



Series: Sustainable Water Developments

6

# Geothermal Water Management



Editors: Jochen Bundschuh & Barbara Tomaszewska

## GEOHERMAL WATER MANAGEMENT



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# Sustainable Water Developments Resources, Management, Treatment, Efficiency and Reuse

*Series Editor*

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# Geothermal Water Management

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## About the book series

Augmentation of freshwater supply and better sanitation are two of the world's most pressing challenges. However, such improvements must be done economically in an environmental and societally sustainable way.

Increasingly, groundwater – the source that is much larger than surface water and which provides a stable supply through all the seasons – is used for freshwater supply, which is exploited from ever-deeper groundwater resources. However, the availability of groundwater in sufficient quantity and good quality is severely impacted by the increased water demand for industrial production, cooling in energy production, public water supply and in particular agricultural use, which at present consumes on a global scale about 70% of the exploited freshwater resources. In addition, climate change may have a positive or negative impact on freshwater availability, but which one is presently unknown. These developments result in a continuously increasing water stress, as has already been observed in several world regions and which has adverse implications for the security of food, water and energy supplies, the severity of which will further increase in future. This demands case-specific mitigation and adaptation pathways, which require a better assessment and understanding of surface water and groundwater systems and how they interact with a view to improve their protection and their effective and sustainable management.

With the current and anticipated increased future freshwater demand, it is increasingly difficult to sustain freshwater supply security without producing freshwater from contaminated, brackish or saline water and reusing agricultural, industrial, and municipal wastewater after adequate treatment, which extends the life cycle of water and is beneficial not only to the environment but also leads to cost reduction. Water treatment, particularly desalination, requires large amounts of energy, making energy-efficient options and use of renewable energies important. The technologies, which can either be sophisticated or simple, use physical, chemical and biological processes for water and wastewater treatment, to produce freshwater of a desired quality. Both industrial-scale approaches and smaller-scale applications are important but need a different technological approach. In particular, low-tech, cost-effective, but at the same time sustainable water and wastewater treatment systems, such as artificial wetlands or wastewater gardens, are options suitable for many small-scale applications. Technological improvements and finding new approaches to conventional technologies (e.g. those of seawater desalination), and development of innovative processes, approaches, and methods to improve water and wastewater treatment and sanitation are needed. Improving economic, environmental and societal sustainability needs research and development to improve process design, operation, performance, automation and management of water and wastewater systems considering aims, and local conditions.

In all freshwater consuming sectors, the increasing water scarcity and correspondingly increasing costs of freshwater, calls for a shift towards more water efficiency and water savings. In the industrial and agricultural sector, it also includes the development of technologies that reduce contamination of freshwater resources, e.g. through development of a chemical-free agriculture. In the domestic sector, there are plenty of options for freshwater saving and improving efficiency such as water-efficient toilets, water-free toilets, or on-site recycling for uses such as toilet flushing, which alone could provide an estimated 30% reduction in water use for the average household. As already mentioned, in all water-consuming sectors, the recycling and reuse of the respective wastewater can provide an important freshwater source. However, the rate at which these water efficient technologies and water-saving applications are developed and adopted depends on the behavior of individual consumers and requires favorable political, policy and financial conditions.

Due to the interdependency of water and energy (water-energy nexus); i.e. water production needs energy (e.g. for groundwater pumping) and energy generation needs water (e.g. for cooling), the management of both commodities should be more coordinated. This requires integrated energy and water planning, i.e. management of both commodities in a well-coordinated form rather than managing water and energy separately as is routine at present. Only such integrated management allows reducing trade-offs between water and energy use.

However, water is not just linked to energy, but must be considered within the whole of the water-energy-food-ecosystem-climate nexus. This requires consideration of what a planned water development requires from the other sectors or how it affects – positively or negatively – the other sectors. Such integrated management of water and the other interlinked resources can implement synergies, reduce trade-offs, optimize resources use and management efficiency, all in all improving security of water, energy, and food security and contributing to protection of ecosystems and climate. Corresponding actions, policies and regulations that support such integral approaches, as well as corresponding research, training and teaching are necessary for their implementation.

The fact that in many developing and transition countries women are disproportionately disadvantaged by water and sanitation limitation requires special attention to this aspect in these countries. Women (including schoolgirls) often spend several hours a day fetching water. This time could be much better used for attending school or working to improve knowledge and skills as well as to generate income and so to reduce gender inequality and poverty. Absence of in-door sanitary facilities exposes women to potential harassment. Moreover, missing single-sex sanitation facilities in schools and absence of clean water contributes to diseases. This is why women and girls are a critical factor in solving water and sanitation problems in these countries and necessitates that men and women work alongside to address the water and wastewater related operations for improvement of economic, social and sustainable freshwater provision and sanitation.

Individual volumes published in the series are spanning the wide spectrum between research, development and practice in the topic of freshwater and related areas such as gender and social aspects as well as policy, regulatory, legal and economic aspects of water. It covers all fields and facets in optimal approaches to the:

- Assessment, protection, development and sustainable management of groundwater and surface water resources thereby optimizing their use.
- Improvement of human access to water resources in adequate quantity and good quality.
- Meeting of the increasing demand for drinking water, and irrigation water needed for food and energy security, protect ecosystems and climate and to contribute to a social and economically sound human development.
- Treatment of water and wastewater also including its reuse.
- Implementation of water efficient technologies and water saving measures.

A key goal of the series is to include all countries of the globe in jointly addressing the challenges of water security and sanitation. Therefore, we aim to a balanced choice of authors and editors originating from developing and developed countries as well as gender equality. This will help society to provide access to freshwater resources in adequate quantity and good quality, meeting the increasing demand for drinking water, domestic water and irrigation water needed for food security while contributing to social and economically sound development.

This book series aims to become a state-of-the-art resource for a broad group of readers including professionals, academics and students dealing with ground- and surface water resources, their assessment, exploitation and management as well as the water and wastewater industry. This comprises especially hydrogeologists, hydrologists, water resources engineers, wastewater engineers, chemical engineers and environmental engineers and scientists.

The book series provides a source of valuable information on surface water but especially on aquifers and groundwater resources in all their facets. Thereby, it covers not only the scientific and technical aspects but also environmental, legal, policy, economic, social, and gender

aspects of groundwater resources management. Without departing from the larger framework of integrated groundwater resources management, the topics are centered on water, solute and heat transport in aquifers, hydrogeochemical processes in aquifers, contamination, protection, resources assessment and use.

The book series constitutes an information source and facilitator for the transfer of knowledge, both for small communities with decentralized water supply and sanitation as well as large industries that employ hundreds or thousands of professionals in countries worldwide, working in the different fields of freshwater production, wastewater treatment and water reuse as well as those concerned with water efficient technologies and water saving measures. In contrast to many other industries, suffering from the global economic downturn, water and wastewater industries are rapidly growing sectors providing significant opportunities for investments. This applies especially to those using sustainable water and wastewater technologies, which are increasingly favored. The series is also aimed at communities, manufacturers and consultants as well as a diversity of stakeholders and professionals from governmental and non-governmental organizations, international funding agencies, public health, policy, regulators and other relevant institutions, and the broader public. It is designed to increase awareness of water resources protection and understanding of sustainable water and wastewater solutions including the promotion of water and wastewater reuse and water savings.

By consolidating international research and technical results, the objective of this book series is to focus on practical solutions in better understanding ground- and surface water systems, the implementation of sustainable water and wastewater treatment and water reuse and the implementation of water efficient technologies and water saving measures. Failing to improve and move forward would have serious social, environmental and economic impacts on a global scale.

The book series includes books authored and edited by world-renowned scientists and engineers and by leading authorities in economics and politics. Women are particularly encouraged to contribute, either as author or editor.

Jochen Bundschuh  
(Series Editor)



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Tesfaye Tafesse (transboundary water issues, with emphasis on the Nile; natural resources management and institutions; rural development and agricultural problems in the Third World), College of Social Sciences, Addis Ababa University (AAU), Addis Ababa

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#### FEDERATED STATES OF MICRONESIA

Leerenson Lee Airens (water supply for Small Islands Development States (SIDS)), GEF-IWRM Focal Point; Manager, Water Works, Pohnpei Utilities Corporation (PUC), Pohnpei State

#### FIJI

Johann Poinapen (water and wastewater engineering and management; design and operation of water/wastewater treatment plants including membrane systems (MF & RO); brine treatment (thermal technologies); mine water treatment; water recycling), Acting Director, Institute of Applied Sciences, University of the South Pacific (USP), Suva

#### FINLAND

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#### FRANCE

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#### GEORGIA

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#### GERMANY

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Jan Hoinkis (membrane technologies; membrane bioreactor technology; water and wastewater treatment; water reuse; sensor and control systems in water treatment), Institute of Applied Research, Karlsruhe University of Applied Sciences (HsKA), Karlsruhe

Heidrun Steinmetz (resource oriented sanitation (nutrient recovery, energy efficiency), biological and advanced WWT; water quality management), Chair of Sanitary Engineering and Water Recycling, University of Stuttgart, Stuttgart

#### GREECE

Maria Mimikou (hydrology; water resources management; hydro-energy engineering; climate change), School of Civil Engineering, National Technical University of Athens (NTUA), Athens



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#### HAITI

Urbain Fifi (hydrogeology; environment engineering; groundwater quality and pollution;  
water resources management; hydrogeological modeling), President of IHP Haitian National  
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Water Management”, Faculty of Sciences, Engineering and Architecture, University  
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#### HONDURAS

Sadia Irais Lanza (water resources and climate change; physical hydrogeology; hydrology;  
water quality), Physics Department, National Autonomous University of Honduras (UNAH),  
San Pedro Sula, Cortés

#### HONG KONG

Jiu Jimmy Jiao (hydrogeology; influence of groundwater and rainfall on landslides; impact of  
human activities on groundwater regimes; dewatering system design; contaminant fate and  
transport modeling and groundwater remediation design; global optimization approaches for  
parameter identification in flow and transport modeling; parameter sensitivity analysis and its  
influence on parameter estimation), Editor Hydrogeology Journal; The University of Hong  
Kong (HKU), Hong Kong

#### HUNGARY

László Somlyódy (wastewater treatment; environmental engineering), past President of the  
International Water Association (IWA), Head, Department of Sanitary and Environmental  
Engineering, Faculty of Engineering, Budapest University of Technology and Economics  
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#### INDIA

Makarand M. Ghangrekar (wastewater treatment in microbial fuel cell and electricity  
generation), Department of Civil Engineering, Indian Institute of Technology – Kharagpur  
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Ashok Kumar Ghosh (water quality, especially arsenic and fluoride contamination in  
groundwater resources; fluoride removal technology, bioremediation of arsenic; bio-synthesis  
of nano-particles through microbes), Chairman, State Expert Appraisal Committee  
(SEAC-Bihar) and Member, Bihar State Pollution Control Board; Head, Research  
Department, Mahavir Cancer Institute and Research Centre, Patna, Bihar

Arun Kumar (environmental management of water bodies), Alternate Hydro Energy Centre,  
Indian Institute of Technology – Roorkee (IITR), Roorkee, Uttarakhand

Rakesh Kumar (urban hydrology; hydrological modeling; watershed management; drought  
mitigation and management; flood estimation, routing, management and socio-economic  
aspects; impact of climate change on water resources), Head, Surface Water Hydrology  
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Dinesh Mohan (environmental chemistry; water/wastewater monitoring, assessment,  
modeling & remediation using physicochemical methods; development of low cost  
adsorbents/magnetic adsorbents/magnetic nanosorbents for water remediation; biomass fast  
pyrolysis for the development of bio-oils and biochars, biorefineries; climate change  
mitigation: development & application of biochar for carbon sequestration; applications of  
biochars for remediation of contaminated soils), School of Environmental Sciences,  
Jawaharlal Nehru University (JNU), New Delhi

Abhijit Mukherjee (physical, chemical and isotope hydrogeology; modeling of groundwater flow and solute transport; hydrostratigraphy; contaminant fate and transport; surface water-seawater-groundwater interactions; effect of climate change on water resources; mine-site hydrology; environmental geochemistry), Department of Geology and Geophysics, Indian Institute of Technology – Kharagpur (IIT Kgp), Kharagpur, West Bengal

Nanakkumar Santdasani (sustainable water supply and management; defluoridation as a solution to fluorosis in rural areas; community managed water and sanitation programs), Water, Sanitation, Hygiene (WASH), UNICEF, Patna, Bihar

## INDONESIA

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## IRAN

Ahmad Abrishamchi (water resources and environmental systems: analysis and management), Chairholder, UNESCO Chair in Water and Environment Management for Sustainable Cities; Department of Civil Engineering, Sharif University of Technology (SUT), Tehran

## ISRAEL

Ofer Dahan (vadose zone and groundwater hydrology; quantitative assessment of water infiltration and groundwater recharge; water flow and contaminant transport through the vadose zone; arid land hydrology; monitoring technologies for deep vadose zone), Department of Hydrology & Microbiology, Zuckerberg Institute for Water Research, Blaustein Institute for Desert Research, Ben Gurion University of the Negev (BGU), Sde Boker Campus, Ben Gurion

Michael Zilberbrand (groundwater resources; hydrogeochemical processes and hydrogeological and hydrogeochemical modeling in aquifers and in the unsaturated zone), Israeli Water Authority, Hydrological Service, Jerusalem

## ITALY

Alessandra Criscuoli (membrane science and technology; membrane distillation and membrane contactors; integrated membrane processes; water and wastewater treatment; desalination of brackish water and seawater), Institute on Membrane Technology, ITM-CNR, Rende (CS)

Enrico Drioli (membrane science and engineering; membrane preparation and transport phenomena in membranes; desalination of brackish and saline water; integrated membrane processes; membrane distillation and membrane contactors; catalytic membrane and catalytic membrane reactors; salinity gradient energy fuel cells), Institute on Membrane Technology, ITM-CNR, Rende (CS)

Alberto Figoli (membrane science and technology; membrane preparation and characterization; transport phenomena in membranes; pervaporation; water and wastewater treatment; desalination of brackish and saline water), Institute on Membrane Technology, ITM-CNR, Rende (CS)

Marco Petitta (groundwater pollution, management, and protection), President IAH Chapter Italy, Department of Earth Sciences, Sapienza University of Rome, Rome

Ludovico Spinosa (sludge management), (retired) National Research Council (CNR); Consultant at Governmental Commissariat Environmental Emergencies in Region Puglia; Convenor at ISO/TC275/WG6 (Thickening and Dewatering) and CEN/TC308/WG1 (Process control methods) on sludge standardization

## JAMAICA

Arpita Mandal (hydrology; hydrogeology; water resources and impacts of climate change; water supply; climate variability; flood risk and control; hydrochemistry of groundwater; saline water intrusion), Department of Geography and Geology, University of the West Indies (UWI), Mona Campus, Mona, Kingston

## JAPAN

Hiroaki Furumai (build-up and wash-off of micropollutants in urban areas; characterization of DOM/NOM in lakes and reservoirs for drinking water sources; fate and behavior of DOM in flocculation and advanced oxidation processes; biological nutrient removal from wastewater; modeling activated sludge in aerobic/anaerobic SBR; characterization of domestic sewage from the viewpoint of nutrient removal), Board of Directors, IWA; Department of Urban Engineering, The University of Tokyo (Todai), Tokyo

Makoto Nishigaki (modeling groundwater and multiphase flow and solute transport in porous media; modeling seepage in the saturated-unsaturated zone; development of methods of measuring hydraulic properties in rock mass), Department of Environmental and Civil Design, Faculty of Environmental Science and Technology, Okayama University, Okayama

Taikan Oki (global water balance and world water resources; climatic variation and the Asian monsoon; land-atmosphere interaction and its modeling; remote sensing in hydrology; temporal and spatial distribution of rainfall), Institute of Industrial Science, The University of Tokyo, Komaba, Tokyo

Yuichi Onda (hillslope hydrology; hydro-geomorphology; radionuclide transfer; forest hydrology), Center for Research in Isotopes and Environmental Dynamics, University of Tsukuba, Tsukuba, Ibaraki

Kaoru Takara (innovative technologies for predicting floods; global environmental changes; risk and emergency management; interactions between social changes and hydrological cycle/water-related disasters; disaster mitigation strategy; policy development; integrated numerical modeling for lakes and surrounding catchments), Director, Disaster Prevention Research Institute, Kyoto University (Kyodai), Kyoto

## JORDAN

Fawzi A. Banat (desalination), Department of Chemical Engineering, Jordan University of Science and Technology (JUST), Irbid

Samer Talazi (irrigation and water resources engineering, planning and policy), Civil Engineering Department, Jordan University of Science and Technology (JUST), Irbid

## KENYA

Daniel Olago (environmental geology; surface and sub-surface water chemistry and dynamics; water-energy and related nexuses; human impact on the environment, global change processes, vulnerability and adaptation to climate change: past and present; environmental policies, laws and regulations and capacity development in global environmental change), Chairman, Network of African Science Academies (NASAC) Water Program; Member, International Lake Environment Committee; Member and focal point for water, Kenya National Academy of Sciences (KNAS); Institute for Climate Change and Adaptation (ICCA) & Department of Geology, University of Nairobi, Nairobi

Mwakio Tole (water and geothermal energy resources; waste disposal; environmental impact assessment), School of Environmental and Earth Sciences, Department of Environmental Sciences, Pwani University, Kilifi

**KOREA**

Jaeweon Cho (water reuse; membrane filtration; ecological engineering (treatment wetland); desalination), School of Urban and Environmental Engineering, Ulsan Institute of Science and Technology (UNIST), Ulsan

Yong Sik Ok (bioavailability of emerging contaminants; bioenergy and value-added products such as biochar; waste management; fundamental soil science and remediation of metals in soils and sediments), Director, Korea Biochar Research Center, School of Natural Resources and Environmental Science, Kangwon National University, Chuncheon

**KYRGYZSTAN**

Bolot Moldobekov (hydrogeology; engineering geology; geographic information systems – GIS; geoinformatics; interdisciplinary geosciences; natural hazards), Co-Director, Central-Asian Institute for Applied Geosciences (CAIAG), Bishkek

**LATVIA**

Māris Kļaviņš (aquatic chemistry; geochemical analysis; environmental pollution and its chemical analysis; environmental education, including also political and social sciences), Head, Department of Environmental Science, University of Latvia (LU), Riga

**LITHUANIA**

Robert Mokrik (groundwater resources, flow and transport modeling; hydrogeochemistry and groundwater isotopes; palaeohydrogeology), Department of Hydrogeology and Engineering Geology, Faculty of Natural Sciences, Vilnius University, Vilnius

**LUXEMBOURG**

Joachim Hansen (wastewater treatment; micropollutants; wastewater reuse; water-energy nexus), Engineering Science – Hydraulic Engineering, Faculty of Science, Technology and Communication, University of Luxembourg – Campus Kirchberg, Luxembourg

**MADAGASCAR**

Désiré Rakotondravaly (hydrology; hydrogeology; hydraulics; geology; rural water supply; vulnerability mapping; water and sanitation; GIS; project management; capacity building; community development; conservation; development cooperation), Ministry of Mines, Antananarivo

**MALAWI**

Victor Chipofya (urban water utility operation and management; groundwater development, monitoring and management; groundwater quality; rural water supply; water and sanitation in peri-urban and rural areas; water reuse; hygiene promotion), Executive Director, Institute of Water and Environmental Sanitation (IWES); National Coordinator of the Malawi Water Partnership (MWP); Steering Committee Member: Water Supply and Sanitation Collaborative Council (WSSCC) for Eastern and Southern Africa, Blantyre

**MALAYSIA**

Mohamed Kheireddine Aroua (separation processes; water and wastewater treatment), Director, Centre for Separation Science & Technology (CSST), Department of Chemical Engineering, Faculty of Engineering, University of Malaya (UM), Kuala Lumpur

Hamidi Abdul Aziz (water supply engineering; wastewater engineering; solid waste management), School of Civil Engineering, University of Science Malaysia (USM), Engineering Campus, Nibong Tebal, Penang

Ali Hashim (separation processes – flotation; liquid-liquid extraction; water and wastewater treatment; ionic liquids – synthesis and applications), Department of Chemical Engineering, Faculty of Engineering, University of Malaya (UM), Kuala Lumpur

Ahmad Fauzi Ismail (development of membrane technology for reverse osmosis, nanofiltration, ultrafiltration and membrane contactor), Deputy Vice Chancellor (Research & Innovation) & Founder and Director, Advanced Membrane Technology Research Center (AMTEC), University of Technology – Malaysia (UTM), Johor Bahru, Kuala Lumpur

Hilmi Mukhtar (membrane development; membrane modeling; membrane applications including wastewater treatment engineering and natural gas separation), Department of Chemical Engineering, Faculty of Engineering, Petronas University of Technology (UTP), Bandar Seri Iskandar, Perak

Mohd Razman Bin Salim (water and wastewater treatment), Deputy Director, Institute of Environmental and Water Resource Management (IPASA), Faculty of Civil Engineering, University of Technology – Malaysia (UTM), Johor Bahru, Johor

Saim Suratman (hydrogeology; groundwater management), Deputy Director General, National Hydraulics Research Institute of Malaysia (NAHRIM), Seri Kembangan Selangor Darul Ehsan, Malaysia

Wan Azlina Wan Ab Karim Ghani (chemical and environmental engineering; biochar and composites for water, wastewater and soil treatment; biomass conversion; biomass energy), Research Coordinator, Department of Chemical & Environmental Engineering, Faculty of Engineering, Putra University (UPM), Serdang

#### MALTA

Kevin Gatt (governance, policy and planning issues related to water resources; waste management and sustainable development), Faculty for the Built Environment, University of Malta (UoM), Tal-Qroqq, Msida

#### MAURITIUS

Arvinda Kumar Ragen (wastewater engineering; constructed wetlands for household greywater; water pollution control in sugar factories; environmental impact assessment), Department of Chemical & Environmental Engineering, Faculty of Engineering, University of Mauritius (UoM), Le Reduit, Moka.

#### MEXICO

Ma. Teresa Alarcón Herrera (water resources; water treatment using artificial wetlands), Director, Durango Unit of the Advanced Materials Research Center (CIMAV), Durango, Dgo.

Maria Aurora Armienta (hydrogeology; trace element contaminants; water treatment using geological materials), Institute of Geophysics, National Autonomous University of Mexico (UNAM), Ciudad Universitaria, Mexico City, D.F.

Sofia Garrido Hoyos (drinking water; collection and treatment of rainwater; biological wastewater treatment; treatment and/or utilization of sludge and biosolids), Mexican Institute of Water Technology (IMTA), Jiutepec, Mor.

Luz Olivia Leal Quezada (environmental engineering; environmental chemistry; automation of chemical analysis techniques for environmental monitoring, particularly for the determination and speciation of trace elements; techniques for determining water quality and chemical aspects of their treatment), Advanced Materials Research Center (CIMAV), Environment and Energy Department, Chihuahua, Chih.

**MOROCCO**

Lhoussaine Bouchaou (hydrology; water quality; aquatic ecosystems; environmental impact assessment; climatology; climate change), President IAH Chapter Morocco; Applied Geology and Geo-Environment Laboratory, Faculty of Sciences, University Ibn Zohr (UIZ), Agadir

**MOZAMBIQUE**

Catine Chimene (municipal water and infrastructure; water supply engineering; agricultural water; rural development), Higher School of Rural Development (ESUDER), Eduardo Mondlane University (UEM), Inhambane, Vilankulo

**MYANMAR**

Khin-Ni-Ni Thein (hydroinformatics, integrated water resources management, river basin management, coastal-zone management, sustainable hydropower assessment, disaster risk reduction, climate change; sustainability; capacity building; community development; water and environmental policy; public policy analysis; green economy and green growth), Secretary, Advisory Group, Member, National Water Resources Committee; Advisory Group Member, National Disaster Management Committee, Founder and President, Water, Research and Training Centre (WRTC); Visiting Senior Professor, Yangon Technological University (YTU), Yangon, Myanmar; Regional Water Expert for Green Growth, UNESCAP

**NAMIBIA**

Benjamin Mapani (groundwater recharge and vulnerability mapping; groundwater development, management, monitoring and modeling; environmental hydrogeology; climate change), Board of Trustees, WaterNet; Department of Geology, University of Namibia (UNAM), Windhoek

**NEPAL**

Bandana K. Pradhan (environment and public health), Department of Community Medicine and Public Health, Institute of Medicine, Tribhuvan University (TU), Maharajgunj

**NEW ZEALAND**

David Hamilton (modeling of water quality in lakes and reservoirs; sediment-water interactions in lakes; boom-forming algae, particularly cyanobacteria; ice cover in lakes), Environmental Research Institute (ERI), University of Waikato, Waikato

**NICARAGUA**

Andrew Longley (hydrogeology; groundwater engineering; catchment studies and groundwater modeling; international development: projects in the water, geothermal, agriculture, environment and health sectors; rural water supply; arsenic contamination: mapping, hydrogeology, epidemiology; bridging the gap between academia, industry, public and charity sectors), Director, Nuevas Esperanzas UK, León

Katherine Vammen (aquatic microbiology; climate change and water resources; water supply and sanitation for the poor; urban waters), Co-Chair of the Water Programme of the Interamerican Network of the Academies of Science; Nicaraguan focal point for water programme in the InterAmerican Network of Academies of Sciences (IANAS); Central American University, Managua

**NIGERIA**

Peter Cooley (sustainable water/wastewater management in developing countries), Rivers State College of Health Science and Technology, Port Harcourt, Nigeria and Earthwatch Research Institute (EWRI), Port Harcourt

## NORWAY

Torleiv Bilstad (water, oil and gas separation; environmental science and engineering), Former President of EWA-Norway; Department of Mathematics and Natural Sciences, University of Stavanger (UiS), Stavanger

Hallvard Ødegaard (water and wastewater treatment; innovative solutions for integrated approaches to urban water management), Department of Hydraulic and Environmental Engineering, Norwegian University of Science and Technology (NTNU), Trondheim

## OMAN

Mohammed Zahir Al-Abri (thermal desalination; water and wastewater treatment; nanotechnology), Petroleum and Chemical Engineering Department, Sultan Qaboos University (SQU), Al Khoudh, Muscat

## PAKISTAN

Ghani Akbar (agricultural engineering; integrated water management; soil & water conservation and climate smart agricultural practices), Program Leader, Integrated Watershed Management Program (IWMP), Climate Change, Alternate Energy and Water Resources Institute (CAEWRI), National Agricultural Research Centre (NARC), Chak Shahzad, Islamabad

## PALESTINIAN AUTONOMOUS AREAS

Marwan Haddad (interdisciplinary approaches to water resources and quality management; renewable energy; recycling), Director, Water and Environmental Studies Institute, An Najah National University, Nabus

## PANAMA

José R. Fábrega (sustainable water and wastewater management; environmental fate of chemicals in water and soil systems), Panamanian focal point for water in the InterAmerican Network of Academies of Sciences (IANAS); Hydraulic and Hydrotechnical Research Center (CIHH), Technological University of Panama (UTP), Panama City

## PARAGUAY

Alicia Eisenkölbl (environmental management; environmental impact assessment; trans-boundary aquifers; rural development), Faculty of Agricultural Sciences Hohenau, Catholic University Our Lady of the Assumption (UCA), Campus Itapúa, Encarnación

## PERU

Nicole Bernex Weiss de Falen (integrated water resources management; human sustainable development; climate change adaptation; integrated ecosystemic services, water management and risks (droughts and floods) with land planning at a water basin, regional and national level), Peruvian focal point for water in the InterAmerican Network of Academies of Sciences (IANAS); member of the technical Committee of Global Water Partnership GWP; LAC Chair in the CST of the UNCCD; Center of Research in Applied Geography (CIGA), Pontifical Catholic University of Peru (PUCP), Lima

## PHILIPPINES

Victor Ella (surface and groundwater hydrology; irrigation and drainage engineering; water quality; simulation modeling; wastewater engineering; contaminant transport in soils; geostatistics; hydraulic engineering), Land and Water Resources Division, Institute of Agricultural Engineering, College of Engineering and Agro-Industrial Technology, University of the Philippines Los Baños (UPLB), College, Laguna

Nasreen Islam Khan (water quality assessment; modeling and mapping geogenic contaminants; arsenic in food chain and mitigation; human health risk assessment and mapping; willingness to pay; climate change impact on land use; GIS and remote sensing), GIS Social Science Division, International Rice Research Institute (IRRI), Los Banos, Laguna, Philippines & Fenner School of Environment and Society, Australian National University (ANU), Canberra, ACT

#### POLAND

Marek Bryjak (adsorption based water treatment), Department Polymer & Carbon Materials, Wrocław University of Technology, Wrocław

Wiesław Bujakowski (geothermics), Mineral and Energy Economy Research Institute, Polish Academy of Sciences (PAN), Kraków

Jacek Makinia (wastewater treatment; nutrient removal and recovery from wastewater), Faculty of Hydro and Environmental Engineering, Vice-Rector for Cooperation and Innovation, Gdańsk University of Technology (GUT), Gdańsk

Barbara Tomaszewska (monitoring of the aquatic environments; geothermics; scaling of geothermal systems; membrane technologies for geothermal water treatment for water resource purposes), AGH University of Science and Technology; Mineral and Energy Economy Research Institute, Polish Academy of Sciences (PAN), Kraków

#### PORTUGAL

Maria do Céu Almeida (sewer processes and networks), National Laboratory of Civil Engineering (LNEC), Lisbon

Helena Marecos (water reuse), Civil Engineering Department, Lisbon Engineering Superior Institute (ISEL), Lisbon

Helena Ramos (water-energy nexus; energy efficiency and renewable energies; hydraulics; hydrotransients; hydropower; pumping systems; leakage control; water supply; water vulnerability), Department of Civil Engineering, University of Lisbon (ULisboa), Lisbon

#### QATAR

Farid Benyahia (immobilized nitrifiers in wastewater treatment; membrane distillation desalination; water quality and energy efficiency analysis; airlift bioreactors; low-grade heat in membrane distillation for freshwater production; bioremediation of oil spills; development, design and evaluation of advanced refinery wastewater treatment processes), College of Engineering, Department of Chemical Engineering, Qatar University (QU), Doha

Patrick Linke (design, engineering and optimization of efficient processes, integrated systems and associated infrastructures; efficient utilization of natural resources (energy, water and raw materials); water-energy-food nexus), Chair, Chemical Engineering Program, Texas A&M University at Qatar (TAMUQ), Managing Director of the Qatar Sustainable Water and Energy Utilization Initiative (QWE), at TAMUQ, Qatar Environment and Energy Research Institute (QEERI), Doha

#### REPUBLIC OF GUINEA

Hafiziou Barry (integrated water resources management), Polytechnic Institute, University Gamal Abdel Nasser, Conakry

#### ROMANIA

Anton Anton (pumping stations; municipal water networks), Hydraulics and Environmental Protection Department, Technical University of Civil Engineering (UTCB), Bucharest



## RUSSIAN FEDERATION

Sergey Pozdniakov (water resources; water quality; hydrogeology; contaminant transport; geostatistics; water balance; climate change), Faculty of Geology, Moscow State University (MSU), Moscow

## RWANDA

Omar Munyaneza (hydrology; climate change and water resources management), College of Science and Technology, Department of Civil Engineering, University of Rwanda (UR), Kigali

## SAUDI ARABIA

Noreddine Ghaffour (renewable energy for desalination and water treatment), Water Desalination and Reuse Research Center, King Abdullah University of Science and Technology (KAUST), Thuwal

Mattheus Goosen (renewable energy for desalination and water treatment; membranes), Office of Research and Graduate Studies, Alfaisal University, Riyadh

## SENEGAL

Alioune Kane (water quality; hydraulics; water-poverty relationships; climate variability and water availability), Director of the Master Programme GIDEL (Integrated Management and Sustainable Development of Coastal West Africa); Coordinator of WANWATCE (Centres Network of Excellence for Science and Water Techniques NEPAD), Department of Geography, Cheikh Anta Diop University (UCAD), Dakar

## SERBIA

Petar Milanović (karst hydrogeology; theory and engineering practice in karst), President IAH Chapter Serbia and Montenegro, Belgrade

## SINGAPORE

Vladan Babovic (hydroinformatics; data assimilation; data mining), Department of Civil and Environmental Engineering, National University of Singapore (NUS), Singapore

Jiangyong Hu (water treatment technology; water quality; water reuse; health impacts), Department of Civil and Environmental Engineering & Co-Director, Centre for Water Research, National University of Singapore (NUS), Singapore

## SLOVAKIA

Ján Derco (environmental engineering; nutrients removal; ozone-based oxidation processes; water resources protection; water and wastewater technology), Department of Environmental Engineering, Faculty of Chemical and Food Technology, Slovak University of Technology (SUT), Bratislava

## SLOVENIA

Boris Kompare (wastewater treatment; modeling), Past President EWA-Slovenia; Faculty of Civil Engineering and Geodesy, University of Ljubljana (UL), Ljubljana

## SOMALIA

Abdullahi Mohamed Abdinisir (water resources management; groundwater governance; water supply), Ministry of Water, Petroleum, Energy and Mineral Resources, Mogadishu

## SOUTH AFRICA

Tamiru A. Abiye (community water supply problems; water quality assessment and monitoring; hydrochemical modeling; groundwater flow and solute transport; trace metals in groundwater; surface and groundwater interactions; climate change impact study on groundwater; spatial and temporal variability of groundwater recharge), School of Geosciences, Faculty of Science (East Campus), University of the Witwatersrand (Wits University), Johannesburg

Hamanth C. Kasan (sustainable water and wastewater management in developing countries), General Manager, Scientific Services Division, Rand Water; President, African Water Association (AfWA), Johannesburg

Sabelo Mhlanga (water-energy nexus; nano-structured materials for water purification and recovery; energy-efficient and antifouling membrane filtration technologies for water treatment; community involvement in water related problems in rural communities; green chemistry), Deputy Director, Nanotechnology and Water Sustainability (NanoWS) Research Unit, College of Science Engineering and Technology, University of South Africa (Unisa), Johannesburg

Anthony Turton (water-energy-food nexus; hydropolitical risk model; mine water management; mine closure planning and strategies; groundwater governance; wastewater reuse), Director, Environmental Engineering Institute of Africa; Centre for Environmental Management, University of Free State (UFS), Bloemfontein; professor at UNESCO Chair in Groundwater, Department of Earth Sciences, University of Western Cape (UWC)

## SPAIN

José Ignacio Calvo (membrane technologies; modifications of structure and surface properties of membranes to increase selectivity), School of Agriculture, Food Technology and Forestry, ETSIIAA, University of Valladolid (UVa), Palencia

Jesús Colprim (small water supply and wastewater systems), Laboratory of Chemical and Environmental Engineering (LEQUIA), Institute of Environment, University of Girona (UdG), Girona

Elena Giménez-Forcada (hydrogeology; hydrogeochemistry; water quality; groundwater contamination; trace elements), Geological Survey of Spain (IGME), Salamanca

J. Jaime Gómez-Hernández (stochastic hydrogeology; geostatistics; inverse modeling; nuclear waste disposal), Head of the Group of Hydrogeology, Research Institute of Water and Environmental Engineering, UPV, Valencia

Aurora Seco Torrecillas (nutrient removal and recovery from wastewater; anaerobic membrane bioreactor for wastewater treatment (WWT); microalgae cultivation for WWT), Chemical Engineering Department, University of Valencia (UV), Valencia

Guillermo Zaragoza (solar energy for desalination; thermal and membrane technologies for water treatment), Solar Platform of Almería (PSA-CIEMAT), Almería

## SRI LANKA

Nadeeka S. Miguntanna (urban stormwater quality and monitoring; surrogate water quality parameters; urban water pollution; rainwater harvesting), Environmental Engineering Laboratory, Department of Civil and Environmental Engineering, Faculty of Engineering, University of Ruhuna (UOR), Hapugala, Galle

Meththika Suharshini Vithanage (water quality; water chemistry; impact of tsunamis on aquifers; groundwater modeling; soil and water monitoring for pollution; mechanistic

modeling of biochar and nano materials for water and soil remediation (landfill leachates, nutrients and toxic metals)), Group Leader – Chemical and Environmental Systems Modeling Research Group, National Institute of Fundamental Studies (NIFS), Kandy

#### SUDAN (REPUBLIC OF)

Abdin Mohamed Ali Salih (environmental sciences with emphasis on water resources management in arid and semi-arid zones), Board Member at UNESCO-IHE; Civil Engineering Department, Faculty of Engineering, The University of Khartoum (UofK), Khartoum

#### SURINAME

Sieuwnath Naipal (hydrology; climate change impact on climate variability; marine and coastal engineering), Anton De Kom University of Suriname (AdeKUS), Tammenga

#### SWAZILAND

Absalom M. Manyatsi (land and water resources management; environmental impact assessment; remote sensing; GIS and spatial climate change impacts; climate change adaptation and mitigation; climate smart agriculture; climate change and climate variability impacts on water resources and agriculture), Head of Department, Agricultural and Biosystems Engineering Department, University of Swaziland (UNISWA), Luyengo

#### SWEDEN

Prosun Bhattacharya (groundwater resources; hydrogeochemistry; arsenic), Coordinator, KTH-International Groundwater Arsenic Research Group, Department of Sustainable Development, Environmental Science and Engineering, Royal Institute of Technology (KTH), Stockholm

Joydeep Dutta (application of nanotechnology for water treatment; water-environment-energy nexus; photocatalytic materials, electrocatalysis and capacitive desalination of water, plasmon resonance sensors for heavy metal ion detection), Chair, Functional Materials Division, Materials- and Nano Physics Department, ICT School, Kista, Stockholm

Gunnar Jacks (hydrology; hydrogeology; hydrochemistry; groundwater chemistry; groundwater arsenic and fluoride; acidification of soil and groundwater; artificial groundwater recharge; water supply and sanitation in suburban areas), (retired), Department of Sustainable Development, Environmental Science and Engineering, Royal Institute of Technology (KTH), Stockholm

Erik Kärrman (sustainable wastewater management; decision support and multi-criteria analysis of municipal and local water and wastewater systems), Director of Research and Development, Urban Water & Royal Institute of Technology (KTH), Stockholm

Andrew Martin (membrane distillation for desalination and water purification; biomass and municipal solid waste; polygeneration), Department of Energy Technology, Royal Institute of Technology (KTH), Stockholm

Aapo Sääsk (development of polygeneration and zero liquid discharge), CEO, Scarab Development AB, Stockholm

Nury Simfors (geothermal exploration, geogenic trace contaminants, GIS and hazard mitigation), MVI/MTA, Swedish National Defence University (FHS), Stockholm

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## Editors' foreword

The rational use of geothermal water resources requires the repeated involvement of specialists and engineers from many fields of technology. In effect, this interaction primarily involves geologists, hydrogeologists, and hydrogeochemists, whose knowledge allows them to determine the feasible resources and potential for the utilization of geothermal energy under the specific hydro-geothermal conditions, as well as engineers, technologists and power engineers specialising in the field of energy recovery in surface installations. The sustainable management of geothermal energy resources should be geared towards the optimisation of energy recovery, but also towards the aspect of the rational management of water resources since geothermal water constitutes both an energy carrier and also a valuable raw material. Geothermal waters, depending on their hydro-geothermal characteristics, the lithology of the rocks involved, the depth at which the resources occur and the sources of water supply may be characterized by very varied physicochemical qualities. This factor largely determines the technology to be used in their exploitation and the manner in which the geothermal water can be used. Closed systems, based on the re-injection of used/cooled waters back into the rock, are employed in many areas of the world as an optimal solution in the context of the rational management of highly mineralized waters. On the other hand, open systems in which waters are discharged into surface receivers are used in the case of lightly mineralized waters with the proviso that all the specified requirements for the discharge of wastewater into the environment must be met.

This book is focused on the effective use of geothermal water and renewable energy for future needs in order to promote modern, sustainable and effective management of water resources.

Drinking water shortages in many regions of the world have contributed to the development of water treatment technologies. Not only are arid and semiarid regions increasingly exposed to water shortage, but also many other regions face limitations of freshwater resources.

Geothermal energy is being used in many countries for both heating and power generating purposes. As was mentioned, in some cases cooled geothermal waters are discharged into rivers. The use of cooled waters for drinking water purposes may be taken into consideration as an alternative method of disposing of them.

The main objective of the proposed book is to determine the potential of desalination processes for reducing total dissolved solids (TDS), enhancing the removal of microelements (such as arsenic and boron) and also removing natural radionuclides so making geothermal waters suitable for reuse for drinking, irrigation, and other purposes. The key issue of the research is utilizing the retentate, which contains a concentrate of the chemical elements and compounds removed from the geothermal water.

The research field includes crucial new areas of study:

- An improvement in the management of freshwater resources through the use of residual geothermal water.
- A review of the technologies available for its use in the field of geothermal water treatment.
- The development of balneotherapy, tourist, and leisure sector opportunities for using treated geothermal water.

The book is divided into four parts: Part I contains studies on the “*Resources, geochemical properties and environmental implications of geothermal water*” and it provides a general overview on the state of geothermal resources worldwide, and information on the trends in their use and the manner of their utilization. It also presents examples of varied geological conditions

related to the distribution of geothermal waters of both low and high enthalpy. Chapter 1 presents a global assessment of geothermal resources, the definition and classification of geothermal resources and also the results of the assessment of World and European geothermal resources. In Chapter 2, the problems related to the re-injection of used geothermal water back into the rock formation are raised. Also, the equations applied in mathematical modeling are presented, equations that enable the specialist to produce a prediction of the occurrence of colmatage in the active zone of an injection well, or the assessment of changes in the receptivity index and the injection pressure. Chapters 3 and 4 discuss experiences with the utilization of geothermal energy resources in Slovakia (low enthalpy resources) and in Turkey (high enthalpy resources). The crucial issues connected with both the geological and hydrogeological characteristics of the distribution of geothermal water, together with their hydro-geochemical variability, are comprehensively explained. Furthermore, the concepts of the utilization of geothermal resources are presented together with the environmental implications of the exploitation being conducted.

Part II "*Treatment of geothermal water for reuse*" contains 6 chapters dedicated to the subject area covering the opportunities for applying water treatment techniques to ensure the comprehensive use of spent and cooled geothermal waters. Chapter 5 constitutes a presentation of analytical procedures for ion quantification supporting water treatment processes, taking into account the procedure of quality assurance/quality control (QA/QC) in the monitoring of geothermal water. Chapters 6 and 7 present the opportunities for analysing the treatment of geothermal waters for industrial and agricultural purposes, as well as a detailed overview of techniques enabling the effective removal of toxic components, such as boron and arsenic, from geothermal waters. The extensive Chapter 8 contains a detailed discussion of the technological solutions available in terms of membranes and integrated techniques of water conditioning for fresh and potable water production. The authors took a position on the issues of energy consumption, the possibility of using renewable energy sources, and the economic aspects associated with the operation of water treatment installations. The use of membrane water treatment techniques requires the recognition of the possibility that concentrate can be reprocessed. A comprehensive review and state of the art analysis of direct discharge and the recovery of RO concentrates is presented in Chapter 9. The second section ends with Chapter 10, which describes the results of the treatment of geothermal water in Poland, which has been done using a hybrid system based on the processes of reverse osmosis and ultrafiltration. The quality tests conducted for the treatment of geothermal waters with respect to the requirements for water intended for human consumption have demonstrated compliance with these requirements in terms of physical, chemical, microbiological and radiological indicators.

The third part of the book is devoted to the issue of "*The uses of geothermal water in agriculture*". Chapter 11 presents a critical review of potential geothermal applications and recent developments in the direct application of geothermal water in agriculture and the agri-food sector such as processing, distribution, retail, preparation and cooking. Topics linking agriculture and the agri-food sector to questions such as (i) energy demands in agriculture, (ii) energy management processes, (iii) the water-energy-food-climate nexus, (iv) greenhouse gas emissions and (v) carbon footprint of agriculture are not dealt with as they are treated elsewhere.

For thousands of years, people have been using thermal baths to stay healthy and feel well. In consequence, balneology, which uses natural spring water for medicinal purposes, has a very long history. The last part of the book "*The uses of geothermal water in balneotherapy*" contains three chapters. The first two (Chapters 12 and 13) present the history of bathing as a technique of thermal healing in America, Asia, the Middle East and European countries (Chapter 12) and the balneological use of geothermal springs in selected regions of the world. Chapter 14 deals with the importance of an integrated analytical approach to the study of the physico-chemical characteristics of natural geothermal waters used for pelotherapy purposes. The chapters present perspectives for reusing cooled geothermal waters for treatments related to thermal applications, also in the field of thermal peloid treatments on the skin surface. Two contrasting thermal water systems have been analysed in this work: (i) the Euganean geothermal system (Veneto region, Italy) and (ii) the Jelenia Gora geothermal system (the Sudetes Mountains, Poland).

We believe that this book will provide readers with a thorough understanding of the different approaches available for the sustainable management of geothermal water, which can include new reasons for the treatment of geothermal water for useful purposes. In addition and at the same time, water treatment technologies which are designed to obtain permissible levels for drinking water and/or irrigation water are presented in the book and these will be helpful for readers who are interested in investigating the potential of new directions, and of enhancing the optimization of geothermal systems and installations and also of water treatment technologies.

We hope that this book will help all readers, professionals, academics and non-specialists, as well as key institutions that are working on geothermal energy use and water treatment projects. It will be useful for leading decision and policy makers, water sector representatives and administrators, policy makers from governments, business leaders, business enterprises specialising in renewable energy management and water treatment, as well as engineers/scientists from both industrialised and developing countries. It is expected that this book will become a standard text used by educational institutions and research and development establishments involved in the respective issues.

Jochen Bundschuh  
Barbara Tomaszewska  
(editors)  
June 2017





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## About the editors



Jochen Bundschuh (1960, Germany), finished his PhD on numerical modeling of heat transport in aquifers in Tübingen in 1990. He is working in geothermics, subsurface and surface hydrology and integrated water resources management, and connected disciplines. From 1993 to 1999 he served as an expert for the German Agency of Technical Cooperation (GTZ, now GIZ) and as a long-term professor for the DAAD (German Academic Exchange Service) in Argentine. From 2001 to 2008 he worked within the framework of the German governmental cooperation (Integrated Expert Program of CIM; GTZ/BA) as adviser in mission to Costa Rica at the Instituto Costarricense de Electricidad (ICE). Here, he assisted the country in evaluation and development of its huge low-enthalpy geothermal resources for power generation. Since 2005, he is an affiliate professor of the Royal Institute of Technology, Stockholm, Sweden. In 2006, he was elected Vice-President of the International Society of Groundwater for Sustainable Development (ISGSD). From 2009–2011 he was visiting professor at the Department of Earth Sciences at the National Cheng Kung University, Tainan, Taiwan.

Since 2012, Dr. Bundschuh is a professor in hydrogeology at the University of Southern Queensland, Toowoomba, Australia where he leads the Platform for Water in the Nexus of Sustainable Development working in the wide field of water resources and low/middle enthalpy geothermal resources, water and wastewater treatment and sustainable and renewable energy resources. In November 2012, Prof. Bundschuh was appointed as president of the newly established Australian Chapter of the International Medical Geology Association (IMGA).

Dr. Bundschuh is author of the books “Low-Enthalpy Geothermal Resources for Power Generation” (2008) (CRC Press/Balkema, Taylor & Francis Group) and “Introduction to the Numerical Modeling of Groundwater and Geothermal Systems: Fundamentals of Mass, Energy and Solute Transport in Poroelastic Rocks”. He is editor of 18 books and editor of the book series “Multiphysics Modeling”, “Arsenic in the Environment”, “Sustainable Energy Developments” and “Sustainable Water Developments” (all CRC Press/Balkema, Taylor & Francis Group). Since 2015, he is an editor in chief of the Elsevier journal “Groundwater for Sustainable Development”.



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Barbara Tomaszewska (1971, Poland), finished her PhD degree in 2001 at the Faculty of Geology, Geophysics and Environmental Protection (Poland) in AGH – University of Science and Technology in Krakow. She has conducted broad ranging research in the area of changes within the aeration zone in soil and aquatic environments under the influence of atmospheric pollution and the migration of contaminants from landfill sites. Studies on spatial and temporal change in the quality of groundwaters and on pore solutions, focusing on specific indicators of pollution, including fluoride and boron ions, alongside other macro and micronutrients, have been presented in her thesis. Since December 2001, she has worked as the senior geology and environment inspector at the Mining District Authority in Krakow where she was working as supervisor of mining operations in the Małopolska region until February 2007. During that time, she had the opportunity to gain further knowledge on the practice of underground, open-cast and drilling operations. In March 2007, Dr. Tomaszewska joined the Department of Renewable Energy and Environmental Research at the Mineral and Energy Economy Research Institute, Polish Academy of Science (PAS MEERI) in Krakow, where she has held an independent researcher position until the present day. In 2011, Dr. Tomaszewska was awarded the Ministry of Environment's badge of honour "Zasłużony dla polskiej geologii" (For Merit in Polish Geology). She finished her habilitation procedure in 2013 on the basis of her important contribution to the development of Earth Science, especially in the field of Geology, which is found in eleven of her published papers which she decided to present under one heading: "Evaluation of the possibilities for the efficient utilisation of cooled geothermal waters for drinking and economic purposes". Since 2015, Dr. Tomaszewska has been a professor of hydrogeology and geothermics at the Faculty of Geology, Geophysics and Environmental Protection in the AGH – University of Science and Technology in Krakow, where she has been working in the broad field of water resources and low enthalpy geothermal resources, water and wastewater treatment and sustainable and renewable energy resources.

Her full specific research interests include: 1) monitoring the soil and aquatic environment and the assessment of the chemical condition of groundwaters, according to spatial and temporal perspectives; 2) the occurrence and consequences of increased boron concentration in water; 3) stability of the chemical composition of waters suitable for health treatment; 4) the impact of geological studies on the occurrence of health treatment and geothermal waters; 5) forecast and prevention of clogging in geothermal systems; 6) sustainable and efficient management of mineral resources as well as groundwaters in order to maintain the state of environment; 7) treatment of geothermal waters using selected membrane processes; 8) legal regulations in geology and protection of the environment.

Dr. Tomaszewska has conducted Poland's first research assessing the potential for treating cooled geothermal wastewaters for drinking and household purposes. She has been an author or co-author of ten books, among others "Atlas of the possible use of geothermal waters for combined

production of electricity and heat using binary systems in Poland”, “Atlas of geothermal waters and energy resources in the Western Carpathians” and “Geothermal Atlas of the Eastern Carpathians”, being editor or co-editor of four of them. One of these volumes was given an award by the Rector of the AGH – University of Science and Technology in Krakow. She has also contributed to, or cooperated with other authors in, publishing 29 chapters of larger publications and 104 papers for journals with national and worldwide availability. She has been actively contributing to work on practical applications, including as a co-author of a patent application. Furthermore she has been author or co-author of more than 100 confidential studies, including collective studies, expert opinions and research documentation within practical projects.

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*Section I*  
*Resources, geochemical properties and*  
*environmental implications of geothermal water*





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# CHAPTER 1

## A global assessment of geothermal resources

Marek Hajto & Anna Sowizdzal

### 1.1 INTRODUCTION

Geothermal energy is the internal heat of the earth that has accumulated in hydrothermal systems or in dry rocks within the earth's crust, in amounts which constitute energy resources. Thermal energy accumulated in hydrothermal systems or in hot dry rocks is available in enormous, practically inexhaustible reserves. At the same time, the distribution of this energy in the world is uneven and some resources are located at considerable depths, which makes the exploitation of huge energy reserves uneconomic at the current technological level.

Geothermal energy comes from the natural heat of the earth, primarily due to the decay of naturally occurring radioactive isotopes of uranium, thorium and potassium. Because of the internal heat, the earth's surface heat flow averages  $82 \text{ mW m}^{-2}$ , which amounts to a total heat of about 42 million megawatts. The total heat content of the earth is in the order of  $12.6 \times 10^{24} \text{ MJ}$ , and that of the crust is of the order of  $5.4 \times 10^{21} \text{ MJ}$  (Dickson and Fanelli, 2004).

Particularly favorable conditions for the formation of high-temperature geothermal systems, for example those potentially most suitable for industrial utilization, occur within the crustal plates, in rifts and in subduction zones (Fig. 1.1). Rifts are sites where hot magma ascends from the mantle. In subduction zones the crust is generated, along with intensive tectonic movements and volcanism. The geothermal potential of active plate boundaries is directly related to anomalous heat flow caused by intensive magmatism and volcanism. Most of the prospective geothermal fields related to high-temperature systems occur within the plate marginal zones. In such zones reserves of water/steam at temperatures above  $150^\circ\text{C}$  occur at depths from several hundreds to several thousands of meters. Their manifestations at the surface are hot springs and geysers.

Most of the plate boundaries are below sea level, but in cases where the volcanic activity has been intensive enough to build islands or where active plate boundaries transect continents, high-temperature geothermal fields are scattered along the boundaries. A spectacular example of this is the "ring of fire" that surrounds the Pacific Ocean (the Pacific Plate) with intense volcanism and geothermal activity. Other examples are Iceland, which is located on the Mid-Atlantic Ridge plate boundary, the East African Rift Valley and "hot spots" such as Hawaii and Yellowstone (WEC, 2013). Reservoirs accumulating relevant steam reserves are utilized in many countries for power generation in geothermal plants.

Low-temperature systems are more common and cover much larger areas in comparison to high-temperature ones. These systems contain water with temperatures below  $150^\circ\text{C}$ . The heat source is mainly the earth's natural heat flux. In most countries, geothermal waters are exploited mainly for direct use (heat production, recreation, etc.). In the areas of low-temperature systems accumulating hot waters of temperatures over  $85^\circ\text{C}$ , such as those in the Polish Lowlands, electricity generation is possible on the basis of the Rankine cycle (Górecki *et al.*, 2006a, 2006b).

Substantial quantities of energy are included in hot dry rocks, which do not contain water or vapor, but are reservoirs of heat. Such rocks are associated with rift zones, subduction zones and with other areas within continents. In some areas, it is possible to obtain geothermal energy for electricity generation.

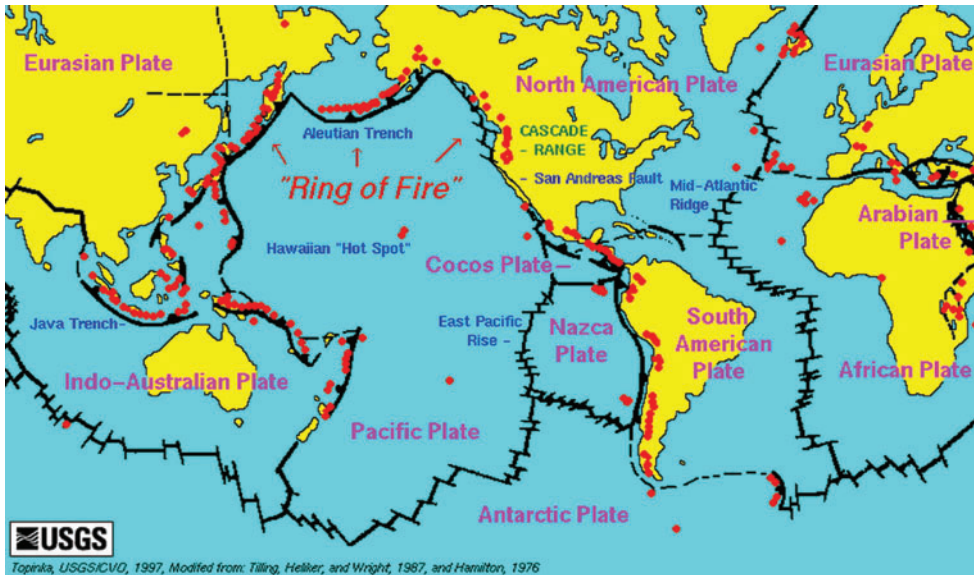


Figure 1.1. World map showing the lithospheric plate boundaries (USGS, 2016).

## 1.2 DEFINITIONS AND CLASSIFICATION OF GEOTHERMAL RESOURCES

### 1.2.1 *Definitions of geothermal energy and geothermal resources*

Unfortunately, there is no standard international terminology in use throughout the geothermal community, which would facilitate mutual comprehension between estimated resources. Lack of global standardization can be caused also by a different understanding of what are “geothermal energy” and “geothermal resources”. An overview of legal and regulatory frameworks and legal acts in the field of geothermal energy in Europe and the wider world indicates that they can vary in many respects between countries, and even within them (Haraldsson, 2012).

The differences can be seen when existing definitions of geothermal energy and geothermal resources are taken into consideration. These differences result mainly from how the geothermal energy is defined, who has ownership of geothermal resources, and what kind of legislation governs the aspects relating to the use of geothermal resources. From this point of view, existing definitions can be classified into three categories (Haraldsson, 2012):

- a part of the mineral estate, handled by mineral legislation (usually mining law);
- as water resources, handled by water legislation;
- resources unique in themselves.

The term “geothermal energy” is commonly used nowadays, even throughout the geothermal community, to indicate that part of the earth’s heat that can, or could, be recovered and exploited by man, although worldwide legislation very often refers also to “geothermal resources”. As an example, in EU countries there exists a term “geothermal energy”, which is given definition in Article 2(c) of the RES Directive 2009/28/EC. According to the aforementioned formal regulations: “*geothermal energy means energy stored in the form of heat beneath the surface of solid earth*”.

Germany uses the definition which applies in the EU. Geothermal energy is the energy stored beneath the surface of the solid earth in the form of heat (VDI, 2012). Synonyms include

geothermal heat (BMW, 2014). Geothermal resources in Germany belong to the mining estate and the legal standard is the Federal Mining Act (*Bundesberggesetz*). Laws exist both at the federal level (Bund) and at the state level (Länder) (Agemar *et al.*, 2014). The utilization of shallow geothermal energy (e.g. by heat pumps) is mainly subject to water laws and those can differ between the German federal states (Gassner, 2010).

In Italy, in contrast to the German legal system, there are laws that exclusively regulate the use of geothermal energy. The most important of these rules is the Legislative Decree 22 of 11/02/2010. The geothermal resource in Italy is not owned by the surface owner, but by the central and regional governments. Furthermore, a subdivision of the geothermal resources is provided in various types of deposits, after which the property status is defined (Dumas *et al.*, 2013).

The Icelandic Act on the “Survey and Utilization of Ground Resources” defines geothermal energy as reserves of energy in the bedrock on one hand, and on the other, a constant flow of heat from the depths of the earth which does not constitute groundwater (Parliament of Iceland, 1998). While this definition treats geothermal energy as unique in itself, it is categorized by the act as a ground resource along with minerals and groundwater.

In French legal regulations, geothermal deposits are classified as “mines” according to Article 3 of the mining code (1st Article of Law 77–620 of 16 June 1977) (EGEC, 2012).

In Poland, according to the legislation only the term “thermal water” exists. There is no clear definition of “geothermal energy”, especially in the context of heat pump use and “geothermal resources”, nor any methodology for its assessment. Thermal water is a mineral product and comes under the Geological and Mining Law of 2011 (PGG, 2016). Its temperature is, by definition, 20°C at the outflow from a well or spring (Article 5, Section 2.2), while, in accordance with this act (Article 5, Section 4), the waters draining from mining excavations are not “thermal waters”. Furthermore, when Poland considers water injection, the Water Law and some provisions of the Environmental Protection Act are also applicable.

In the US, where the use of geothermal energy and legal regulation in that field has a long history, “geothermal resources” were defined in the early 1970s (Geothermal Steam Act of 1970). The provisions of the act are found under 30 USCS §1001 through 1027. The act regulates, among others, the principles related to the development and conservation of geothermal steam and associated geothermal resources, the prevention of waste and protection of the public interest, the protection of water quality, and other environmental qualities. According to section 270.2(g) of the act, “geothermal resources” were defined as: (i) all products of geothermal processes, embracing indigenous steam, hot water and hot brines; (ii) steam and other gases, hot water and hot brines resulting from water, gas, or other fluids artificially introduced into geothermal formations; (iii) heat or other associated energy found in geothermal formations; and (iv) any byproduct derived from them. Nowadays in the US, the definition of “geothermal resources” is regulated by 30 USCS §1001 and 1102. In parallel, geothermal energy production and use are governed by numerous federal, state, and local laws ranging from environmental protection statutes to zoning regulations (including, for example, specific laws and regulations applicable to geothermal energy development on tribal lands). Unique laws at the federal and state level also govern the leasing and permitting of geothermal resources on federal and state land. One of the early state attempts to introduce specific geothermal legislation was the California Geothermal Resources Act of 1967 (Miethling, 2011). Moreover, states have their own definitions of geothermal resources, which differ from state to state. More detailed information of selected states can be found in Reed and Bloomquist (1995) and Callison (2010).

In Australia, too, there are no clear rules regarding the geothermal energy sector. In South Australia and Western Australia, the situation has much in common with the mining of petroleum. In New South Wales and Tasmania, a geothermal resource is defined as a mineral and is regulated under mining legislation, and in Queensland, Victoria and the Northern Territory, geothermal energy is regulated by a dedicated act (Collyer *et al.*, 2010; Haraldsson, 2012).

To conclude, it must be emphasized that the differentiated understandings of the nature of geothermal energy, arising from cultural factors, the nature of geothermal resources

(steam, hydrothermal, petrothermal) and the possibility of their use for heating, electricity production and other things, means that different definitions of geothermal water, geothermal energy and geothermal resources exist in different countries on a global scale.

### 1.2.2 *Classification of geothermal resources*

Resource classification is a key aspect of the characterization, assessment, reporting and development of overall energy resources, including geothermal energy.

Terminology must cover both the fundamentally geological nature of geothermal resources and the practical technological and economic aspects of resource exploitation to remain understandable to the broad community as well as non-specialists (Williams *et al.*, 2011).

For decades, classification of resources has been an integral part of comprehensive efforts within the framework of regular geothermal surveys. The first works aiming to classify geothermal resources were published in the US at the beginning of the 1960s and 1970s (e.g. Grossling, 1972; Hickel, 1973; Kruger and Otte, 1973; Nathenson and Muffler, 1975; Rex and Howell, 1973; White, 1965; White and Williams, 1975; White *et al.*, 1971) and were continued by, for example, Muffler (1979) and Reed (1983). These reports evaluated various methodologies for geothermal resource assessments and provided estimates of potential electric power generation and associated production of heat.

Parallel research aimed at the normalization of rules for classification of geothermal resources, and the methodology of their evaluation, was carried out in Italy. A leading role in this regard was played by the Geothermal Research Center of the National Electric Agency of Italy (ENEL), which has prepared an appraisal of the pre-Apennine belt from Pisa to Naples (Batelli *et al.*, 1975).

The milestone in the subject of classification and development of methodology of geothermal resources evaluation was published by Muffler and Cataldi (1978). The characterization and assessment methods presented in the paper are fundamental also to the recent resource assessment. Some approaches including in particular the basic framework for the classification of geothermal resources have continued to be in use until the present.

Most of the concepts regarding classification and assessment of geothermal resources that have assumed geothermal as “mineral” make reference to classifications and terminology derived from the mining industry, including mineral and fossil fuels (coal and petroleum as well). These methods usually describe the quantity or volume of valuable materials in the earth that can be excavated on the surface with intrinsic economic interest. The authors emphasize that the uniqueness and specificity of geothermal phenomena imply that when terminology is applied to mineral resources, several assumptions must be taken into consideration, for example, the commodity to be extracted is thermal energy, rather than a substance only subsequently to be converted to thermal energy, thermal energy is contained in rock (itself a multicomponent mixture) and in fluids (water, steam and noncondensable gases), only part of the thermal energy is recoverable (even at depths reachable by drilling), some of the thermal energy may be replaced or renewed from greater depths, and this possible replacement is accelerated by the extraction process itself (Muffler and Cataldi, 1978). Elaborated at that time, this classification is still in use worldwide, regard being given to only minor corrections relating to the terminology used in individual countries.

According to the main concept of the classification, geothermal resources were divided into degree of economic feasibility (vertical axis) and degree of geologic assurance (horizontal axis), following the scheme of McKelvey (1972). Classification of geothermal resources with derivation of particular resource classes is shown in Figure 1.2.

The following are definitions of the basic concepts and terms, essential to understand the structure and meaning of the worldwide used classification of geothermal resources:

- Geothermal resource base (GRB) – all of the geothermal energy in the earth’s crust beneath a specified area, referenced to local mean annual temperature. It refers to an instant in time, neglects transfer of heat from mantle, and takes no regard of whether or not it would ever be technically or economically feasible to recover the geothermal energy;

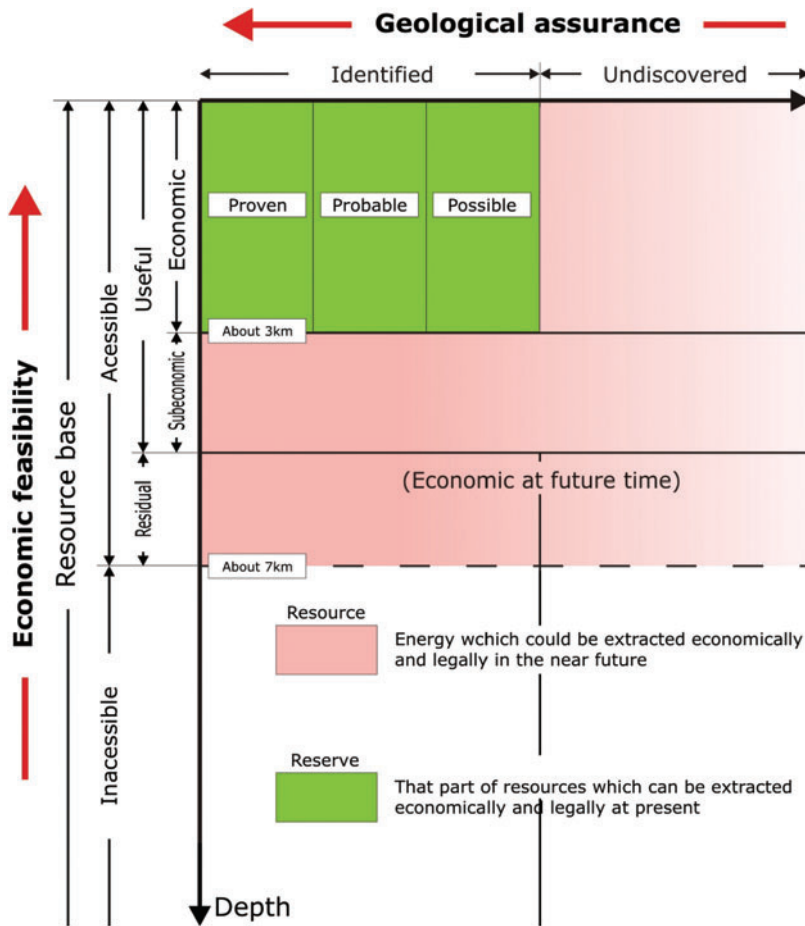


Figure 1.2. McKelvey diagram for geothermal energy showing derivation of particular resource classes (based on McKelvey, 1972).

- Geothermal resource (=useful accessible resource base) (RESOURCE) – fraction of the accessible resource base that could be extracted economically and legally at some reasonable future time. It can be subdivided into sub-classes in a subjective aggregate of predicted technology and economics at some reasonable and specified future time  $\leq 100$  years;
- Inaccessible resource base (IRB) – all of the geothermal energy stored between the base of the crust and a specified depth in the crust, beneath a specified area and referenced to local mean annual temperature. It refers to an instant in time, and neglects transfer of heat from mantle. Depth chosen for the upper limit is a matter of convenience, but must be specified in each case. IRB implies that geothermal energy beneath the specified depth is unlikely to be tapped by production drilling at a reasonable time in the future;
- Accessible resource base (ARB) – all of the geothermal energy between the earth's surface and a specified depth in the crust, beneath a specified area and referenced to local mean annual temperature. It refers to an instant in time, and neglects transfer of heat from deeper levels. Depth chosen for the upper limit is a matter of convenience, but must be specified in each case. ARB implies that geothermal energy beneath the specified depth is unlikely to be tapped by production drilling at a reasonable time in the future;

- Residual accessible resource base (RARB) – part of the accessible resource base unlikely to be extracted economically and legally at some specified time in the future. It can be subdivided into sub-classes in a subjective aggregate of predicted technology and economics at some reasonable and specified future time;
- Subeconomic resource (SER) – part of the resource of a given area that cannot be extracted legally at a cost competitive with other commercial energy sources at the time of determination, but might be extracted economically and legally at some specified time in the future;
- Economic resource (ER) – part of the resource of a given area that can be extracted legally at a cost competitive with other commercial energy sources at the time of determination;
- Undiscovered economic resource (UER) – part of the economic resource in unexplored parts of regions known to contain geothermal resources, or in regions where geothermal resources are suspected but not yet discovered;
- Identified economic resource (RESERVE) – part of the economic resource known and characterized by drilling or by geochemical, geophysical and geological evidence.

Classification of geothermal resources based on the McKelvey diagram is widely used and appreciated within the geothermal community, including the International Geothermal Association (IGA), the European Geothermal Energy Council (EGEC), and other organizations of practitioners and researchers dealing with estimation of geothermal potential and assessment of possibility of using geothermal energy to produce electricity and for heat purposes. The classification and terminology were adapted by the EU standards and used for resources assessment of EU countries (Haenel and Staroste, 1988; Hurter and Haenel, 2002). In some countries, for example in Poland, the classification was modified in order to include traditional terminology and definitions applied in the country.

Instead of the classification shown in the McKelvey diagram, which defines a framework and principles for resources assessment, many other different classifications exist. The most commonly applied classification criterion is the temperature of geothermal fluids that act as the carrier transporting heat from the deep hot rocks to the surface. Enthalpy, which can be considered more or less proportional to temperature, is used to express the heat (thermal energy) content of the fluids, and gives a rough idea of their “value” (Dickson and Fanelli, 2004).

Classification based on energetic value – temperature (enthalpy) enables one to distinguish a variety of *geothermal systems*, which are characterized by the dominant presence of specific geothermal resources related to: hot water, steam, hot dry rocks or geopressure.

A summary of classifications applied in the world literature is shown in Table 1.1.

Practically, those classifications are based upon the energetic value of geothermal resources with regards to possible direction of its use for electricity generation or for direct heating purposes. Generally, according to assumed division, geothermal systems can be divided into: low, intermediate and high enthalpy, and associated types of geothermal resources (low, medium and high enthalpy). The diversification of temperature boundaries among particular classes (types) results both from the level of technical knowledge and from the ability to use of certain types of geothermal resources for production of electricity or heat as well. International growth of the geothermal industry and technology, and more detailed understanding of geologic and tectonic processes foster the potential development of new types of resources, for example the enhanced geothermal system (EGS), which refers to an underground reservoir that has been created or improved artificially.

Newly established classifications are usually faced with new requirements of technology, legal frameworks and licensing rules. Also, their application depends on the targeted geothermal resource (e.g. shallow or deep geothermal).

The most common and widely used temperature classification of geothermal systems relates to the classification of Muffler and Cataldi (1978) (Table 1.1). In Europe, the most popular classification divides geothermal systems into two categories: low- and high-temperature (enthalpy) (Kepińska *et al.*, 2014; Nicholson, 1993; Rowley, 1982).

Table 1.1. Example classifications of geothermal resources by temperature and enthalpy.

Geothermal resources	Geothermal medium temperature [°C]							
	(a)	(b)	(c)	(d)	(e)	(f)		
Low-enthalpy resources	<90	<125	<100	≤150	≤190	Non-electrical	<100	
						Very low temperature	100–150	
						Low temperature	150–190	
Intermediate-enthalpy resources	90–150	125–225	100–200	–	–	Moderate	190–230	
High-enthalpy resources	>150	>225	>200	>150	>190	High temperature	230–300	
						Ultra-high temperature	300+	
						Steam field	240 (3.35 MPa pressure; 2800 kJ kg <sup>−1</sup> enthalpy)	

(a) Muffler and Cataldi (1978); (b) Hochstein (1990); (c) Benderitter and Cormy (1990); (d) Rowley (1982), Nicholson (1993); (e) Axelsson and Gunnlaugsson (2000); (f) Sanyal (2005).

High-temperature systems include both liquid- and vapor-dominated resources. Moderate-temperature systems are almost exclusively liquid-dominated. The heat source of the systems comes mainly from magma in magma chambers located at shallow depth (reaching the surface as lava during volcanic eruption). Low-temperature systems are liquid-dominated, where hydrogeothermal reservoirs are present. Heat sources are mainly due to the natural earth's heat flux. Low-temperature systems and related hydrogeothermal reservoirs occupy much larger areas of the world.

All three temperature classes are suitable for direct-use applications, but in general moderate- and high-temperature systems are viable for electric power generation. Additionally, low temperature range systems can be exploited for electric power generation if sufficiently low temperatures are available for cooling the working fluid in a binary power plant.

However, it must be emphasized that temperature is acceptable as a classification parameter only for its simplicity and for being a measure quantity. Take for example, as discussed by Lee (1996), two geothermal resources both at 200°C, but where one is saturated water and one saturated steam. Both are classified as intermediate-enthalpy resources by Hochstein (1990), although high-enthalpy by others, but the specific enthalpy of saturated steam is three times that of saturated water. Indeed, the steam is five times “better” than the water in its ability to do work. That is, the steam can produce five times more power than the water, per unit mass (Lee, 1996).

There are other, more complex classifications which characterize geothermal systems by additional attributes important for practical utilization of geothermal energy, such as: steam fraction in the mobile fluid phase in the reservoir, type of power generation technology applicable, production mechanism and the state of the fluid at the wellhead, high content of non-condensable gases. An example of such a classification has been discussed by Sanyal (2005).

Due to the form of storage of energy accumulated in the earth's crust, geothermal systems (geothermal resource types) can be classified into the following groups (White and Williams, 1975 – modified):

- hydrogeothermal convection – (a) vapor-dominated, (b) hot water systems – the energy carrier is hot groundwater produced with the wells. Vapor-dominated systems are well known from: Larderello, Italy, and The Geysers, California (White and Williams, 1975). Many regions throughout the world are characterized by deep basins filled with sedimentary rocks of high



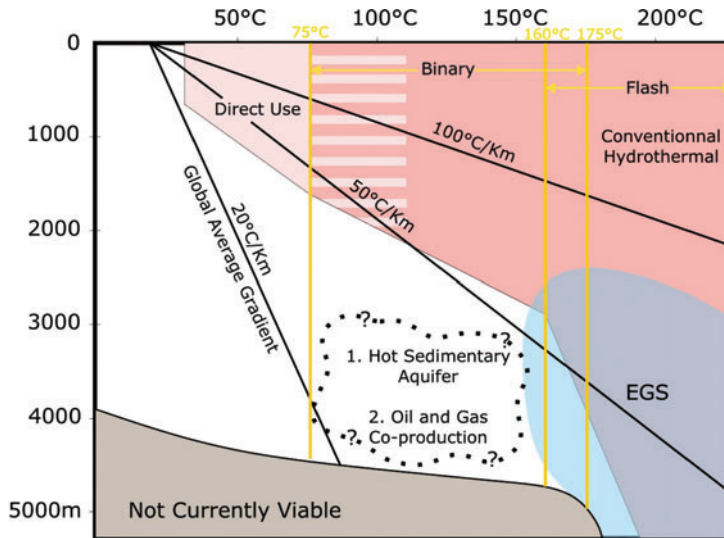


Figure 1.3. Schematic depth-temperature plot for geothermal resources (EGS, 2016).

porosity and permeability. If these are properly isolated from surface groundwater by impermeable strata (caprock), the water in the sediments is heated by the regional heat flow. The geothermal reservoirs in the sedimentary basins can be very extensive, as the basins themselves are commonly hundreds of kilometers in diameter. The temperature of the thermal water depends on the depth of the individual aquifers and the geothermal gradient in the area concerned, but is commonly in the range of 50–100°C (in wells less than 3 km deep) in areas that have been exploited. Geothermal resources of this type are rarely seen on the surface, but are commonly detected during deep drilling for oil and gas. Hot-water systems are well known in Europe, for example, the Pannonian Basin (Hungary, Slovakia, Romania), the North European Basin (North German Basin, Polish Lowlands Basin, Paris Basin), the Aquitaine Basin in southwest France, and the South German Molasse Basin;

- petrogeothermal – for which the energy carriers are media (usually water) injected through wells into the hot rock formations (so-called hot dry rocks (HDR)) and salt diapirs;
- geopressed (conduction-dominated) – which is hydraulic energy accumulated in the earth's crust, in fluids subjected to lithostatic pressure higher than normal, hydrostatic pressure (e.g. dissolved methane);
- igneous-related – where sources of geothermal energy are magma bodies or intrusions penetrating the fault zones and heating both the enclosing rock formations and the infiltrating meteoric waters;
- new developments: drilling for higher temperatures – production wells in high-temperature fields are commonly 1.5–2.5 km deep and the production temperature 250–340°C. The energy output from individual wells is highly variable, depending on the flow rate and the enthalpy (heat content) of the fluid, but is commonly in the range of 5–10 MWe and rarely over 15 MWe per well (Fridleifsson *et al.*, 2007). Producing supercritical fluids requires drilling wells, sampling fluids and rocks to depths of 3.5–5 km, and at temperatures of 450–600°C (WEC, 2013).

A schematic depth-temperature plot comprising location of distinguished geothermal systems and related geothermal resources is shown on Figure 1.3.

Distinction of these geothermal systems, supplemented with definition of dominant type of energy stored in the system and detailed analysis and description of the main geothermal parameters, may determine the most appropriate methods for estimating energy resources.

### 1.3 METHODS OF REGIONAL ASSESSMENT OF GEOTHERMAL RESOURCES

*“Geothermal resource assessment can be defined as the broadly-based estimation of supplies of geothermal energy that might become available for use, given reasonable assumptions about technology, economics, governmental policy, and environmental constraints”* (Muffler and Christiansen, 1978).

This assessment implies not merely the determination of how geothermal energy is distributed in the upper part of the earth's crust but also the evaluation of how much of this energy could be extracted for man's use. A resource assessment is regional or national in scope and thus provides a framework for long-term energy policy and strategy decisions by industry and government. A resource assessment is intended to give an overall perspective at a particular time, using uniform methodology and data (Muffler and Guffanti, 1978).

Methods for assessing geothermal resources can be grouped into four classes (Muffler and Cataldi, 1978):

- surface thermal flux – method is conceptually the simplest. It is based on the calculation of thermal energy that, in a given unit of time, is transferred from the soil to the atmosphere and surface waters by means of conductive heat flow and thermal effluents from springs, fumaroles, etc.
- planar fracture – method was developed by Bodvarsson (1951, 1962, 1970) primarily for use in the flat-lying, late Cenozoic basalts of Iceland. The method is presented systematically as the “single fracture method” in Bodvarsson (1974), with additional computational details being found in Bodvarsson (1970, 1972). The model used in the planar fracture method consists of a planar fracture in otherwise impermeable rock. Heat is transferred to the fracture by conduction and along the fracture by means of flowing water. Using a synthesis of Bodvarsson's symbology,  $t_0$  is the initial temperature of the rock and  $T_r$  is the temperature of recharge water entering the fracture. The temperature of the outflow water will decrease from  $T$  at the beginning of fluid extraction to a minimum temperature ( $T_m$ ) after a production period ( $t_0$ ). Using classical heat-conduction theory, Bodvarsson (1974) calculates the heat theoretically extractable per unit fracture area, as a function of  $T$  and of the “end temperature ratio”. Bodvarsson emphasizes that according to the above assumptions we obtain theoretical values for extractable thermal energy, and that these values must be reduced substantially in real field situations. The planar fracture model can be extended to multiple fractures (Bodvarsson, 1974; Nathenson, 1975). The planar fracture method, and in particular its multiple-fracture variant, can readily be applied to a sequence of gently dipping basalt flows, where the subsurface fracture geometry is simple and predictable with confidence. More details can be found at the literature.
- magmatic heat budget – method is based on the fact that, in volcanic areas, magma is being supplied intermittently to the upper crust. Much of this magma passes through the upper crust and is erupted on the surface as volcanic rocks. A fraction of the magma, however, lodges in the upper crust as igneous intrusions, which either act as heat sources for overlying geothermal systems or are themselves targets for exploration and development. Accordingly, an estimate of the number, size, position and age of young igneous intrusions, combined with an analysis of the cooling history, provides a means of estimating the geothermal potential of a region or even of a specific restricted area. By its very nature, this method does not provide a precise categorization of resources, but gives a broad overview of the accessible resource base; inherently, the method gives little quantitative insight into the fraction of this resource base that might be recoverable. Noguchi (1970) has estimated the geothermal resources of Japan using a variant of the magma thermal budget method. Smith and Shaw (1975) have analyzed the resource base associated with young intrusive rocks in the United States. They consider that basic magmas usually rise directly to the earth's surface without forming magma chambers at high levels in the crust, but that more silicic magmas do form storage chambers in the upper 10 km of the crust. Hence, their approach is to estimate the volumes of these silicic magma chambers, to estimate their age of emplacement, and to calculate the amount of

geothermal energy still remaining in the intrusion and adjacent country rock using conventional calculations of conductive heat loss.

- volume method – method uses estimates of subsurface temperature, volume, specific heat and density to calculate the *accessible resource base*, multiplying the resultant value by a *recovery factor* to get the *recoverable thermal energy*. Methodology of assessment is similar to methods used commonly in petroleum and mineral resource estimation. Accordingly, of all the methods described above, the volume method tends itself to be best for the assessment of individual *hydrothermal convection systems*. More detailed description of the principles and methodology of the method is provided in Section 1.3.1.

### 1.3.1 Volume method of resource assessment

The basics of the volume method has been discussed in detail (Górecki *et al.*, 1995, 2006a, 2006b, 2011, 2012, 2013; Gosk *et al.*, 1982; Gringarten, 1978; Gringarten and Sauty, 1975; Haenel and Staroste, 1988; Haenel *et al.*, 1988; Hurter and Haenel, 2002; Koppe *et al.*, 1983; Lovekin, 2004; Muffler, 1979; Muffler and Cataldi, 1978; Nathenson and Muffler, 1975; Sorey *et al.*, 1983; Williams, 2004).

Due to the broad application of this method and numerous publications considering various aspects of its application, only a brief summary of the relevant aspects of the methodology for estimation of geothermal resources used in Europe for the low-temperature (enthalpy) hydrogeothermal convection systems has been presented.

To simplify, the methodology for estimating of geothermal resources used in Europe for low-temperature geothermal systems, related to hydrogeothermal has been presented. The methodology of geological resources estimation was based upon the EU standards available, for example, in the Atlas of geothermal resources in the European Community (Haenel and Staroste, 1988) and the Atlas of geothermal resources in Europe (Hurter and Haenel, 2002).

The challenge in the resource assessment lies in quantifying the size and thermal energy of a reservoir as well as the constraints on extracting that thermal energy. Under typical conditions, fluid extraction is governed by the hydraulic conductivity or transmissivity. Determination of aforementioned hydrogeological factors during regional exploration is rather difficult, especially when we deal with oil and gas borehole data, usually with poor, hydrogeological documentation, including lack of the pumping test results. In contrast to poor hydrogeological documentation, oil and gas boreholes are well documented when considering petrophysical parameters, in particular the effective porosity of the rock.

- Thus, in the volume method, to obtain an estimate of the total heat content of an area at drillable depth, the *ARB* down to a given depth (e.g. 7 km depth\*) could be calculated as:

$$ARB = V_s \rho_s c_s \frac{T_h - T_o}{2A} \quad [\text{J m}^{-2}] \quad (1.1)$$

where:

$V_s$ : volume of rocks from the earth's surface down to 7000 m depth [ $\text{m}^3$ ]

$\rho_s$ : mean density of rocks down to 7000 m depth [ $\text{kg m}^{-3}$ ]

$c_s$ : mean specific heat capacity of rocks down to 7000 m depth [ $\text{J kg}^{-1} \text{ } ^\circ\text{C}^{-1}$ ]

$T_h$ : temperature at 7000 m depth or at the top surface of crystalline basement [ $^\circ\text{C}$ ]

$T_o$ : mean annual temperature at the earth's surface [ $^\circ\text{C}$ ]

$A$ : area of calculation block [ $\text{m}^2$ ].

According to Poland terminology, we call it *accessible resources*.

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\*from a practical point of view and availability of drilling data the resource estimation might be limited to 3 km.

- The *heat in place* contained within a given aquifer can be determined after Muffler and Cataldi (1978) as:

$$H_o = Am_p \cdot [(1 - p_e)\rho_r c_r + p_e \rho_w c_w] \cdot (T_s - T_o) \quad [\text{J}] \quad (1.2)$$

where:

- $m_p$ : cumulative thickness of groundwater horizons in the reservoir [m]
- $p_e$ : effective porosity [–]
- $T_s$ : temperature at the top surface of groundwater reservoir [°C]
- $T_o$ : mean annual temperature at the Earth's surface [°C]
- $\rho_r$  and  $\rho_w$ : mean density of rock framework and water, respectively [ $\text{kg m}^{-3}$ ]
- $c_r$  and  $c_w$ : mean specific heat of rock framework and water, respectively [ $\text{J kg}^{-1} \text{ } ^\circ\text{C}^{-1}$ ]
- $A$ : area of calculation block [ $\text{m}^2$ ].

The *heat in place* (*static resources*) resource of geothermal energy are the amounts of free (gravitational) geothermal water hosted in pores, fractures or caverns of given hydrogeothermal horizon, expressed in [ $\text{m}^3$ ] or [ $\text{km}^3$ ] and energy stored in the rock framework, recalculated into the energy units [J].

In Poland, the *heat in place resources* are referred to as *static resources*. These resources are calculated if the recognition of continuous groundwater reservoirs or horizons is possible in the given area. Based on determined properties of groundwater horizons (lithology, thickness, porosity and permeability), the identification of producing reservoirs and horizons is possible. It can be concluded from this formula that  $H_o$  is a total amount of heat accumulated in free water and in rock framework, with reference to the given area of calculation. According to Muffler and Cataldi (1978), in nearly all reservoirs roughly 90% of the geothermal energy is contained in the rock and only 10% in the water.

- **recoverable geothermal energy** – constitute only a part of the *heat in place* diminished by the recovery index  $R_o$ , expressed in [ $\text{m}^3$ ] or [ $\text{km}^3$ ], recalculated into the energy units [J]. *Recoverable geothermal energy* resources are a part of the *heat in place* of a given groundwater reservoir or horizon, which can be produced with the given exploitation systems: either doublet (or triplet, etc.) systems (production and injection wells) in which extracted geothermal water is injected back into the reservoir or horizon after heat recovery, or single systems (production well) in which the geothermal waters extracted are not returned to the reservoir. It is applied for geothermal reservoirs or their fragments in which fresh or low-TDS (total dissolved solids) waters occur. Usually in deep wells (e.g. in the Polish Lowlands Basin) where high-TDS groundwaters occur, the *recoverable geothermal energy* resources were calculated for a doublet system. The recoverable part of geological resources is represented as the recovery index  $R_o$  of thermal energy from the given reservoir or horizon. For geothermal doublet, this parameter is calculated from the following formula (Lavigne, 1978):

$$R_o = \frac{A_{\text{cool}}}{A_{\text{tot}}} \frac{T_{\text{top}} - T_{\text{inj}}}{T_{\text{top}} - T_o} \quad [-] \quad (1.3)$$

where:

- $A_{\text{cool}}$ : cooled area of the doublet [ $\text{m}^2$ ]
- $A_{\text{tot}}$ : total area affected by the doublet [ $\text{m}^2$ ]
- $T_{\text{top}}$ : temperature at the top surface of groundwater horizon [°C]
- $T_{\text{inj}}$ : temperature of water injected back to the horizon (=25°C)
- $T_o$ : mean annual temperature at the earth's surface [°C].

The ratio of cooled area to total area affected by geothermal doublet was taken as an empirical constant value based upon long-term experience gained from the operating geothermal installations in the Paris Basin (France). The following, simplified values of this parameter were taken for calculations: for geothermal doublet  $R_o = 0.33$ . If a production well alone, without reinjection, is considered (a singlet), the recovery factor is  $R_o = 0.1$  (Gringarten, 1978).

The  $R_o$  allows the expression of recoverable geothermal energy as a percentage of the thermal energy contained in a given subsurface volume. The geothermal recovery factor in most cases is poorly known, and usually can only be estimated subjectively. It depends on many items, the most important of which seem to be: the type of geothermal system (hydrothermal convection, geopressured, conduction-dominated, magma), porosity, nature of fluid in pores, reservoir temperature, and extraction technology.

Recoverable geothermal energy resources ( $H_1$ ) can be calculated according to the following formula:

$$H_1 = H_o R_o \quad [\text{J}] \quad (1.4)$$

where:

$R_o$ : recovery index

$H_o$ : heat in place (*static resources*) [J].

Recoverable geothermal energy resources are also known from literature as static-recoverable geothermal resources (Górecki *et al.*, 1995, 2011, 2006b; Hajto, 2006a, 2006b, 2013; Hajto and Górecki, 2010, 2013; Hajto and Kotyza, 2012; Hajto *et al.*, 2011, 2012; Kuźniak and Hajto, 2006a).

As mentioned before, only a part of the geothermal energy resources can be exploited economically at present. The proven reserves at wellhead, commonly abbreviated as “RESERVES”, depends on site-specific geological conditions, as well as on the cost of drilling, installation and the other economic factors including the cost of alternative sources of energy, which when economically reasonable can be replaced by geothermal source.

### 1.3.2 *Economic evaluation of hydrogeothermal aquifers*

Reserves of geothermal energy of given aquifer constitute an assessed part of recoverable geothermal energy, which utilization is efficient from an economic point of view. Estimation of disposable reserves requires the effectiveness analysis of geothermal energy use in order to select those parts of geothermal aquifer where exploitation of thermal energy will be cost-effective. The methodology of economic evaluation of geothermal resources in regional scale assessment is presented. It must be emphasized that, although financial criteria are crucial for investment decisions, these are not always the only factors considered during evaluation of geothermal reservoir, particularly if infrastructural investments are discussed, which stimulate development of various existing and new environmentally friendly branches of the local economy. However, additional social and economic benefits can be known in detail, not earlier than during the analysis of a particular investment project, whereas the regional analyzes should instead provide information on potentially most profitable localizations of future investments.

Principal factors affecting the economic effectiveness of geothermal energy can be categorized into three groups:

- reservoir properties;
- utilization modes of extracted heat;
- social and economic constraints.

Properties of hydrogeothermal aquifers are controlled by geological and hydrogeological factors, which values are objective and constant. On the contrary, the remaining two categories are only partly and indirectly dependent (in most cases independent) on reservoir properties.

Taking into account specific assumptions and identifying relationships between the variables, it is possible to present the economic effectiveness of geothermal energy exploitation in particular aquifer as a function of only its reservoir properties. Determination of investment expenditures, production costs of installation and recovery of accumulated thermal energy in respect to reservoir properties of a hydrogeothermal aquifer leads to the selection of a criterion, which can

justify the incipient decision on exploitation of the reservoir. The resulting mathematical formulae should consider those reservoir properties which decisively influence the economic efficiency, for example:

- hydraulic transmissivity of rocks – which determines the capacity of rocks to convey fluids and which influences the power of production and injection pumps;
- temperature of produced geothermal water – which controls the thermal power of heating installation;
- depth to geothermal reservoir – which decisively controls drilling costs, that is, the main component of investment expenditures.

In order to assess the resources of geothermal aquifer, these properties can be expressed as a dimensionless coefficient, so-called “power factor”, given by the following formula (Gosk, 1982):

$$F = \frac{\text{effective power output}}{\text{equivalent thermal power}} = \frac{P_{\text{out}}}{P_{\text{inp}}} \quad [-] \quad (1.5)$$

Effective power output – it is assumed that effective power output corresponds to mean annual thermal power of geothermal waters intake (=geothermal installation, understood here as a set of devices enabling production of geothermal waters and recovery of accumulated heat), which is given by the following formula:

$$P_{\text{out}} = LF Q q_w c_w (T - T_{\text{inj}}) \quad [\text{W}] \quad (1.6)$$

where:

$LF$ : mean annual load factor of an intake

$Q$ : rated discharge of geothermal water [ $\text{m}^3 \text{s}^{-1}$ ]

$\rho_w$ : density of geothermal water [ $\text{kg m}^{-3}$ ]

$c_w$ : specific heat of geothermal water [ $\text{J kg}^{-1} \text{°C}^{-1}$ ]

$T$ : temperature of produced geothermal water [ $\text{°C}$ ]

$T_{\text{inj}}$ : temperature of waste water (e.g. geothermal water after heat recovery) [ $\text{°C}$ ].

Mean annual load factor of an intake ( $LF$ ) reflects the degree to which rated thermal power of a geothermal intake is utilized. Its value depends on planned system of heat utilization and falls into the range 0 to 1. The  $LF = 1$  corresponds to continuous operation of an intake at constant, rated thermal power. Assuming some parameters and constants ( $\rho_w c_w = 4.1 \text{ MJ kg}^{-1} \text{°C}^{-1}$ ) and assuming the temperature of injected water as  $25\text{°C}$ , the effective power output can be expressed as:

$$P_{\text{out}} = 1.14 \times 10^{-3} LF Q (T - T_{\text{inj}}) \quad [\text{W}] \quad (1.7)$$

If  $LF = 1$ , the rated thermal power of geothermal waters intake (=geothermal installation) is:

$$P_{\text{out}} = 1.14 \times 10^{-3} Q (T - T_{\text{inj}}) \quad [\text{W}] \quad (1.8)$$

- Equivalent thermal power – equivalent energy input corresponds to capital expenditures required for construction of geothermal waters intake and its running cost, expressed as an equivalent of thermal power. It can be interpreted as the amount of heat which can be recovered in time unit if given financial resources were used for construction and operation of an alternative energy source:

$$P_{\text{inp}} = 3.17 \times 10^{-8} \left( \frac{I}{t} \right) + \frac{K_a W}{CP} \quad [\text{W}] \quad (1.9)$$

where:

$I$ : total capital expenditures spent for geothermal waters intake [US\$]

- $T$ : life time of installation in years (25 years was taken for calculations)  
 $I/t$ : annual investment expenditures [US\$ year<sup>-1</sup>]  
 $K_a$ : annual running costs of geothermal doublet [US\$ year<sup>-1</sup>]  
 $W$ : calorific value of alternative fossil fuel [MJ unit<sup>-1</sup>] (unit of fuel, e.g. ton or cubic meter)  
 $CP$ : unit price of alternative fossil fuel [US\$ unit<sup>-1</sup>].

Estimation of capital costs necessary for construction of geothermal waters intake requires the calculation of expenditures for principal installations: production and injection wells, heat exchangers, pumps, supply pipeline, buildings and engineering works. Additionally, development and incidental expenditures must be included. All these costs were estimated based upon cost calculations and applying the exponential and factor expenditure interpolation methods, and expressing them as functions of, for example, hydrogeothermal reservoirs properties.

In order to simplify the estimation of running costs of geothermal water intakes, these costs were divided into the two groups: costs determined as percentage of investment expenditures spent for construction of intakes (including repairs, maintenance, overheads, administration) and costs proportional to production rates of intakes (costs of electric energy used for pumping). Similar to capital expenditures, the running costs were expressed as functions of hydrogeothermal reservoirs properties.

- Power factor – based upon the formulae and assumptions discussed above, the following dependence between power factor  $F$  and the principal reservoir properties of hydrogeothermal aquifers was determined:

$$F = \frac{1.14 \times 10^{-3} LF Q(T - 25)}{1.078 \times 10^{-3} \left( 312 \times 10^{-3} \exp(0.00078H) + 825[Q(T - 25)]^{0.6} + 2.55 \left[ \frac{Q^2}{(k m)} \right]^{0.6} + 1.033 \times 10^{-5} \left[ \frac{Q^2}{(k m)} \right] \right)} \quad (1.10)$$

where:

- $k$ : hydraulic conductivity coefficient [m s<sup>-1</sup>]  
 $m$ : thickness of groundwater reservoir [m]  
 $H$ : depth to groundwater reservoir [m]  
 $LF$ : mean annual load factor of an intake  
 $Q$ : rated discharge of geothermal water [m<sup>3</sup> h<sup>-1</sup>]  
 $T$ : temperature of produced water [°C].

It was assumed that alternative fuel considered in the calculations will be hard coal of calorific value 6000 kcal/kg (about 25 GJ t<sup>-1</sup>) and unit price 70 US\$ t<sup>-1</sup>, as the average price of coal on the European market (International Coal Report steam coal market price) for the years 2005–2010. The power factor is a value which expresses how many times the thermal power of a geothermal intake exceeds the thermal power equivalent of capital expenditures and running costs of this intake. Such definition corresponds to an effectiveness criterion, that is, the ratio of effects to expenditures, which means that the higher is the ratio, the higher is the effectiveness.

The power factor value <1 points out that “thermal equivalent” of expenditures is higher than the thermal energy produced. Hence, this is an indicator which reflects both the energetic value of geothermal resources and the economic sense of their exploitation. The power factor is a quasi-economic indicator because it is a comprehensive representation of economic and energetic aspects of groundwater heat exploitation. However, it cannot be the base for conclusions on competitiveness of geothermal heat production in relation to conventional heat generation technologies.

- Estimation of reserves – Power factor can be applied to determination of reserves (*disposable geothermal energy resources*) of studied aquifers (Górecki *et al.*, 1995, 2006a, 2006b, 2011, 2012, 2013; Hajto and Górecki, 2010). Such resources were calculated for the areas in which

power factor value  $F > 1$  and load factor value  $LF = 1$ , for example, for the areas where economic efficiency of geothermal waters utilization is probable. The condition  $LF = 1$  results from an assumption that for calculations of disposable reserves the power factor value should not have to be limited by the planned utilization mode of the geothermal energy.

- Reserves (disposable reserves) (RES) is defined as the assessed part of recoverable geothermal energy resources (static-recoverable resources), which exploitation is economically efficient, are determined as the amount of energy which can be generated during the year. The disposable geothermal waters and energy resources are the amounts of free (gravitational) geothermal water within the horizon or other calculation unit, which can be developed under given conditions but without detailed localization as well as technical and economic specification of an intake, expressed in  $[\text{m}^3 \text{ day}^{-1}]$ ,  $[\text{m}^3 \text{ year}^{-1}]$ ,  $[\text{J year}^{-1}]$  or  $[\text{TOE year}^{-1}]$ . Estimation of disposable reserves should be preceded by parametric/economic evaluation of given geothermal reservoir. The methodology of such evaluation was presented in several publications (e.g. Górecki *et al.*, 1995, 2006a, 2006b, 2011, 2012, 2013; Hajto and Górecki, 2010). Reserves (*disposable reserves*) constitute a part of assessed static-recoverable resources, which utilization would be economically effective. The disposable reserves *RES* is determined as the amount of energy recoverable during one year from a geothermal doublet:

$$RES = Q(T_{\text{top}} - 25)\rho_w c_w \times 8760^* \quad [\text{J year}^{-1}] \quad (1.11)$$

where:

$Q$ : rated discharge of potential production well  $[\text{m}^3 \text{ h}^{-1}]$ , ( $Q_{\text{max}} = 300 \text{ m}^3 \text{ h}^{-1}$ )

$T_{\text{top}}$ : temperature at the top surface of groundwater horizon  $[^\circ\text{C}]$

$\rho_w$ : water density  $[\text{kg m}^{-3}]$

$c_w$ : water specific heat  $[\text{J kg}^{-1} \text{ }^\circ\text{C}^{-1}]$ , ( $=4180 \text{ J kg}^{-1} \text{ }^\circ\text{C}^{-1}$ )

\*: coefficient resulting from lifetime of geothermal doublet (1 year = 8760 hours).

For calculation of disposable reserves, it was assumed that maximum discharge of geothermal water intake will not exceed  $300 \text{ m}^3 \text{ h}^{-1}$ . This limit results from technical constraints, among others from delivery rate of submersible pumps and quality of boreholes.

To conclude it must be emphasized that both the accessible resource base and heat in place have exclusively the cognitive meaning whereas the reserves is of practical importance. Therefore, the results of worldwide geothermal energy resources commonly cited in various papers and reports as tens or even over  $4.19 \times 10^{21} \text{ J}$  (100 billions TOE), are only the theoretical values of heat accumulated in groundwaters and rocks. These values, by no means, can be identified as *resources*, which can be practically (=commercially) recovered and utilized under economically effective conditions, as in the meaning of RESERVES of Muffler and Cataldi (1978).

#### 1.4 NEW CONCEPTS OF GEOTHERMAL RESOURCES CLASSIFICATION

In recent years, the geothermal community has intensified discussion, indicating the need to harmonize the rules of the international classification and reporting of geothermal resources.

In September 2014, the IGA and the United Nations Economic Commission for Europe (UNECE) signed a Memorandum of Understanding (MoU) to develop a globally applicable harmonized standard for reporting geothermal resources. Such a standard will ensure greater consistency and transparency in financial reporting and enhance management of geothermal resources. Under this MoU, the IGA will work towards providing technology-specific rules (“specifications”) for the application of the United Nations Framework for Fossil Energy and Mineral Reserves and Resources 2009 (UNFC) to geothermal resources (Falcone and Beardsmore, 2015).



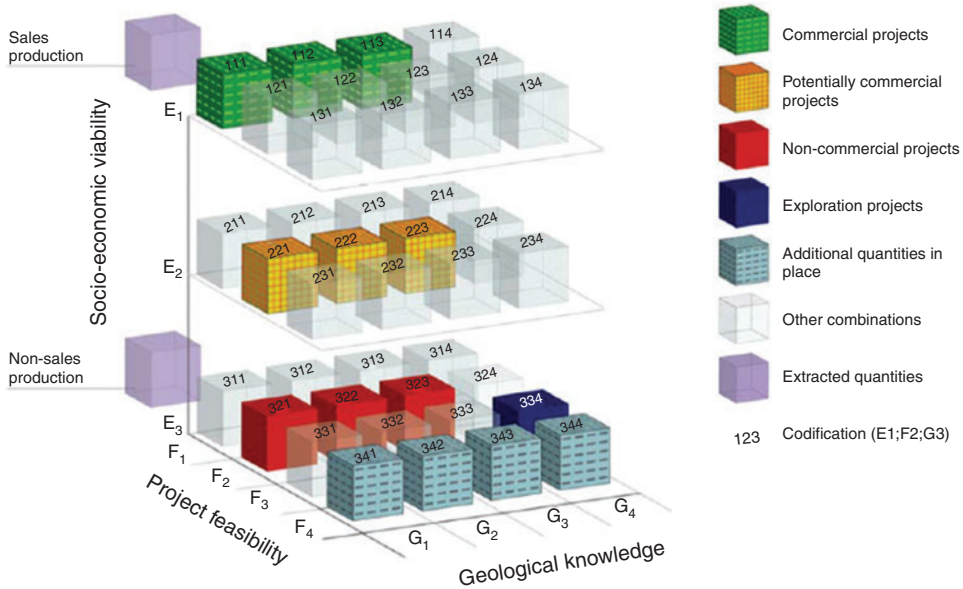


Figure 1.4. UNFC-2009 categories and examples of classes (ECE, 2013).

The United Nations Framework Classification for Fossil Energy and Mineral Reserves and Resources 2009 (UNFC-2009) differs from other systems as it classifies estimated resource quantities using three axes: socio-economic variability (E), project feasibility (F) and geological knowledge (G) (Fig. 1.4). The first set of categories (the E axis) designates the degree of favorability of social and economic conditions in establishing the commercial viability of the project, including consideration of market prices and relevant legal, regulatory, environmental and contractual conditions. The second set (the F axis) designates the maturity of studies and commitments necessary to implement mining plans or development projects (Falcone, 2015).

Additionally, the IGA Resources and Reserves Committee actively engages in matters related to the global standardization of geothermal terminology, methods of geothermal resources and reserves estimation, and classification systems for geothermal potential. The committee collaborates with the IGA Service Company, the World Bank, the UNECE, the International Renewable Energy Agency, and other bodies to progress its programs.

Geothermal classification standards among the others are needed to reduce risk to investor and increase confidence in geothermal development. Multiple parallel activities within the geothermal community have led to duplication of the efforts to avoid biased estimation of resources that could not be comparable with one another.

UNFC-2009 (ECE, 2013) geothermal classification tries to consider other existing geothermal classification schemes, including:

- The Canadian Geothermal Code for Public Reporting, by the Canadian Geothermal Code Committee (Deibert *et al.*, 2010);
- A Protocol for Estimating and Mapping Global EGS Potential (Beardsmore *et al.*, 2010);
- The New Geothermal Terms and Definitions, by the Geothermal Energy Association (GEA, 2010);
- The Resource Assessment Protocol for GEO-ELEC (van Wees *et al.*, 2011).

The standard for reporting geothermal resources with reference to the UNFC-2009 protocol is still under development.

## 1.5 RESULTS OF GEOTHERMAL RESOURCES ASSESSMENT

### 1.5.1 World geothermal resources

The total thermal energy contained in the earth is of the order of  $12.6 \times 10^{12}$  EJ and that of the crust of the order of  $5.4 \times 10^9$  EJ to depths of up to 50 km (Dickson and Fanelli, 2004). The main sources of this energy are due to the heat flow from the earth's core and mantle, and that generated by the continuous decay of radioactive isotopes in the crust itself. Heat is transferred from the interior towards the surface, mostly by conduction, at an average of  $65 \text{ mW m}^{-2}$  on continents and  $101 \text{ mW m}^{-2}$  through the ocean floor. The result is a global terrestrial heat flow rate of around  $1400 \text{ EJ year}^{-1}$ . Continents cover  $\sim 30\%$  of the earth's surface and their terrestrial heat flow has been estimated at  $315 \text{ EJ year}^{-1}$  (Stefansson, 2005).

Stored thermal energy down to 3 km depth on continents was estimated to be  $42.67 \times 10^6$  EJ by EPRI (1978), consisting of  $34.14 \times 10^6$  EJ (80%) from hot dry rocks (or EGS resources) and  $8.53 \times 10^6$  EJ (20%) from hydrothermal resources. Within 10 km depth, Rowley (1982) estimated the continental stored heat to be  $403 \times 10^6$  EJ with no distinction between hot dry rock and hydrothermal resources, and Tester *et al.* (2005) estimated it to be  $110.4 \times 10^6$  EJ from hot dry rocks and only  $0.14 \times 10^6$  EJ from hydrothermal resources. A linear interpolation between the EPRI (1978) values for 3 km depth and the values from Rowley (1982) results in  $139.5 \times 10^6$  EJ down to 5 km depth, while linear interpolation between the EPRI (1978) values and those from Tester *et al.* (2005) only for EGS resources results in  $55.9 \times 10^6$  EJ down to 5 km depth. Based on these estimates, the theoretical potential is clearly not a limiting factor for global geothermal deployment. In practice, geothermal plants can only utilize a portion of the stored thermal energy due to limitations in drilling technology and rock permeability. Commercial utilization to date has concentrated on areas in which geological conditions create convective hydrothermal reservoirs where drilling to depths up to 4 km can access fluids at temperatures of  $180^\circ\text{C}$  to more than  $350^\circ\text{C}$  (Goldstein *et al.*, 2011).

Bertani (2003) found that, based on a compilation of estimates produced by a number of experts, the expected geothermal electricity potential ranges from a minimum of 35–70 GWe to a maximum of 140 GWe. The potential may be orders of magnitude higher, based on EGS technology. If the target of 140 GW will be reached, it would be possible to produce from geothermal up 8.3% of total world electricity production, serving 17% of world population. Moreover, 40 countries (located mostly in Africa, Central/South America and the Pacific) can be 100% geothermally powered (Bertani, 2015). Theoretical examinations indicate that the magnitude of hidden resource can be 5–10 times larger than the estimate of identified resources.

The geologic potential (heat in place) for geothermal power in Europe and the world is very large and exceeds the current electricity demand in many countries. However, only a small portion of the heat in place can be realistically extracted for power production (Sigfússon and Uihlein, 2015).

Regarding geothermal technical potentials, defined as the amount of renewable energy output obtainable by full implementation of demonstrated technologies or practices, one recent and comprehensive estimate for conventional hydrothermal resources in the world was presented by Stefansson (2005). For electric generation, he calculated the global geothermal technical potential for identified hydrothermal resources as 200 GWe (equivalent to  $5.7 \text{ EJ year}^{-1}$  with a capacity factor (*CF*) of 90%), with a lower limit of 50 GWe ( $1.4 \text{ EJ year}^{-1}$ ). He assumed that unidentified, hidden resources are five to ten times more abundant than the identified ones and then estimated the upper limit for the worldwide geothermal technical potential as between 1000 and 2000 GWe ( $28.4$  and  $56.8 \text{ EJ year}^{-1}$  at 90% *CF*), with a mean value of 1500 GWe ( $\sim 42.6 \text{ EJ year}^{-1}$ ). Mainly based on those numbers, Krewitt *et al.* (2009) estimated geothermal technical potential for 2050 at  $45 \text{ EJ year}^{-1}$ , largely considering only hydrothermal resources.

Global EGS technical potential for electricity to depths of 0–10 km was estimated by Tester *et al.* (2005) as  $288.1 \text{ EJ year}^{-1}$  and by Rowley (1982) as  $1051.8 \text{ EJ year}^{-1}$ .

Geothermal technical potentials for continents, specifically the International Energy Agency (IEA) regions, are presented in Table 1.2.

Table 1.2. Geothermal technical potentials on continents for the International Energy Agency (IEA) regions (after Goldstein *et al.*, 2011).

Region	Electric technical potential [EJ year <sup>-1</sup> ] at depth to:						Technical potentials [EJ year <sup>-1</sup> ] for direct uses	
	3 km		5 km		10 km		Lower	Upper
	Lower	Upper	Lower	Upper	Lower	Upper		
OECD North America	25.6	31.8	38.0	91.9	69.3	241.9	2.1	68.1
Latin America	15.5	19.3	23.0	55.7	42.0	146.5	1.3	41.3
OECD Europe	6.0	7.5	8.9	21.6	16.3	56.8	0.5	16.0
Africa	16.8	20.8	24.8	60.0	45.3	158.0	1.4	44.5
Transition Economies	19.5	24.3	29.0	70.0	52.8	184.4	1.6	51.9
Middle East	3.7	4.6	5.5	13.4	10.1	35.2	0.3	9.9
Developing Asia	22.9	28.5	34.2	82.4	62.1	216.9	1.8	61.0
OECD Pacific	7.3	9.1	10.8	26.2	19.7	68.9	0.6	19.4
Total	117.5	145.9	174.3	421.0	317.5	1108.6	9.5	312.2

Despite of the increase of power production in many parts of the world, there is still large unused geothermal resources potential.

At the end of 2014, 82 countries used geothermal energy in a direct way. An estimation of the installed thermal power for direct utilization equals 70,329 MWt, almost a 45% increase over the 2010 data, growing at a compound rate of 7.7% annually with a capacity factor of 0.265. The thermal energy used is 587,786 TJ year<sup>-1</sup> (163,287 GWh year<sup>-1</sup>), about a 38.7% increase over 2010, growing at a compound rate of 6.8% annually (Lund and Boyd, 2015). The total installed capacity from worldwide geothermal power plant is 12.6 GW. The estimated value of 21 GWe for 2020 is in line with the long-term forecasting for standard hydrothermal fields (Bertani, 2015).

### 1.5.2 European geothermal resources

The geothermal resources of most European countries were comprehensively presented in the Atlas of geothermal resources in Europe (Hurter and Haenel, 2002). The participating countries were: Albania, Austria, Belarus, Belgium, Bosnia-Herzegovina, Bulgaria, Croatia, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Netherlands, Poland, Portugal, Romania, Russia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Ukraine and the UK. An assessment of geothermal energy on a European scale, using data from many countries, requires a standardized procedure that will allow comparisons between regions and facilitate regional planning of investments in every kind of geothermal application. This was the philosophy of the European project that led to the publication of the Atlas of geothermal resources in the European Community, Austria and Switzerland (Haenel and Staroste, 1988) and of the Atlas of geothermal resources in Europe (Hurter and Haenel, 2002). The latter contains updated information on geothermal resources provided by the contributors to the first atlas as well as new information from 19 other countries. Together these two atlases provide information on a total of 32 countries, practically all of the European continent: Albania, Austria, Belarus, Belgium, Bosnia-Herzegovina, Bulgaria, Croatia, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Netherlands, Poland, Portugal, Romania, Russia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Ukraine and the UK (Hurter and Schellschmidt, 2003).

Atlas of geothermal resources in Europe contains more than 500 maps on a national and regional scale. The geothermal resources of a geothermal aquifer are displayed with a set of four maps:

- The map of the depth to the top of the aquifer showing the range of depth variation of the reservoir;

- The map of aquifer thickness, which is a measure of the magnitude of the resource;
- The temperature at the top of the aquifer;
- The distribution of geothermal resources over a given region shown in the map of isolines representing the resources per unit area [in  $\text{GJ m}^{-2}$ ].

The information presented in the atlas shows that practically all European sedimentary basins have low-enthalpy geothermal resources that could be utilized in some form and, moreover, countries with no geothermal application are rather the exception in Europe. The largest reservoirs of geothermal waters exploited in Europe occur in the Paris Basin (France), in the Pannonian Basin (shared by Hungary, Serbia, Slovakia, Slovenia and Romania), in the European Lowlands (e.g. in Germany, Denmark and Poland), in Paleogene basins of the Inner Carpathians (Poland, Slovakia), as well as in Alpine and older structures in Southern Europe (Bulgaria, Romania, Greece, Turkey). In some areas overheated water and steam (high-enthalpy accumulations) occur, as in Italy, Turkey, Greece, Greek Islands, Azores (Portugal), Canary Islands (Spain) and, most particularly, in Iceland (Górecki *et al.*, 2006a).

More detailed information about national geothermal resources is contained in local research works. Both the European Geothermal Congress and the World Geothermal Congress are relevant events at which the newest information about geothermal resources is presented. Held every five years, the World Geothermal Congress is a unique event organized by IGA in cooperation with national geothermal associations, which brings together members of the geothermal community from across the globe.

The organization that represents the geothermal sector in Europe is the EGEC. EGEC publications are a valuable source of information about different aspects of geothermal energy utilization in Europe, and also in terms of geothermal resources. Over the last 100 years, the production of geothermal energy has been concentrated in areas where rich hydrothermal resources are available. However, the development of advanced technologies has enabled the production of geothermal energy at low temperature in all European countries. One of the technologies which is very promising for the future of geothermal electricity production is EGS, which is an underground reservoir that has been created or improved artificially. The concept of EGS is going to greatly increase geothermal potential as it allows for the production of geothermal electricity nearly anywhere in Europe with medium or low temperature.

Also, some European projects tend to assess geothermal potential are very being informative.

Geothermal potential for district heating was assessed during the realization of the GeoDH project. Results of the project (GeoDH Report, 2014) shows that more than 25% of the EU population lives in areas directly suitable for geothermal district heating. There is a large potential, with similar geothermal district heating systems in operation in 22 European countries. Central and eastern Europe, with geothermal district heating systems in operation in Hungary, Poland, Slovakia, Slovenia, the Czech Republic and Romania, is a very promising region. Existing heat networks are well developed in these countries. The geothermal potential is recognized by some EU member states in their national renewable energy action plans. However, the actual potential is significantly larger. In order to increase awareness, the GeoDH project has assessed and presented for the first time the potential in Europe on an interactive map of geothermal potential ([www.geodh.eu](http://www.geodh.eu)).

Effects of project indicate that:

- geothermal district heating can be developed everywhere;
- geothermal can be installed with existing district heating systems during extension or renovation, replacing fossil fuels;
- new geothermal district heating systems can be built in many regions of Europe at competitive costs;
- the Pannonian Basin is of particular interest when looking at potential development in central and eastern Europe.

Geothermal potential for electricity generation in Europe was assessed during the realization of project GeoElec (GeoElec, 2011). The project produced an action plan towards more geothermal electricity generation in Europe, with the objective of doubling the installed geothermal power capacity in Europe by 2020. The project also looked at concrete actions to reach these objectives, for example conditions for financial feasibility, regulatory frameworks, and public acceptance. The resource assessment is the product of the integration of existing data provided by the EU-28 countries and a newly defined methodology building on Canadian, Australian, and American methodology. The geological potential (heat in place) has been translated to an economical potential, using a levelized cost of energy (LCoE) value of less than 150 € MWh<sup>-1</sup> for the 2030 scenario and less than 100 € MWh<sup>-1</sup> for the 2050 scenario:

- The production of geothermal electricity in the EU in 2013 was 6 TWh;
- The NREAP (National Renewable Energy Action Plan) forecasts a production in the EU-28 of ~11 TWh in 2020;
- The total European geothermal electricity potential in 2030 is 174 TWh;
- The economic potential grows to more than 4000 TWh in 2050 (GeoElec, 2011).

### 1.5.3 Polish geothermal resources

Comprehensive information about Polish geothermal resources provides seven geothermal atlases of different part of Poland issued by the Department of Fossil Fuels at the Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology in Kraków over the years 1990–2013 (e.g. Górecki *et al.*, 2015). For many years, the department has conducted scientific research and has issued many publications related to the occurrence of geothermal waters in the sedimentary basins of Poland. Geothermal energy resources are analyzed and technologies for development of geothermal water resources are examined by the Department in the Polish Lowlands, Carpathians and Carpathian Foredeep.

Hot groundwaters represent carriers of environmentally clean energy which can be important for numerous regions in Poland. Similar to other European countries, Poland has natural sedimentary-structural basins filled with geothermal waters of diversified reservoir temperatures, from 20 to 80–90°C, in some cases even over 100°C. The country is characterized by significant low-enthalpy geothermal potential, connected mostly with the Mesozoic sediments. In 2013, the last atlas (Górecki *et al.*, 2013) dealing with Polish sedimentary basins was published, thereby closing the series of geothermal atlases of Poland.

The atlases represent a result of interdisciplinary, constructive cooperation of specialists from various fields of science. The selected geothermal aquifers were characterized from the point of view of geological setting, extent, depth and thickness of the aquifers, water temperature and mineralization, discharge of hydrogeological intakes and reservoir properties. Results of the research allowed calculation of geothermal resources and indicated the best locations for a variety of uses: balneotherapeutic, recreation and heating. Geothermal atlases of Poland constitute essential information on geothermal waters and the possibility of their utilization. The atlases comprise important information for investors involved in recognition and production of warm brines for practical uses. The atlases show that geothermal energy can be commercially utilized in vast areas of Poland. The best geothermal conditions are predicted in the Polish Lowlands and Podhale area although in many areas of Carpathian and Carpathian Foredeep favorable geothermal conditions also occur. The scale of this utilization will depend on numerous factors. A very significant challenge is to break the continuing bad habits and improper standards that have dominated state energy policy in recent decades.

Geothermal waters can be utilized for heat generation used in houses, industrial buildings, greenhouses, agriculture, for generation of warm water, and for therapeutic and recreational purposes. Use of ecologically clean geothermal energy resources is realistic and economically justified in vast areas of the Poland.

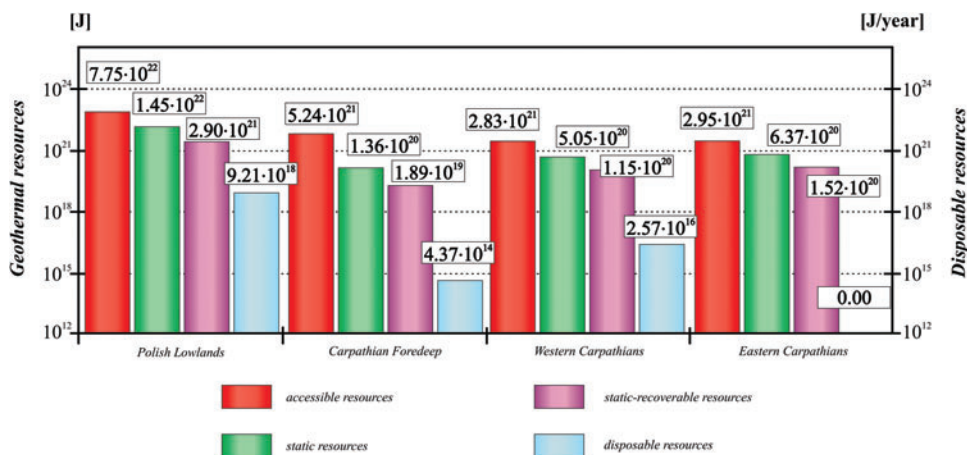


Figure 1.5. Distribution of geothermal resources within particular resource classes for different areas of Poland.

The estimates of the geothermal resources in the classes of the accessible, static (*heat in place*), and static-recoverable (*recoverable geothermal energy*) resources in different parts of Poland confirm the biggest geothermal potential of the Polish Lowlands (Fig. 1.5). The lowest potential (expressed by value of disposable geothermal resources) is associated with the Eastern Carpathians. Analysis of geological, hydrogeological, and petrophysical/volumetric parameters of the flysch rocks, Miocene deposits and the Mesozoic-Paleozoic basement of the Eastern Carpathians, supplemented by the economic indicator analysis considering the present economic conditions (including the geothermal drilling costs), are indicative of very limited potential for utilization of heat from geothermal waters for heating purposes in the study area. However, hydrogeological parameters of the analyzed geothermal aquifers of the Eastern Carpathians, principally discharges of intakes and predicted water temperatures, indicate the possibility of building small heating installations with thermal powers ranging from several hundred kilowatts to as much as 5 MWt (Górecki *et al.*, 2014).

Since 2010, the work connected with analysis of the possibility of using hot dry or wet rocks for building the closed geothermal systems has been carried out. The results of the project were presented in numerous publications (e.g. Górecki *et al.*, 2013; Sowiżdżał and Kaczmarczyk, 2014; Sowiżdżał *et al.*, 2013a, 2013b; Wójcicki *et al.*, 2013). It was the first enterprise of this type, which tends to recognize the potential of HDR for heat and electricity production. Considering the resources accumulated in sedimentary, volcanic and crystalline rocks, it should be noted that the most abundant resources occur in three locations: in the central part of the Polish Lowlands (the Mogilno-Łódź Trough), Gorzów block (Dębno area) and Karkonosze pluton (Szklarska Poręba area).

In 2014, the Atlas of the possible use of geothermal waters for combined production of electricity and heat using binary systems in Poland (Bujakowski and Tomaszewska, 2014) was issued. As the result of this work, the areas characterized by the best hydrogeothermal conditions for use of binary technologies were indicated. The most promising region for hydrogeothermal energy utilization (including electricity production) is Podhale Basin. In the Polish Lowlands, the best prospects for the utilization of geothermal water in binary systems occur in the central part of Polish Lowlands, especially in the Konin area where the temperature of the water accumulated in the Lower Jurassic reservoir exceeds 90°C, as well as the Szczecin Through area. Due to the existence of geothermal anomalies, the Sudetic Region appears to be appropriate for the location

of a binary system. All the above-mentioned works are an excellent source of information about geothermal water and/or energy resources in Poland.

In 1987, geothermal energy resources in Poland were preliminarily estimated as  $7 \times 10^9$  TCE, which corresponds  $2.1 \times 10^{20}$  J ( $4.9 \times 10^9$  TOE) (Ney and Sokołowski, 1987). Szargut (1990) recalculated geothermal resources in Poland assuming their utilization only for heat generation and obtained an estimate of  $1.8 \times 10^6$  TOE. Such extreme differences result from the variety of calculation methodologies and the various possibilities for geothermal energy recovery and utilization.

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## CHAPTER 2

### Reinjection of cooled water back into a reservoir

Leszek Pająk & Barbara Tomaszewska

#### 2.1 INTRODUCTION

In the case of low-temperature geothermal resources, direct use of geothermal energy consists of extracting the formation fluid to the surface and directing it to the so-called surface installation. In the surface installation, heat energy is transferred from the formation fluid to the intended recipients. The process of transfer of the heat energy accumulated in the fluid results in the cooling of the formation fluid. In order to maintain appropriate pressure conditions in the rock formation, the cooled formation fluid (cooled geothermal water) is reinjected into the formation at many geothermal plants. This method of disposal of used water also plays an important role where this water exhibits high mineral content. This solution is safe for the environment, but unfortunately often involves numerous problems of a technical nature. It also generates additional costs related to drilling the required number of absorption wells, and also operating costs related to the operation of high-pressure pumps.

Key formation fluid parameters that change during the energy recovery process are temperature and pressure. Temperature and pressure are intensive state parameters and their changes affect many other processes associated with the use of geothermal energy. The pressure and temperature of formation fluids and the physicochemical properties of geothermal water determine other parameters that directly affect certain conditions of geothermal energy extraction, such as viscosity, density, specific heat, and substance (solid and gas) solubility in formation fluid. Apart from the parameters that describe the formation fluid, there are also other factors that affect geothermal energy extraction conditions. These can be conventionally assigned to the production well (fluid extraction process), connecting pipelines and surface installation (energy extraction process), and the absorption well (injection process). The production and absorption wells interact directly with the formation and the hydrogeothermal structure, and therefore reservoir conditions also have a significant impact on geothermal energy extraction conditions. In the production well zone, a decrease in formation pressure is observed, while in the absorption well zone this pressure increases. The maximum decrease in pressure below the natural formation pressure in the production well zone is referred to as depression, and the maximum pressure increase above the natural pressure in the absorption well zone is referred to as repression.

#### 2.2 MATHEMATICAL MODEL FOR ASSESSING THE CONDITIONS FOR INJECTING WATER INTO A ROCK FORMATION

##### 2.2.1 *Estimation of power and energy demand associated with reinjection*

The electric power consumed by the injection pump (or pumps),  $P_{el}$ , can be determined using the following equation:

$$P_{el} = \frac{\Delta p V}{\psi} \quad (2.1)$$

where:

$P_{el}$ : electric power used to drive the injection pump(s) [W]

$\Delta p$ : total required excess pressure to be generated by the injection pumps [Pa]

$V$ : flow rate of reinjected water [ $\text{m}^3 \text{s}^{-1}$ ]

$\psi$ : pump efficiency (this is usually in the range of 0.65 to 0.80 for correctly selected pumps).

Injection pump operation directly affects the key parameters related to the efficiency of extracting geothermal energy, which includes the share of the costs associated with the purchase of electricity to drive injection pumps in the overall thermal energy production costs. In some cases, the electricity that drives injection pumps is produced using conventional fuels and the degree of conversion of the chemical energy stored in fuel into electricity (taking transmission losses into account) can be as low as  $\sim 30\%$ . This can significantly affect the energy, economic and environmental effects of using geothermal energy.

The required energy to drive pumps over a certain period,  $\Delta\tau = \tau_2 - \tau_1$ , can be calculated from instantaneous power demand values using the following relationship:

$$E_{el} = \int_{\tau_1}^{\tau_2} P_{el} d\tau \quad (2.2)$$

where:

$\tau_1, \tau_2$ : the start and end time of the  $\Delta\tau$  period during which the required driving power consumed by injection pumps is determined [s].

### 2.2.2 Estimation of required pressure for reinjection

Injecting cooled thermal water into the reservoir requires some overpressure,  $\Delta p$ , to overcome the flow resistance in the absorption well and in the zone surrounding the well filter, as well as the pressure in the reservoir.

The required injection pressure,  $\Delta p$ , can be determined with the following formula:

$$\Delta p = \Delta p_p + \Delta p_w + \Delta p_s - H_z \rho_{sg} - (H_w - H_z) (\rho_{srz} - \rho_{srn}) g \quad (2.3)$$

where:

$\Delta p$ : total required excess pressure to be generated by the injection pumps [Pa]

$\Delta p_p$ : flow resistance in the absorption well [Pa]

$\Delta p_w$ : resistance associated with the injection of water into the reservoir [Pa]

$\Delta p_s$ : resistance associated with skin effect [Pa]

$H_z$ : level of the static water table, calculated versus ground surface [m]

$H_w$ : depth of the borehole [m]

$\rho_{sr}$ : averaged density of the liquid injected in the borehole, above the static water table [ $\text{kg m}^{-3}$ ]

$\rho_{srz}$ : average density of the liquid injected into the source formation layer at the depth interval of  $H_z$  to  $H_w$  [ $\text{kg m}^{-3}$ ]

$\rho_{srn}$ : average density of the liquid in the borehole, under natural conditions, at the depth interval from  $H_z$  to  $H_w$  [ $\text{kg m}^{-3}$ ]

$g$ : earth gravity [ $\text{m s}^{-2}$ ].

Flow resistance in the absorption well is estimated by the following equation (Recknagel *et al.*, 2008):

$$\Delta p_p = \lambda \frac{L}{d} \frac{\rho}{2} w^2 \quad (2.4)$$

where:

$\lambda$ : coefficient of friction [—]

$L$ : borehole length [m]

$d$ : inner borehole diameter [m]  
 $\rho$ : water density [ $\text{kg m}^{-3}$ ]  
 $w$ : water flow speed in the borehole [ $\text{m s}^{-1}$ ].

The resistance associated with the injection of water into the reservoir can be estimated by the following equation (Kapuściński *et al.*, 1997):

$$\Delta p_w = \frac{V\mu}{4\pi k_h h} \ln\left(\frac{2.25k_h \tau}{\varphi \mu c_t r_w^2}\right) \quad (2.5)$$

where:

$\tau$ : repressure settling time ( $\Delta p_w$ ) [s]  
 $V$ : flow rate of reinjected water [ $\text{m}^3 \text{s}^{-1}$ ]  
 $\mu$ : dynamic viscosity of water [Pa s]  
 $k_h$ : horizontal permeability [ $\text{m}^2$ ]  
 $h$ : thickness of water-bearing layer [m]  
 $\varphi$ : effective aquifer porosity [–]  
 $r_w$ : well radius [m]  
 $c_t$ : compressibility factor of rocks [ $\text{Pa}^{-1}$ ].

The resistance associated with the skin effect may be calculated as follows (Kapuściński *et al.*, 1997):

$$\Delta p_s = s \frac{V\mu}{4\pi k_h h} \quad (2.6)$$

where:

$s$ : the skin-effect coefficient, aquifer resistance in the zone adjacent to the filter (so-called skin effect) [–].

According to Kapuściński *et al.* (1997), the skin-effect coefficient may be calculated as:

$$s = \left(\frac{k}{k_s} - 1\right) \ln\left(\frac{r_{wa}}{r_w}\right) + \left(\frac{h}{h_p} - 1\right) \left[ \ln\left(\frac{h}{r_w} \sqrt{\frac{k_h}{k_v}}\right) - 2 \right] + \left[ \frac{\mu_{t_1} \rho_{t_0}}{\mu_{t_0} \rho_{t_1}} \ln\left(\frac{r_s}{r_w}\right) + \ln\left(\frac{r_d}{r_s}\right) \right] \quad (2.7)$$

where:

$k$ : aquifer permeability [ $\text{m}^2$ ]  
 $k_s$ : permeability of the near-well zone [ $\text{m}^2$ ]  
 $r_{wa}$ : damaged zone range [m]  
 $h_p$ : thickness of the active layer [m]  
 $k_v$ : vertical aquifer permeability [ $\text{m}^2$ ]  
 $\mu_{t_1}$ : dynamic viscosity of water at injection temperature [Pa s]  
 $\mu_{t_0}$ : dynamic viscosity of water at natural reservoir temperature [Pa s]  
 $\rho_{t_1}$ : water density at injection temperature [ $\text{kg m}^{-3}$ ]  
 $\rho_{t_0}$ : water density at natural reservoir temperature [ $\text{kg m}^{-3}$ ]  
 $r_s$ : cold front radius [m]  
 $r_d$ : radius of pressure changes caused by injection [m].

Assuming that the formation fluid is mineralized geothermal water with a mineral content of  $S$ , its density under standard conditions can be calculated for the entire salinity range using the following relationship (McCain, 1991):

$$\rho_0 = 16.018 \times (62.368 + 0.438603S + 1.60074 \times 10^{-3}S^2) \quad (2.8)$$



where:

$\rho_0$ : mineralized fluid density under standard conditions [ $\text{kg m}^{-3}$ ]

$S$ : salinity (the percentage of substances dissolved in the brine by mass) [%].

The density of mineralized water can be converted from standard conditions to formation conditions using the following relationship (McCain, 1991):

$$\begin{aligned}\rho &= \frac{\rho_0}{B_w} \\ B_w &= (1 + \Delta V_{wp})(1 + \Delta V_{wT}) \\ p' &= \frac{p}{6894.757} \quad \text{conversion of units [Pa] to [psi]} \\ T' &= 32 + \frac{9}{5}(T - 273.15) \quad \text{conversion of units [K] to [°F]} \\ \Delta V_{wp} &= -1.95301 \times 10^{-9} p' T' - 1.72834 \times 10^{-13} (p')^2 T' - 3.58922 \times 10^{-7} p' \\ &\quad - 2.25341 \times 10^{-10} (p')^2 \\ \Delta V_{wT} &= -1.0001 \times 10^{-2} + 1.33391 \times 10^{-4} T' + 5.50654 \times 10^{-7} (T')^2\end{aligned} \quad (2.9)$$

where:

$\rho$ : mineralized water density under standard conditions [ $\text{kg m}^{-3}$ ]

$B_w$ : volume coefficient of mineralized water [–]

$p'$ ,  $p$ : pressure  $p'$  [psi],  $p$  [Pa]

$T'$ ,  $T$ : temperature  $T'$  [°F],  $T$  [K].

The relationship holds within the entire salinity range for temperatures of up to  $\sim 127^\circ\text{C}$  and pressures of up to  $\sim 34.5$  MPa.

The dynamic viscosity of mineralized water at formation temperature and at atmospheric pressure,  $\mu_0$ , can be calculated using the following relationship (McCain, 1991):

$$\begin{aligned}\mu_0 &= A(T')^{-B} \times 10^{-3} \\ A &= 109.574 - 8.40564S + 0.313314S^2 + 8.72213 \times 10^{-3}S^3 \\ B &= 1.12166 - 2.63951 \times 10^{-2}S + 6.79461 \times 10^{-4}S^2 + 5.47119 \times 10^{-5}S^3 \\ &\quad - 1.55586 \times 10^{-6}S^4\end{aligned} \quad (2.10)$$

In this relationship (Equation (2.10)), salinity  $S$  should be expressed as a percentage, that is,  $S = 20$  for brine with a salinity of 20%. The relationship holds for temperatures ranging from  $38$  to  $204^\circ\text{C}$  and for salinity values of up to 26%.

Dynamic viscosity can be converted from atmospheric pressure to formation pressure using the following relationship (McCain, 1991):

$$\mu = \mu_0[0.9994 + 4.0295 \times 10^{-5} p' + 3.1062 \times 10^{-9} (p')^2] \quad (2.11)$$

The relationship (Equation (2.11)) holds for temperatures ranging from  $30$  to  $75^\circ\text{C}$  and for pressures of up to  $103.4$  MPa.

The compressibility of the conducting medium (active during the flow) can be described by the following relationship (Kapuściński *et al.*, 1997):

$$c_t = \varphi c_s + c_r \quad (2.12)$$

where:

- $c_t$ : compressibility of the conducting medium (active during the flow) [ $\text{Pa}^{-1}$ ]
- $c_s$ : compressibility of mineralized water [ $\text{Pa}^{-1}$ ]
- $c_r$ : compressibility of rock skeleton [ $\text{Pa}^{-1}$ ]
- $\varphi$ : effective aquifer porosity [—].

The compressibility of mineralized water as a function of salinity, pressure and temperature can be determined using the following equation (McCain, 1991):

$$c_s = \frac{1}{7.033 \frac{p}{6894.757} + 0.5415s - 537 \left[ \frac{9}{5}(T - 273) + 32 \right] + 403.3 \times 10^3} \cdot \frac{1}{6894.757} \quad (2.13)$$

where:

- $c_s$ : compressibility of mineralized water [ $\text{Pa}^{-1}$ ]
- $p$ : mineralized water pressure [Pa]
- $s$ : mineral content of mineralized water (salinity) [ $\text{mg L}^{-1}$ ]; ( $s = S\rho$ )
- $S$ : the fraction of substances dissolved in the water by mass [—]
- $\rho$ : mineralized water density (under the conditions specified by  $S$ ,  $p$  and  $T$ ) [ $\text{kg m}^{-3}$ ]
- $T$ : mineralized water temperature [K].

Equation (2.13) is valid for temperatures ranging from 93 to 132°C, pressures ranging from 6.89 to 13.79 MPa, and salinity of up to 200  $\text{mg L}^{-1}$ . Outside these temperature, pressure and salinity ranges, the isothermal compressibility of mineralized water can be determined from the following relationship (Kapuściński *et al.*, 1997):

$$c_s = -\frac{1}{\rho} \left( \frac{\delta \rho}{\delta p} \right)_T = -\frac{1}{B_w} \left( \frac{\delta B_w}{\delta p} \right)_T \quad (2.14)$$

where:

- $B_w$ : volume coefficient of mineralized water [—].

This relationship enables  $c_s$  to be determined for temperatures of up to 127°C and for pressures of up to 34.5 MPa.

The isothermal compressibility coefficient of the rock skeleton,  $c_r$ , may be determined from Hall's relationship (Kapuściński *et al.*, 1997):

$$c_r = \left( \frac{194.184}{\varphi^{0.438}} \right) \times 10^{-6} \quad (2.15)$$

where:

- $c_r$ : isothermal compressibility coefficient of rock skeleton [ $\text{Pa}^{-1}$ ].

### 2.2.3 Heat transfer between saline water and the geological medium in the vicinity of the absorption well

The equations presented in Section 2.2.2 require knowledge of the temperature of the saline water injected into the formation. This is because most parameters describing the state of the water are functions of temperature, including viscosity and density, which have an effect on nearly all values in the equations presented. The temperature of the mineralized fluid changes as it flows through the well, as a result of heat exchange with the formation. In these conditions, the water/brine can be both cooled and heated. The situation in the case of injection is much more complicated than in the case of extraction, where we are basically dealing only with the cooling of the fluid that flows

from the formation to the surface. The temperature of the injected fluid is usually much higher than the temperature of the near-surface soil layer. As a result, the fluid is cooled. Eventually, the fluid reaches a depth at which the temperature of the geological formations is higher than that of the fluid and, from this depth down, the fluid is heated. The temperature of the fluid in the filter zone before it enters the formation depends on many parameters. The approximate value of the unit power exchanged between fluid and rock can be calculated using the following relationship (Carslaw and Jaeger, 1948):

$$q_{\text{str}} = \frac{-4\pi\lambda_g(t_s - t_\infty)}{\ln\left(\frac{4a_g\tau}{r_w^2} - 2\gamma\right)} \quad (2.16)$$

where:

$q_{\text{str}}$ : unit power losses occurring during heat transfer between fluid and geological medium per 1 m of well length [ $\text{W m}^{-1}$ ]

$\lambda_g$ : coefficient of thermal conduction through the geological medium [ $\text{W m}^{-1} \text{K}^{-1}$ ]

$t_s$ : saline water temperature [ $^{\circ}\text{C}$ ]

$t_\infty$ : natural geological medium temperature before injection starts or at a large distance from the well (i.e. beyond the range of thermal influence) [ $^{\circ}\text{C}$ ]

$a_g$ : temperature compensation factor for the rock medium [ $\text{m}^2 \text{s}^{-1}$ ]

$\tau$ : heat settling time [s]

$\gamma$ : Euler's constant ( $\gamma = 0.577216\dots$ ) [—].

Equation (2.16) holds if  $4a_g\tau/r_w^2 \gg 1$ . The minus sign in the relationship determines the proper sign for  $q_{\text{str}}$ : negative if  $t_s > t_\infty$  and positive if  $t_\infty > t_s$ . Unfortunately, if heat transfer effects are to be accounted for in calculations,  $q_{\text{str}}$  has to be determined in an iterative manner for certain depth intervals, and this means that in order for this relationship to yield more accurate results, iterative calculations are required. In these, the assumption made is that the temperature of fluid when leaving one zone is its temperature as it enters another zone.

The mathematical model presented has been successfully used in studies whose purpose was to assess injection conditions in active zones around absorption wells. Practical experience related to forecasting the efficiency of injecting water into rock formation under varying hydrogeothermal conditions is presented, inter alia, in Tomaszewska and Pająk (2012a, 2012b) and Tomaszewska *et al.* (2014).

## 2.3 INJECTION OF SALINE WATER INTO ROCK FORMATION

### 2.3.1 Parameters of water and borehole construction

The process of injection of a saline water into a rock formation was presented based on case study. The input parameters and received results are presented below.

- Mineralization of the geothermal water analyzed, pumped from the exploitation well ranges from 101.5 to 113.8  $\text{g dm}^{-3}$  (11% salinity). The ion pool is dominated by chloride anions,  $\text{Cl}^-$  (99.3% mval), and sodium cations,  $\text{Na}^+$  (86.3% mval). Carbonate hardness varies within the  $\text{CaCO}_3$  range of 39.4–214.5  $\text{mg dm}^{-3}$  and the general hardness range (as  $\text{CaCO}_3$ ) from 11,000.5–12,431  $\text{mg dm}^{-3}$  (Tomaszewska and Pająk, 2012b).
- A stream of highly saline brine injected into the rock formation at  $40 \text{ m}^3 \text{ h}^{-1}$ .
- Temperature of the injected brine:  $50^{\circ}\text{C}$  at the head of the injection borehole.
- Construction of the injection borehole:

Depth interval [m]	Borehole diameter ( $d_w$ ) [inch]
0–278	$13 \frac{7}{8}$
278–2769.4	$9 \frac{5}{8}$
2769.4–2886	$6 \frac{5}{8}$

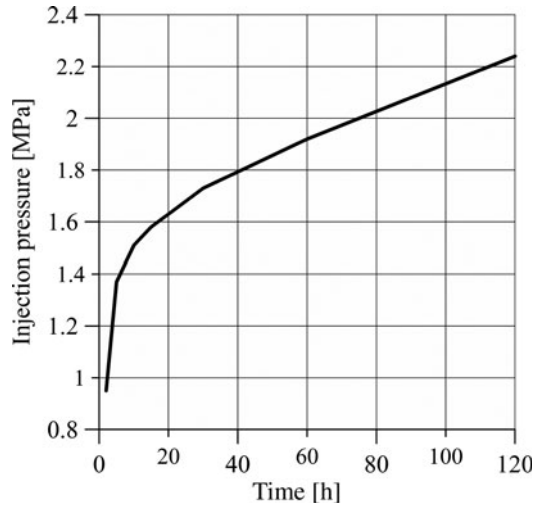


Figure 2.1. Forecast changes in the injection pressure required over time, assuming a  $40 \text{ m}^3 \text{ h}^{-1}$  constant flow of brine injection (after Tomaszewska and Pająk, 2012b).

- Heat transfer coefficient of the geological environment ( $\lambda_g$ ):  $2.5 \text{ W m}^{-1} \text{ K}^{-1}$ ; density of the rock formation environment:  $2.4 \text{ Mg m}^{-3}$ ; specific heat of the rock formation:  $0.8 \text{ kJ kg}^{-1} \text{ K}^{-1}$ .
- Change in temperature in the borehole area in line with the geothermal gradient, from the source layer temperature of  $70^\circ\text{C}$  to the surface temperature of  $8^\circ\text{C}$ .
- Effective porosity of the water-bearing stratum: 15%.
- Thickness of the water-bearing horizon: 64 m; thickness covered by the borehole and thickness of the permeable layer: 19 m.
- Permeability of the water-bearing stratum: horizontal, 210 mD; vertical, 21 mD.
- Level of the static water table: 125 m u.l.s.l. (under land surface level).
- Range of the zone affected by the skin effect: 1.25 m; and its permeability: 10 D (the commissioning documentation suggested a negative value of the hydraulic skin-effect coefficient, giving rise to this high value of permeability).
- The forecast time of water injection is counted from the start-up of the borehole after cleaning of the scale products causing clogging (following acid treatment).
- The quantity of products causing clogging in the filter zone is  $0.063 \text{ kg m}^{-3}$ . The value has been determined based on analyses that take into account chemical composition of water (Tomaszewska and Pająk, 2012b).
- It has been assumed that the products of secondary clogging are sedimenting in the internal parts of the filter and gravel pack and have a permeability of 7 mD.

### 2.3.2 Dynamics of the clogging process in the active area

A gradual change in the injection pressure required is shown in Figure 2.1, which resulted from clogging in the active zone. The forecast shows the injection pressure increasing particularly rapidly in the first 24 hours of pumping. In the subsequent hours of the period analyzed, the increase in pressure is close to linear and continual, reaching a value of  $\sim 2.2 \text{ MPa}$  at 120 hours. The value of the absorbance index declines, more particularly in the first six hours (Fig. 2.2). In the period investigated, the value decreased from more than 42 to approximately  $18 \text{ m}^3 \text{ h}^{-1} \text{ MPa}^{-1}$  at 120 hours after initiation of the injection (Tomaszewska and Pająk, 2012b). The results of analyses based on the model were verified with absorbance tests in the injection borehole, using the same flow intensity and temperature of the water injected into the source rock formation (Tomaszewska *et al.*, 2013). The results of the forecasts and the real measurements taken at the

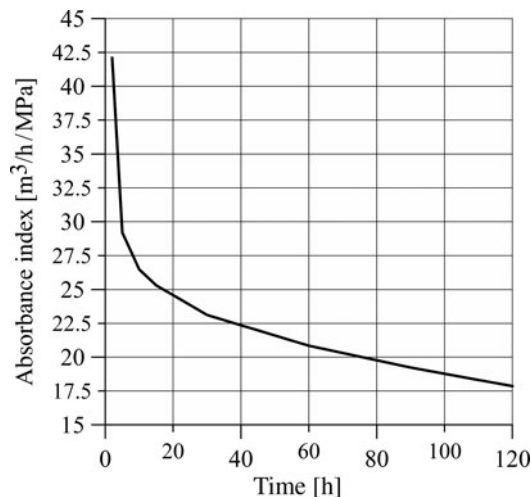


Figure 2.2. Forecast changes in the absorbance index with time, assuming a  $40 \text{ m}^3 \text{ h}^{-1}$  flow of brine injection (after Tomaszewska and Pająk, 2012b).

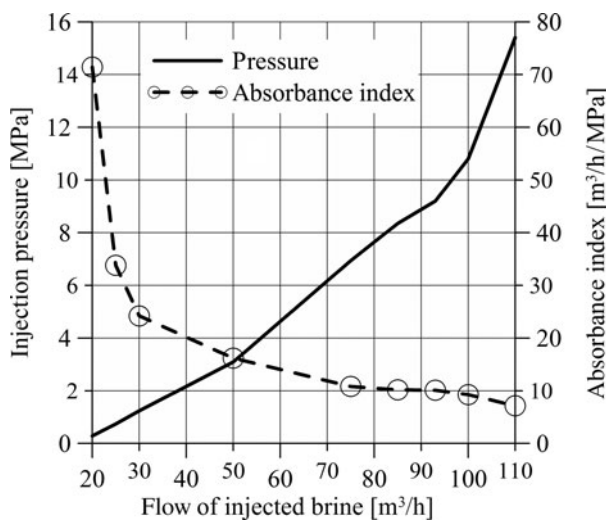


Figure 2.3. Forecast variation of the absorbance index and injection pressure with flow of the injected liquid, 120 h from initiation of injection into the source rock formation (after Tomaszewska and Pająk, 2012b).

borehole were comparable. The absorbance index measured during hydrodynamic tests dropped to approximately  $20 \text{ m}^3 \text{ h}^{-1} \text{ MPa}^{-1}$  after 120 h.

Figure 2.3 shows the variability of the absorbance index and injection pressure over 120 h as a function of a stream of brine exploited by the geothermal doublet. In the hydrogeothermal conditions analyzed, a sudden drop in absorbance index was observed when the injection capacity was  $50 \text{ m}^3 \text{ h}^{-1}$ . Above the value of  $50 \text{ m}^3 \text{ h}^{-1}$ , the value of the absorbance index decreased at a much slower pace.

The key product of secondary mineral precipitation from the geothermal water in the system investigated is calcium carbonate, in the form of aragonite and calcite. The presence of these minerals has been demonstrated in samples of materials discharged from the borehole during implementation of the source zone cleaning procedures (Tomaszewska and Pająk, 2012b). Secondary precipitation products and products of corrosion of the pipes coat the filter and the gravel pack, and are carried with the injected water, so penetrating the reservoir rock formations (they are also probably deposited and form accumulation clusters in the structures of the reservoir rock). As a result, the absorbance of the boreholes, borehole zone and source rock formations is decreasing and this has been clearly demonstrated in the analyses performed based on the model, and in the practical results from injection of water into the rock formations (Tomaszewska and Pająk, 2012b; Tomaszewska *et al.*, 2013).

## 2.4 SUMMARY

The mathematical description of the injection process has been derived using a significant number of assumptions made to simplify the process. To that, one must add the changes in permeability of the filter zone and the source formation itself, caused by the precipitation of various types of substances and the products of corrosion processes. Because of all these factors, the calculation of the pressure that must be overcome to inject brine into the source rock formation can only be estimated and approximated. However, having a well-prepared mathematical or numerical model, we can describe reality with better approximation.

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## CHAPTER 3

### Geothermal and hydrogeological conditions, geochemical properties and uses of geothermal waters of the Slovakia

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Zlatica Ženišová & Renáta Fl'aková

#### 3.1 INTRODUCTION

Slovakia has always been known for its curative mineral water springs. In number and quality of mineral springs it is among the richest countries in the world. Based on the archaeological findings, human presence can be assumed in the thermal springs in prehistoric times (Bešeňová, Dudince, Gánovce), many of which were already known to the Romans.

The use of geothermal waters in Slovakia is historically associated primarily with the implementation of the spa facilities. Written records of the realization of these objects are known from the late 14th and early 15th century from the areas of Turčianske Teplice, Dudince, Piešťany and Rajecké Teplice (Mulík, 1981). The utilization of geothermal water as a source of energy was launched in Slovakia in the 1950s. At that time in the spa premises, the use of geothermal water was tested for heating buildings in the spas Piešťany, Kováčová and Sklené Teplice. Trial tests of heat pump operation in Piešťany, and Turčianske Teplice were performed, along with the use of heat exchangers and heating of buildings in Piešťany, Turčianske Teplice and Kováčová (Uhlíarik, 1977).

The source of geothermal energy in the Slovak Republic is mostly geothermal water, which was tapped during the geothermal research by prospection or exploratory geothermal wells.

The first overview report summarizing the basic results of 37 research and exploratory geothermal wells was compiled by Franko (1986). The overview of geothermal wells and basic data about them, including the utilization and ownership (at that time), is given in *Inventory of geothermal resources and their potential utilization in Slovakia* (Franko *et al.*, 1993). It was the first inventory of geothermal resources.

Summaries of the results of the geothermal wells drilled in the years 1971–1994 in Slovakia are presented by Remšík and Fendek (1995) and Fendek *et al.* (1995). A comprehensive list of geothermal wells with geothermal installations is given in *The atlas of geothermal energy of Slovakia* (Franko *et al.*, 1995). In this work, there was, for the first time, a comprehensive evaluation and summary of the knowledge gained during more than two decades of geothermal review investigations, along with maps and descriptions of geothermal structures. The occurrence of geothermal water in Slovakia in cartographic form is given in a map of geothermal resources and mineral water, published in *The landscape atlas of the Slovak Republic* (Fendek *et al.*, 2002).

Based on the results of research and geological exploration works carried out in the 1970s and 1980s, Franko *et al.* (1995) have earmarked 26 prospective geothermal areas (Fig. 3.1). In 2007, the 27th geothermal area (Fig. 3.1) was identified in Lučenská Kotlina Basin (Dzúrik *et al.*, 2007; Vass and Dzúrik, 2007). After completion of geological works the existing wells gradually began to be used for recreational purposes and heating of greenhouses, when the physical-chemical characteristics of geothermal water were found suitable for the above purposes.



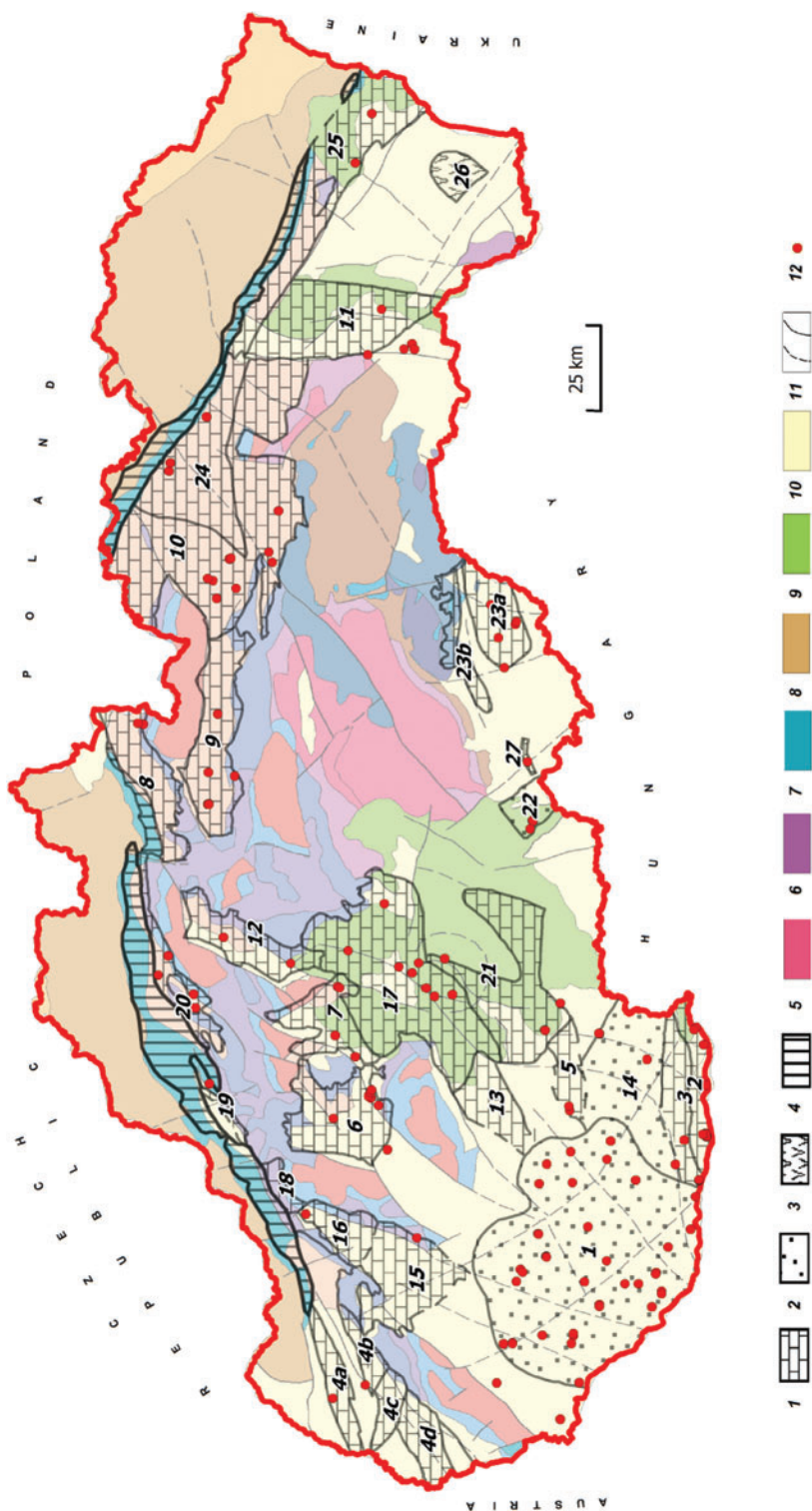


Figure 3.1. Geothermal prospective areas according to Remšik *et al.* (2011), based on Fendek *et al.* (2002) and on geological map of Biely *et al.* (1996). Explanation: (1–3 are main aquifers of geothermal water) 1: Triassic carbonates; 2: Neogene sands, sandstones and conglomerates; 3: Neogene andesites and related pyroclastics; 4: Klippen belt; (5–10 are geological structures) 5: Early Paleozoic metapsammities, metapelites, predominantly acid metavolcanic and volcanoclastic rocks; 6: Late Paleozoic (crystalline) granitoids and metamorphic rocks; 7: Mesozoic predominantly carbonate rocks (limestones and dolomites), minor sandstones, claystones, quartzite; 8: Paleogene sandstones and claystones; 9: Neogenic volcanic and volcanoclastic rocks, predominantly andesites; 10: Neogene sandstones and claystones; 11: main faults; 12: geothermal wells. Corresponding numbers for prospective geothermal areas are listed in Table 3.1.

Table 3.1. Overview of the geothermal prospective areas and wells in Slovakia (based on Remšík, 2012).

Area no.	Name of geothermal perspective area	Code of geothermal water body	No. of geothermal wells	Depth of wells [m]	Age and lithology of the collectors	Temperature at wellhead [°C]
1	Danube Basin Central Depression	SK300240PF	45	290–2800	Dacian – Badenian, sand, sandstone, basal clastic sediments, andesites	18–91
2	Komárno high block	SK300010FK	10	125–1021	Lias – Triassic, limestones, dolomites	20–40
3	Komárno marginal block	SK300020FK	4	1184–1970	Neogene – conglomerates, Triassic – limestones, dolomites	42–64
4	Vienna Basin	SK300030FK	2	2100–2605	Eggenburgian – clastic sediments, Triassic – limestones, dolomites	73–78
5	Levice marginal block	SK300210FK	2	1470–1900	Badenian – clastic sediments, Triassic – limestones, dolomites	69–80
6	Topolčany embayment and Bánovce Basin	SK300090FK	7	102–2106	Paleogene – breccias, Triassic – carbonates	20–55
7	Upper Nitra Basin	SK300100FK	5	150–1851	Paleogene – breccias, Triassic–Permian – carbonates, sandstones	19–59
8	Skorušiná Basin	SK300120FK	2	600–1601	Triassic – dolomites	28–56
9	Liptov Basin	SK300130FK	6	400–2500	Triassic – carbonates	25–66
10	Levoča Basin W and S part	SK300140FK	9	607–3616	Mesozoic, dolomites, limestones	25–62
11	Košice Basin	SK300140FK	7	160–3210	Neogene – gravel, sand, Triassic – dolomites	18–129
12	Turiec Basin	SK300110FK	2	1503–2461	Triassic – carbonates	54
13	Komjatice depression	SK300250FK	0	–	–	–
14	Dubník depression	SK300180FP	4	350–1927	Neogene – sand, sandstones, clastic sediments	18–75
15	Trnava embayment	SK300040FK	1	118	Triassic – dolomites	24
16	Piešťany embayment	SK300050FK	1	1206	Mesozoic – carbonates	19.4
17	Central Slovakian Neogene volcanics NW part	SK300190FK	10	64–2500	Neogene – porphyres, Mesozoic – limestones, dolomites	27–57
18	Trenčín Basin	SK300060FK	0	–	–	–
19	Ilava Basin	SK300070FK	1	1761	–	–
20	Žilina Basin	SK300080FK	4	600–2258	Paleogene – sandstones, Triassic – carbonates	24–41
21	Central Slovakian Neogene volcanics SE part	SK500200FK	4	63–910	Neogene – andesites, sandstones, Triassic – carbonates	25–46
22	Horné Strháre – Trenč graben	SK300260FK	4	320–625	Neogene – sand	21–38
23	Rimava Basin	SK300220FK	5	158–1050	Triassic – carbonates	18–33
24	Levoča Basin NE part	SK300150FK	3	3400–3500	Paleogene – sandstones, Triassic – carbonates	53–85
25	Humenné ridge	SK300160FK	2	600–823	Neogene – sand, sandstones, Mesozoic – dolomites, limestones	29–34
26	Beša – Čičarovce structure	SK300230FP	0	–	–	–
27	Rapové structure		1	1501	Triassic – carbonates	38
Summary of defined geothermal areas				64–3616	Neogene – sand, sandstone breccias, andesites, Mesozoic – carbonates	18–129

(continued)

Table 3.1. Continued.

Area no.	Name of geothermal perspective area	Total yield of geothermal area [L s <sup>-1</sup> ]	Total thermal power of geothermal area	TDS [g L <sup>-1</sup> ]	Chemical type of geothermal water
1	Danube Basin Central Depression	479.7	99.17	0.5–21	Na-HCO <sub>3</sub> , Na-HCO <sub>3</sub> -Cl, Na-Cl-HCO <sub>3</sub> , Na-Cl
2	Komárno high block	265.0	17.42	0.7–0.8	Ca-Mg-HCO <sub>3</sub> , Ca-Mg-HCO <sub>3</sub> -SO <sub>4</sub>
3	Komárno marginal block	15.9	2.62	2.2–90	mixed-type, Na-Cl
4	Vienna Basin	37.0	9.50	6.8–10.9	Na-Ca-Cl-SO <sub>4</sub> , Na-Cl
5	Levice marginal block	81.0	20.74	19.2–19.6	Na-Cl
6	Topol'čany embayment and Bánovce Basin	68.8	5.26	0.7–5.9	Ca-Mg-HCO <sub>3</sub> , Ca-Mg-HCO <sub>3</sub> -SO <sub>4</sub>
7	Upper Nitra Basin	57.9	7.05	0.4–1.9	Ca-Mg-HCO <sub>3</sub> , Ca-Mg-SO <sub>4</sub> -HCO <sub>3</sub>
8	Skorušíná Basin	135.0	18.29	0.8–1.3	Ca-HCO <sub>3</sub> , Ca-Mg-HCO <sub>3</sub>
9	Liptov Basin	121.4	20.36	0.5–4.7	Mg-Ca-HCO <sub>3</sub> , prevailing Ca-Mg-HCO <sub>3</sub> -SO <sub>4</sub>
10	Levoča Basin W and S part	226.3	34.24	0.6–4	Ca-Mg-HCO <sub>3</sub> -SO <sub>4</sub> , Ca-Mg-HCO <sub>3</sub>
11	Košice Basin	207.4	78.88	0.7–31	prevailing Na-Cl, Na-Ca-Cl-HCO <sub>3</sub>
12	Turiec Basin	12.2	2.02	2.5	Ca-Mg-HCO <sub>3</sub> -SO <sub>4</sub>
13	Konjatice depression	–	–	–	–
14	Dubník depression	36.0	3.7	1.6–30	Na-Cl, Na-Ca-HCO <sub>3</sub> , Na-SO <sub>4</sub> -Cl
15	Trnava embayment	–	–	2.52	Ca-Mg-HCO <sub>3</sub> -SO <sub>4</sub>
16	Piešť any embayment	–	–	1.41	Ca-Mg-SO <sub>4</sub> -HCO <sub>3</sub> , Ca-Mg-SO <sub>4</sub> , Ca-Mg-HCO <sub>3</sub>
17	Central Slovakian Neogene volcanics NW part	80.6	9.47	0.4–5	–
18	Trenčín Basin	–	–	–	–
19	Ilava Basin	–	–	–	Ca-Mg-HCO <sub>3</sub> , Ca-Mg-HCO <sub>3</sub> -SO <sub>4</sub>
20	Žilina Basin	57.4	2.95	0.4–0.5	Ca-Mg-HCO <sub>3</sub> -SO <sub>4</sub> , Na-Ca-SO <sub>4</sub> -HCO <sub>3</sub>
21	Central Slovakian Neogene volcanics SE part	64.1	3.84	1.0–5.7	Na-HCO <sub>3</sub>
22	Horné Strháre – Trenč graben	16.0	1.04	0.4–3.1	Ca-Mg-HCO <sub>3</sub> , Ca-HCO <sub>3</sub>
23	Rimava Basin	61.3	1.76	1.7–5.9	Na-Cl, Na-HCO <sub>3</sub> -Cl-SO <sub>4</sub>
24	Levoča Basin NE part	19.0	4.55	9.4–12.3	–
25	Humenné ridge	6.0	0.41	4.4–11.9	–
26	Beša – Čičarovce structure	–	–	–	–
27	Rapove structure	–	–	12.6	Na-HCO <sub>3</sub>
Summary of defined geothermal areas		2083.9	345.04	0.4–90	Na-HCO <sub>3</sub> , Na-Cl, Ca-Mg-HCO <sub>3</sub> -SO <sub>4</sub> , mixed-type

### 3.2 GEOLOGICAL STRUCTURE

The majority of the Slovak territory is occupied by the West Carpathian mountain system; only part of eastern Slovakia (Nízke Beskydy, Poloniny and Vihorlat) is assigned into the East Carpathians. The West Carpathians are characterized by extensive long mountain ranges, which in Slovakia are separated from one another by conspicuous basins. The southern section of the territory is made up of vast lowlands – extensions of the Pannonian Basin (Biely and Fusán, 1987 in Fusán *et al.*, 1987).

The essential feature of the West Carpathians is their nappe structure composed of rock complexes ranging in age from the pre-Cambrian to Tertiary. With respect to areal distribution of individual rock complexes and time of their principal folding, the West Carpathians are divided into several zones. The Inner Carpathians are located in the south and the Outer or Flysch Carpathians in the north. They are separated by the narrow Klippen Belt which is located in the Outer Carpathians.

#### 3.2.1 *Inner Carpathians*

The characteristic features of this zone are the pre-Senonian (Mediterranean) age of nappe thrusting, manifestations of Alpine metamorphism and magmatism and the large areal extent of post-nappe sedimentary and volcanogenic formations. The pre-Senonian nappe structure consists of nappes of two kinds. The first type is composed of the pre-Upper Carboniferous fundament overlain by Late Paleozoic and Mesozoic in normal position. This nappe group includes the Tatricum, Veporicum and Gemicum. The second type comprises rootless nappes composed of Mesozoic and sometimes also Late Paleozoic rocks which are entirely separated from their substratum. This type includes nappes in the Fatricum, Hronicum and Silicicum.

The Tatricum is widespread in the core mountains (Malé Karpaty, Považský Inovec, Strážovské vrchy, Malá Fatra, Tatra, Veľká Fatra, Nízke Tatry and Branisko) in the outer section of the Inner Carpathians. It is dominated by crystalline schists, granitoids and the envelope which in some mountain chains starts with Permian continental sediments. The Tatric Mesozoic sediments range in age from the Lower Triassic to Cenomanian (in the Tatra Mts. to the Lower Turonian). The Mesozoic succession of strata is interrupted by hiatuses in the Upper Triassic and Lower Cretaceous. It is dominated by carbonate rocks, except for the Lower and Upper Triassic where detrital sediments prevail.

The Veporicum also consists of crystalline schists, granitoids and the Late Paleozoic and Mesozoic envelope. It is fringed by the Čertovica line in the north and the Lubeník-Margecany line in the south. The envelope of the crystalline was preserved mostly in the northern Veporic subzones where its Lower Triassic Neocomian succession of strata is similar in character to the Fatricum. The Mesozoic rarely occurs in the southern subzones. The Late Paleozoic formations have a detrital character. The whole envelope is mildly metamorphosed. The Veporicum is overthrust onto the Tatricum.

The Gemicum is widespread in the Inner Carpathians southern tract. This term now refers only to the Paleozoic part of the originally larger unit. It comprises the Early Paleozoic Gelnica Group dominated by flysch rocks with abundant acid effusive volcanics and the Rakovec Group composed of flyschoid and mafic effusive volcanic rocks. In addition, it includes Upper Carboniferous detrital sediments, Permian continental sediments with acid effusive volcanics and in the south also Permian marine detrital sediments. In the Alpine period, the Early Paleozoic sequences were intruded by granitoids.

The Meliaticum and Tornaicum in the southern Inner Carpathians, which were formerly assigned into the Gemicum, are now regarded as separate units. Their areal extent is very small, and their mutual relationships and position have not yet been clarified sufficiently. The Gemicum is overthrust onto the Veporicum.

The Fatricum consists of rootless nappes overlying the Tatricum (Křížna and Vysoká nappes). Its succession of strata ranges from the Lower Triassic to Cenomanian. Only in the Staré Hory

area the Křižna nappe also includes earlier rocks – Permian and crystalline ones. The Fatric basin of deposition is likely to have been situated between the Tatricum and Veporicum.

The Hronicum is made up of higher rootless nappes resting on the Fatricum largely in the Tatric and partly also in the Veporic area. The nappe rocks are Carboniferous to Neocomian in age. The Permian continental sediments are accompanied by mafic volcanics. The Triassic in the Choč nappe has a variegated marine carbonate character whereas the Šturec nappe is essentially dolomitic. The Hronic basin of deposition was probably situated south of the Gemicum.

The Silicicum (Mesozoic of the Slovak Karst, Galmus, Muráň Plateau, Drienok nappe, etc.) is the highest group of rootless nappes composed of the Lower Triassic shaly facies but mainly Middle to Upper Triassic carbonates. They were probably deposited in the same sedimentary area as the Hronicum.

The Middle Cretaceous Inner Carpathian tectogenesis is characterized by complete reduction of the crystalline basement which originally underlay the rootless nappes. After the nappes were overthrust, this area was partly inundated by a Senonian sea whose sediments were preserved only very rarely. In the Paleogene, the Inner Carpathians became a basin of deposition. Thick flysch formations, the Inner Carpathian Paleogene, were deposited in the northern section. The Buda- (Pannonian-) Paleogene facies were deposited in the south. Late tectonic and post-tectonic molasse basins evolved in the Inner Carpathians after the Sava folding, a process accompanied by intensive volcanism. The filling of these basins is dominated by brackish and freshwater sediments. The Neogene tectonic regime crushed the Inner Carpathians into blocks. Tectonic activity of the blocks resulted in the ascent of magma, particularly along the block limits. The volcanics belong to the effusive series rhyolite – andesite – basalt, and the intrusive rocks into granite – granodiorite group.

### 3.2.2 *Outer Carpathians*

From a tectonic point of view, the Klippen Belt is the most complicated unit in the Carpathians. It is characterized by the absence of pre-Mesozoic rocks, insignificant Triassic, variable Jurassic and Cretaceous, klippe tectonic style, and location between the Inner and Outer Carpathians. The klippees are made up of Jurassic and Lower Cretaceous limestone lenses amidst Cretaceous and Paleogene flysch sediments. Until the Senonian, the Pieniny geosyncline underwent the same evolution as the Inner Carpathian one. During the Laramian stage the geosyncline was folded into a system of north-vergent folds and nappes, and deformed once again in the uppermost Paleogene and throughout the Miocene.

The Flysch Belt forms an arc along the outer rim of the West Carpathians. Its principal characteristics include the absence of pre-Mesozoic units, flysch sediments of Cretaceous and Paleogene age, Tertiary overthrusting of the nappe system, and minor extent of post-nappe formations. Several nappes were overthrust here. They are assigned into the Magura, Silesian and Dukla nappe groups. Only the southern ones, i.e. the Magura and Dukla groups, occur in the Slovak territory.

Structural units present in the Slovak territory have different depth ranges. The units in the Outer Carpathians, ordered from the north to the south, are as follows. The Flysch Belt whose depth is 5000–6000 m in the west and 10,000–12,000 m in the east (Nizke Beskydy). The very steep Klippen Belt stretches to a depth of more than 10 km. The Inner Carpathians consist of both nappe crystalline-Paleozoic-Mesozoic tectonic units and post-nappe formations, such as Inner Carpathian Paleogene sediments of extremely variable thickness of 1500–2000 m in basins and 3000–3500 m in the Levočské vrchy Mts. Neogene formations, mainly in basins, are as much as 5000–7000 m thick. These are closely associated with Neogene volcanic complexes up to 2500 m thick. Late Paleozoic and Mesozoic units, both autochthonous and allochthonous relative to their substratum, are widespread, mainly in the northern section of the Inner Carpathians, their presence in the southern section being smaller. They make up primarily western and northern slopes of mountain ranges mostly in the Strážovské vrchy, Veľká Fatra and Chočské vrchy Mts. They also

underlie Tertiary rocks in the inner basins, Levočské vrchy and Skorušinské vrchy Mts. and their depth is greater in these areas. Their assumed maximum depths are 3000–3200 m, but in the near-Klippen area the Mesozoic units may stretch to much greater depths as a result of complex tectonics. The Slovak part of the Vienna Basin has a special character in this respect because the well LNV-7 intersected Mesozoic complexes here as deep as 6405 m. In the southern section of the Inner Carpathians, that is, in the Danube Basin, Central Slovakian Neogene volcanics, Rimava Basin and Eastern Slovakian Basin, the Mesozoic underlies the Tertiary to a much smaller extent. In the Danube Basin it occurs only on its northeastern edge and between Štúrovo and Komárno. The crystalline unit here mostly lies at a depth of 3000 m. In the Central Slovakian Neogene volcanic area, Mesozoic occurs at substantial depths only in the Žiar Basin (around 5000 m), while elsewhere its depth does not exceed 2000–3000 m. Over vast areas the Mesozoic is absent and the Neogene volcanics rest directly on the crystalline unit. In the Rimava Basin, Lower Triassic shale complexes probably start at a depth of 1500 m and Paleozoic formations at 2000 m. In the Eastern Slovakian Basin, the Tertiary is likely to be underlain primarily by Late Paleozoic formations of the Zemplinicum. Mesozoic units are either absent or occur only exceptionally at substantial depths (5000–7000 m).

The crystalline complexes (crystalline schists, granitoids) crop out in central tracts of mountain ranges and stretch to very great depths. Given the nappe structure of the West Carpathians, the crystalline unit is believed to be underlain by Mesozoic elements (at depths of 10–12 km) which are nowhere exposed on the surface (e.g. the Pieninicum, etc.).

### 3.3 CHARACTERISTICS OF GEOTHERMAL BODIES

In line with the Water Framework Directive (WFD) and following EU guidelines for classifying groundwater bodies, with regard to long-term information database in the assessment of groundwater in Slovakia and national specifics, three independent levels of groundwater bodies were identified: (i) Quaternary groundwater bodies, (ii) pre-Quaternary groundwater bodies and (iii) geothermal groundwater bodies. Delineation of the geothermal groundwater bodies respects the delineation of geothermal areas as shown in Figure 3.1.

Sources of geothermal energy in Slovakia are represented by geothermal waters, which are bound mainly to the Triassic dolomites and limestones of Inner Carpathians nappes; less to the Neogene sands, sandstones and conglomerates, or the Neogene andesites and pyroclastics. Geothermal aquifers are located at the depths of 200–5000 m. In general, the temperature of geothermal water ranges from 15 to 240°C. Aquifers where the temperature of the geothermal water exceeds 150°C are located in Danube Basin Central Depression, Vienna Basin, Central Slovakian Neogene volcanics NW part (Žiar Basin), Humenné ridge, Beša – Čičarovce structure (Table 3.2).

The link of geothermal waters to those aquifers is evident from their natural discharges. Geothermal water flow regime is determined by the fold-nappe tectonics of Mesozoic strata, and by presence of nappes plunging from the mountain slopes to greater depths. Young fault tectonics affected the Mesozoic strata by longitudinal and transverse faults as well. Far-reaching folds provide the connection of infiltration areas with the transition-accumulation ones. The crossing of longitudinal and transverse faults allows the groundwater to ascend to the surface through the Tertiary and Quaternary sediments. This is particularly the case of the intra-mountain depressions. An example of such a hydrogeothermal structure is the western part of the Liptovská kotlina Basin with natural outflows in Bešeňová (Fig. 3.1). Other examples of geothermal structure are geothermal reservoirs without natural springs (Danube Basin Central Depression, Komárno Marginal block), or without infiltration areas (Levice block).

In terms of geothermics the Western Carpathians can be divided into two parts, which vary widely in their geothermal activity and spatial distribution of the earth's heat (Fig. 3.2). Relatively low temperatures and densities of surface heat flux are characteristic for the central and northern

Table 3.2. Geothermal water bodies, predicted water temperatures at the surface in relation to the expected depth of the aquifer (based on Remšík *et al.*, 2011).

Type sources and their GTW temperature	Geothermal water body	No. of GTW bodies
Low temperature ( $T < 100^{\circ}\text{C}$ )	Danube Basin Central Depression, Komárno high block, Komárno marginal block, Vienna Basin, Levice block, Topol'čany embayment and Bánovce Basin, Upper Nitra Basin, Skorušina Basin, Liptov Basin, Levoča Basin W and S parts, Košice Basin, Turiec Basin, Komjatice Depression, Dubník Depression, Trnava embayment, Piešť'aný embayment, Central Slovakian Neogene volcanics SE part, Žilina Basin, Horné Strháre – Trenč graben, Rimava Basin, Trenčín Basin, Ilava Basin, Levoča Basin NE part, Humenné ridge, Beša – Čičarovce structure, Lučenec Basin	27
Medium temperature ( $T = 100\text{--}150^{\circ}\text{C}$ )	Danube Basin Central Depression, Komárno marginal block, Vienna Basin, Topol'čany embayment and Bánovce Basin, Liptov Basin, Košice Basin, Turiec Basin, Trnava embayment, Piešť'aný embayment, Central Slovakian Neogene volcanics NW part, Trenčín Basin, Ilava Basin, Žilina Basin, Levoča Basin NE part, Humenné ridge, Beša – Čičarovce structure	16
High temperature ( $T > 150^{\circ}\text{C}$ )	Danube Basin Central Depression, Vienna Basin, Central Slovakian Neogene volcanics NW part (Žiar Basin), Humenné ridge, Beša – Čičarovce structure	5

Legend: GTW – geothermal water.

part of the Inner Western Carpathians and for the western part of the Outer Flysch zone ( $30\text{--}40^{\circ}\text{C}$  at a depth of 1000 m;  $50\text{--}60\text{ mW m}^{-2}$ ). In contrast, high subsurface temperatures and high heat flux densities are typical for the Neogene sedimentary basins and volcanic mountains of the Inner Western Carpathians ( $40\text{--}70^{\circ}\text{C}$  at a depth of 1000 m;  $70\text{--}120\text{ mW m}^{-2}$ ). The boundary between these geothermically different areas forms a zone of intensive horizontal temperature gradients, especially at the contact with volcanoclastic complex of the Pre-Neogene units of the Western Carpathians. The mean temperature at a depth of 1000 m within the Western Carpathians is  $45^{\circ}\text{C}$ ; the mean heat flux density (arithmetic average of 136 wells) is  $82.1 \pm 20.5\text{ mW m}^{-2}$ .

The highest temperatures and surface heat flow densities were found in the Eastern Slovakia Neogene Basin (Fig. 3.2) with its maximum values in the central and SE parts ( $60\text{--}70^{\circ}\text{C}$  at a depth of 1000 m;  $100\text{--}120\text{ mW m}^{-2}$ ). The high values, namely from  $74.0$  to  $109.0\text{ mW m}^{-2}$  with a mean value of  $94.3\text{ mW m}^{-2}$ , were also found in the Central Slovakia Neovolcanites; values higher than  $90\text{ mW m}^{-2}$  are typical for central and eastern part of the Danube Basin. Surprisingly low values, from  $40.6$  to  $69.0\text{ mW m}^{-2}$  with a mean value of  $55.0\text{ mW m}^{-2}$  were detected in the Vienna Basin. Significantly variable values (from  $52.0$  to  $79.4\text{ mW m}^{-2}$ ) characterize the inner depressions of the Western Carpathians (Franko *et al.*, 1995).

The largest in extent in Slovakia is the Danube Basin geothermal water body in the northern tip of the Pannonian Basin. The Danube Basin Central Depression is fringed by the Malé Karpaty Mts. in the northwest, by the Dobra Voda fault (Ludince line) in the northeast, roughly by the Nitra River in the southeast and by the River Danube between Bratislava and Komárno in the southwest. The geothermal aquifer continues further south to Hungary. Based on accessible and published data, the Danube Basin area between Slovakia, Hungary and Austria was investigated during the international cooperation. The outcome was incorporated into geological models (Kronome *et al.*, 2014), hydrogeological models (Švasta *et al.*, 2014) and geothermic models (Goetzl and Zekiri, 2012) of the Danube Basin area.

The Danube Basin pre-Tertiary substratum is morphologically fairly rugged. Away from the above mountains, the pre-Tertiary substratum plunges rather regularly towards the basin center, thus forming a vast central depression whose deepest part, the Gabčíkovo depression, is  $7000\text{--}8000\text{ m}$  deep, as is indicated by geophysical investigations (Figs. 3.3 and 3.4).

Several drillholes in the northwestern and southeastern tracts of the depression have revealed that the Tertiary filling here rests on crystalline rocks (crystalline schists, granitoids). The geologic

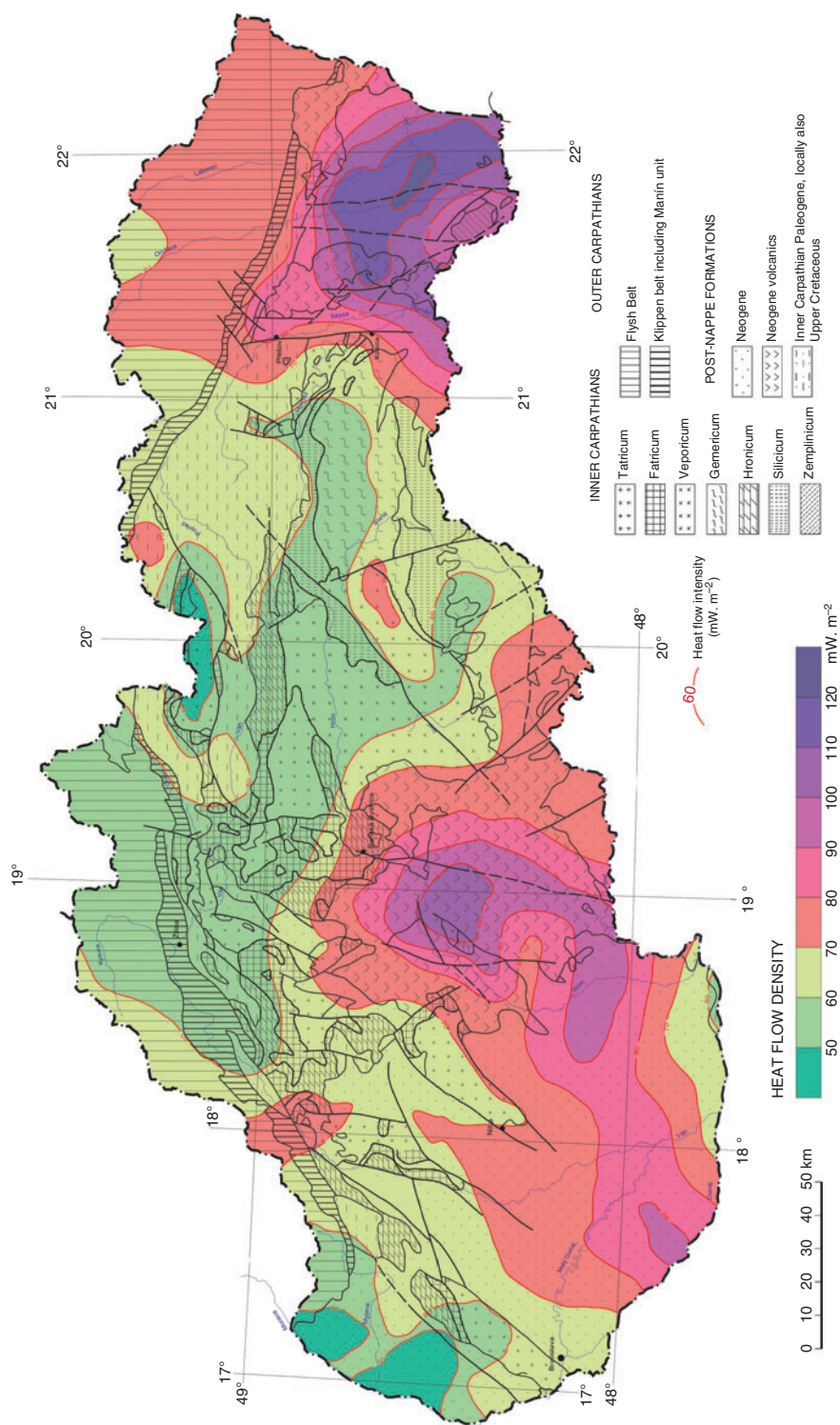


Figure 3.2. Map of surface heat flow density of Slovakia on the background of geologic units (after Franko *et al.*, 1995).



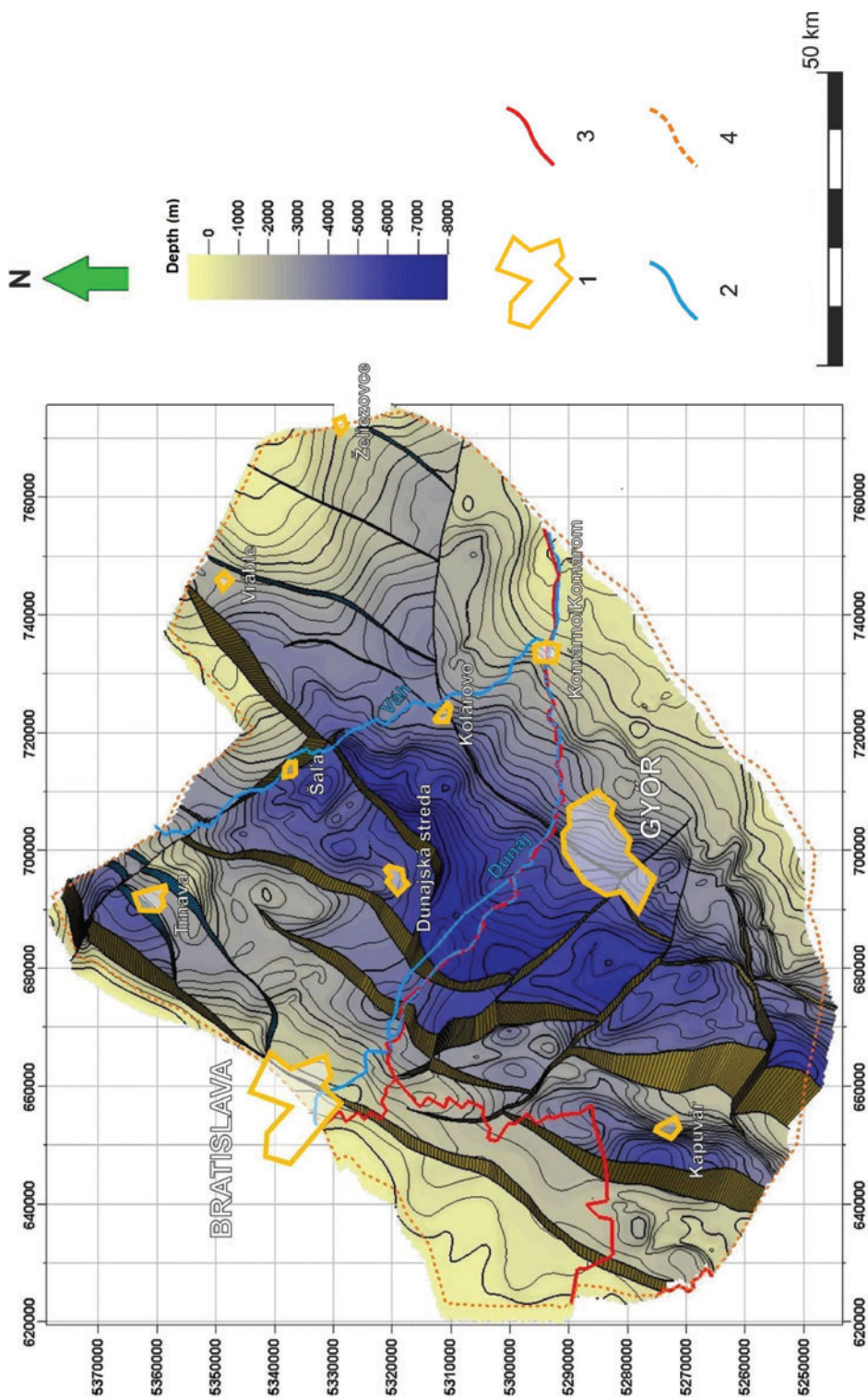


Figure 3.3. Top surface of pre-Tertiary basement in 2D (output from the model) (after Kronome *et al.*, 2014). Legend: 1: major cities; 2: rivers; 3: state borders; 4: area investigated by the project TRANSENERGY.



history of the Danube Basin suggests that the whole Tertiary filling of the Central Depression is underlain by the Carpathian crystalline unit which contains no suitable geothermal aquifers (suitable aquifers include sands to sandstones of Pannonian, Pontian and Dacian age). However, geothermal activity of the Central Depression is high (Král, 1992). The highest heat flow densities have been recorded in the middle of the depression ( $q > 85\text{--}90\text{ mW m}^{-2}$ ) and do not correspond to lower temperatures ( $T < 45^\circ\text{C}$ ) nor thermal gradients. While  $Q$  values decrease towards the margins,  $T$  increases. This irregularity is caused by a cold-water body bound to the first hydrogeological unit up to 460 m thick. The colder zone gradually diminishes downward and then the temperature field corresponds to the heat flow field. The Badenian volcanoclastics at depths of 5–6 km may contain geothermal waters whose aquifer temperature exceeds  $200^\circ\text{C}$ . They can be exploited through reinjection. Due to its post-Sarmatian evolution, the Central Depression has a bowl-like brachysynclinal shape (Priehodská and Vass, 1986). A hydrogeothermal characteristic of the depression was described by Franko and Mucha (1974, 1975), Franko *et al.* (1984, 1985, 1989, 1990), Fendek *et al.* (1988), Remšík *et al.* (1989b, 1990), Bodiš and Franko (1990) and Fendek and Bodiš (1992). The upper limit of the geothermal water body is 1000 m below surface and at the bottom it is confined by a fairly impervious substratum – an aquitard (clays) which plunges from the periphery towards the middle of the basin to a depth of 3400 m. The structure is likely to have interlayer leakage, intergranular permeability and confined groundwater level. Circulation of geothermal water ( $42\text{--}92^\circ\text{C}$ ) is connected to sands to sandstones of Dacian, Pontian and Pannonian age. Clays form an aquiclude. The percentage of aquifers falls from the edge of the basin towards its center as the aquifers disappear with increasing depth. With respect to lithology, the aquifer and overlying beds have been divided into six hydrogeological units:

- An aquifer complex (sandy gravels and sands, exceptionally clays).
- A complex where aquifers prevail over aquicludes (thick and thin sand or sandstone layers alternating with thin clay and marlstone layers), characteristic transmissivity values range from  $TR = 1 \times 10^{-4}\text{--}1 \times 10^{-3}\text{ m}^2\text{ s}^{-1}$ .
- A complex where the percentage of aquifers and aquicludes is roughly equal (alternating sands, gravels, clays and sandy clays), characteristic  $TR = 1 \times 10^{-4}\text{--}3.2 \times 10^{-3}\text{ m}^2\text{ s}^{-1}$ , lower or higher  $T$  occur rarely.
- A complex where aquicludes prevail over aquifers (clay beds from 18 to 88 m thick alternating with thin sand beds from 3 to 12 m in thickness), characteristic  $TR = 1 \times 10^{-4}\text{--}1 \times 10^{-3}\text{ m}^2\text{ s}^{-1}$ .
- A complex where aquicludes prevail over aquifers (less thick clay beds from 3 to 17 m in thickness alternating with thin sand beds from 3 to 7 m thick), characteristic  $TR = 1 \times 10^{-4}\text{--}1 \times 10^{-3}\text{ m}^2\text{ s}^{-1}$ .
- An aquiclude complex (clay beds clearly prevail over exceptional thin sand or sandstone beds),  $TR < 1 \times 10^{-4}\text{ m}^2\text{ s}^{-1}$ .

Aquifers with the highest  $TR$  ( $TR > 1 \times 10^{-3}\text{ m}^2\text{ s}^{-1}$ ) at the  $-1500\text{ m}$  level are widespread in several parts of the depression, away from which  $T$  decreases towards the N, NE, SE and E to  $3 \times 10^{-4}\text{ m}^2\text{ s}^{-1}$ .

### 3.4 GEOTHERMAL WATERS' CHEMICAL COMPOSITION

As to the origin of geothermal waters' chemical composition, three basic genetic types have been distinguished (Bodiš and Franko, 1986) (Fig. 3.5):

1. Geothermal waters with marinogene mineralization which include:
  - (a) connate waters whose mineralization corresponds to the paleosalinity of their aquifers and which were metamorphosed only in the water-rock system and/or by  $\text{CO}_2$  addition;
  - (b) connate waters infiltrated, biogenic or petrogenic degraded to various degrees and at different periods;

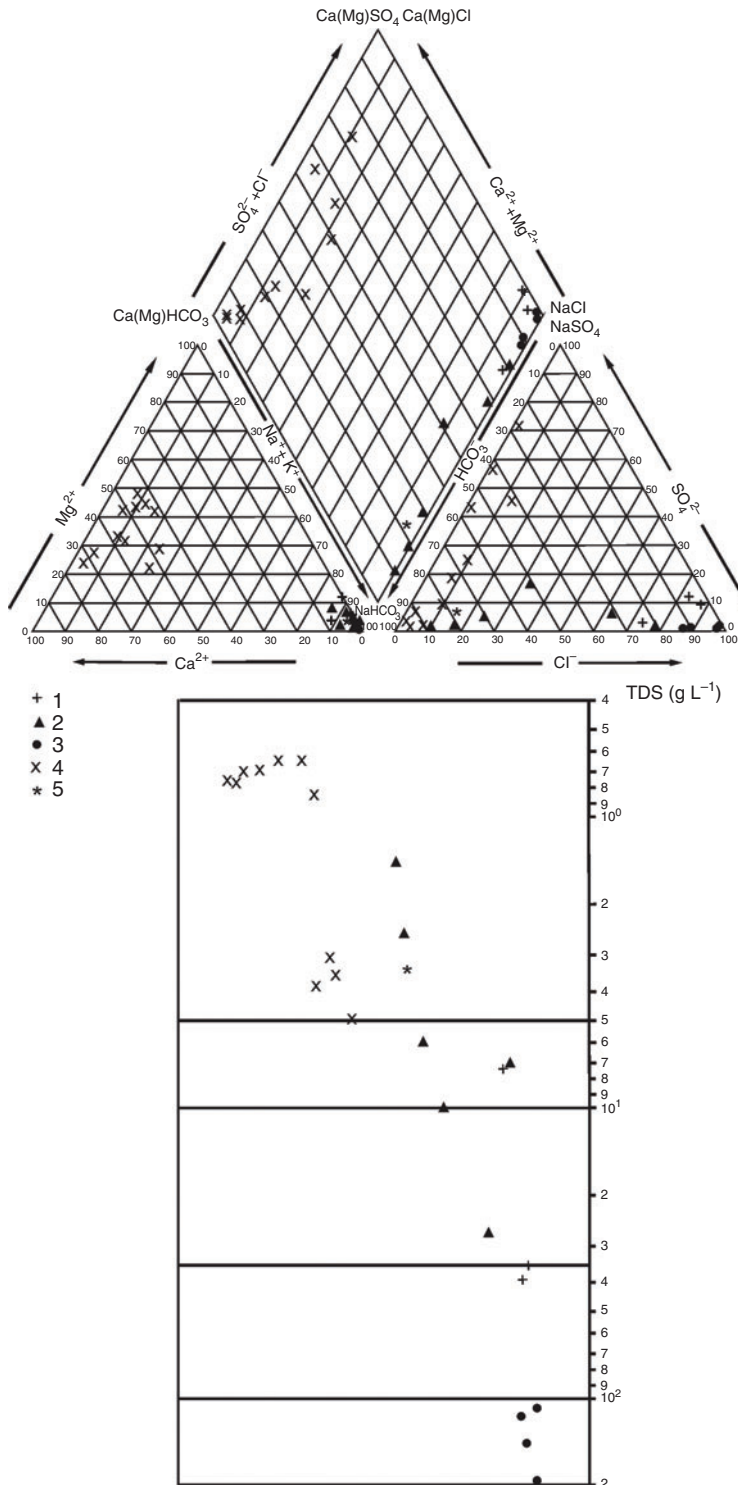


Figure 3.5. Piper diagram of West Carpathian geothermal waters: 1: connate waters; 2: degraded connate waters; 3: highly mineralized waters; 4: waters with petrogenic mineralization; 5: waters of mixed origin.

- (c) highly mineralized geothermal waters formed through halite dissolution by seawater or through local concentrating of seawater;
2. Geothermal waters with petrogenic mineralization whose TDS does not exceed  $5 \text{ g L}^{-1}$  exemplified by meteoric waters of fairly deep or deep circulation;
3. Geothermal waters of mixed origin and complex chemistry.

Connate waters are characteristic of the whole investigated section of the Pannonian in the Danube Basin Central Depression (Franko *et al.*, 1989), subjacent Triassic carbonates in the Lakšárska Nová Ves elevation (Remšík *et al.*, 1989a), Levice block, southern tract of the Košice Basin, andesites and related pyroclastics in the Beša – Čičarovce structure and deeper Miocene sediments of the Komárno block. Their chemistry typically is sodium-chloride with a minimum presence of sodium-hydrogencarbonate component. The waters were metamorphosed only in the water-rock system. The main metamorphic process was ion-exchange controlled by chemical potentials of the solid-liquid phase at equivalent stoichiometric ratios. The ion-exchange kinetics is controlled by diffusion processes on the surface and inside solid phase. The metamorphism of connate waters results in lower concentrations of  $\text{Mg}^{2+}$  ions and higher concentrations of  $\text{Ca}^{2+}$  ions in comparison with their original chemistry. According to Valjaško (1963), these changes were caused by cation exchange of  $\text{Mg}^{2+}$  in solution for  $\text{Ca}^{2+}$  from the rock, cation exchange of  $2\text{Na}^+$  in solution for  $\text{Ca}^{2+}$  from the rock or by the reaction  $\text{MgCl}_2 + 2\text{CaCO}_3 = \text{CaMg}(\text{HCO}_3)_2 + \text{CaCl}_2$ .

Of course, the changes also depend on further factors, such as chemical composition of sedimentary rocks and, according to a multitude of authors, also on the changes in chemistry of ocean waters and atmosphere over geologic history, aquifer depths which control *P-T* conditions, biochemical processes, among others.

The basins underwent a complex paleohydrogeologic and tectonic evolution and therefore their connate waters could not have been preserved and were infiltration-degraded to a varying degree (often as a result of geologic openness in the geologic history or even recently). This degradation typically leads to substantial reduction in sodium-chloride component which is replaced by sodium-bicarbonate, and to higher  $\text{HCO}_3/\text{Cl}$  coefficients (up to 10, locally even more). The maximum degree of degradation was noted in the Trnava embayment (well Krupá-1) where meteoric waters infiltrate into subjacent Mesozoic through its outcrops, and in geothermal waters (tapped by wells at Vlčany, Tvrdošovce, Horná Potôň and Topol'níky) accumulated in hydrogeologically semi-open structures in Pontian sands of the Danube Basin Central Depression. It is worth mentioning that the basin of deposition became gradually brackish during the Pontian, its salinity being 0.5–3‰ (Vass, 1981).

Infiltration-degraded connate waters were also discovered in the Mesozoic substratum of the central Vienna Basin by wells Šaštín-9, 10, RGL-2 and Studienka-37. High sulfate contents in these waters originated from gypsum (anhydrite) dissolution. Their hydrogen-sulfide contents are anomalously high as well ( $200\text{--}400 \text{ mg L}^{-1}$ ).

Geothermal waters of similar character are genetically associated with Triassic carbonates in the northern tract of the Košice Basin and in the Levoča Basin.

Highly mineralized geothermal waters after Palmer-Gazda's classification (Gazda, 1971) are of clear sodium-chloride chemical type ( $S_1(\text{Cl})$  range from 87 to 96 eq. %) whose TDS exceeds  $50 \text{ g L}^{-1}$  occur in the Danube, Vienna and Trebišov basins. Gazda (1977) assumes that these waters in the Danube and Vienna basins are so-called relict salt solutions formed by local thickening of the basins' waters below the critical point of NaCl solubility. Such waters in the Eastern Slovakian Basin are of halogenous origin, i.e. were formed through halite dissolution by seawater, or meteoric waters.

The central and eastern tracts of the Komárno high block (Remšík *et al.*, 1992) are characterized by the occurrences of geothermal waters with petrogenic mineralization of calcium-magnesium-hydrogencarbonate chemical type whose temperature is  $20\text{--}30^\circ\text{C}$  and TDS around  $0.7 \text{ g L}^{-1}$ . These typical carbonatogenic acratothermae are genetically associated with Triassic carbonates of the Central Hungarian Mountains. High Mg/Ca coefficients of these thermal springs indicate that they originate in dolomites while low  $\text{SO}_4/\text{TDS}$  coefficients attest to the absence of major gypsum (anhydrite) occurrences in their circulation routes. The only so far known hydrogeochemical



anomaly is at Štúrovo where well FGŠ-1 tapped roughly equally mineralized acratothermae 40°C warm with a fairly high calcium-sulfate content ( $S_2(SO_4) = 28.44$  eq. %).

Carbonate geothermal waters are also known in the Topol'čany embayment (Vel'ké and Malé Bielice), Upper Nitra Basin (Bojnice) and Žilina Basin (Rajecké Teplice).

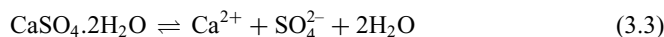
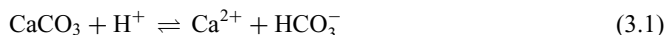
Carbonate-sulfatogenic geothermal waters are characteristic of the Mesozoic substratum of the Liptov Basin (Bešeňová, Vlachy, etc.) and Mesozoic carbonates underlying the Central Slovakian Neogene volcanics (Zlatno R-3).

TDS of geothermal waters with petrogenic mineralization attains  $5 \text{ g L}^{-1}$  (locally even more) and depends mostly on the amount of abyssal  $CO_2$  added and time during which they were in contact with rocks along their circulation routes. The chief mineralization process controlling the chemistry of these waters is carbonate and/or gypsum dissolution.

Geothermal waters of mixed origin were tapped by wells FGK-1, M-3 and M-1 in the Komárno area (Remšík, 1979). From a genetic point of view, these thermal sources are a mixture of carbonate-sulfatogenic waters of the Mesozoic and considerably infiltration-degraded waters of the overlying Miocene, which latter seeped into the carbonate complexes mainly in the beginning of Miocene marine transgression. As to their TDS, four types of geothermal waters have been distinguished (Franko *et al.*, 1975): low-mineralized (up to  $5 \text{ g L}^{-1}$ ), medium-mineralized ( $5\text{--}10 \text{ g L}^{-1}$ ), high-mineralized ( $10\text{--}35 \text{ g L}^{-1}$ ) and very high-mineralized ( $>35 \text{ g L}^{-1}$ ).

When assessing the state of a system with respect to chemical equilibrium, which controls the deposition of incrustations and therefore plays a key role in the exploitation, it is necessary to evaluate interactions of water with carbonate rocks and with sands that are important for mixed-type and petrogenic mineralization waters. In the case of sand aquifers, their  $Ca^{2+}$  content is made up entirely of carbonates through reversible equilibrium because the remains of feldspars and micas as well as the presence of clay minerals create a system similar to that in acid aluminosilicate rocks. Reversible equilibrium with evaporites can take place in waters with marinogenic mineralization.

Chemical equilibriums of the following reactions were considered:



A thermodynamic analysis was used to calculate activities and saturation indices (SI). Program PHREEQC (Parkhurst and Appelo, 1999) was used for speciation modeling.

The SI values for gypsum suggest that connate waters tapped by well LNV-7 in depth interval 5576–5547 m, all high-mineralized waters with marinogenic mineralization and sulfato-carbonatogenic waters, are at equilibrium or are oversaturated with respect to gypsum. That is why sulfate contents are controlled by chemical equilibrium between gypsum (and/or anhydrite) and water.

Calcite saturation indices in the vast majority of geothermal waters attain positive values indicating tendency to form incrustations. In practice, thick carbonate incrustations were often deposited in casing, effluent and distribution tubes.

Saturation indices for carbonate minerals are reduced by the influx of endogenous  $CO_2$ , which shifts the equilibrium to the right side of the equation, or by shorter duration of the contact between water and rocks along circulation routes.

Different conditions under which geothermal waters in individual areas were formed result in different physico-chemical and consequently also technological properties of these waters. For instance, a comparison between geothermal waters in the Danube Basin Central Depression and those in the Liptov Basin reveals that the former, aside from a few exceptions, deposit little incrustations, but the latter readily deposit incrustations even when degassed only partly (the only exception being well FGL-1 Pavčina Lehota). The properties of waters in the Skorušiná and Levoča basins are very similar to those in the Liptov Basin. Waters in the Vienna Basin are very different from waters in the other areas because of their high content of dissolved  $H_2S$  and related corrosive effects and therefore can hardly be exploited without reinjection.

Table 3.3. Descriptive statistics of water chemistry data in carbonate geothermal aquifers.

Parameter	Average	Median	Minimum	Maximum
Na	344.641	44.500	2.500	11,470.00
K	32.397	11.700	0.800	684.00
NH <sub>4</sub>	1.655	0.100	bld	53.77
Ca	289.443	248.496	4.010	816.00
Mg	83.334	62.259	2.918	289.41
Fe	1.150	0.100	bld	34.60
Mn	0.116	0.030	bld	2.73
As	0.722	0.005	0.0004	36.70
Cd	0.009	0.001	bld	0.20
Cr	0.005	0.003	0.0001	0.11
Cu	0.016	0.010	bld	0.51
Li	1.177	0.130	0.0005	39.82
Pb	0.005	0.001	bld	0.23
Sr	4.417	3.405	0.0106	15.00
Zn	0.062	0.020	bld	2.43
F	1.311	1.300	bld	3.63
Cl	429.939	14.600	1.060	17,778.30
Br	0.810	0.500	bld	20.05
I	0.175	0.050	bld	3.74
SO <sub>4</sub>	584.144	524.070	1.630	1560.00
HCO <sub>3</sub>	797.657	530.857	190.900	4051.73
H <sub>2</sub> SiO <sub>3</sub>	27.600	23.205	0.286	92.88
HBO <sub>2</sub>	38.283	2.260	0.020	1074.13
CO <sub>2</sub>	342.734	102.000	bld	1640.00
H <sub>2</sub> S	0.907	0.005	bld	8.86
TDS	2632.666	1510.710	374.130	32,562.23

Note: bld: below limit of detection; TDS: total dissolved solids,  $n = 155$ . Units are in mg L<sup>-1</sup>.

Chemical composition of most representative geothermal waters, which are bound to the Triassic dolomites and limestones, is shown in Table 3.3.

Geothermal waters of carbonate reservoirs mostly belong to non-metamorphosed or slightly metamorphosed geothermal waters of Mesozoic formations of Western Carpathians; in this group, there are waters of Ca-Mg-HCO<sub>3</sub>-(SO<sub>4</sub>) type, Ca-Mg-SO<sub>4</sub>-(HCO<sub>3</sub>) type and mixed types (Vranovská *et al.*, 2015).

Concentrations of trace elements are very low, except for high arsenic concentrations in geothermal sources in Ďurkov. The geothermal structure at Ďurkov is a part of the Košice Basin, located between Slanské vrchy Mts. and Slovenské Rudohorie Mts. This is a depression of Neogene age, where thickness of Mesozoic dolomites reaches 2000 m over an area of 33.6 km<sup>2</sup>. The geothermal reservoir is located in Mesozoic carbonates (Upper and Middle Triassic) and also in basal clastics of Carpathian. However, the thickness of Carpathian sediments (86–155 m) is insignificant compared to Mesozoic sediments (more than 200 m). Neogene sediments are represented by Sarmathian clays (thickness 500–1000 m), carbonate-sandy clays of Badenian (thickness up to 1300 m) and Carpathian carbonate claystones with basal conglomerates about 400 m thick. Thickness of Mesozoic dolomites increases towards the east from 300 m to 1000 m, and their depth also increases.

Geothermal gradient at Ďurkov in Neogene sediments is 51.2°C km<sup>-1</sup> and in Mesozoic carbonates it is 29.4°C km<sup>-1</sup>. Temperatures at the top of the reservoir at depths 1800–2600 m are 100–135°C and they reach 120–185°C at the base of the reservoir at 2500–4200 m depths. Thermal conductivity of Neogene sediments is 2088–2413 W m<sup>-1</sup> K<sup>-1</sup> and in geothermal reservoir in Mesozoic carbonates it is 3922 W m<sup>-1</sup> K<sup>-1</sup>. Average heat flux in the geothermal structure is 110 mW m<sup>-2</sup> (Vranovská *et al.*, 1999, 2015).

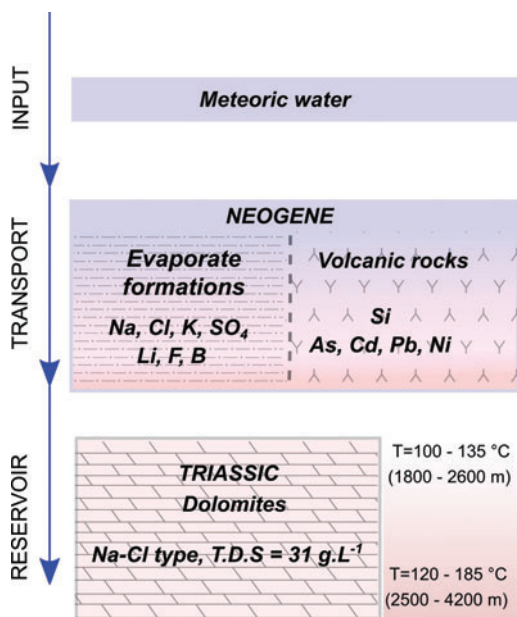


Figure 3.6. Conceptual model of As enrichment at Ďurkov site.

Based on hydrodynamic tests, values of transmissivity are from  $8.16 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$  to  $3.41 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$  and hydraulic conductivity from  $9.44 \times 10^{-8} \text{ m s}^{-1}$  to  $8.5 \times 10^{-6} \text{ m s}^{-1}$ . Two-phase flow regime starts from 750 m depth in well GTD-1 to 1146 m depth in well GTD-3. Suggested exploited amount of geothermal water from GTD-1 was  $56 \text{ L s}^{-1}$ .

Concentrations of arsenic are generally relatively low, with an average  $0.722 \text{ mg L}^{-1}$  (Table 3.3) except for the Ďurkov structure, where they reach  $36.7 \text{ mg L}^{-1}$ . Average concentrations of geothermal indicators Li and F are  $1.177$  and  $1.311 \text{ mg L}^{-1}$ , respectively. Concentrations of B, also a typical geothermal indicator, reach  $38.28 \text{ mg L}^{-1}$ . Concentrations of silica are considerable, up to  $92.88 \text{ mg L}^{-1}$  in spite of predominant carbonates in reservoir rocks.

Based on available data, the source of mineralization is in overlying Neogene evaporate formation comprising halite of Carpathian or Badenian age. A link to the Neogene sediments is also confirmed by the presence of spores *Cedripites miocaenicus*, *Pinuspollenites* sp. and *Juglandipollis* sp. found in sediments and incrustations from the well GTD-3.

A probable source of As and Si is in neo-volcanic rocks in Neogene formation and their mineralization. In the area of Neogene magmatism principal mineralization is of Hg-As-Sb type.

A conceptual model of geothermal water chemistry formation is in Figure 3.6. Meteoric water infiltrates into Neogene sediments and dissolves halite. In the next stage the formed brine dissolves minerals of As, for example, arsenopyrite and As-rich pyrite present in Neogene sediments. Simultaneously the water dissolves quartz. In the final stage the water infiltrates farther down to underlying Triassic dolomites, where it accumulates and interacts with carbonates in the presence of endogenous CO<sub>2</sub>.

Geochemical modeling of equilibrium reaction of water with arsenopyrite was able to reproduce measured As concentrations for a typical range of reservoir temperatures.

### 3.5 ABSTRACTION AND THERMAL ENERGY POTENTIAL OF GEOTHERMAL WATERS

In the period 2000–2010, 141 geothermal wells were registered in Slovakia, which made it possible to verify the conditions for the geothermal waters' formation. Geothermal water was



Table 3.4. Overview of exploited geothermal wells with the highest exploitation values (mean yearly exploitation of the geothermal water for the period 2000–2010).

Name of geothermal water body	Locality	Well	AAGTW [m <sup>3</sup> y <sup>-1</sup> ]	% from WPW
Liptov Basin	Bešeňová	ZGL-1	835687	74
Levoča Basin W and S parts	Vrbov	Vr-2	716091	83
	Vrbov	Vr-1	694794	110
Komárno high block	Štúrovo	FGŠ-1	408683	81
Levoča Basin W and S parts	Poprad	PP-1	304558	29
Danube Basin Central Depression	Senec	BS-1	295132	78
	Galanta	FGG-2	230661	70
	Galanta	FGG-3	294255	89
	Vel'ký Meder	Č-2	232512	92
	Horné Saliby	Di-2	198459	43
	Topol'níky	FGT-1	179314	59
	Bánovce nad Bebravou	BnB-1	156396	45
Upper Nitra Basin	Nováky-Laskár	Š1 NBII	149992	26
Danube Basin Central Depression	Vel'ký Meder	Č-1	148333	47
	Horná Potôň	FGHP-1	120015	67
	Dunajská Streda	DS-2	99704	109

AAGTW: annual average amount of geothermal water abstraction; WPW: water abstraction permit for well.

utilized from 46 wells situated in 36 sites within 13 geothermal water bodies. This list does not include geothermal wells, which are used as curative sources under the supervision of the Ministry of Health of Slovak Republic, with exemption of the source FGČ-1 in Čilistov.

In the period 2000–2010, 6,323,167 m<sup>3</sup> year<sup>-1</sup> (236.65 L s<sup>-1</sup>) were summarily taken from 46 operating geothermal wells. For all of these wells permits have been issued by relevant state water authorities for the abstraction of geothermal water, totaling 17,476,731 m<sup>3</sup> year<sup>-1</sup> (721 L s<sup>-1</sup>). The use of the wells represents 33% of allowances under the reported data on Slovak Hydrometeorological Institute of Slovak Republic customers. However, many data are notified as an estimate, since some sampling devices lack the necessary functional measuring capabilities.

The largest average amount of geothermal water was collected from the following units of the geothermal waters in the years 2000–2010: Danube Basin Central Depression, Levoča Basin, W and S parts, Liptov Basin and Komárno high block. During this period, from the perspective of individual geothermal wells, geothermal water was collected with the highest exploited volumes in the range of 100,000 to 1,000,000 m<sup>3</sup> year<sup>-1</sup> per well (Table 3.4).

The geothermal water from 23 exploited wells (50%) is taken from the Neogene rocks (sands or sandstones) and 23 wells (50%) from the Mesozoic rocks (Triassic carbonates). According to the value of the average annual utilization of geothermal water (2000–2010) from the Mesozoic rock environment were withdrawn 142 L s<sup>-1</sup> (60%) and from the Neogene geological environment 95 L s<sup>-1</sup> (40%).

The active part of the wells in the Neogene aquifers is approximately at the depth level of about 1200–1550 m and in the Triassic aquifers at intervals of about 635–1130 m. The water temperature at the wellheads in the Neogene sediments is 19–91°C (an average of about 60°C), the temperature of the water at the wellheads in the Triassic carbonates is 20–80°C (average of 42.5°C).

The prevailing type of geothermal energy utilization in Slovakia is currently for recreational purposes (87% of the sources used). Geothermal energy from 22 wells (48% of the sources used) is utilized for the purpose of building heating. The most important is the hospital complexes heating in Galanta as well as mining air heating in the lignite mine in Nováky. In the year-round opened aquaparks and thermal pools based on geothermal water, hotel rooms are also heated. This involves the sites of Dunajská Streda, Vel'ký Meder, Galanta, Horné Saliby, Senec, Čilistov,

Table 3.5. Thermal energy potential of geothermal waters in Slovakia (after Remšík *et al.*, 2011).

Geothermal water body	Category	Predicted amount		Proven amount		$\Sigma$ TEP	
		GW [L s <sup>-1</sup> ]	GE [MW <sub>t</sub> ]	GW [L s <sup>-1</sup> ]	GE [MW <sub>t</sub> ]	GW [L s <sup>-1</sup> ]	GE [MW <sub>t</sub> ]
Danube Basin Central Depression	ARE	731.0	150.0	488.7	101.11	1219.7	251.11
Komárno high block	ARE	133.0	9.7	265.0	17.42	398	27.12
Komárno marginal block	ANE		227.5	15.9	2.62	15.9	230.12
Vienna Basin	ANE		511.0	37.0	9.5	37	520.5
Levice block	ANE		126.0	81.0	20.74	81	146.74
Bánovce Basin	ARE	141.7	12.469	68.8	5.26	210.5	17.73
Upper Nitra Basin	ARE	140.0	29.12	57.9	7.05	197.9	36.17
Skorušiná Basin	ARE	166.0	24.0	135.0	18.29	301	42.29
Liptov Basin	ARE	248.0	34.589	121.4	20.36	369.4	54.95
Levoča Basin W and S parts	ARE	424.6	75.4	226.3	34.24	650.9	109.64
Košice Basin	ANE		1276.4	207.4	78.88	207.4	1355.28
Turiec Basin	ARE		22.5	19.9	2.65	19.9	25.15
Komjatice Depression	ANE		392.64				392.64
Dubník Depression	ANE		808.3	36.0	3.70	36	812
Trnava embayment	ARE		33.5	14.5	0.55	14.5	34.05
Piešťany embayment	ARE		10.5	10.0	0.18	10	10.68
Central Slovakian Neogene volcanics NW part	ARE		82.6	80.6	9.47	80.6	92.07
Trenčín Basin	ARE		4.6				4.6
Ilava Basin	ARE		1.1				1.1
Žilina Basin	ARE		13.2	57.4	2.95	57.4	16.15
Central Slovakian Neogene volcanics SE part	ARE		26.4	64.1	3.84	64.1	30.24
Horné Strháre – Trenč graben	ARE		6.2	16.0	1.04	16	7.24
Rimava Basin	ARE	284.74	21.121	61.3	1.76	346.04	22.88
Levoča Basin NE part	ANE		1316.0	19.0	4.55	19	120.55
Humenné ridge	ARE	341.0	750.5	6.0	0.41	347	750.91
Beša-Čičarovce structure	ANE		268.7				268.7
Lučenec Basin	ANE			11.20	1.04	11.2	1.04
$\Sigma$ ARE	ARE	2610.04	1307.5	1692.9	226.6	4302.9	1534.08
$\Sigma$ ANE	ANE		4926.5	407.5	121.0	407.5	5047.57
$\Sigma$ ARE + $\Sigma$ ANE	ARE + ANE	2610.04	6234.0	2100.4	347.6	4710.4	6581.65

Legend: TEP: thermal-energy potential; GW: geothermal water; GE: geothermal energy; ARE: amount of renewable energy; ANE: amount of non-renewable energy (need to use reinjection).

Pol'ný Kesov, Štúrovo, Podhájska, Bánovce nad Bebravou, Malé Bielice, Chalmová, Oravice, Bešeňová, Liptovský Mikuláš, Vrbov, Poprad and Veľká Lomnica.

In agriculture, the geothermal water is exploited from 11 wells (24% of the sources used) at 10 sites to heat winter greenhouses, or plastic greenhouses, to force the production of vegetables as well as the cultivation of flowers. In the Central Depression of the Danube Basin these wells are in Tvrdosovce, Gabčíkovo Topol'níky, Topol'ovec, Čiližská Radvaň, Horná Potôň and Dunajská Streda; in Levice block in Podhájska, and in Liptov Basin in Bešeňová. In Levoča Depression at the site Vrbov the geothermal water is also used for fish farming.

On a single site in Slovakia (Podhájska), the geothermal water is exploited using a reinjection system. Water from the exploitation borehole Po-1 passes through the heat exchangers, which transfer the heat to technological water. Thermally utilized geothermal water for greenhouse heating is reinjected into the well GRP-1 by pipe of length 2300 m. Operating parameters of reinjection are for exploitation well Po-1 ( $T = 83.4^{\circ}\text{C}$ ,  $Q = 5.6 \text{ L s}^{-1}$ ,  $P_{\text{wellhead}} = 0.385 \text{ MPa}$ )

and reinjection well GRP-1 ( $T = 40^{\circ}\text{C}$ ,  $Q = 5.0 \text{ L s}^{-1}$ ) during winter period (Marcin *et al.*, 2014).

For evaluation of the thermal energy potential of Slovakia in 1994, data from 61 geothermal wells for the period 1971–1991 were processed (Franko *et al.*, 1995). Wells proved amount of geothermal water  $900 \text{ L s}^{-1}$  with a temperature from 20 to  $92^{\circ}\text{C}$  and thermal energy 176 MWt. That represented around 3.2% from the total predicted amount of thermal energy. These quantities were linked to hydrogeological structures with renewable amounts of geothermal energy. Taking into account only the amount renewed, then it represented almost 32% of the total renewable and usable quantity of geothermal energy in Slovakia.

In 1999 and 2009, thermal energy potential in Slovakia was estimated and assessed at 5538 MWt and 6653 MWt, respectively. The actual use of this potential has been documented at the level of 130.97 MWt in 1999 (Fendek and Franko, 2000) and 163.86 MWt in 2009 (Fendek and Fendeková, 2010).

Thermal energy potential was assessed in 2011 and in individual geothermal areas of Slovakia its value was in the range of 1.1 MWt to 1316.0 MWt. The total calculated amount of geothermal energy in defined geothermal areas in Slovakia is currently at the level of 6,234,039 MWt (Table 3.5). These values were calculated by geothermal balance, volumetric method and mathematical modeling. In percentage terms, the identified amount of geothermal energy (345.04 MWt) compared to total calculated amount of geothermal energy in Slovakia represents only 5.58%.

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## CHAPTER 4

### Resources, geochemical features and environmental implications of the geothermal waters in the continental rift zone of the Büyük Menderes, Western Anatolia, Turkey

Nevzat Özgür

#### 4.1 INTRODUCTION

In Turkey, the eastern Mediterranean area between the Eurasian and African plates is controlled tectonically by the Anatolian and Aegean microplates. This plate tectonic evolution has resulted in the uplift of the Menderes Massif, which shows a dome-shaped structure due to compressional tectonic features formed through the Oligocene and Miocene. During the Early and Middle Miocene, the continental rift zones of the Büyük Menderes, Küçük Menderes and Gediz were formed by extensional tectonic features striking generally E–W and representing a great number of active geothermal systems, epithermal mineralizations and volcanic rocks from the Middle Miocene to recent times. The geothermal waters are associated with the faults that strike preferentially NW–SE and NE–SW and are also located diagonal to the general strike of the rift zones of the Menderes Massif in the Western Anatolia. These NW–SE and NE–SW striking faults were probably generated by compressional tectonic regimes, which led to the deformation of uplift between two extensional rift zones in the Menderes Massif. In addition to heat flow anomalies in the rift zone of the Büyük Menderes, there occurs very intensive volcanic activity, which is represented by various localities of a great number of calcalkaline-through-acidic volcanic rocks, and ranges in age from the Middle Miocene to 10,000 a. Based on isotope analyses of  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{144}\text{Nd}/^{143}\text{Nd}$ , the volcanic rocks are the products of the continental crust and can be considered as a heat source for the heating of the geothermal waters in the rift zone of the Büyük Menderes and elsewhere. In addition, the geothermal gradients may contribute to heating of the geothermal waters in the reservoir consisting of limestones, marbles, quartzites and gneisses. One of these continental rift zones is the rift zone of the Büyük Menderes, which represent a great number of geothermal waters such as Kızıldere, Salavathı, Germencik and others (Figs. 4.1 and 4.2).

The aim of this chapter is to give an overview and to present enhanced hydrogeological, hydro-geochemical and geochemical isotope data for the geothermal waters in the rift zone of the Büyük Menderes, in combination with interpretation of the origin and evolution of these waters as well as their potential for electricity generation and consideration of the environmental impacts of geothermal energy.

#### 4.2 GEOLOGIC SETTING

The geothermal field of Kızıldere has about 28 production and reinjection wells up to a depth of 2872 m and is located in the north of the eastern part of the Büyük Menderes rift zone (Figs. 4.1 and 4.2), where three geothermal power plants with a capacity of approximately 100 MWe have been installed (Mertoğlu *et al.*, 2015; Parlaktuna *et al.*, 2013) (Fig. 4.3). In Kızıldere, the Paleozoic basement rocks are overlain by Pliocene sedimentary rocks that consist of Kızılkaya, Sazak, Kolonkaya and Tosunlar formations (Özgür, 1998; Şimşek, 1985) (Fig. 4.4) and play an important

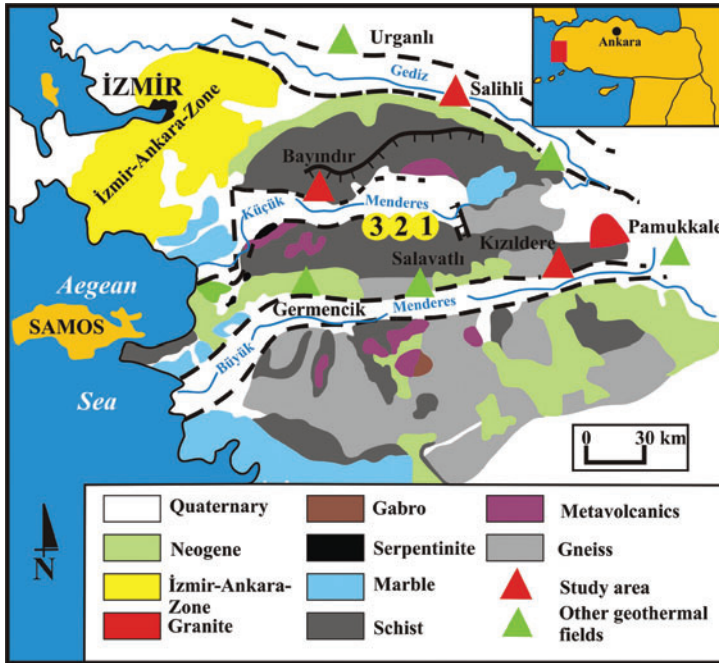


Figure 4.1. Geologic setting of the Menderes Massif and location map of the investigated geothermal fields of Kızıldereli, Salavatlı and Germencik. Epithermal mercury (1), antimony (2) and (3) arsenopyrite-gold deposits (Özgür, 1998).

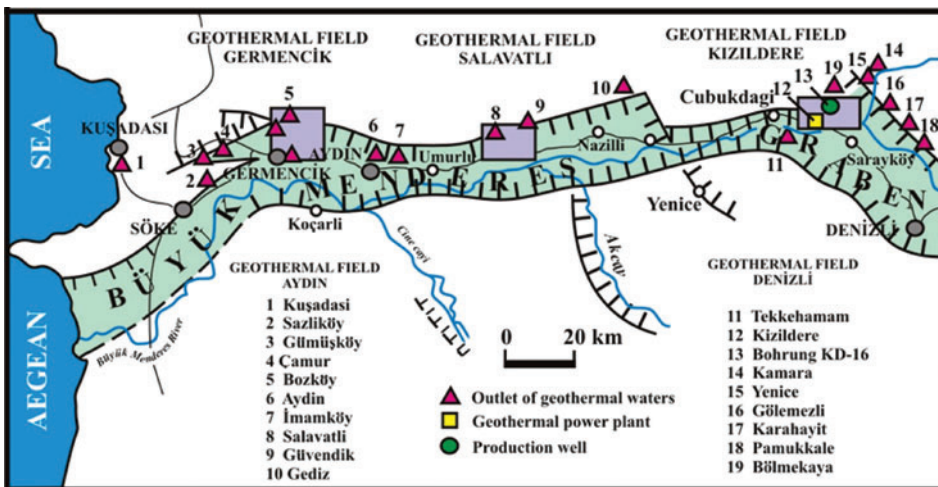


Figure 4.2. Distribution of the geothermal fields in the rift zone of the Büyük Menderes within the Menderes Massif (Özgür, 1998).





Figure 4.3. Geothermal power plant of Kızıldere in the rift zone of the Büyük Menderes.

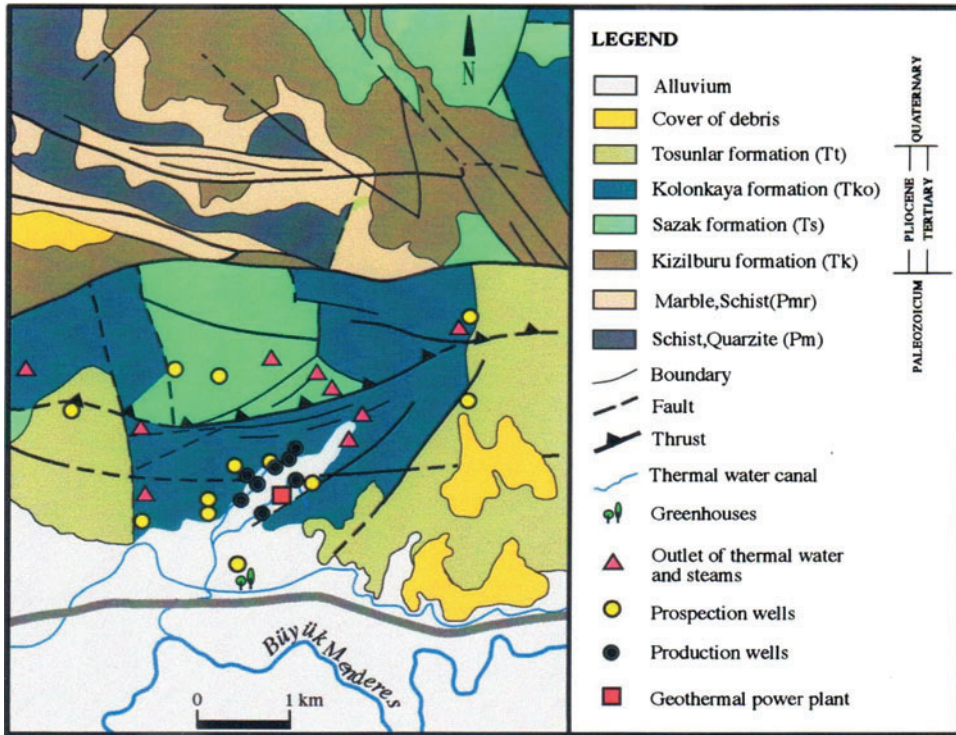


Figure 4.4. Geological map of the geothermal field of Kızıldere in the continental rift zone of the Büyük Menderes (Özgür, 1998).



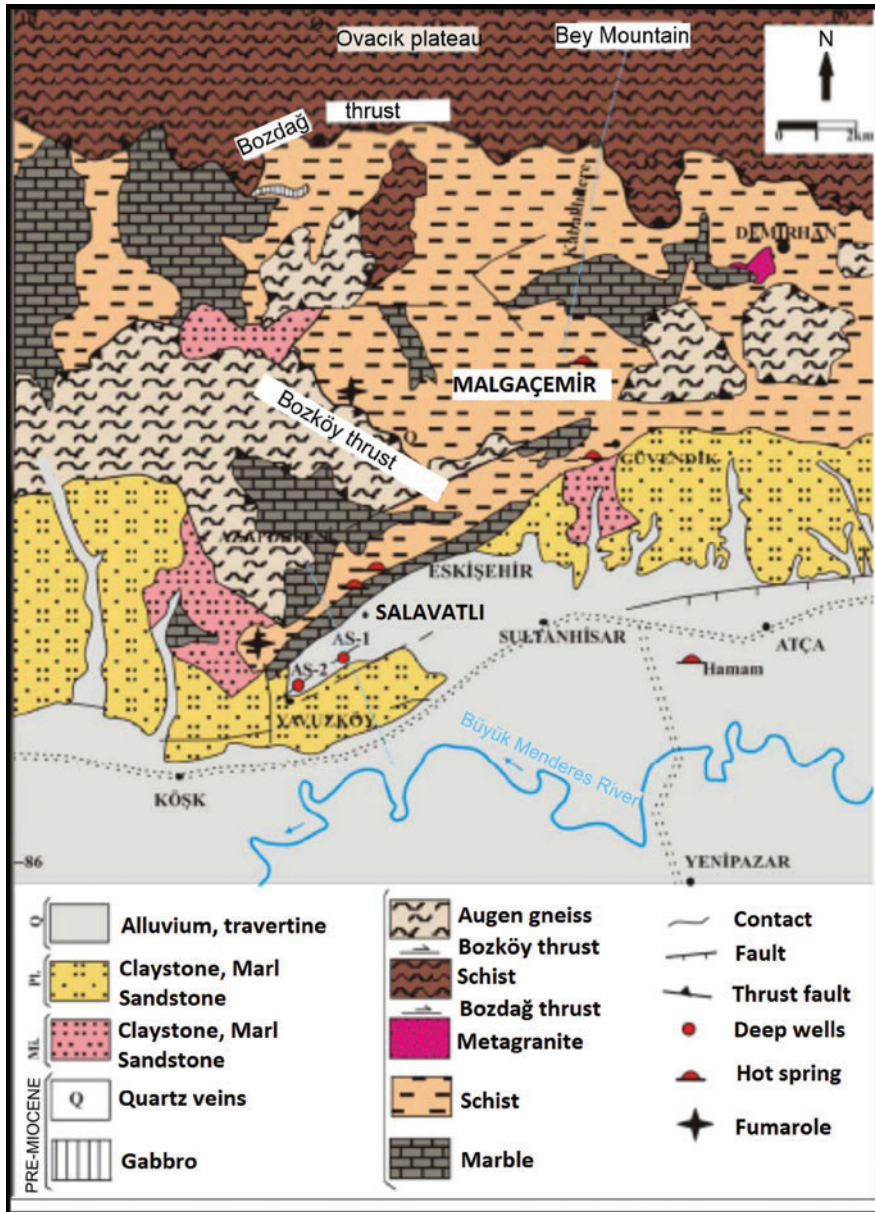


Figure 4.5. Geological map of the thermal field of Salavatlı and environs (modified from Karamandereci, 1997).

role as basement and cap rocks. The Sazak formation composed of silicified limestones forms the first shallow reservoir. The Paleozoic İğdecik formation consisting of quartzites, marbles and mica schists is the next-deepest reservoir.

The geothermal field of Salavatlı has at least ten production wells to a depth of 1510 m and is located in the north of the middle part of the rift zone of the Büyük Menderes (Figs. 4.1 and 4.2). It consists of Paleozoic metamorphic rocks and Miocene to Pliocene sedimentary rocks (Karamandereci, 1997) (Fig. 4.5). Paleozoic marbles and quartzites, in alternation with mica



Figure 4.6. Geothermal power plant of Salavatlı in the rift zone of the Büyük Menderes.

schists, marbles and quartzites, form the thermal water reservoir in the field of Salavatlı. The capacity of geothermal power plants in the area is about 51 MWe (Fig. 4.6) and, by 2018, an additional plant with a capacity of 17 MWe is planned.

The geothermal field of Germencik has approximately 100 production and reinjection wells to a depth of 2800 m and is one of the geothermal areas with high enthalpy, located in the north of the western part of the rift zone of the Büyük Menderes. It consists of Paleozoic metamorphic rocks and Miocene to Pliocene conglomerates (Correia *et al.*, 1990) (Figs. 4.1 and 4.2). In the area, the conglomerates form the shallow reservoir, whereas marbles and quartzites in alternation with marble, quartzite and mica schists comprise the deep reservoir rocks (Fig. 4.7). The total capacity of geothermal power plants is about 115.4 MWe (Fig. 4.8) and, by 2018, an additional plant capacity of 256.5 MWe is planned.

In addition, the capacity of existing geothermal fields at Pamukören in Kuyucak, with 45 MWe, and Gümüşköy in Germencik, with 13 MWe, total 58 MWe. Furthermore, the geothermal fields of Efeler in Umurlu, Yılmazköy, Pamukören in Kuyucak, Sultanhisar, Durasallı (Nazilli) and Atça (Sultanhisar) will all contribute to an increase of the geothermal potential by 203.5 MWe as of 2018. These geothermal fields are composed of Paleozoic metamorphic rocks and Miocene to Pliocene sedimentary rocks (Figs. 4.1 and 4.2). Marbles and quartzites, in alternation with mica schists, marbles and quartzites, form the reservoir rocks in these geothermal fields, with temperatures up to 180°C.

### 4.3 HYDROGEOLOGY AND HYDROGEOCHEMISTRY

#### 4.3.1 Hydrogeology

The groundwater provisions in the drainage area of the geothermal fields in the rift zone of the Büyük Menderes can be reconstructed from morphological features and analogous comparisons. The groundwater flow occurs on the northern side of the rift zone of the Büyük Menderes at the

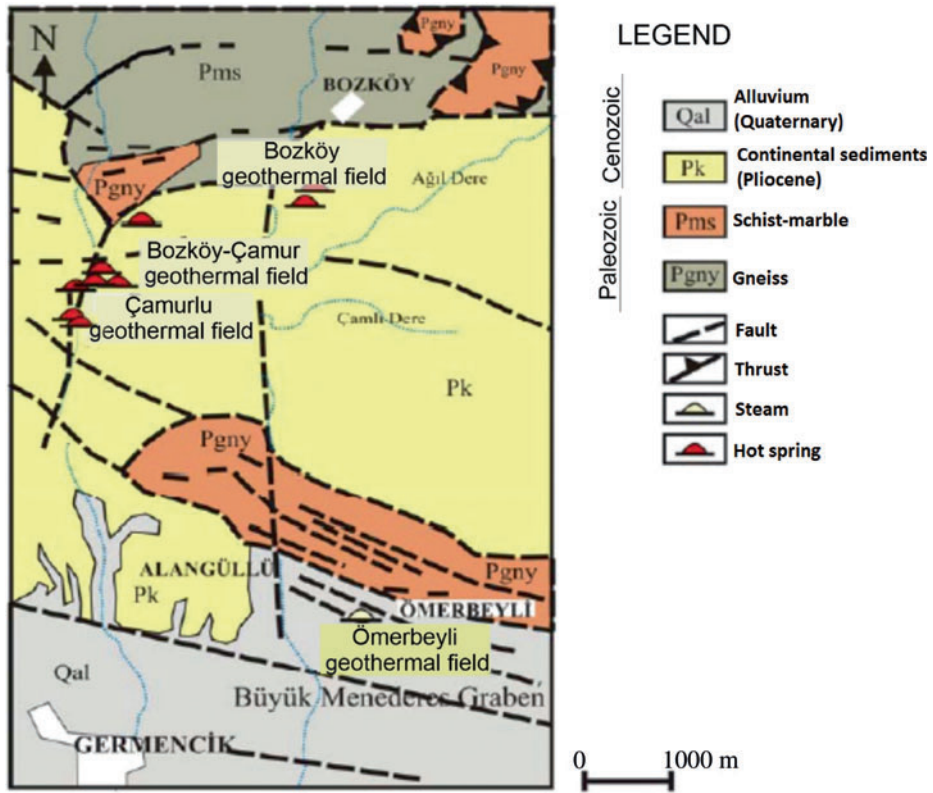


Figure 4.7. Geological map of the geothermal field of Germencik in the continental rift zone of the Büyük Menderes (Yaman, 2005).



Figure 4.8. Geothermal power plant of Germencik in the rift zone of the Büyük Menderes (<http://www.guris.com.tr>).



Buldan Horst to the south in which the geothermal water reservoirs are recharged. The distance from the watershed to the geothermal fields in the rift zone of the Büyük Menderes is as much as 10 km. Thus, the drainage area of every geothermal field is between 100 and 150 km<sup>2</sup>.

The rift zone of the Büyük Menderes experiences semiarid climatic conditions, with an annual rainfall of 430 mm and an annual average temperature of 17.6°C. The largest proportion of the precipitation takes place in the winter months from December to March; during the remaining part of the year aridity predominates. This aridity contributes to a groundwater deficit, for which reason the surface waters there play an insignificant role except for the supply of geothermal waters. The Büyük Menderes is the river which rises at Dinar near Isparta as karst spring and passes Sarayköy, close to Aydın and Söke and flows into the Aegean Sea near Akköy. The stream discharge of this river is about 15–20 m<sup>3</sup> s<sup>-1</sup> in winter and 2 m<sup>3</sup> s<sup>-1</sup> in summer.

At the surface, the metamorphic and sedimentary rocks in the geothermal fields of the rift zone of the Büyük Menderes, at very important localities such as Kızıldere, Salavatlı, Germencik and others, are intensively altered. This is recognizable in a distinct color change of the rocks, studies of rock microscopy on various thin sections, and X-ray diffractometry analyses. The hydrothermal alteration is distinguished by phyllic, argillic, and silicic  $\pm$  haematization zones. The phyllic and argillic alteration zones occur in the Paleozoic metamorphic rocks, whereas silicic  $\pm$  haematization alteration zones are an overprinting type and are observed in Paleozoic metamorphic and sedimentary rocks. In addition, a new alteration type of carbonatization has been recognized in sedimentary rocks that can be observed in the geothermal fields of Kızıldere in particular (Özgür and Pekdeğer, 1995). Due to high temperature, pressure, and CO<sub>2</sub> content in the geothermal water reservoir of the study area, high-temperature acidic water infiltrates the soil formations and dissolves CaCO<sub>3</sub>. The solution seeks equilibrium constantly, but does not reach suitable parameters in the surrounding environment and, thus, the solution loses temperature, pressure and CO<sub>2</sub> on its way to the surface, for which reason the pH values increase to 9.2. Consequently, the geothermal fluid is unable to retain CaCO<sub>3</sub> in solution, which instead precipitates and occurs in sedimentary rocks near the surface. The silicic alteration zone can be observed in both Paleozoic metamorphic rocks and Miocene to Pliocene sedimentary rocks (Özgür, 1998).

#### 4.3.2 Hydrogeochemistry

During the present study, the outflow of 14 geothermal springs and 14 production wells has been sampled in different seasons since 1992. Additionally, about 240 rock samples were collected. The geothermal waters flow out of clastic sediments of Miocene to Pliocene age. The discharge of geothermal waters is linked to the faults which strike in an E–W direction with a vertical incline. The surface temperatures of the geothermal waters are 99°C in Kızıldere, 45 to 95°C in Salavatlı, and 30 to 92°C in Germencik, whereas geochemical thermometers show reservoir temperatures of 200 to 240°C in Kızıldere, 162 to 180°C in Salavatlı, and 216 to 232°C in Germencik. The total dissolved solids of the geothermal waters range from 1800 to 6000 mg L<sup>-1</sup>. At the surface, scale formations are generated by decreasing temperature and pressure. The scale formations consist of carbonates with high Sr anomalies and minor contents of silicates and sulfides. These minerals are mostly aragonite and calcite with high Au and Sb contents. Hydrogeochemically, the geothermal waters can be considered as Na-(Cl)-(SO<sub>4</sub>)-HCO<sub>3</sub> type (Fig. 4.9) and are distinguished by an increase and a decrease of dominantly cations, anions, and trace elements from marine towards continental environment. Trace elements that indicate intensive high-temperature water-rock interaction, such as B<sup>(III)</sup> and F<sup>-</sup>, are found in high concentrations in these waters. With the exception of As, Sb, and Hg, the geothermal waters in the investigated fields are very poor in heavy metals. As, Sb, and Hg are known to precipitate mostly at the surface. There is a close correlation between F and B in dependence on the increasing Na content and decreasing Ca content of high-temperature waters (Özgür, 2001, 2002; Özgür and Pekdeğer, 1995). The origin of B<sup>(III)</sup> can be attributed to mineral phases, that is, tourmaline and biotite in metamorphic rocks, and boron deposits at depth (Özgür, 2001). Fluorine can lead either to volcanic activity or to lower Ca content in the fluids (Pekdeğer and Özgür, 1992).

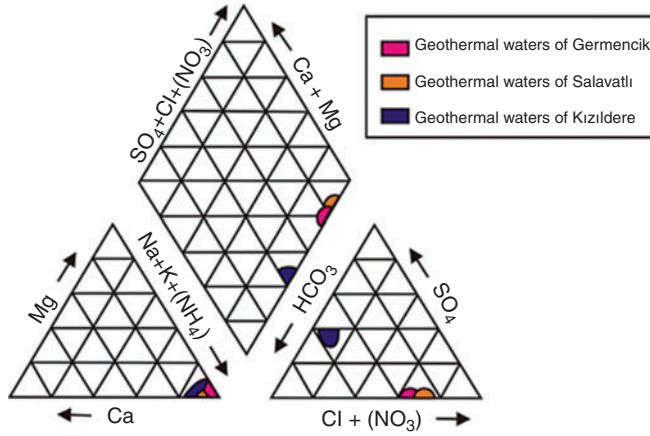


Figure 4.9. Geothermal waters of Kızıldere, Salavatlı and Germencik in the continental rift zone of the Büyük Menderes (Özgür *et al.*, 1998).

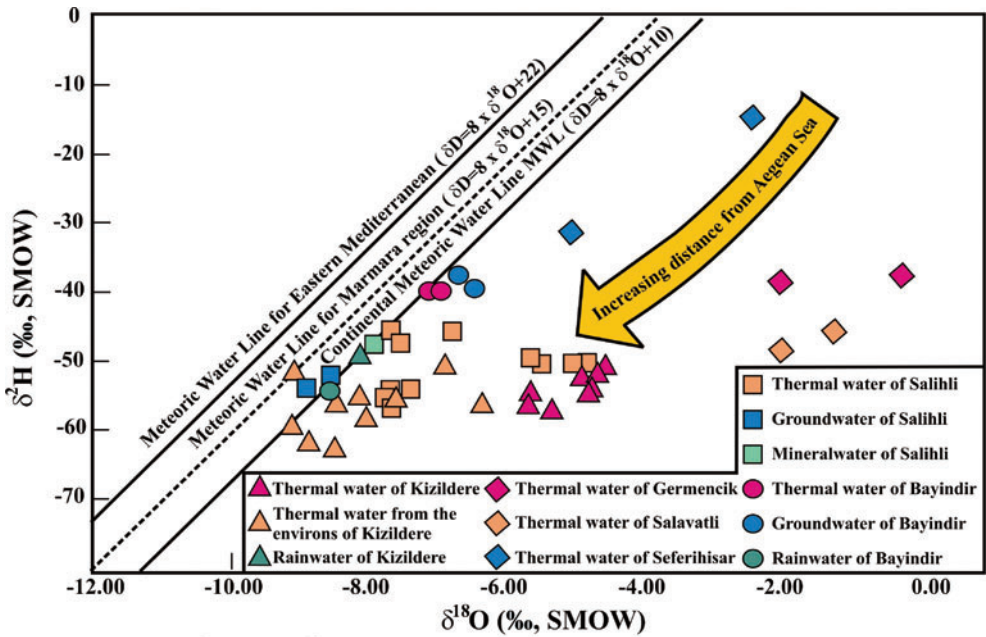


Figure 4.10. Plot of  $\delta^2\text{H}$  versus  $\delta^{18}\text{O}$  for geothermal waters of Kızıldere, Salavatlı, Germencik and other localities in the continental rift zone of the Büyük Menderes (Özgür, 1998).

#### 4.3.3 Isotope geochemistry

Samples from hot springs, production wells and groundwaters in the rift zone of the Büyük Menderes have been analyzed for their oxygen-18, deuterium and tritium contents. In addition, the geothermal waters of Kızıldere were considered due to their content of  $\delta^{13}\text{C}$  and  $^{14}\text{C}$ .

The sample contents of the stable isotopes  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  are shown in Figure 4.10. The sampled rainwaters and mixed groundwater-geothermal water systems lie along the Meteoric Water Line (MWL), whereas the high-temperature deep groundwater systems deviate from the MWL,

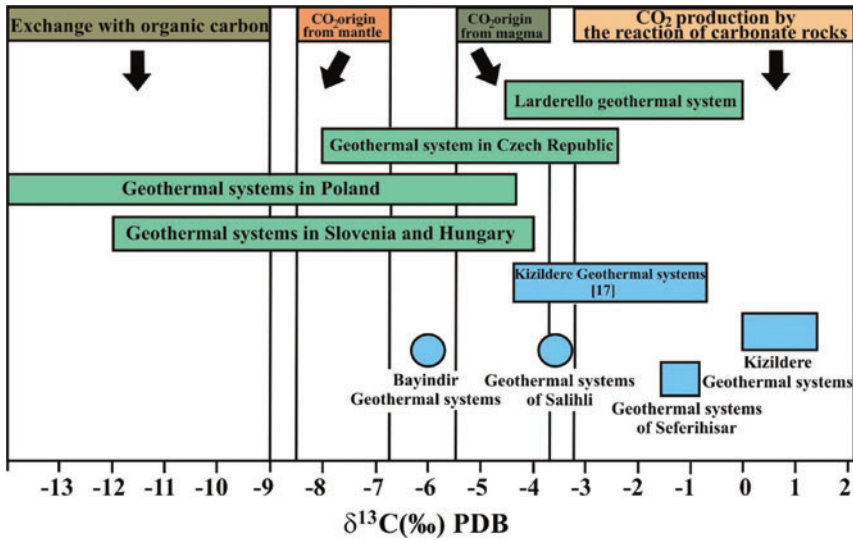


Figure 4.11.  $\delta^{13}\text{C}$  values in the geothermal waters of Kızıldere and environs within the continental rift zone of the Büyük Menderes (Özgür, 1998).

suggesting a fluid-rock interaction under high-temperature conditions. The differences in the degree of isotope shift from Kızıldere to Germencik indicate a mixing between three geothermal waters, which are characterized by  $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ,  $^3\text{H}$  and  $^{14}\text{C}$  values.

The tritium measurements reveal that (i) the geothermal waters of Kızıldere, Salavatlı and Germencik do not contain any measurable tritium and (ii) the mineralized groundwater and groundwater-geothermal water systems contain both atmospheric and anthropogenic tritium. Therefore, the tritium content is not suitable for age determination of the geothermal waters of Kızıldere, Salavatlı and Germencik. According to  $^{13}\text{C}$  data, the origin of  $\text{CO}_2$  might be attributable to magmatic activity as well as to the reaction of geothermal waters with carbonate rocks at depth. These geothermal waters show  $^{14}\text{C}$  content below the limit of detection because of the dilution of  $^{14}\text{C}$  by a high content of  $\text{CO}_2$  (Fig. 4.11). Given this fact, the geothermal waters of Kızıldere, Salavatlı and Germencik might be interpreted as old waters, with an age of 10,000 to 30,000 years.

#### 4.4 RESOURCES AND GEOTHERMAL POTENTIAL

##### 4.4.1 Kızıldere

In Kızıldere, the Sazak formation forms the first shallow reservoir. In the course of this, the Upper Pliocene Tosunlar and Kolonkaya formations constitute impermeable cap rocks against which the Pliocene Kızılburun formation creates impermeable basement rocks. The geothermal water reservoir in limestones of the Sazak formation is at a depth of 800 m and shows a thickness of 400 m and temperatures ranging from 150 to 198°C (Fig. 4.6). The marbles, quartzites and quartz schists form the second geothermal water reservoir. In the course of this, the Early Pliocene Kızılburun formation forms the impermeable cap rocks whereas the Paleozoic bedrock forms its impermeable basement (Fig. 4.6). Due to well-developed fractures, the rocks of the İğdecik formation form the next-deepest geothermal water reservoir, at a depth of 1700 to 2800 m with temperatures up to 250°C. Thus, the geothermal field of Kızıldere and environs has a potential of 120 MWe.

#### 4.4.2 *Salavatlı*

The geothermal field of Salavatlı has at least ten production and reinjection wells to a depth of 1500 m and is situated in the north of the middle part of the continental rift zone of the Büyük Menderes (Figs. 4.1 and 4.2). It consists of Paleozoic metamorphic rocks composed of mica schists, marbles and quartzites and Miocene to Pliocene sedimentary rocks. Mica schists, marbles and quartzites form the geothermal water reservoirs with temperatures up to 200°C. The geothermal field of Salavatlı and environs shows a geothermal potential of 68 MWe for the near future.

#### 4.4.3 *Germencik*

The geothermal field of Germencik has about 100 production and reinjection wells to a depth as great as 2800 m and is located in the north of the western part of the Büyük Menderes rift zone (Figs. 4.1 and 4.2). It consists of Paleozoic mica schists, marbles and quartzites and Miocene to Pliocene sedimentary rocks. Paleozoic mica schists, marbles and quartzites form the geothermal water reservoirs with temperatures up to 240°C. In the near future, the geothermal potential in Germencik and its environments can be extended up to 450 MWe.

#### 4.4.4 *Other geothermal reservoirs*

Other geothermal fields are located in various parts of the continental rift zone of the Büyük Menderes, for example, Efeler in Umurlu, Köşk, Yılmazköy, Pamukören, Sultanhisar, Durasallı and Atça (Figs. 4.1 and 4.2). In these locations, the Paleozoic mica schists, marbles and quartzites form the geothermal water reservoirs with temperatures up to 180°C. By 2018, the geothermal potential in these locations can be assumed as up to 203.5 MWe.

### 4.5 ENVIRONMENTAL IMPLICATIONS

In some regions, the most widely developed types of geothermal power plant are located near hot spots where hot molten rocks are close to the earth's crust and produce geothermal waters. In other regions, enhanced geothermal waters or hot dry rock systems, which involve drilling into the earth's surface to reach deeper geothermal resources, can allow broader access to geothermal energy. Geothermal power plants differ in terms of the technology used to convert the resource to electricity, by direct steam, flash and binary systems, and the type of cooling technology used, either water-cooled or air-cooled. The environmental implications of geothermal energy are described in the rest of this section.

#### 4.5.1 *Water quality and use*

Geothermal power plants can have implications for water quality and consumption. Geothermal waters pumped from both shallow and deep reservoirs often contain high concentrations of sulfur, salt, heavy metals and other chemical ions, including silica, boron, fluorine, chloride, arsenic, mercury, antimony, nickel, bicarbonate and carbonate (Kagel, 2007). Most geothermal power plants are closed-loop water systems in which extracted waters are pumped back into the reservoir after they have been used for heat and electricity production. In these systems, the waters are contained within steel well casings cemented to the surrounding rocks (Kagel, 2008). Nowadays, there are no cases of water contamination from geothermal power plants in the rift zone of the Büyük Menderes, due to the reinjection of these geothermal waters into the reservoirs. Before the beginning of the year 2000, extracted geothermal wastewaters were discharged into the river of the Büyük Menderes at a flow rate of about 250–300 L s<sup>-1</sup> and were polluting the river waters, especially due to boron concentrations of 1.3 mg L<sup>-1</sup> (Figs. 4.12 and 4.13; Özgür, 2001).

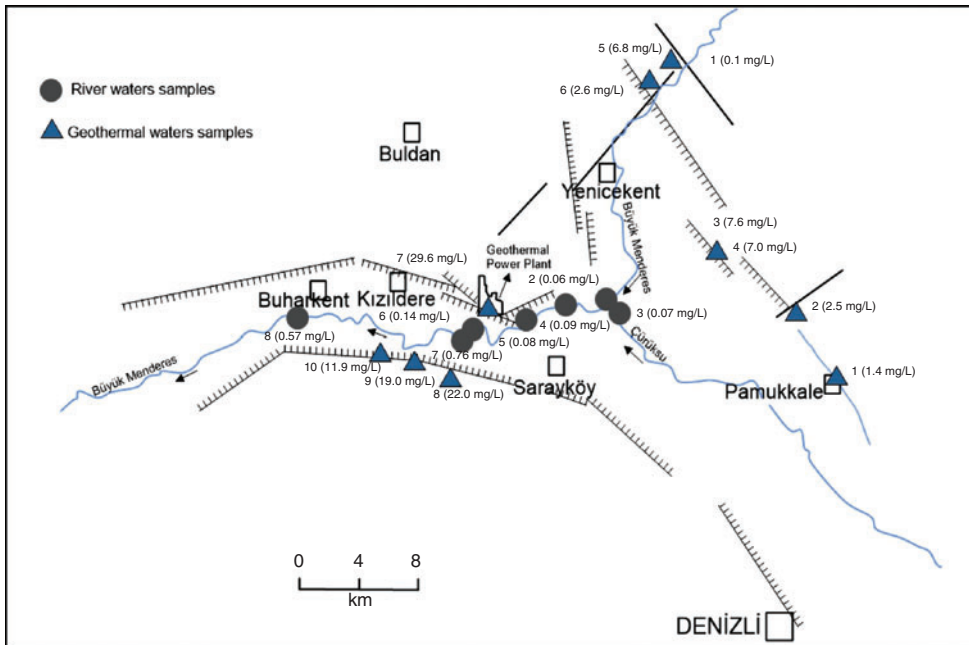
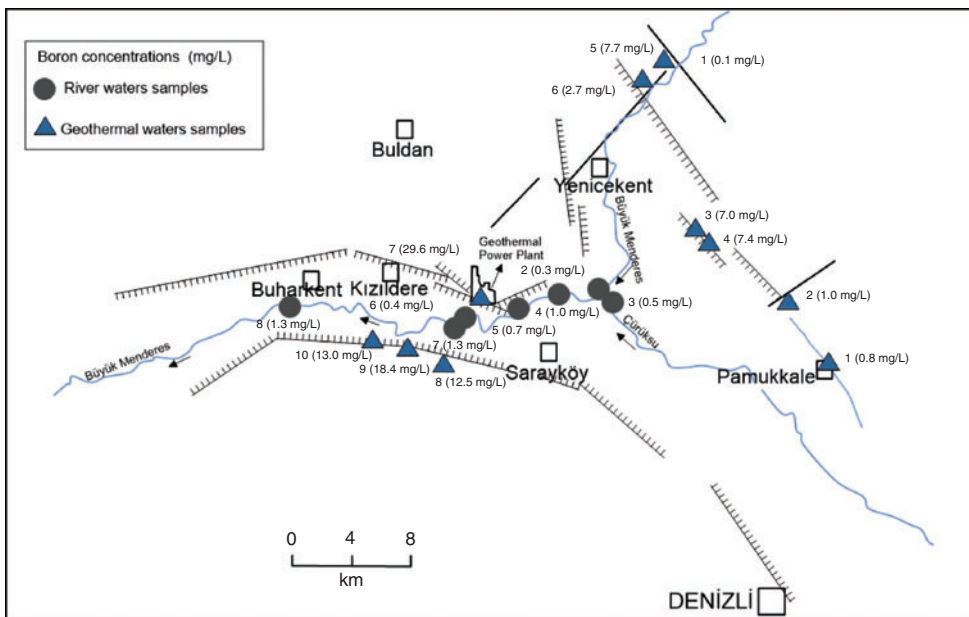


Figure 4.12. Boron concentrations in winter of the geothermal waters of Kızıldere and environs and river waters of the Büyük Menderes prior to 1995 (for B analyses of these waters, see Özgür, 1998, 2001).





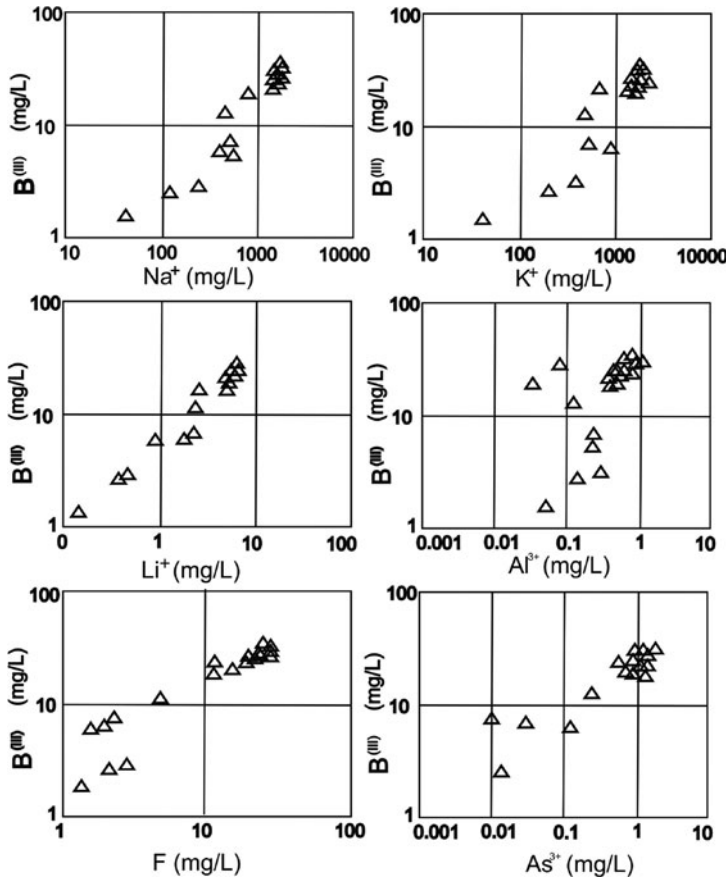


Figure 4.14. Plot of  $B^{(III)}$  versus  $Na^+$ ,  $K^+$ ,  $Li^+$ ,  $Al^{3+}$ ,  $F^-$  and  $As^{(III)}$  in the geothermal waters of Kızıldere and environs (for analyses of  $B^{(III)}$  versus  $Na^+$ ,  $K^+$ ,  $Li^+$ ,  $Al^{3+}$ ,  $F^-$  and  $As^{(III)}$  in the geothermal waters of Kızıldere, see Özgür, 1998, 2001).

The flow rate of the river of the Büyük Menderes in the winter/spring half of the year is  $16 \text{ m}^3 \text{ s}^{-1}$ , which is a nearly tenfold increase compared to the summer/autumn flow rate ( $2 \text{ m}^3 \text{ s}^{-1}$ ). In the case of continuous operation of the Kızıldere geothermal power plant (and consequent production of geothermal wastewaters), there was an observed flow rate of up to  $300 \text{ L s}^{-1}$  into the Büyük Menderes river, with a boron input ranging from  $850$  to  $1100 \text{ kg day}^{-1}$ , and mean values of  $20$  to  $25 \text{ mg L}^{-1}$ . In March 1995, boron concentrations in the river waters into which geothermal waters from the Kızıldere geothermal power plant were discharged amounted to  $0.76 \text{ mg L}^{-1}$  (Özgür, 2001) (Fig. 4.12). By comparison, boron concentrations in the river waters increased to  $1.3 \text{ mg L}^{-1}$  in October 1995 in conjunction with a decreased flow rate of  $6 \text{ m}^3 \text{ s}^{-1}$  (Özgür, 2001) (Fig. 4.13). The boron concentrations of the Kızıldere geothermal waters and environs are positively correlated with Na, K, Li, Al, F, As and Sb under increasing temperature conditions (Özgür, 2001) (Fig. 4.14). On the other hand, these boron concentrations are negatively correlated with Ca and Mg content in the thermal waters of Kızıldere and environs (Özgür, 2001).

The solubility of boron in boron-bearing minerals, such as biotites, white micas, feldspars, tourmalines and hornblendes, in metamorphic rocks within water-rock interaction may contribute to an increase of boron in the geothermal waters of Kızıldere and environs in the continental rift zone of the Büyük Menderes. Experimental leaching tests of various rocks of the Kızıldere environments show that gneisses and mica schists play an important role as boron sources (Özgür, 2001).

In addition, magmatic input of boron increases these concentrations in geothermal waters of meteoric origin, having been corroborated by  $\delta^{11}\text{B}$  (Giese, 1997; Gallo, 1998),  $\delta^{13}\text{C}$  (Özgür, 1998) and  $\delta^{34}\text{S}$  (Özgür, 1998) isotopic analyses of geothermal waters. The sampling of the geothermal waters of Kızıldere encompassed a range of  $\delta^{11}\text{B}$  (‰), from  $-4.7$  to  $-1.5$  (Giese, 1997), apparently indicating a continental boron source in the study area (relative to the  $\delta^{11}\text{B}$  values of Barth, 1993). Moreover, Neogene boron deposits, which occur in connection with recent volcanism in northeastern Turkey (e.g. the Bigadiç deposits in Balıkesir, and Kırka deposits in Eskişehir; Palmer and Helvacı, 1997), should be taken into consideration as potential boron sources (Özgür, 2001). Finally, it can be noted that there is no single reason for the high boron concentrations measured in the geothermal waters of various localities in the rift zone of the Büyük Menderes ( $25\text{--}30\text{ mg L}^{-1}$  in Kızıldere in the east, and up to  $100\text{ mg L}^{-1}$  in the west). Rather, a concurrence of several natural factors is likely.

The waters are also used by geothermal power plants for cooling and reinjection. The majority of geothermal power plants use wet-recirculation technology with cooling towers. Depending upon the cooling technology, geothermal power plants require between  $6.5$  and  $15.0\text{ m}^3\text{ MWh}^{-1}$  of cooling water. Most geothermal power plants use either geothermal waters or freshwater for cooling. The use of geothermal waters instead of freshwater reduces the overall water impact of the power plants (Macknick *et al.*, 2011). Most geothermal power plants reinject their wastewaters into reservoirs to prevent contamination and land subsidence. In most cases, it is not possible to reinject all of the water removed from a reservoir because some of it is lost as steam. To maintain a constant volume of water in the reservoirs of geothermal power plants, water from external sources must be added. The amount of water needed depends upon the size of the geothermal power plant and the technology in use.

#### 4.5.2 Air emissions

The distinction between open- and closed-loop geothermal plants is very important with respect to air emissions. In closed-loop geothermal power plants, gases such as  $\text{H}_2\text{S}$ ,  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{HB}^-$  and  $\text{HF}^-$  that are removed from the reservoirs are not exposed to the atmosphere and are reinjected into the reservoirs after giving up their heat, so that air emissions are very minimal. By contrast, open-loop geothermal plants emit  $\text{H}_2\text{S}$ ,  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{HF}^-$  and  $\text{HB}^-$ .  $\text{H}_2\text{S}$ , which has a distinctive “rotten egg” smell, is the most common emission (Kagel, 2007). In the atmosphere,  $\text{H}_2\text{S}$  is converted to  $\text{SO}_2$ , which contributes to the formation of small acidic particulates that can be absorbed by the bloodstream and cause heart and lung disease (National Research Council, 2010).  $\text{SO}_2$  also causes acid rain, which damages crops, forestry and soils, and acidifies lake and stream waters. Finally,  $\text{SO}_2$  emissions from geothermal power plants are 30 times lower per megawatt-hour than from coal power plants, which are the largest  $\text{SO}_2$  source in all countries. In some geothermal power plants, there is a small amount of mercury content, which is mitigated by using mercury filter technology. Air emissions can be reduced by using scrubbers. These scrubbers produce a watery sludge composed of captured materials, including sulfur, silica compounds, vanadium, chlorides, arsenic, nickel, mercury, and other heavy metals. These toxic sludges must often be disposed of at hazardous waste sites (Kagel, 2007).

The geothermal power plants in the rift zone of the Büyük Menderes are of closed-loop design, in which gases removed from the reservoirs are not exposed to the atmosphere but are reinjected into the reservoirs after giving up their heat, so that air emissions are very minimal.

#### 4.5.3 Land use

The amount of land use of geothermal power plants depends upon (i) the properties of the resource reservoir, (ii) the power capacity, (iii) the type of energy conversion system, (iv) the type of cooling system, (v) the arrangement of wells and piping systems and (vi) the substation and auxiliary needs (NREL, 2012). For instance, The Geysers (California), the largest geothermal field in the world, has a capacity of approximately 1517 MWe and the area of the plant is approximately 78 km<sup>2</sup>, which translates to approximately 13 acres per MWe. Like The Geysers, many geothermal waters are located in remote and ecologically sensitive areas, so that geothermal power plants must take these features into account in the planning process.

In some cases, land subsidence can be attributed to the removal of waters from geothermal reservoirs. Most geothermal power plants mitigate this risk by reinjection of wastewaters into the reservoirs after the heat of the geothermal waters has been captured. Moreover, geothermal waters are located on geological “hot spots”, with higher levels of earthquake risk. There is evidence that geothermal power plants can contribute to an even greater earthquake frequency (NREL, 2012). In addition, enhanced geothermal systems such as hot dry rock systems can also increase the risk of some small earthquakes. In this process, groundwater is pumped under high-pressure conditions into fractures of reservoirs in a system similar to the technology used in natural gas hydraulic fracturing (fracking). Here, the earthquake risk can be minimized by siting geothermal power plants an appropriate distance away from major fault lines. If siting a geothermal power plant in a heavily populated area, continued monitoring and transparent communication with local communities is essential.

#### 4.5.4 Life-cycle global warming emissions

In open-loop geothermal power plants, air emissions consist of approximately 10% CO<sub>2</sub>, and a smaller amount of methane, an even more potent global warming gas. Estimates of global warming emissions for open-loop geothermal power plants are approximately 45.3 g per kWh. In closed-loop geothermal power plants, the gases cannot be released to the atmosphere. Nevertheless, there are some small emissions in connection with power plant construction and infrastructure in the environs. Enhanced geothermal systems, which require energy to drill and pump water into hot rock reservoirs, indicate life-cycle global warming emissions of approximately 90 g CO<sub>2</sub> per kWh (IPCC, 2011). In order to put this into context, estimates of life-cycle global warming emissions for electricity generated from natural gas are between 271.8 and 906 g CO<sub>2</sub> per kWh (IPCC, 2011), and for coal-generated electricity are between 634.2 and 1630.8 g CO<sub>2</sub> per kWh.

### 4.6 MODEL OF THE GEOTHERMAL WATERS IN THE RIFT ZONE OF THE BÜYÜK MENDERES

The investigated geothermal waters of Kızıldere, Salavatlı, and Germencik are of meteoric origin. The meteoric waters in the drainage area percolate at fault zones and permeable clastic sediments into the reaction zone of the roof area of a magma chamber, situated at a probable depth of up to 4 km, where meteoric fluids are heated by the cooling magmatic melt and ascend to the surface due to their lower density caused by convection cells (Fig. 4.15). The heating of the geothermal waters by subvolcanic activity is proven by the distinctive enrichment of mantle helium in the geothermal fluids of Kızıldere (Ercan *et al.*, 1992; Güleç, 1988), which might be interpreted as <sup>3</sup>He surplus in comparison to pure continental crustal fluids. This high value of mantle helium might indicate that basic volcanic rocks from the earth's mantle show an interaction with the geothermal fluids in the environs of the geothermal field of Kızıldere. Besides some intrusive rocks in the rift zones of the Menderes Massif, calcalkaline basic to intermediate volcanic rocks

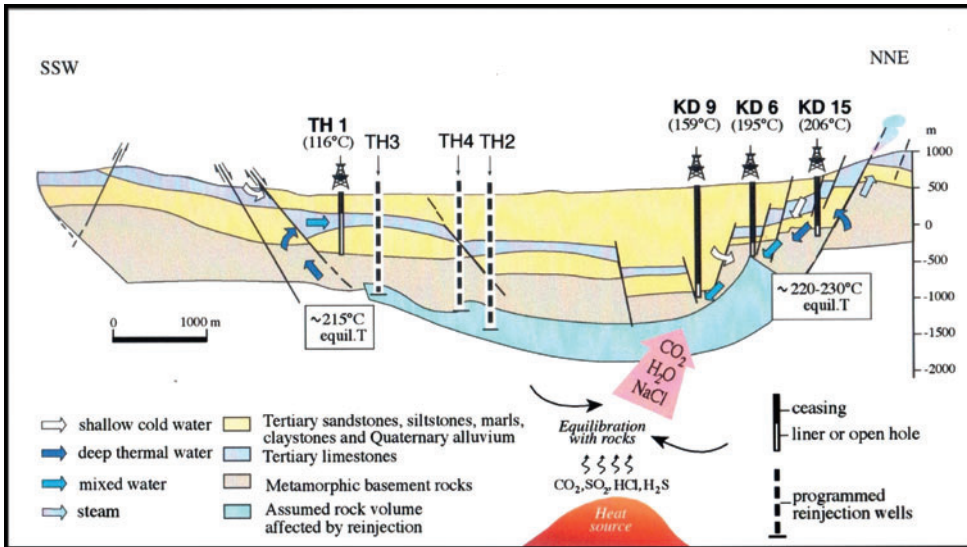


Figure 4.15. Geothermal model of the geothermal waters in Kızıldere and environs within the continental rift zone of the Büyük Menderes (modified from Özgür, 1998; note that the programmed reinjection wells, TH2, TH3 and TH4, are not in operation).

exist that have been generated from the Middle Miocene to recent times. For example, the Kula volcano, located 150 km north of the investigated area, had its last eruptions/activity 18,000 years ago. Thereby, the presence of magma chambers at the depth of the rift zone of Büyük Menderes cannot be excluded and must be taken into consideration, that is, volcanic activities in Denizli and Söke.

In addition, it is noticeable that the geothermal gradients form a second possibility for heating of the meteoric waters in the area, which correspond to the intensity of heat flow and earthquake activity. Nevertheless, the waters at depth react with heated rocks which leads to water–rock interaction. The volatile components of  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{HCl}$ ,  $\text{H}_2\text{S}$ ,  $\text{HB}$ ,  $\text{HF}$  and  $\text{He}$  from the magma reach the geothermal water reservoir where an equilibrium between altered rocks, gas components and fluids is established. Thus, the geothermal waters ascend in the tectonic zones of weakness in the rift zone of the Büyük Menderes in terms of hot springs, gases and steams.

The well-investigated geothermal waters of Kızıldere, Salavatlı, Germencik and many others located in the continental rift zone of the Büyük Menderes represent typical examples of active geothermal systems and together suggest a great potential of up to 750 MWe (Kızıldere: 150 MWe; Salavatlı: 150 MWe; Germencik: 300 MWe; other locations in the rift zone of the Büyük Menderes: 150 MWe) in the area for the immediate future.

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*Section II*  
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## CHAPTER 5

### Analytical procedures for ion quantification supporting water treatment processes

Ewa Kmiecik

#### 5.1 INTRODUCTION

Rational and optimal use of existing water resources, including geothermal waters, is an extremely important issue. Geothermal waters can be used not only to extract energy but also in the context of improving the water balance and reducing or eliminating the need to inject waters into the formation as well as meet local needs (as drinking water and water for other household purposes). To this end, however, the water must be treated. The concentrate remaining after the treatment process contains valuable ingredients, which enables its use for industrial and residential purposes, in spas and/or for recreation purposes (Tomaszewska, 2011; Tomaszewska and Szczepański, 2014).

The effectiveness of the treatment process is monitored on the basis of the results of physical and chemical analyses of raw thermal waters, retentate and permeate. It is therefore important that these results be highly reliable. Obtaining sufficiently certain and reliable measurements of physicochemical parameters of water in practice entails the need for the laboratory to implement a quality assurance/quality control (QA/QC) system with respect to both field and laboratory testing.

The problem of controlling the quality of the data obtained in the process of monitoring the quality of groundwater has been discussed in both international (e.g. Fresenius *et al.*, 1988; Garrett, 1969; Kolpin and Burkart, 1991; Kolpin *et al.*, 1991; Nielsen, 1991, 2005; Ramsey, 1998; Ramsey and Thompson, 2007; Ramsey *et al.*, 1992; Thompson and Howarth, 1976) and Polish literature (Kmiecik, 2011; Osmęda-Ernst *et al.*, 1995a, 1995b, 1995c, 1996; Szczepańska and Kmiecik, 1998, 2005; Szczepańska *et al.*, 1996; Witczak and Adamczyk, 1994, 1995) for a long time. Since there was no legislation that would make controlling the quality of such data mandatory, QA/QC programs were introduced only in exceptional cases.

The situation changed after the introduction of EU legislation: the Water Framework Directive (EU, 2000), Groundwater Directive (EU, 2006) and the so-called Technical Directive (EU, 2009). EU directives set new challenges for hydrogeologists linked to the implementation of new testing methods related to groundwater monitoring, hydrogeochemical data quality control and the methodology for assessing chemical status on the basis of verified data, taking into account their uncertainty.

The 2009 Directive (EU, 2009) clarified the technical specifications for the analysis and monitoring of the chemical status of waters, and set minimum criteria for the performance of analysis methods and the rules for demonstrating the quality of analytical results. Pursuant to its guidelines, laboratories that perform water chemical monitoring should follow the quality management system practices described in the EN ISO/IEC 17025: 2005 standard (ISO, 2005).

According to the EN ISO/IEC 17025: 2005 standard, laboratories must provide uncertainty estimates in their test reports because if uncertainty is not known, this may adversely affect the interpretation of results. ILAC (2002) recommends that uncertainty be stated in reports at least when test results must be compared to the results of other tests or to other numerical values, for example, those stated in specifications (threshold values). This is the case for example, with

evaluating the suitability of geothermal waters for particular purposes (for human consumption after treatment, or for being discharged to surface waters).

The quality of geothermal waters directly in the well or within installations is evaluated on the basis of the results of chemical analyses covering a certain number of samples collected from a certain point/network/installation within a specified time interval. The results of chemical analyses obtained are dependent on the samples collected (small volumes of water that are subject to analysis). If the quality of water varies temporally or spatially, successive samples (from the point or installation in question) will exhibit different values of the physicochemical parameters measured. Each such set of results will allow the quality of the water to be assessed, but the estimates will differ.

Each single measurement is encumbered with uncertainty. In the measurement uncertainty estimation process, one must take into account all stages of hydrogeochemical data collection – from sampling through sample transport, storage and analytical procedures to analysis results, since errors are generated at each of these stages.

This chapter discusses the quality control/quality assurance procedures applied to geothermal water testing. A detailed analysis has been carried out for one of the main indicators that usually determine the hydrogeochemical type of water, that is, calcium.

The main source of calcium in fresh groundwater is the leaching of rocks, and especially of carbonate minerals (calcite, dolomite) (Witczak *et al.*, 2013). In typical drinkable water, the ratio of calcium to magnesium equivalent concentrations is around 3:4, with the exception of water circulating in dolomite rocks where this ratio approaches unity. The calcium content of water is most often controlled by the carbonate equilibrium and strongly depends on the CO<sub>2</sub> content and pH of water (Hem, 1989; Macioszczyk, 1987; Macioszczyk and Dobrzyński, 2007). Calcium is actively involved in the processes of sorption and ion-exchange with the clay substance contained in the rocks (Małeck *et al.*, 2009).

Elevated levels of calcium in waters may have natural causes or may be related to anthropogenic pollution. Geogenic anomalies are mainly linked to the presence of gypsum where the Ca concentrations found are at levels of several hundred mg L<sup>-1</sup> (Motyka and Witczak, 1992).

Calcium in the form found in water is non-toxic. However, the calcium and magnesium content of water (total hardness) affects human health and can be troublesome in households and in the industry since it necessitates excessive consumption of detergents, and causes boiler scaling, etc. (WHO, 2011). Soft waters have an adverse effect on health (Selinus *et al.*, 2005; Witczak *et al.*, 2013). Polish regulations provide for an optimal range of concentrations resulting in a total hardness water level ranging from 60–500 mg L<sup>-1</sup> of CaCO<sub>3</sub>. Hardness is mainly determined by calcium, so indirectly this is also the maximum allowable calcium concentration in water intended for human consumption. These are however, only additional requirements and regulations do not provide for mandatory water hardness supplementation.

In a number of countries, calcium content is not regulated directly since it is governed by the conductivity (EC) standard or, as in the United States, the standard for total dissolved solids (TDS). According to (Reimann and Birke, 2010), there are countries that regulate calcium content in water intended for consumption, for example, Austria (400 mg L<sup>-1</sup>), Albania, Bosnia, Serbia (200 mg L<sup>-1</sup>), Bulgaria (150 mg L<sup>-1</sup>), Czech Republic (30–80 mg L<sup>-1</sup>), Russia (130 mg L<sup>-1</sup>), Slovakia (more than 30 mg L<sup>-1</sup>) and Sweden (100 mg L<sup>-1</sup>) (Witczak *et al.*, 2013).

Calcium is also an important component of geothermal waters from the point of view of extracting them. Clogging is a problem that accompanies the extraction of thermal waters and directly influences the energy production cost for example. The intensity of this process depends mainly on the physicochemical composition of water and the presence of, *inter alia*, calcium ions. During the geothermal water cooling process, several physicochemical reactions take place, as a result of which the thermodynamic state of water changes. This leads to the precipitation of the minerals dissolved in the water (scaling), causing the clogging of the near-well zone and the active zone and limiting the productivity and absorption capacity of wells (Tomaszewska, 2008; Kleszcz and Tomaszewska, 2013).

## 5.2 GROUNDWATER SAMPLING

Sampling of groundwater, including geothermal waters, is more difficult than in the case of other elements of the environment due to the considerable spatial variability and the absence of a simple hierarchical flow.

Detailed guidance on the principles of designing networks, selecting monitoring points and sampling methods is contained in ISO 5667-11: 2009 (Water quality – Sampling – Part 11: Guidance on sampling of groundwater). This standard applies to tests conducted in order to determine the overall chemical composition of groundwater and does not cover the sampling related to the daily control of groundwater extracted for human consumption or other purposes.

Owing to the complexity of groundwater systems, many specific sampling applications – for example, monitoring to assess the chemical status of water – require specialist hydrogeological guidance. This is included, *inter alia*, in the following publications (Jousma and Roelofsen, 2004; Nielsen, 1991, 2005; Staniewicz-Dubois, 1995; WFD-CIS, 2003, 2007a, 2007b, 2009; Witczak and Adamczyk, 1994, 1995; Witczak *et al.*, 2006, 2013).

Procedures for collecting and analyzing geothermal water samples can be found for example, in Ármannsson and Ólafsson (2007).

Details concerning the use of statistical techniques to define the frequency of sampling and information on the selection of materials for equipment and sampling containers are included in ISO 5667-1: 2006 (ISO, 2006).

Guidelines for the preservation and handling of samples during transport are contained in ISO 5667-3: 2012 (Water quality – Sampling – Part 3: Preservation and handling of water samples) (ISO, 2012).

Guidance on how to estimate and minimize common errors present in the monitoring of groundwater can be found in numerous publications and regulations (including ISO, 2004a, 2004b, 2005; Nielsen, 1991, 2005; Nordtest, 2003, 2005, 2006; Szczepańska and Kmiecik, 1998, 2005).

Quality control/quality assurance procedures while collecting samples are described in ISO 5667-14: 2014 (ISO, 2014).

Recommendations that enable a large proportion of errors generated during water sampling to be avoided are also included in the other standards from the 5667 series (e.g. Kmiecik, 2011):

- ISO 5667-7: 1993. Water quality – Sampling – Part 7: Guidance on sampling of water and steam in boiler plants (recommends procedures and equipment for sampling water and steam in boiler plants including examples of sampling apparatus, to provide samples for physical and chemical analysis that are representative of the main body of water or steam from which they are taken);
- ISO 5667-20: 2008. Water quality – Sampling – Part 20: Guidance on the use of sampling data for decision-making – Compliance with thresholds and classification systems (establishes principles, basic requirements, and illustrative methods for dealing with the use of sample data for decision-making based on the assessment of the confidence that water quality meets targets and complies with thresholds, has changed, and/or lies in a particular grade in a classification system);
- ISO 5667-21: 2010. Water quality – Sampling – Part 21: Guidance on sampling of drinking water distributed by tankers or means other than distribution pipes (establishes principles to be applied to the techniques of sampling water provided for drinking and for use in the manufacture of food and beverage products);
- ISO 5667-22: 2010. Water quality – Sampling – Part 22: Guidance on the design and installation of groundwater monitoring points (gives guidelines for the design, construction and installation of groundwater quality monitoring points to help ensure that representative samples of groundwater can be obtained).

However, the use of standards and textbooks does not give assurance that no errors were made during the sampling process. An extremely important aspect is the adequate training of the personnel carrying out sampling, and common sense in solving the problems emerging during fieldwork, and this cannot be taught without proper practice.

### 5.3 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) PROGRAM

The quality of geothermal water testing results depends on the entire measurement process, starting from the correct sampling, proper sample preservation, storage and transportation to the laboratory, sample processing and chemical composition analysis using specific analytical methods.

Obtaining sufficiently certain measurements of physicochemical parameters of water entails the need to implement a quality assurance/quality control (QA/QC) system with respect not only to laboratory tests, but also field ones.

#### 5.3.1 *Laboratory QA/QC program*

Laboratories accredited in accordance with EN ISO/IEC 17025: 2005 (ISO, 2005) must meet the recommendations of Clause 5.9 of the standard: 'Internal quality control. Assuring the quality of test results'.

Measures in this area include:

- testing certified reference materials;
- participation in proficiency testing or inter-laboratory comparisons;
- repeating tests using the same or other methods;
- re-testing of stored samples; and
- correlation of results concerning different characteristics of samples.

According to Thomson (2012), the three main pillars of the quality of analytical testing at accredited research laboratories are as follows:

- The suitability of the tests proposed by the laboratory for the customer's purposes – what accuracy of the results the customer expects.
- Test procedure validation or standardized method verification – what the guaranteed accuracy is of the analytical method proposed by the laboratory to the customer.
- Quality control – whether the method used by the laboratory guarantees appropriate accuracy for the customer at all times.

Within the framework of internal quality control, laboratories perform tests on control samples – blank, spiked or duplicate samples – to ensure that the uncertainty found during validation remains true for successive runs of the measurement and the factors determining the magnitude of uncertainty have remained constant.

Internal quality control should be carried out at the laboratory on a regular basis and its results should also be verified on a regular basis by both the staff performing the testing and supervisors. The laboratory must have measurement result acceptance criteria. Control results should be marked on control charts (blanks, relative range from real samples, recovery from matrix reference materials or real samples spiked with a standard) (Pasałowski, 2016).

Table 5.1 lists the types of control samples used within the framework of internal quality control at the accredited Hydrogeochemical Laboratory of the Hydrogeology and Engineering Geology Department of the AGH University of Science and Technology that also conducts geothermal water testing. For the determination of calcium in water, the laboratory uses the ICP-MS and ICP-OES methods.

Table 5.1. Laboratory control samples (after Wątor, 2015).

Analytical method	Type of control samples	Sampling frequency
ICP-MS ICP-OES	CRM (Certified Reference Material)	Once a month <i>acceptance criterion: the true value is in the (result <math>\pm</math> uncertainty) range</i>
	Laboratory blanks	1 sample per series (up to 20 samples) <i>acceptance criterion: the result is below the quantification limit</i>
	Laboratory control sample (environmental control sample)	1 sample per series (up to 10 samples) <i>acceptance criterion: the true value is in the (result <math>\pm</math> uncertainty) range</i>
	Laboratory duplicate samples	1 sample per series (up to 20 samples) <i>acceptance criterion: the differences between the results plotted on a control chart should fall between the control limits</i>

Zhong-he and Ármannsson (2005) suggest running a QA/QC program for geothermal water monitoring related to calcium determination using the ICP method according to the following scheme:

- Instrument check standard – once per 10 samples to determine if significant instrument drift has occurred. If agreement is not within  $\pm 5\%$  of the expected values (or within the established control limits, whichever is lower), terminate analysis of samples, correct problem, and recalibrate instrument.
- Reanalyze one sample analyzed just before termination of the analytical run. Results should agree to within  $\pm 5\%$ , otherwise all samples analyzed after the last acceptable instrument check standard analysis must be reanalyzed.
- Spiked sample – once per every 10 samples (or with each batch of samples, whichever is less) add a known amount of the metal of interest and reanalyze to confirm recovery. Recovery of the added metal should be between 95–105%. Otherwise, reanalyze the whole batch.

### 5.3.2 Field QA/QC program

In accordance with the requirements of EN ISO/IEC 17025: 2005 (ISO, 2005) standard, a quality system at an accredited laboratory that performs water quality testing covers both the work performed at permanent laboratory premises and field testing.

According to Nielsen (1991, 2005), the field program within the quality assurance system is used to detect any errors made during the process of collecting water samples, their preservation and storage, transport to the laboratory and chemical analysis at the laboratory.

The field quality control program covers the collection from the monitoring network (using the same equipment as for normal samples) and analysis (within the same scope as normal samples) of additional control samples. These samples should account for 10–30% of the total number of normal samples collected from the monitoring network (Nielsen, 1991).

Under the field QA/QC program in groundwater monitoring, the following types of control samples are collected (Kolpin and Burkart, 1991; Leidel *et al.*, 1977; Ramsey, 1998; Ramsey *et al.*, 1992; Szczepańska and Kmiecik, 1998, 2005; Witczak and Adamczyk, 1994, 1995):

- field blanks (so-called zero samples – at least 3% of the total number of normal samples collected from the monitoring network) – collected using the same equipment as normal samples but using high-purity deionized water as a medium; subject to the same processing,

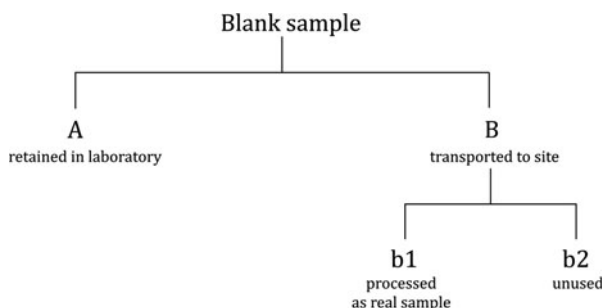


Figure 5.1. Field blank samples – sampling contamination errors (ISO, 2014).

transport and storage as normal samples, they are used to determine the practical detection limit (PDL);

- duplicate samples (at least 6% of normal samples collected – one duplicate sample per 20 normal samples at a minimum) – collected from randomly selected monitoring points as duplicates of normal samples, they are used to assess the precision and uncertainty associated with the sampling process;
- spiked samples (a minimum of 1% normal samples collected) with known composition or spiked with selected substance standards (reference material (RM) or certified reference material (CRM)) make it possible to evaluate accuracy and thus detect bias.

The quality assurance level should be higher for those monitoring points where the concentrations observed are close to the limit of quantification of the method in question or the threshold/limit specified in the relevant regulations concerning water quality (Nielsen, 2005).

ISO 5667-14: 2014 includes quality assurance procedures to be used during the manual collection of environmental samples, i.e. also geothermal water samples. This issue is particularly important in connection with the possibility of monitoring the effectiveness of the sampling methodology and demonstrating that the different stages of the sampling process are properly supervised and suitable for their intended purposes. Moreover, quality assurance procedures also make it possible to quantify and control the sources of errors that arise during the sampling process.

In accordance with the above standard, at least 2% of the analysts' working time should be allocated to procedures related to the quality assurance of the samples collected.

ISO 5667-14: 2014 mentions sample quality assurance techniques similar to those recommended in groundwater monitoring (Leidel *et al.*, 1977; Nielsen, 1991, 2005):

- field blanks – used to monitor sources of sample contamination;
- duplicate (replicate) samples – used to assess sampling precision;
- samples spiked with analyte (spiked samples) – used to test the durability/stability of samples during transport and storage.

The *field blank sample* collection scheme is shown in Figure 5.1.

Blank sample (deionized water) is divided into two parts (A and B). Part A is retained in the laboratory, and Part B is transported into the field and then divided into Portions b1 and b2. Sample b1 should be placed in the sampling container and processed as a real sample. Sample b2 should be returned to the laboratory unused (ISO, 2014).

Table 5.2 lists the types of errors that can be estimated using test results for these samples.

The same type of control samples can be used to identify errors related to the contamination of sampling equipment or resulting from the filtration process that accompanies sampling. In this case, sample b1 is only used to rinse the sample container in a manner as close as possible to the

Table 5.2. Estimates based on results for field blank samples (ISO, 2014).

Difference of the results	Estimation
A-b1	errors due to sampling, processing and transportation
A-b2	errors due to sample transportation

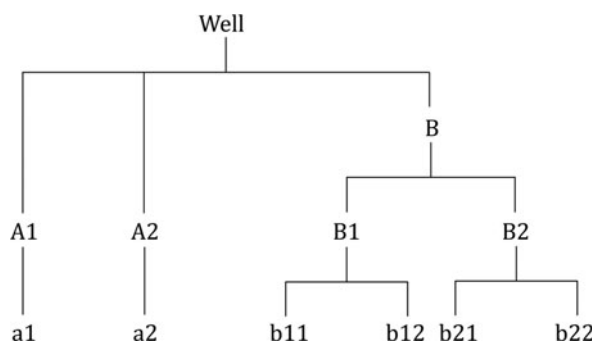


Figure 5.2. Duplicate samples – relationship between different sampling variances (ISO, 2014).

Table 5.3. Estimates based on results for duplicate samples (ISO, 2014).

Difference of the results	Estimation
A1-A2	Total sampling variance (sampling, containers, storage, analysis)
B1-B2	Analytical and sampling (measurement) variance (including storage, excluding sampling container)
b11-b12 (b21-b22)	Analytical precision

procedure followed with real samples or is filtered and further treated as a real (normal) sample (ISO, 2014).

The *duplicate sample* collection scheme is shown in Figure 5.2.

Explanation:

- A1, A2 – two discrete samples,
- B – single sample,
- B1, B2 – replicate samples taken in the field,
- a1, a2, b11, b12, b21, b22 – analyses.

Table 5.3 lists the estimates based on the results of determinations for duplicate samples.

*Spiked samples* (spiked with analyte) can be prepared on the basis of blanks (deionized water) or environmental samples. Figure 5.3 shows the scheme for preparing a marked blank sample and handling it in the field.

At the laboratory, deionized water is divided into two parts. Part A is retained in the laboratory, Part B is transported to site, then divided into three portions. Sample b1 should be placed in the sampling container and processed as a real sample. Sample b2 should be returned to the laboratory unused. Sample b3 should be spiked with a known concentration of the determinant and subdivided into two portions – b3<sub>(I)</sub> and b3<sub>(II)</sub>. Sample b3<sub>(I)</sub> should be placed in the sampling container and processed as a real sample, sample b3<sub>(II)</sub> should be retained and returned to the laboratory without any further processing (ISO, 2014).



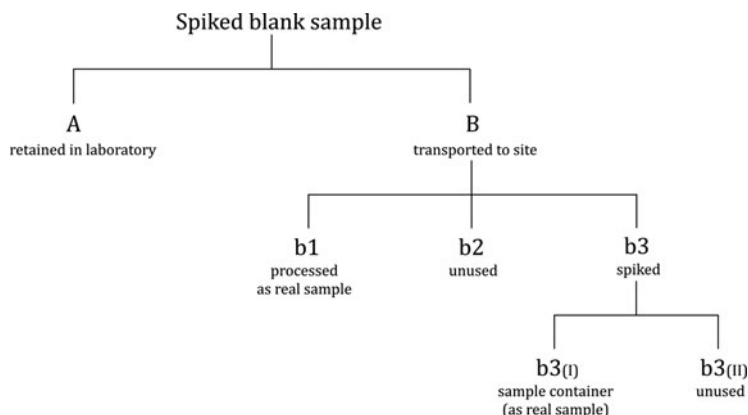


Figure 5.3. Spiked deionized water samples – contamination from sampling container and process (ISO, 2014).

Table 5.4. Estimates based on results for spiked samples (ISO, 2014).

Difference of the results	Estimation
A-b1	Errors due to sampling, processing and transportation
A-b2	Errors due to sample transportation
A-b3 <sub>(II)</sub>	Errors due to any instability and contamination of sample and transportation
A-b3 <sub>(I)</sub>	Errors due to sample processing and transportation and any errors due to instability and contamination of the sample
b1-b2	Errors due to contamination of sampling containers and sampling processing (eliminates transportation errors)
b2-b3 <sub>(II)</sub>	Errors due to instability and contamination of the sample
b3 <sub>(I)</sub> -b3 <sub>(II)</sub>	Errors due to contamination of sampling containers or sampling processes

Table 5.4 lists the estimates based on the results of determinations for spiked samples.

Figure 5.4 shows the scheme for preparing a spiked sample using an environmental sample matrix.

This sample may be prepared in the laboratory or in the field. In the field, however, this may be impractical and encumbered with too large an error if the analyte is added by an untrained sampler. It is best to prepare such a sample in the laboratory using a previously analyzed sample. The amount of standard/analyte added should be such that the measurements are conducted in the range in which the best determination accuracy is achieved.

Examples of concentration levels of analytes added to spiked samples are summarized in Table 5.5.

The sample spiked with analyte is divided into two parts A and B at the laboratory (Fig. 5.4). Part A is retained in the laboratory. Part B is transported in the field and then divided into two portions. Sample b1 should be placed in the sampling container and processed as a real sample. Sample b2 should be returned to the laboratory unused (ISO, 2014).

Table 5.6 lists the estimates based on the results of determinations for spiked environmental samples.

These samples should be used at different stages of the sampling process in order to estimate the uncertainty associated with a given testing stage.

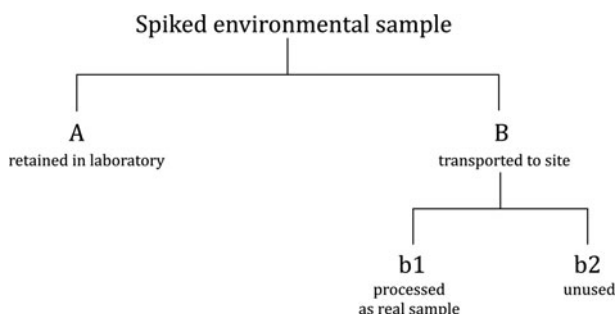


Figure 5.4. Spiked environmental samples – contamination from sampling container and process (ISO, 2014).

Table 5.5. Sample analytes and spiking concentrations.

Analytes	Spiking solution concentration [mg L <sup>-1</sup> ]
Major chemistry (Ca, Mg, Na, K, Br, Cl, SO <sub>4</sub> )	4–100
Minor chemistry and trace elements (Al, Fe, Mn, Cu, Zn, Ba, Ag, As, Be, Co, Cr, Ni, Pb, V, Hg)	0.005–0.5
Fluoride and iodide	2.0
Nitrate-N and total oxidized nitrogen-N	5
Ammonia-N and orthophosphate-P	1

Table 5.6. Estimates based on results for spiked environmental samples (ISO, 2014).

Difference of the results	Estimation
A-b1	Errors due to sampling, processing and transportation
A-b2	Errors due to sample transportation
b1-b2	Errors due to contamination of sampling containers as well as sampling processes and errors due to instability and contamination of the sample

To develop the data obtained from the QA/QC program, control charts (individual measurements, parallel determinations or recovery control charts) are used. Examples of application of this technique for developing groundwater monitoring data are described in Szczepańska and Kmiecik (2005) and Postawa (2012), and in the 7870 series of standards:

- ISO 7870-1:2014. Control charts – Part 1: General guidelines,
- ISO 7870-2:2013. Control charts – Part 2: Shewhart control charts,
- ISO 7870-3:2012. Control charts – Part 3: Acceptance control charts,
- ISO 7870-4:2011. Control charts – Part 4: Cumulative sum charts,
- ISO 7870-5:2014. Control charts – Part 5: Specialized control charts.

A control chart is shown in Figure 5.5.

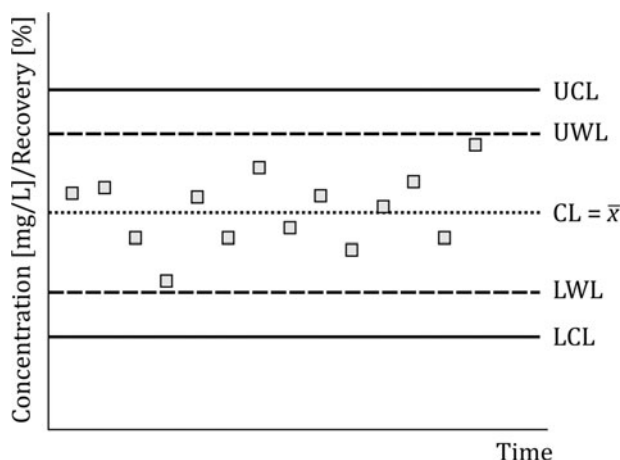


Figure 5.5. Control chart.

Each point plotted on the chart represents an individual process measurement, difference of results or a summary statistic. The Central Line (CL) is the average of the data ( $\bar{x}$ ). The two continuous lines are the upper and lower control limits (UCL and LCL,  $\pm 3$  standard deviations (3s) of the mean). The two dashed lines are the upper and lower warning limits (UWL and LWL,  $\pm 2$  standard deviations (2s) of the mean).

When an analytical process is within control, approximately 68% of all values fall within  $\pm 1$  standard deviation (1s). Likewise, 95.5% of all values fall within  $\pm 2$  standard deviations (2s). About 4.5% of all data will be outside the  $\pm 2$ s limits when the analytical process is in control. Approximately 99.7% of all values are found to be within  $\pm 3$  standard deviations (3s) of the mean. As only 0.3% – or three out of 1000 points – will fall outside the  $\pm 3$ s limits, any value outside of  $\pm 3$ s is considered to be associated with a significant error condition.

Individual values are also tested to determine if they are in or out of control, using a set of rules called the Westgard rules (Westgard, 2016):

- Rule 1 2S: One value beyond  $2 \times s$  of the mean.
- Rule 1 3S: One value beyond  $3 \times s$  of the mean.
- Rule 2 2S: Two consecutive values either greater than, or less than,  $2 \times s$  of the mean.
- Rule R 4S: A difference between consecutive values greater than  $4 \times s$  (one measurement is greater than two standard deviations of the mean and the previous measurement is greater than two standard deviations of the mean in the opposite direction such that the difference is greater than four standard deviations).
- Rule 4 1S: Four consecutive values greater than, or less than,  $1 \times s$  of the mean.
- Rule 10 X: Ten consecutive values all greater than, or less than, the mean.

According to Closceri *et al.* (2012), we should respect the following rules during control chart analysis:

- One out of 20 points, on average, would exceed the warning limit (WL,  $\pm 2$ s), whereas only one out of 100 would exceed the control limits (CL,  $\pm 3$ s).
- If one measurement exceeds a CL, repeat the analysis immediately. If the repeated measurement is within the CL, continue analyses; if it exceeds the CL, discontinue analyses and correct the problem.
- If two out of three successive points exceed a WL ( $\pm 2$ s), analyze another sample. If the next point is within the WL, continue analyses; if the next point exceeds the WL, evaluate potential bias and correct the problem.

- If four out of five successive points exceed 1s, or are in decreasing or increasing order, analyze another sample. If the next point is less than 1s, or changes the order, continue analyses; otherwise, discontinue analyses and correct the problem.
- If seven successive samples are on the same side of the CL, discontinue analyses and correct the problem.

There are several publications concerning QA/QC issues at testing laboratories, including the topic of test method validation (the suitability of methods for specific applications), also in environmental testing (AMC, 2001a, 2001b, 2001c, 2002, 2003, 2005, 2006; Bulska, 2008; Coleman *et al.*, 1997; Currie, 1995; Daszykowski *et al.*, 2007; Dobkowski, 2001; Eurachem, 1998a, 1998b; Feinberg and Laurentie, 2006; Fleming *et al.*, 1997; Fresenius *et al.*, 1988; Gluschke, 2008; Hibbert, 2006; Huber, 1997; ISO, 2002a, 2002b, 2002c, 2002d, 2002e; IUPAC, 1995, 1997, 2003; Mazerski, 2009; Miller and Miller, 2005; Namieśnik *et al.*, 2003, 2007; Nordtest, 2005, 2006; Otto, 2007; Prichard, 2004; Quevauviller, 1995, 2002; Roux, 2004; Shotyk and Krachler, 2009; Srnkova and Zbiral, 2009; Thompson *et al.*, 2002a, 2002b).

There are also publications on data quality control in groundwater monitoring (Garrett, 1969; Gibbons, 1995; Kłojzy-Karczmarczyk *et al.*, 2001; Kmiecik, 2001a, 2001b, 2004, 2008, 2011; Kmiecik *et al.*, 2005; Nawalany *et al.*, 2009; Osmęda-Ernst *et al.*, 1995b, 1996a; Postawa, 2012; Ramsey *et al.*, 1992; Szczepańska and Kmiecik, 1998, 2005; Thompson and Howarth, 1976; Witczak *et al.*, 2006, 2013) and geothermal water monitoring (Amorsson, 2000; Ármannsson and Ólafsson, 2007; Kmiecik and Korzec, 2015; Kmiecik *et al.*, 2017; Zhong-he and Ármannsson, 2005).

#### 5.4 QA/QC PROGRAM IN GEOTHERMAL WATER MONITORING – THE CASE OF BAŃSKA PGP-1 WELL (BAŃSKA NIŻNA, POLAND)

Pursuant to the applicable provisions contained in Polish Geological and Mining Law (PGG, 2016), geothermal water is groundwater that has a temperature of not less than 20°C at intake. Geothermal waters are among the greatest assets of the Podhale region (southern Poland). In addition to their use for heating purposes, they are increasingly used in recreation, medicine and rehabilitation (Kępińska, 2009; Tomaszewska and Bodzek, 2013a, 2013c); they can also be treated and subsequently used as drinking water or for other household purposes (Bujakowski and Tomaszewska 2007; Tomaszewska, 2011; Tomaszewska and Bodzek, 2013a, 2013b, 2013c; Tomaszewska and Szczepański, 2014).

##### 5.4.1 Characteristics of the study object

The Bańska PGP-1 geothermal well is located in the town of Bańska Niżna in the Nowy Targ district, in the Małopolska province (Poland). This well, together with the PGP-2 well, forms a geothermal doublet and is included in the Geotermia Podhalańska S.A. geothermal district heating system (Kleszcz and Tomaszewska, 2013). Geothermal water reservoir levels are Eocene carbonate series with underlying Mesozoic formations, mainly Middle Triassic limestones and dolomites and Jurassic sandstones and carbonate rocks. The chemical composition of geothermal waters in the Podhale Basin is affected by the conditions of their circulation, reservoir rock lithology, oxidation-reduction conditions, pressure, temperature and the activity of microorganisms (Kępińska and Ciągło, 2008).

The geothermal water sourced from the Bańska PGP-1 Well is a sulfate-chloride-sodium-calcium water with a total mineralization of up to ca. 3 g L<sup>-1</sup> (Chowaniec, 2009).

The chemical composition of geothermal waters from the Bańska PGP-1 Well is tested by PEC Geotermia Podhalańska S.A. on average once a quarter. From 2001 to 2012, the analysis of water commissioned by ZG PEC was conducted by the accredited Hydrogeochemical Laboratory of the Department of Hydrogeology and Engineering Geology of the AGH University of Science and

Table 5.7. Comparison of analysis methods used to determine calcium concentrations in geothermal water from Bańska PGP-1 Well.

Indicator	Methods of determination (range of determination)	
	KGHI AGH Laboratory (PCA accreditation No. AB 1050)	SGS EKO-PROJEKT Laboratory (PCA accreditation No. AB 1232)
Ca <sup>2+</sup> [mg L <sup>-1</sup> ]	PN-EN ISO 17294-2:2006. Inductively coupled plasma mass spectrometry (ICP-MS) (0.05–10,000 mg L <sup>-1</sup> ) or PN-EN ISO 11885:2009. Inductively coupled plasma optical emission spectrometry (ICP-OES) (10–10,000 mg L <sup>-1</sup> )	PN-EN ISO 17294-2:2006. Inductively coupled plasma mass spectrometry (ICP-MS) (1.00–1000 mg L <sup>-1</sup> ) or PN-EN ISO 11885:2009. Inductively coupled plasma optical emission spectrometry (ICP-OES) (1.00–1000 mg L <sup>-1</sup> )

Technology in Kraków (PCA accreditation certificate No. AB 1050), and since 2013 it has been conducted by the accredited SGS EKO-PROJEKT Laboratory in Pszczyna (PCA accreditation certificate No. AB 1232). Samples for testing are collected by employees of PEC Geotermia Podhalańska S.A. in accordance with the procedure described in ISO 5667-11: 2004.

In parallel, since 2014, the quality of water from the Bańska PGP-1 Well has been tested by the Department of Hydrogeology and Engineering Geology at AGH in Kraków within the framework of research projects. Sampling is also carried out in accordance with the ISO 5667-11: 2004 standard – samples are collected by a single sampler on average once a month. The sampler changed in September 2015.

Calcium determination results in the samples tested have been subject to detailed analysis. The methods used by the aforementioned laboratories for the determination of calcium are compared in Table 5.7. The laboratories use a similar methodology for determining calcium ions, but the determination ranges declared for this indicator differ.

#### 5.4.2 Laboratory QA/QC program

The laboratory QA/QC program in relation to major ions (including calcium) is implemented by the accredited laboratory of the Department of Hydrogeology and Engineering Geology at the AGH University of Science and Technology that conducts geothermal water testing according to the scheme shown in Table 5.3. The laboratory has validated both methods (ICP-MS and ICP-OES) for the determination of calcium in water, but mainly uses the ICP-OES method.

In the following, data for blank control samples, CRM and environmental control samples are presented.

The results of repeated analyses for duplicate samples have been compared and developed within the framework of the field QA/QC program.

#### Laboratory blanks

A laboratory blank consists of deionized water and all reagents (including preservatives) that normally are in contact with the sample during the entire analytical procedure. It is used to determine how much reagents and preparative analytical steps contribute to measurement uncertainty.

At minimum one blank sample should be included with each sample set (batch) or on a 5% basis. The blank should be analyzed after the daily calibration standard and after highly contaminated samples. If unacceptable contamination is present in the blank sample, the laboratory should identify and eliminate the source of contamination. Samples analyzed with contaminated blank must be re-prepared and reanalyzed (Closceri *et al.*, 2012).

Table 5.8 shows calcium determination results in laboratory blanks.

Table 5.8. Calcium determination results in laboratory blanks.

Date of sampling	Ca [mg L <sup>-1</sup> ]
3 Jun 2014	0.00364
25 Jul 2014	0.00207
13 Aug 2014	0.00224
8 Oct 2014	0.00201
27 Oct 2014	0.13618
16 Jan 2015	0.00534
3 Mar 2015	0.02559
10 Apr 2015	0.01588
3 May 2015	0.01450
12 May 2015	0.00446

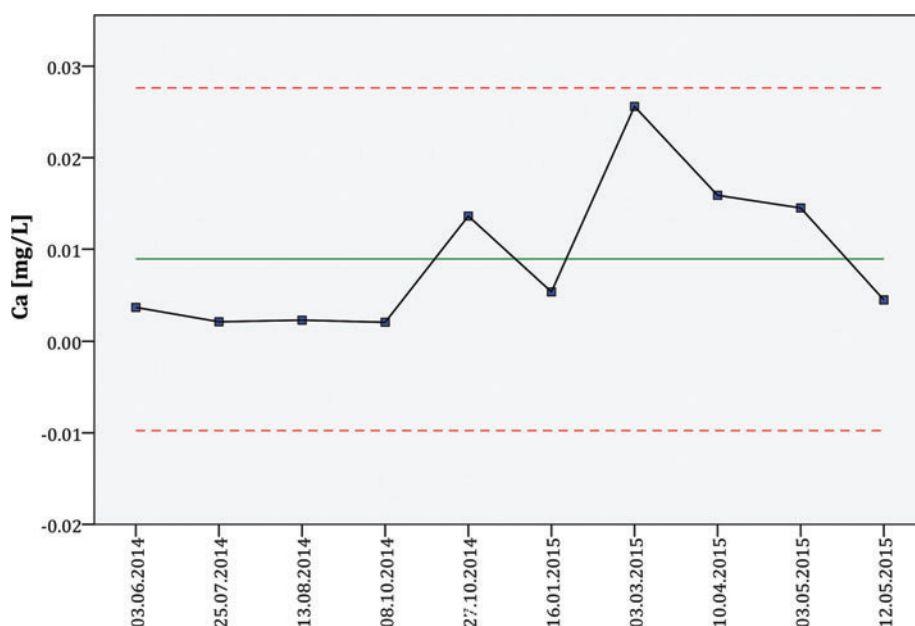


Figure 5.6. Calcium determination results in laboratory blanks. Individual measurement control chart produced using the PS Imago program.

These data are presented on an individual measurement control chart (Fig. 5.6). The chart was produced using the PS Imago program based on the IBM SPSS v. 23.0 system ([www.psimago.pl](http://www.psimago.pl)).

The green central line is the center line, or the average of the data. The two red lines are the upper and lower control limits (*UCL* and *LCL*,  $\pm 3s$ ).

In the case analyzed, determination results for laboratory blanks fit in the area bounded by the control limits. They also meet the  $< DL$  condition stated in Table 5.3. One point is in the range between 2 and 3s.

JMP Statistical Discovery from SAS v. 12.2.0 (JMP Statistical Discovery, 2016) has also been used to produce control charts. The program makes it possible to produce various types of control charts (for individual measurements and for averages in subgroups). Control charts update dynamically as data is added or changed in the data table.

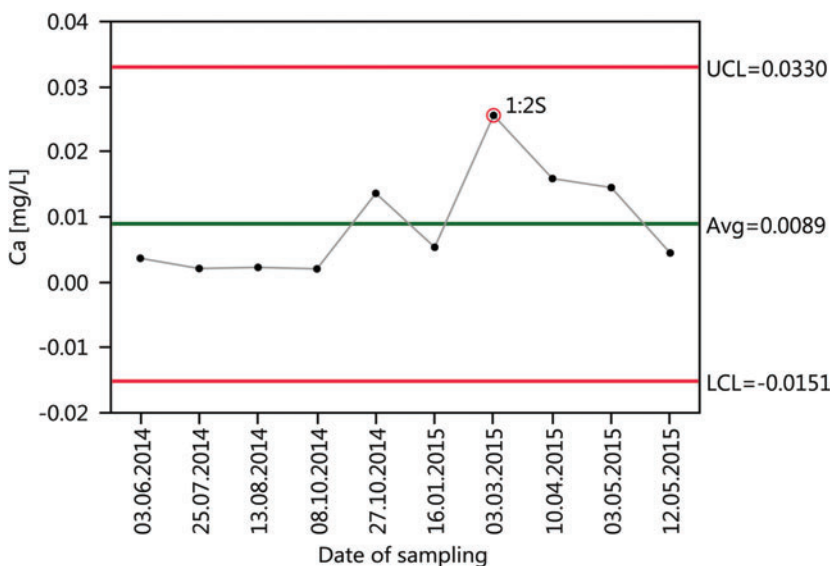


Figure 5.7. Calcium determination results in laboratory blanks. Individual measurement control chart produced using the JMP v. 12.2.0 (SAS) software.

Figure 5.7 shows an individual measurement chart (Levey-Jennings chart) for calcium determination results in laboratory blanks.

The chart also shows that the Westgard 1:2S rule has been broken; one point is in the range between 2 and 3s of the center line, but the subsequent point is already within the 2s inner limit.

#### *Spiked samples (certified reference material – CRM)*

Calcium determination results in CRM (Standard Reference Material, 2009) are shown in Table 5.9.

The certified concentration of calcium in the standard is  $32.3 \text{ mg L}^{-1}$  with an uncertainty of 1.1%. The calcium determination uncertainty declared by the laboratory is 13%.

Figure 5.8 shows a Levey-Jennings control chart for calcium determination results in CRM.

Additionally, these results are shown on a control chart with control limits calculated on the basis of determination uncertainty (Fig. 5.9). The sum of uncertainty of the standard (1.1%) and the uncertainty declared by the laboratory with respect to calcium determination (13%) is taken into account.

Calcium determination results in the certified reference material fall within the range bounded by control limits (Fig. 5.8) and the range of uncertainty (Fig. 5.9) and therefore meet the criteria stated in Table 5.1.

On the control chart in Figure 5.8, it is apparent that the Westgard 1:2S rule is broken (one point is in the range between 2 and 3s of the center line), but the subsequent point is not within this range.

On the chart that takes into account determination uncertainty, a slight bias can also be seen, since all the results are in the area below the target value. The laboratory conducted additional testing to identify the bias.

#### *Environmental control sample*

The environmental control sample used by the laboratory is mineral water with a stable chemical composition ('Cisowianka') spiked with 2 mL of multi-element standard VI. The target calcium

Table 5.9. Calcium determination results in CRM.

Date of sampling	Ca [mg L <sup>-1</sup> ]
3 Jun 2014	29.2
3 Jun 2014	29.1
25 Jul 2014	28.9
13 Aug 2014	28.7
13 Aug 2014	30.5
23 Sep 2014	27.4
8 Oct 2014	31.1
8 Oct 2014	31.1
27 Oct 2014	31.6
27 Oct 2014	29.2
16 Jan 2015	29.6
16 Jan 2015	29.9
3 Mar 2015	29.8
3 Mar 2015	30.3
10 Apr 2015	29.7
10 Apr 2015	29.4
3 May 2015	29.4
3 May 2015	28.8
12 May 2015	28.6

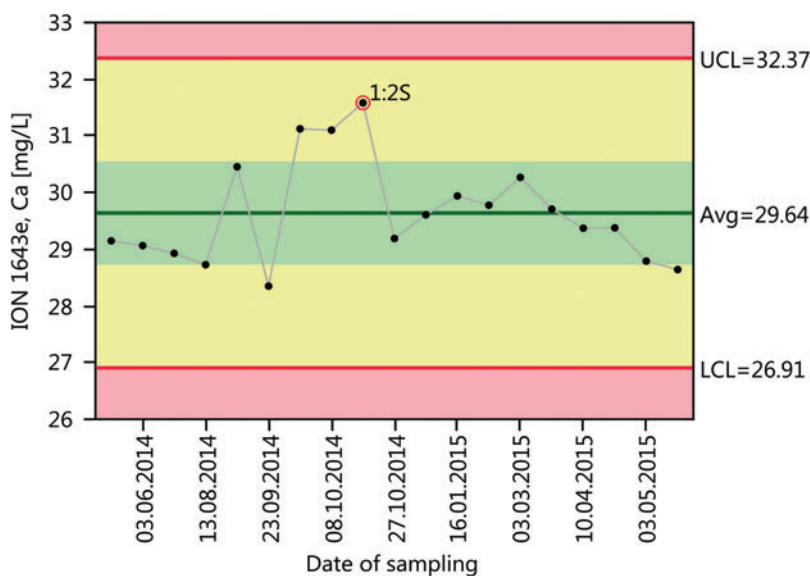


Figure 5.8. Calcium determination results in spiked samples. Levey-Jennings individual measurement control chart. Zones bounded by a specific number of standard deviations are marked with colors:  $\pm 1s$ : green,  $\pm 3s$ : yellow.

concentration value in this sample is  $\mu_0 = 130 \text{ mg L}^{-1}$ . Measurement uncertainty was assumed at 13% in accordance with the laboratory's declaration.

Table 5.10 shows the results of calcium determinations in these samples.

Figure 5.10 shows a control chart with calcium determination results; the limits result from measurement uncertainty (13%).



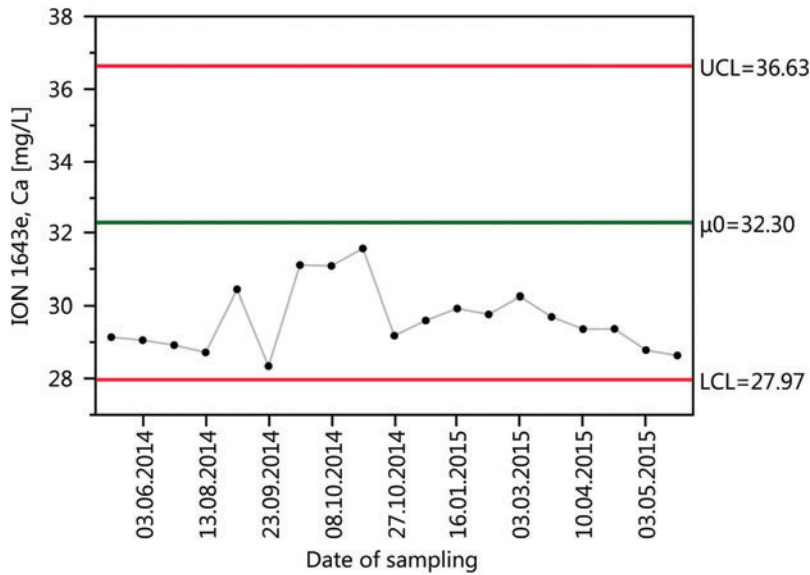


Figure 5.9. Calcium determination results in spiked samples. Individual measurement control chart with limits determined on the basis of determination uncertainty.

Table 5.10. Calcium determination results in spiked environmental samples.

Number of sample	Ca [mg L <sup>-1</sup> ]	Recovery [%]
1	110.3	84.8
2	111.4	85.7
3	131.1	100.9
4	128.3	98.7
5	128.2	98.6
6	132.6	102.0

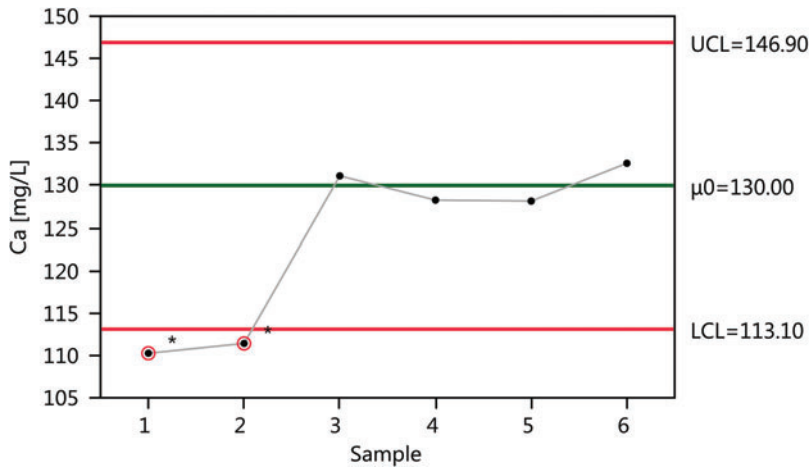


Figure 5.10. Calcium determination results in an environmental control sample. Individual measurement control chart.

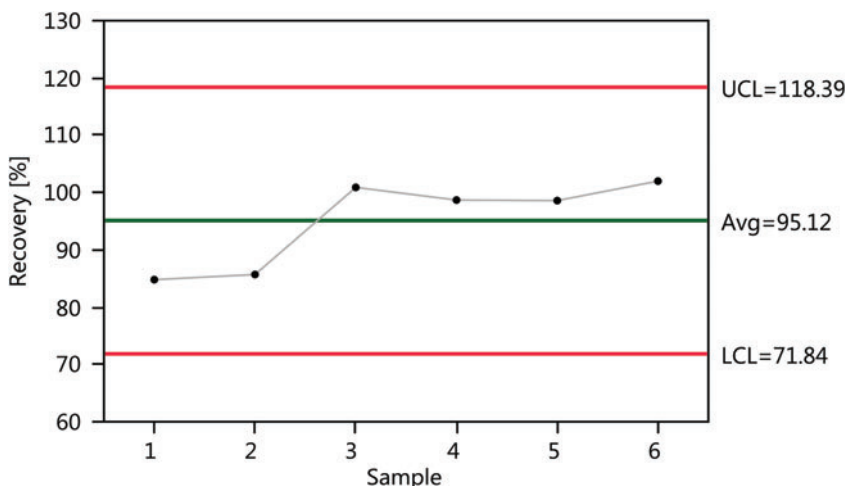


Figure 5.11. Calcium determination results in an environmental control sample. Recovery control chart.

The results for the first two control samples do not fall within the range bounded by measurement uncertainty. The laboratory recalibrated the equipment and subsequent standard analysis results were within the range bounded by measurement uncertainty.

Figure 5.11 shows a calcium recovery control chart for the samples analyzed ( $\% \text{ recovery} = \text{found value}/\text{true value} \times 100\%$ ).

Recovery falls within an acceptable range from 70 to 120%.

#### 5.4.3 Field QA/QC program

In accordance with the guidelines in force at the accredited hydrogeochemical laboratory, the field QA/QC program is designed individually for specific monitoring projects. It includes the collection of field blanks, duplicate and spiked samples.

Within the framework of the projects conducted by the Department of Hydrogeology and Engineering Geology at the AGH University of Science and Technology monitoring of, inter alia, geothermal waters from the Bańska PGP-1 Well, has been conducted since 2014. In parallel with the regular collection of these water samples, field control samples are collected.

On average once every month, field blanks are collected according to the scheme shown in Figure 5.1 and duplicate samples are collected according to the scheme in Figure 5.2. Spiked samples are collected at random for various indicators (specific indicators and major ions).

#### Field blanks

Table 5.11 shows calcium determination results in field blanks and differences between the results.

For the A-b1, A-b2, b1-b2 differences, individual measurement control charts were produced using the JMP program (Figs. 5.12 to 5.14).

The analysis of control charts shows that differences in calcium determination results in field blanks fit within the range bounded by the control limits, which means that the criteria for the analysis of these samples are met.

Field blanks can also be used to determine the so-called practical detection limit, which is a measure of measurement uncertainty. Examples can be found in publications by Kmiecik and Postawa (2009), Postawa and Kmiecik (2010) or Kmiecik and Korzec (2015).

Table 5.11. Calcium determination results in field blanks. Legend as in Figure 5.2.

Date of sampling	A	b1	b2	A-b1	A-b2	b1-b2
3 Jun 2014	0.0059234	0.0771708	0.0009830	-0.0712474	0.0049403	0.0761877
25 Jul 2014	0.0001097	0.0899232	0.0021698	-0.0898134	-0.0020600	0.0877534
13 Aug 2014	0.0001567	0.0390602	0.0061199	-0.0389034	-0.0059632	0.0329402
8 Oct 2014	0.0011589	0.0303284	0.0021502	-0.0291695	-0.0009913	0.0281781
27 Oct 2014	0.0010743	0.0301869	0.0002662	-0.0291125	0.0008081	0.0299206
16 Jan 2015	0.0030623	0.077021	0.0697915	-0.0739590	-0.0667291	0.0072299
3 Mar 2015	0.0176964	0.0779469	0.0111575	-0.060250	0.0065388	0.0667893
10 Apr 2015	0.0154389	0.0386033	0.2289651	-0.0231644	-0.2135262	-0.1903618
3 May 2015	0.0341417	0.0009090	0.0196956	0.0332327	0.0144461	-0.0187865
12 May 2015	0.0025849	0.0886811	0.0099484	-0.0860962	-0.0073635	0.0787326

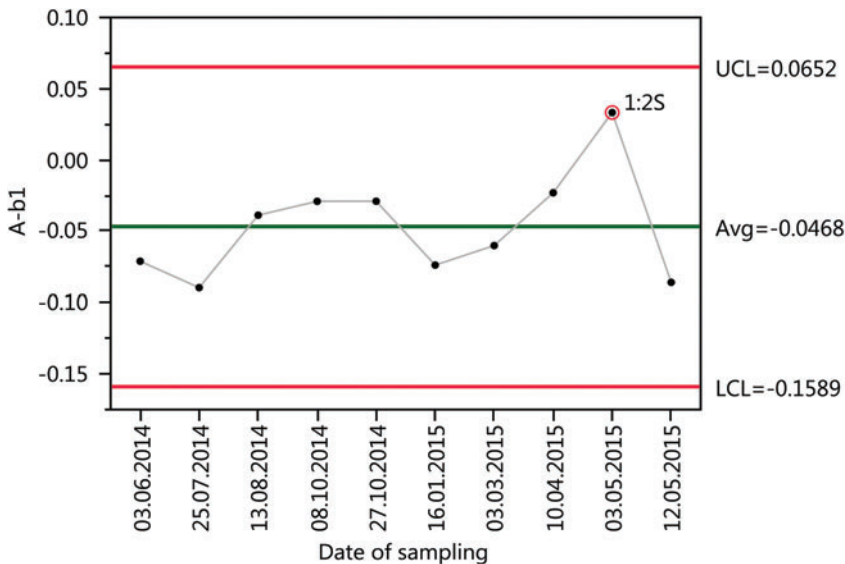


Figure 5.12. Calcium determination results in field blanks. Control chart for A-b1 differences.

### Duplicate samples

Duplicate samples were collected according to an extended balanced design – the normal sample (A) and duplicate sample (B) were each analyzed twice (A1, A2, B1, B2) (Fig. 5.15).

Table 5.12 shows calcium determination results in duplicate samples.

Standard 5667-14 recommends that an individual measurement control chart be used to develop results with respect to differences for duplicate samples (Fig. 5.16).

No signals were identified on the chart, so differences between the results should be regarded as stable.

In groundwater quality monitoring (including thermal water), the total variability of the parameters monitored ( $\sigma_{\text{total}}^2$ ) is derived from three main sources (Fig. 5.15):

- the spatial and/or temporal natural variability of the indicator in question (geochemical variance) –  $\sigma_{\text{geochemical}}^2$ ;

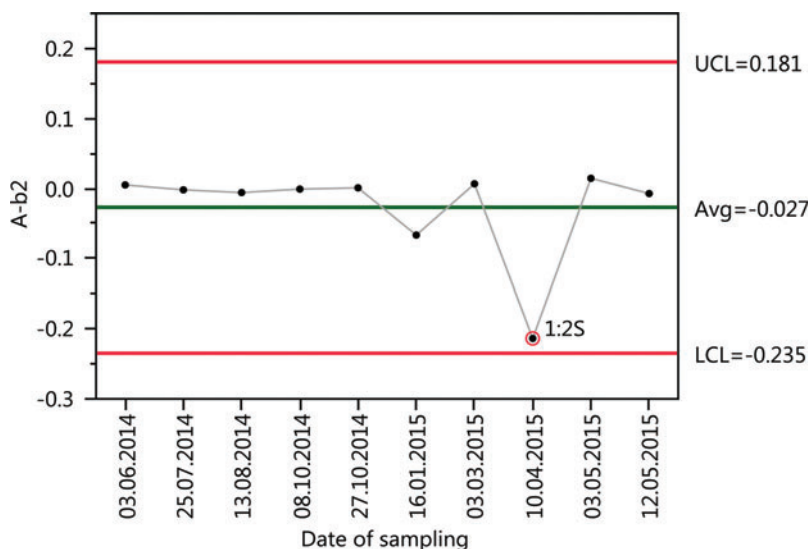


Figure 5.13. Calcium determination results in field blanks. Control chart for A-b2 differences.

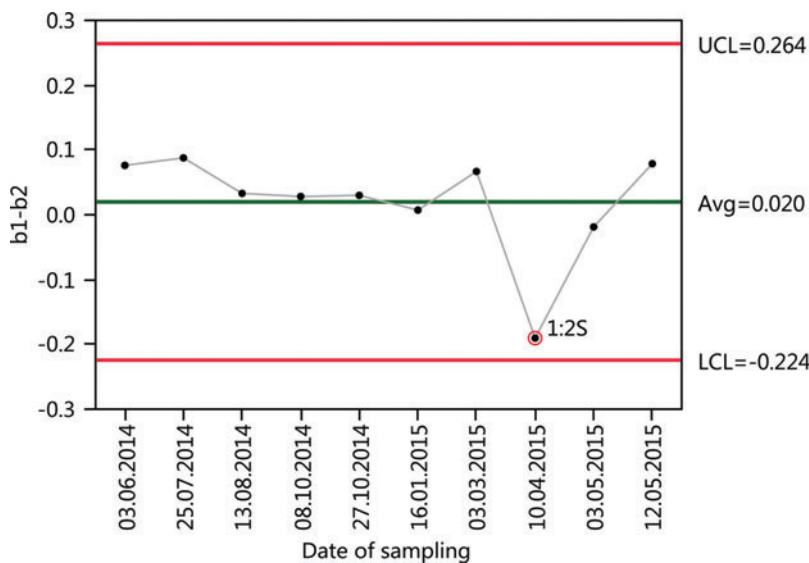


Figure 5.14. Calcium determination results in field blanks. Control chart for b1-b2 differences.

- the errors that occur during sampling, sample transport and storage (sampling variance) –  $\sigma_{\text{sampling}}^2$ ;
  - analytical errors (analytical variance) –  $\sigma_{\text{analytical}}^2$
- $$\sigma_{\text{total}}^2 = \sigma_{\text{geochemical}}^2 + \sigma_{\text{sampling}}^2 + \sigma_{\text{analytical}}^2$$

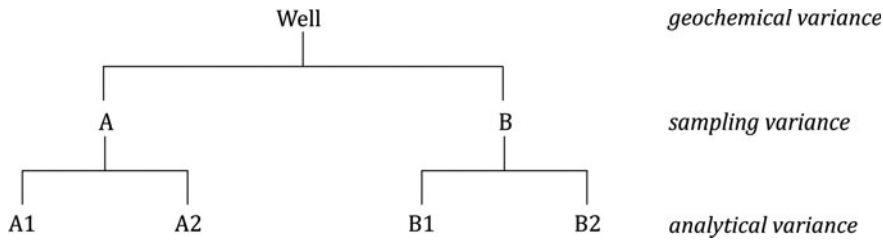


Figure 5.15. Scheme for sampling duplicate control samples and estimating individual types of variance.

Table 5.12. Calcium determination results [ $\text{mg L}^{-1}$ ] in duplicate samples. Legend as in Figure 5.15.

Date	A1	A2	B1	B2
3 Jun 2014	195.69	194.40	196.43	196.55
22 Jul 2014	231.39	233.33	235.27	235.03
13 Aug 2014	191.85	195.16	191.09	190.91
4 Sep 2014	197.31	196.60	199.69	201.23
8 Oct 2014	196.79	199.57	202.40	203.67
27 Oct 2014	199.19	202.90	196.16	204.06
13 Nov 2014	174.42	176.26	177.81	178.16
16 Jan 2015	210.99	211.17	204.57	203.67
5 Feb 2015	203.51	202.89	204.42	203.17
3 Mar 2015	191.92	194.69	187.27	196.25
10 Apr 2015	236.54	238.28	235.89	244.64
3 May 2015	204.38	204.33	203.46	196.77
12 May 2015	199.12	205.63	201.73	203.04

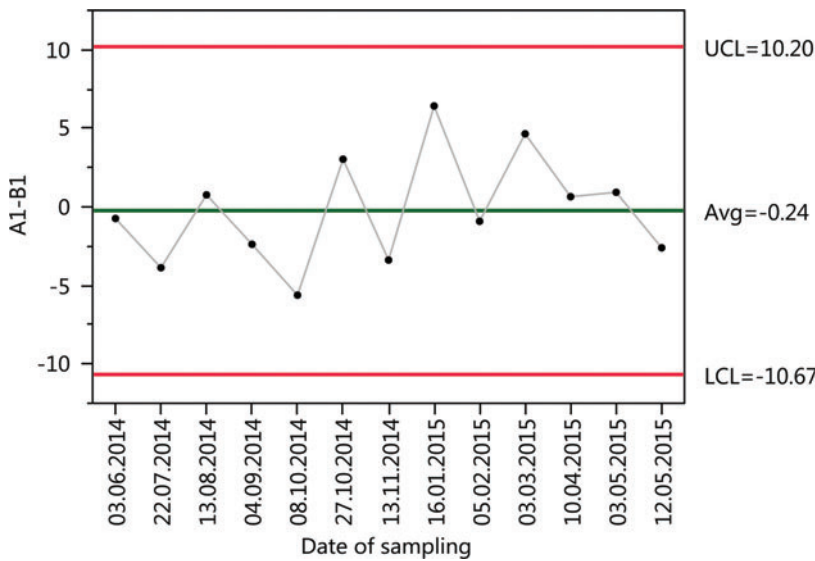


Figure 5.16. Individual measurement charts for concentration differences in normal and duplicate samples.

This variability can be estimated based on the results of determinations for duplicate samples using variance estimators:

$$s_{\text{total}}^2 = s_{\text{geochemical}}^2 + s_{\text{sampling}}^2 + s_{\text{analytical}}^2 \quad (5.1)$$

We use these statistics to estimate standard uncertainties  $u$ :

$$u_{\text{geochemical}} = s_{\text{geochemical}} \quad (5.2)$$

$$u_{\text{sampling}} = s_{\text{sampling}} \quad (5.3)$$

$$u_{\text{analytical}} = s_{\text{analytical}} \quad (5.4)$$

To calculate expanded uncertainty ( $U$ ) at a confidence level of, for example, 95%, we multiply the standard uncertainty value by the  $k$  coverage factor of 2,  $U = 2u$ :

$$U_{\text{geochemical}} = 2s_{\text{geochemical}} \quad (5.5)$$

$$U_{\text{sampling}} = 2s_{\text{sampling}} \quad (5.6)$$

$$U_{\text{analytical}} = 2s_{\text{analytical}} \quad (5.7)$$

Relative uncertainties ( $U'$ ) with respect to the average value of the indicator analyzed in normal and duplicate samples ( $\bar{x}$ ) are calculated using the following formulas (5.8–5.10):

$$U'_{\text{geochemical}} = \frac{2s_{\text{geochemical}}}{\bar{x}} 100 \quad [\%] \quad (5.8)$$

$$U'_{\text{sampling}} = \frac{2s_{\text{sampling}}}{\bar{x}} 100 \quad [\%] \quad (5.9)$$

$$U'_{\text{analytical}} = \frac{2s_{\text{analytical}}}{\bar{x}} 100 \quad [\%] \quad (5.10)$$

Estimates of uncertainty according to the above formulas can be obtained automatically in the ROBAN program (ROBAN, 2016) using the results of analyses of duplicate (replicate) samples.

ROBAN accompanies AMC Technical Briefs No 40 ‘The Duplicate Method for the estimation of measurement uncertainty arising from sampling’ (AMC, 2009).

The program presents, in graphical form, independent estimates of all three components of total variance – geochemical, sampling and analytical variances and their percentage shares.

The estimate is based on the classical variance analysis (classical ANOVA) method and the robust ANOVA method, which uses a flexible statistical approach that allows for the presence of up to 10% of outliers in the data set analyzed. For estimates using the robust method, the program also calculates standard uncertainty (standard deviation)  $u$  and extended relative uncertainty  $U'$  associated with these components.

The analysis of variance makes it possible to gain insights to total uncertainty structure. Figure 5.17 shows the boundary values of relative shares of total uncertainty components resulting from measurements (sampling and analysis) and from the analysis itself (after Ramsey *et al.*, 1992). If relative shares of total variance obtained through the duplicate sample method are higher than the boundary values shown in Figure 5.18, appropriate action should be taken to reduce them.

The introduction of a QA/QC program in relation to duplicate samples in accordance with the extended analysis program is a costly undertaking. However, the use of a simplified program where the normal and duplicate samples are analyzed only once provides no information about sampling and analytical uncertainty because only data on measurement uncertainty, which is the sum of these two components, are obtained. The solution is to apply the unbalanced design and use the U-RANOVA program for estimating uncertainty (Kostka, 2015; Rostron and Ramsey, 2012).

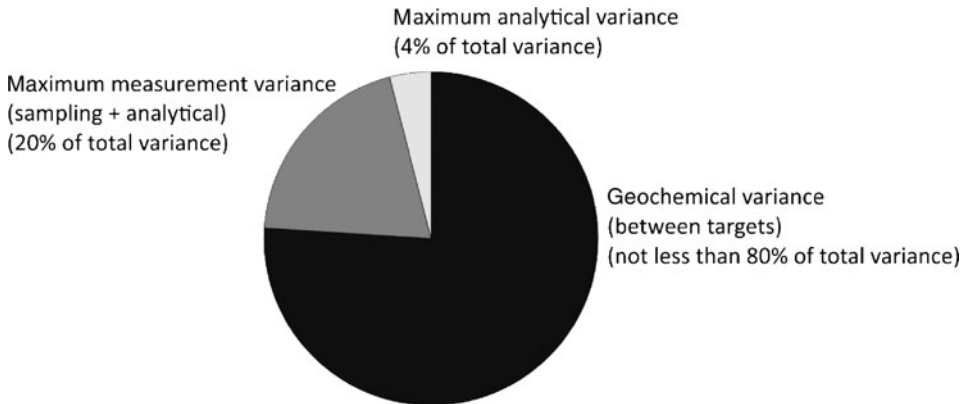


Figure 5.17. Maximum permissible relative shares of sampling variance and analytical variance in total variance (Ramsey *et al.*, 1992).

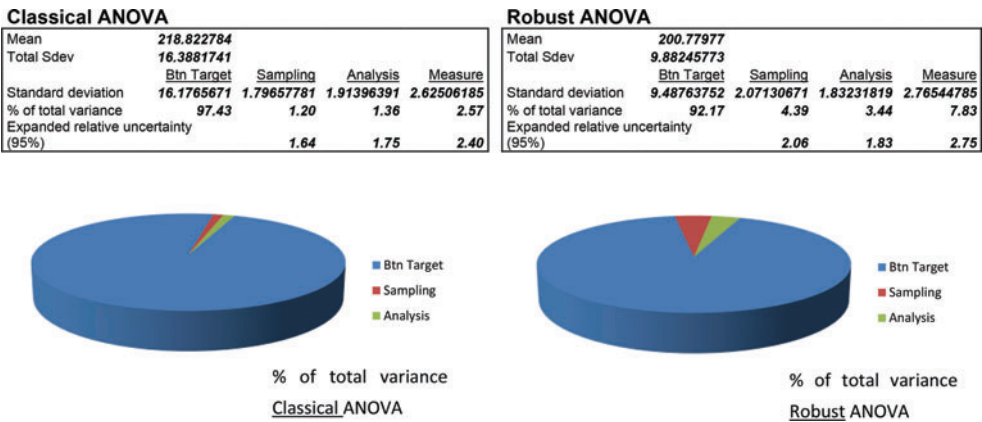


Figure 5.18. U-RANOVA program. Estimates of variance and relative uncertainty  $U'$  for duplicate samples collected from the Bańska PGP-1 Well.

U-RANOVA is an application which assists in the estimation of uncertainty by the duplicate method, which is fully described in the Eurachem guidelines. It is intended for use by analytical chemists, or for anyone else who needs to measure concentrations within a bulk of material through the analysis of a number of discrete samples.

U-RANOVA differs from previous methods in that it permits an unbalanced experimental design to be used. In effect, this enables estimates of the three variances described above to be made with fewer duplicated analyses, thus saving money on the chemical analysis.

U-RANOVA is presented as an easy-to-use Excel application, which allows measurement data from other Excel spreadsheets to be easily pasted into the program, and output to be pasted into other documents as required.

Figure 5.18 shows the results of variance and uncertainty estimation for duplicate samples from the Bańska PGP-1 Well using the U-RANOVA program, assuming an unbalanced design – the normal sample is analyzed twice while the duplicate sample only once.

Table 5.13. Estimates of variance and uncertainty for duplicate samples collected from the Bańska PGP-1 Well obtained using the classical ANOVA variance analysis and robust statistics.

Parameter	ROBAN program		U-RANOVA program	
	ANOVA	Robust	ANOVA	Robust
Geochemical variance (between target) [% total variance]	96.82	90.67	97.43	92.17
Sampling variance [% total variance]	0.63	5.00	1.20	4.39
Analytical variance [% total variance]	2.55	4.33	1.36	3.44
Measurement (technical) variance [% total variance]		9.33	2.57	7.83
Expanded relative uncertainty of sampling [%]		1.98	1.64	2.06
Expanded relative uncertainty of analysis [%]		1.84	1.75	1.83
Expanded relative uncertainty of measurement [%]		2.69	2.40	2.75

Estimates of variance and uncertainty for duplicate samples from the Bańska PGP-1 Well analyzed according to an extended balanced design using the ROBAN program and unbalanced design using the U-RANOVA program are shown in Table 5.13.

In the present case, regardless of the data analysis method used, the sampling variance and analytical variance do not exceed 5% of total variance. Measurement variance does not exceed 20% of total variance.

Estimated measurement uncertainty ranges from 2.40–2.75%. However, this uncertainty is estimated without taking bias into account.

Data on determination uncertainty can be used for assessing the quality of geothermal waters or their fitness for a particular purpose using the probabilistic method. Examples of such assessments in connection with the assessment of chemical water status can be found in publication (Kmiciek, 2008, 2011); with respect to assessing the suitability of water for human consumption in publication (Demetriades, 2010); and with respect to assessing the medicinal qualities of water in publication (Wątor *et al.*, 2016).

#### Spiked samples

Spiked samples were prepared according to the schemes shown in Figures 5.3 and 5.4 by spiking the (laboratory and field) blank samples, the environmental sample (groundwater sample from Jurassic formations from the Królewski Spring in Kraków) and geothermal water sample from the Bańska PGP-1 Well with 5 mL of solution with a calcium concentration of 1000 mg L<sup>-1</sup>.

The results of calcium determinations in these samples together with the method of their preparation for analysis are summarized in Table 5.14.

The calcium determination uncertainty declared by the laboratory is 13% and therefore the results for individual types of spiked samples are within the determination uncertainty range.

The calculated recovery values are at an acceptable level: 91–119% (Table 5.15).

However, differences in recovery should be noted depending on the method of preparation of samples for analysis. Differences between calcium determinations for filtered and unfiltered samples may, for example, result from the precipitation of calcium in the form of CaCO<sub>3</sub> or CaSO<sub>4</sub>. In order to ascertain this, geochemical modeling methods would be required.

The QA/QC program in relation to laboratory and field samples has demonstrated that calcium determination results for thermal water samples obtained at the accredited Hydrogeochemical Laboratory of the Hydrogeology and Engineering Geology Department of the AGH University of Science and Technology are reliable, exhibit acceptable accuracy and precision and their uncertainty does not exceed around a dozen percent. These data can therefore be used, for example, to evaluate the stability of chemical composition of tested waters over time (Kmiciek and Korzec, 2015), as well as to evaluate the effectiveness of the treatment methods used for the geothermal waters from the Bańska PGP-1 Well (Tomaszewska *et al.*, 2017).



Table 5.14. Calcium determination results in spiked samples.

Sample ID	Description	Ca concentration [mg L <sup>-1</sup> ]				
		19 Jan 2016	5 Feb 2016	1 Mar 2016	13 Mar 2016	31 Mar 2016
PGP-1	Water sample from the Bańska PGP-1 Well, filtered, acidified	200.58	202.40	186.55	191.44	202.45
PGP-1+Ca	Water sample from the Bańska PGP-1 Well spiked with the standard, filtered, acidified	217.09	255.78	212.80	233.04	200.72
ZTf	Field blank (deionized water), filtered, acidified	<10	<10	<10	<10	<10
ZTf+Ca	Field blank (deionized water) spiked with standard, filtered, acidified	21.88	20.39	18.38	20.41	19.48
ZL	Laboratory blank (deionized water), unfiltered, unacidified	<10	<10	<10	<10	<10
ZL+Ca	Laboratory blank (deionized water) spiked with standard, unfiltered, unacidified	29.68	22.13	20.17	23.33	21.06
ZK	Environmental sample (water from the Królewski Spring), unfiltered, acidified	98.17	82.21	77.42	78.72	74.45
ZK+Ca	Environmental sample (water from the Królewski Spring) spiked with standard, unfiltered, unacidified, prepared at the laboratory	116.70	99.50	89.26	99.39	87.78

Table 5.15. Calcium recovery in spiked samples. Legend as for Table 5.14.

Sample ID	Recovery [%]				
	19 Jan 2016	5 Feb 2016	1 Mar 2016	13 Mar 2016	31 Mar 2016
PGP-1+Ca	100.2	100.6	104.9	112.2	106.7
ZTf+Ca	109.7	101.9	91.4	101.2	102.0
ZL+Ca	118.4	110.6	100.8	116.6	116.6
ZK+Ca	100.4	98.9	93.1	102.3	106.9

## 5.5 SUMMARY

The results of geothermal water testing depend on the entire process, starting with the proper design of the monitoring point/network, correct sampling, proper preservation, storage and transportation of samples to the laboratory, sample processing and analysis of sample chemical composition using specific analytical methods.

Obtaining sufficiently certain (robust and reliable) measurements of physicochemical parameters of water entails the need to implement a quality assurance/quality control (QA/QC) system with respect not only to laboratory tests, but also field ones.

Ensuring the adequate quality of hydrogeochemical data is also important from the point of view of their comparability between different laboratories on an international scale. A way of verifying this quality is the mandatory participation of laboratories accredited according to the EN 17025: 2005 standard and laboratories performing groundwater tests (EU, 2009) in inter-laboratory comparisons. Details on planning such tests, their implementation and the development of data can be found in ISO/IEC Guide 43 and in publications, for example, Bulska (2008).

The ultimate purpose of testing the quality of waters (including geothermal waters) is always a decision on, for example, the status of these waters, their suitability for a particular purpose, or the effectiveness of the treatment method used. Our awareness of the quality of the result on the basis of which assessment is conducted and knowledge of its parameters, including for example, uncertainty, contributes to the credibility of the decision made.

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## CHAPTER 6

### Treatment of geothermal waters for industrial and agricultural purposes

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#### 6.1 INTRODUCTION

Geothermal resources consist of thermal energy from the earth's interior stored in both rock and trapped steam or liquid water. Geothermal energy is classified as a renewable resource because the heat from an active reservoir is continuously restored by natural heat production, conduction and convection from surrounding hotter regions, and the extracted geothermal fluids are replenished by natural recharge and injection of the cooled fluids (Goldstein *et al.*, 2011).

The first geothermal power plant in the world was installed in Italy in 1904 with a capacity of 0.015 MW. This capacity was upgraded to 0.25 MW in 1913, but it was not until 1938 when modern commercial development began with an expansion to 69 MW. The field was subsequently expanded during the 1950s and 1960s and then upgraded in the 1980s and 1990s to its current capacity of 547 MW. The next significant geothermal development was in New Zealand in 1958. Following the geothermal activities in Italy and New Zealand, additional large-scale international geothermal activities were developed in the 1960s, 1970s and 1980s, especially in Japan, Mexico, and Philippines. In 1999, geothermal power generation occurred in 21 countries from 85 sites, with 94% of the total from eight countries. These eight largest geothermal power producers are: USA (31%), Philippines (19%), Mexico (12%), Indonesia (9%), Italy (9%), Japan (7%), New Zealand (5%) and Iceland (2%). Seventy-five percent of the worldwide total is produced from 20 countries with more than 100 MW installed generating capacity each (Williamson *et al.*, 2001). New 18 geothermal power plants started up and added 313 MW of new capacity to electricity grids globally in 2015. The global geothermal market operating capacity became 13.3 GW with 24 countries in January 2016. The global geothermal market planned capacity was reaching about 12.5 GW with 82 countries at 2016 (Matek, 2016).

Geothermal energy is on the scale of hundreds of MW both for electricity generation and direct use. According to Geothermal Energy Association (GEA), there are expecting about 18,400 MW as total in the global geothermal industry by 2021 and about 32,000 MW of geothermal resources under development could reach 32 GW by the early 2030s (Matek, 2016). The leading countries producing electricity from geothermal energy are listed in Table 6.1.

According to the Geothermal Energy Association (GEA), the global geothermal industry grew slowly but steadily, adding several hundred MWs online each year without pause. The growth in new capacity will most likely come from European, East African, and South Pacific markets as these regions lead geothermal power's growth by substantial capacity additions in the next five years (Matek, 2016).

#### 6.2 GEOTHERMAL POTENTIAL OF TURKEY

For Turkey, geothermal resources are very important renewable energy sources as Turkey is among the top seven countries in the world in terms of its geothermal potential. The first commercial geothermal power plant with 20.4 MW power was installed at Denizli-Sarayköy. Investments in



Table 6.1. Countries producing geothermal power in 2016 (adapted from Matek, 2016).

Country	Installed capacity [MW]
United States	3567
Philippines	1930
Indonesia	1375
Mexico	1069
Italy	944
New Zealand	973
Iceland	665
Turkey	637
Japan	533
Russia	97
Costa Rica	166
Nicaragua	88
Russia	82
Turkey	82

geothermal power plants have increased since 2008. Numerous power plants have been commissioned, or their construction has been ongoing, in Aydın, Manisa, İzmir, Denizli, Kütahya and Çanakkale. Geothermal power plants with a total of 860 MW installed power have been commissioned in December 2016 and planning and under construction power plants of total capacity reach to 600 MW. Total power generation is expected to reach 1700 MW in few years (Jesder, 2017).

At that time, Turkey will be first in Europe and fifth in all over the world in terms of geothermal power generation capacity. Furthermore, integrated with power generation, carbon dioxide production, central heating, drying, greenhousing etc. geothermal applications are being performed in these fields. In Turkey, current geothermal electricity production is at Aydın, Denizli, Manisa and Çanakkale with 570.1 MW, 131.2 MW, 141.4 MW and 15.5 MW of installed capacity, respectively.

### 6.3 MAIN UTILIZATION AREAS OF GEOTHERMAL ENERGY

Geothermal fluid is utilized especially and primarily in power generation and as a heat source for such applications as urban heating and cooling, plant and fish production/cultivation, heating animal farms, streets and airport runways, swimming pools, thermal treatment centers and other tourist facilities, drying and sterilization of foods, production of canned food, paper/textile whitening, drying and processing of leather, at various food industries and cooling plants, for recovery of chemical substances from geothermal fluid, production of chemical substances from salt water, and utilization of waters with high mineral content for the cosmetic industry. Direct utilization of geothermal energy as heat in worldwide for the 1995 to 2015 period summarized in Figure 6.1.

Geothermal district heating is the use of geothermal energy to heat individual and commercial buildings, as well as for industry, through a distribution network. Iceland, Turkey, China and France are the leaders in district heating, whereas Russia, Japan, USA and Italy are the major users in the individual home-heating sector (Lund *et al.*, 2005, 2011). The utilization of geothermal energy for district heating provides the following benefits:

- The use of an environmentally friendly and economically compatible reliable energy source;
- Improving air quality;
- Price stability compared to fossil fuels;
- Applications in various domestic and industrial uses;
- Provides competitive advantages to various industries.

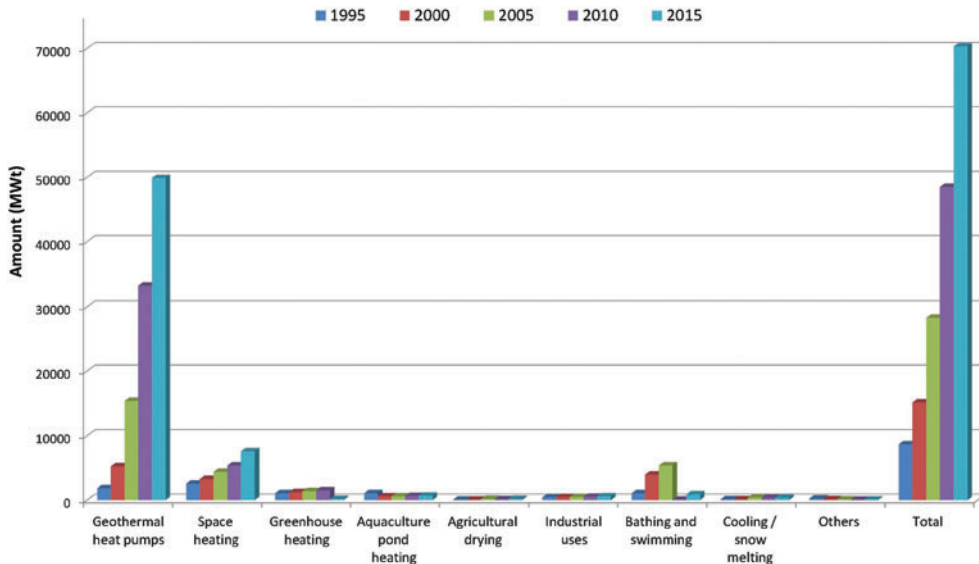


Figure 6.1. Worldwide direct heat energy usage potential of geothermal energy for the period 1995–2015 (adapted from Lund and Boyd, 2015).

Greenhouses have been heated with geothermal energy since 1970. Totally, around thirtyone countries use geothermal greenhouse heating and the leading countries in this field are Turkey, Russia, Hungary, China and Netherlands (Lund and Boyd, 2015).

A number of commercial crops can be raised in greenhouses, making geothermal resources in cold climates particularly attractive, where growth can be optimized in a controlled environment. Some of these crops include vegetables, flowers, house plants and tree seedlings (Barbier and Fanelli, 1977). The major risks to be taken into consideration in the design of a heating system are the losses of heat from transmission through the walls and roof, and infiltration and ventilation losses due to the heating of cold outside air (Boyd and Rafferty, 1998).

One of the main use of geothermal resources for many years has been for bathing and washing. The value of hot springs has been recognized everywhere since ancient times (Fridleifsson, 2001). Such bathing has been used for recreation, relaxation, socializing, therapy, and as part of spiritual practices by cultures in many parts of the world (Kepinska, 2003). While the reason for bathing remains unchanged, bathing practices have evolved into refined cultural traditions and sophisticated therapeutic treatments that rely on modern technology (Haraldsson and Cordero, 2014). Almost every country has spas and resorts that have swimming pools, but many allow the water to flow continuously, regardless of use (Lund *et al.*, 2005, 2011).

It has been demonstrated that more fish can be produced in a shorter period of time if geothermal energy is used for aquaculture pond and raceway heating rather than water dependent upon the sun for its heat. When the water temperature falls below the optimal values, the fish lose their ability to feed because their basic body metabolism is affected (Johnson, 1981).

The use of geothermal steam and hot water was developed for drying some agricultural crops such as seaweed, onion, wheat and other cereals, fruit, lucerne, coconut, and timber (Boyd and Lund, 2003). There is a large potential and great interest in using geothermal heat for drying crops especially in tropical zones (Lund *et al.*, 2005, 2011).

Geothermal heat pumps have the largest energy use and installed capacity, accounting for 54.4% and 32.0% of the worldwide capacity and use (Curtis *et al.*, 2005). Geothermal energy has a considerable economic potential only in areas where thermal water or steam is found

concentrated at depths less than 3 km in restricted volumes. Heat pumps use the ground source of the earth as a heat source or as a heat sink for cooling. This has made it possible for all countries to use the heat of the earth for heating and/or cooling purposes (Fridleifsson, 1998).

Industrial applications are the smallest sector of direct use of geothermal resources. Industrial processes which operate at a high load factor relative to other geothermal applications, offer a concentrated load at a single location and in some cases are characterized by energy as a significant portion of production cost (Rafferty, 2003).

The reasons preventing use of geothermal resources widely in the industrial sector are mostly due to the high-temperature requirements for most processes, the use of steam rather than hot water and the fact that geothermal resources tend to be dominated by low-temperature hot water production (Rafferty, 2003).

Utilization of geothermal for industrial process heat has applications in those countries where the installations tend to be large and have a high energy consumption. The use of geothermal energy in industrial processes has increased slightly since 2000. Concrete curing, bottling of water and carbonated drinks, milk pasteurization, leather industry, chemical extraction, carbon dioxide extraction, mushroom growing and laundry use, salt extraction and diatomaceous earth drying, pulp and paper processing, iodine and salt extraction, and borate and boric acid production are some examples of the use of geothermal sources in industry (Lund *et al.*, 2005, 2011).

In Argentina, geothermal steam is used for highway snow melting in the Andes to keep a resort community open during winter (Boyd and Lund, 2003).

Geothermal power stations produce electricity using conventional processes. For this, geothermal fluid, a naturally occurring mineralized mixture of pressurized water and steam with 100–300°C temperature is drawn from a geothermal field by production wells at depths of 1–3 km. The hot water at high pressure is separated into steam and water. The dry steam is used to spin turbines, generating electricity. All waste fluids are injected back into the geothermal field to help replenish it and to avoid contaminating surface waters with dissolved chemicals (Stewart, 2012).

In Turkey, electricity production potential is calculated at 1500 MW<sub>e</sub>. There are twenty companies licensed for electricity production and seven power plants producing electricity at the moment (Aksoy, 2013).

## 6.4 ENVIRONMENTAL ISSUES

Geothermal is an environmentally friendly, renewable, and sustainable source of energy. It is well positioned to play an important role in mitigating global climate change, increasing national energy security, and safeguarding public health. Emissions rates associated with geothermal power plants are much lower than emissions from coal or natural gas-fired power plants (Holm *et al.*, 2012).

Geothermal fluids contain a variable quantity of gas, largely nitrogen and carbon dioxide, with some hydrogen sulfide and smaller proportions of ammonia, mercury, radon, arsenic and boron. The amounts depend on the geological conditions of different fields. Most of the chemicals are concentrated in the disposal water which is routinely reinjected into drill holes and thus not released into the environment. The concentrations of the gases are usually not harmful, and the removal of, for example, hydrogen sulfide from geothermal steam, is a routine matter in geothermal power stations where the gas content is high (Fridleifsson, 2001).

The range in CO<sub>2</sub> emissions from high-temperature geothermal fields used for electricity production in the world is 13–380 g kWh<sup>-1</sup>, whereas the CO<sub>2</sub> emissions are 453 g kWh<sup>-1</sup> for natural gas, 906 g kWh<sup>-1</sup> for oil and 1042 g kWh<sup>-1</sup> for coal. Sulfur emissions are also significantly less for geothermal than fossil fuel electric power stations. The gas emissions from low-temperature geothermal resources are normally only a fraction of the emissions from the high-temperature fields used for electricity production (Fridleifsson, 2001).

The process of extracting geothermal fluids including gases, steam and water for power generation typically removes heat from natural reservoirs at over 10 times their rate of replenishment.

This imbalance may be partially improved by injecting waste fluids back into the geothermal system (Stewart, 2012).

Surface disturbances may occur during drilling, but will mostly disappear once drilling is completed, the drill rigs have been removed, the ponds drained and the landscape reshaped. Surface disturbances caused by excavation, construction and the creation of new roads will accompany most new activities, but the area involved is relatively small (Kristmannsdottir and Armannsson, 2003).

Natural features such as hot springs, mud pools, sinter terraces, geysers, fumaroles and steaming ground can be easily, and irreparably, damaged by geothermal development (Stewart, 2012).

Landslides are liable to occur in some places and may set constraints on the sites chosen for construction. As geothermal fields are often associated with volcanic rocks such as pumice, and the soil and upper basement in geothermal fields are often thermally altered and can become increasingly so during utilization, the landslide factor has to be carefully monitored (Goff and Goff, 1997).

Extracting geothermal fluids can reduce the pressure in underground reservoirs and cause the land to sink. As the ground sinks it also moves sideways and tilts towards the center. This puts a strain on bores and pipelines, may damage buildings and roads, and can alter surface drainage patterns (Stewart, 2012).

Geothermal fluids may contain high levels of arsenic, mercury, lithium and boron because of the underground contact between hot fluids and rocks. If brine is released into rivers or lakes instead of being injected into the geothermal well back again, these elements can damage aquatic life and make the water unsafe for drinking or irrigation. The main pollutant chemicals in the liquid fraction are hydrogen sulfide, arsenic, boron, mercury and other heavy metals such as lead, cadmium, iron, zinc and manganese. Lithium, ammonia and aluminum could also exist at toxic levels (Stewart, 2012).

The heat efficiency of power production is low, so a considerable amount of energy is wasted. Wastewater causes problems for the environment. Excess heat emitted in the form of steam may affect cloud formation and change the weather locally, and waste brine discharged into streams, rivers, lakes or local groundwater may seriously affect the biology and ecological system.

A serious environmental effect of the geothermal industry is arsenic pollution. Levels of arsenic in some regions exceed the World Health Organization (WHO) standard for drinking water of  $10 \mu\text{g L}^{-1}$  (Stewart, 2012).

Geothermal fluids contain dissolved gases which are released into the atmosphere (Stewart, 2012). The major offenders are carbon dioxide and hydrogen sulfide, although methane, mercury, radon, ammonia and boron can also cause problems. Carbon dioxide, which is usually the major constituent of the gas present in geothermal fluids, and methane, a minor constituent, both require attention because of their role as greenhouse gases. The main toxic gases are carbon dioxide and hydrogen sulfide. These gases could be harmful for people working at geothermal stations or bore fields, and could also be a problem in urban areas. Carbon dioxide is also a greenhouse gas, contributing to potential climate change. However, geothermal extraction releases far fewer greenhouse gases per unit of electricity generated than burning fossil fuels, such as coal or gas, to produce electricity.

Carbon dioxide is already an industrial by-product in several geothermal plants, such as Kizildere, Turkey, thus reducing emissions even further. It has also been pointed out that the carbon dioxide emitted from geothermal plants is not created by power generation but it is vented out gradually through the earth anyway (Kristmannsdottir and Armannsson, 2003). Research from volcanic terrains strongly suggests that the development of geothermal fields makes no difference to the total carbon dioxide emanated from those terrains (Bertani, 2001). Hydrogen sulfide probably causes the greatest concern as it has an unpleasant smell and is toxic at certain concentrations. It has been observed that, as a result of geothermal field exploitation, the concentration of hydrogen sulfide increases relatively more than the concentration of carbon dioxide, probably because of the higher reactivity of hydrogen sulfide. It is reported that most of the

hydrogen sulfide will end up being oxidized to sulfur dioxide, and will thus add to the global acid rain problem, but the fate of the hydrogen sulfide in the atmosphere is a matter of debate. Little evidence has been found of such an effect in the vicinity of power plants and it has not been demonstrated that the hydrogen sulfide is indeed oxidized to sulfur dioxide to any degree. On the contrary, it has been demonstrated that a considerable proportion of the hydrogen sulfide is washed out of the steam and precipitated as elemental sulfur. It was reported that only a small fraction of hydrogen sulfide is oxidized to sulfur dioxide in the climatic conditions of Iceland (Kristmannsdottir and Armannsson, 2000). Geothermal gases will also have an impact on the biology of the region (Webster and Timperley, 1995).

## 6.5 CHEMISTRY OF GEOTHERMAL FLUIDS

Mineral-fluid equilibria play a fundamental role in determining the chemistry of the discharge fluids. The chemical reactions which take place are a function of the temperature, pressure, salinity and host rocks of the geothermal system. The following species are the most common (Barbier, 2002):

- Anions:  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$
- Cations:  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$
- Neutral:  $\text{SiO}_2$ ,  $\text{NH}_3$ ,  $\text{H}_3\text{AsO}_3$ ,  $\text{H}_3\text{BO}_3$ , noble gases.

In water-dominated geothermal systems, the most common type of fluid found at depth, the primary water type, is of near-neutral pH, a sodium chloride brine containing gas, mainly  $\text{CO}_2$ . It is generally agreed that these waters are formed, at some greater depth, from the absorption of magmatic volatiles ( $\text{HCl}$ ,  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ) into deeply circulating meteoric water. The proportion of magmatic volatiles ultimately determines the salinity of the reservoir waters (Barbier, 2002).

### 6.5.1 Toxic elements in geothermal water

#### 6.5.1.1 Arsenic

The presence of arsenic in natural waters may originate from geochemical reactions, industrial waste discharges, or agricultural use of arsenic-containing pesticides (Gupta and Chen, 1978). It can enter the vapor phase as arsenous acid ( $\text{H}_3\text{AsO}_3$ ), but only in very high-temperature systems is arsenic likely to be more than a trace constituent. Arsenic is mobilized by natural weathering reactions, biological activity, geochemical reactions, volcanic emissions and other anthropogenic activities (Mohan and Pittman, 2007).

#### 6.5.1.2 Boron

Boron is readily dissolved by steam condensate, or near-surface steam-heated waters in which it attains elevated concentration, it shows highest concentration in upflow zones (Barbier, 2002). It is vital as a trace element for plant growth and is supplied in fertilizer. However, if it is present in amounts larger than required it becomes toxic. Among the most sensitive crops are citrus trees, which show massive leaf damage at boron levels of more than  $0.3 \text{ mg L}^{-1}$  in irrigation water. Excess boron also reduces fruit yield and induces premature ripening (Kabay *et al.*, 2010, 2015).

#### 6.5.1.3 Mercury

Discharge from natural hot springs or from drill holes producing hot water or steam for geothermal power may constitute an important source of mercury pollution. Inorganic mercury discharged from these sources may accumulate in the sediments of rivers or lakes and, after microbiological methylation, may become concentrated as the more toxic compound, methylmercury (Weissberg and Zobel, 1973). Mercury can be introduced into the atmosphere from fumaroles, hot springs, and magmatic sources. Mercury vapor and gaseous mercury sulfide can both contribute to the mercury content of the steam discharge. Hydrogen sulfide concentration of the deep fluid play an

important role in controlling mercury emissions, with less mercury vapor being produced with increasing  $\text{H}_2\text{S}$  concentrations (Kagel *et al.*, 2007).

## 6.6 TREATMENT OF GEOTHERMAL WATER

For the energy needs of the world, geothermal sources are becoming attractive alternatives as they are one of the most stable renewable energy sources (Kose, 2007). Also in some regions with water scarcity, geothermal fluids are considered as valuable water resources for industry and agriculture, as well as for drinking water supplies (Gallup, 2007).

Geothermal water that ascends to the surface reacts with the wall rocks causing mineral dissolution (Webster and Nordstrom, 2003). Therefore, geothermal waters contain a high concentration of boron, arsenic, fluoride and heavy metals. The presence of some elements, especially boron which exists at high concentrations, prevents the direct use of geothermal waters as irrigation or potable water and causes chemical pollution and environmental problems in groundwater and surface waters (Aksoy *et al.*, 2009; Gemici and Tarcan, 2002; Kristmannsdottir and Armannsson, 2003; Vengosh *et al.*, 2002).

Geothermal waters are generally used as irrigation water in agricultural areas. Their boron contents accumulate in the soil and this may cause a change to its characteristics. Also, these waters could mix with underground waters by passing through the soil and constitute complexes with Pb, Cu, Cd and Ni ions. It was reported that the toxicities of these complexes are higher than those of the heavy metals alone (Gallup, 2007). The environmental impacts of high boron content in geothermal brines discharged to environment and the importance of the removal of boron have been pointed out in many studies. Therefore, removal of boron from geothermal water is an important concern.

### 6.6.1 Boron removal from geothermal water

For many years, boron was not considered as a toxic element. Between 1958 and 1971, there was no mention of boron in the WHO International Standards for drinking water. The first mention of boron in drinking water was encountered in the document, Drinking Water Quality, published in 1984, where the conclusion drawn indicated that no action was required. In other words, boron was not considered harmful at that time. Provisional guidelines for boron concentration in drinking water by WHO were first introduced in 1993. However, since boron has been shown to induce several harmful effects on animals in laboratory studies, the recommended guideline value of  $0.3 \text{ mg L}^{-1}$ , based on NOAEL (no observed adverse effect level) was set in the 1993 guidelines. This guideline value was increased to  $0.5 \text{ mg L}^{-1}$  in the published guidelines in 1998 as it was difficult to comply with the guideline due to the poor performance of boron removal processes encountered in water treatment (Hilal *et al.*, 2011). This value ( $0.5 \text{ mg L}^{-1}$ ) was revised by WHO as  $2.4 \text{ mg L}^{-1}$  in 2011 (Kabay *et al.*, 2010, 2015; WHO, 2011). Although the new guideline value is based on a human health perspective, some utilities may set product water limits as low as  $0.5 \text{ mg L}^{-1}$  to reflect agricultural related issues. These include the herbicidal effect of boron on some plant species, which is of particular concern in areas of low rainfall. On the other hand, if boron concentration in irrigation water is only slightly higher than the minimum, this has a negative effect on plant growth and will present signs of boron toxicity. The tendency of boron to accumulate in vegetable tissue constitutes a potential hazard to the health of those consuming food and water with high boron content. As a result, although boron is vital as a micronutrient element for the growth of plants, it can be detrimental at higher concentrations. Therefore, it is necessary to remove the excess amount of boron from water in an economical and feasible way.

Most of the geothermal waters in Turkey contain a high concentration of boron. When boron-containing thermal waters and geothermal brines are discharged to agricultural areas for irrigation after being used in thermal baths and electricity production, they can cause some environmental problems. Boron species in many geothermal fields and boron rich thermal springs are

undissociated boric acid  $\text{B(OH)}_3$  and borate ions  $\text{B(OH)}_4^-$ . Boric acid is dominant at low pH values ( $\text{pH} < 8.5$ ) and borate at high pH values (Kabay *et al.*, 2009, 2015).

As for irrigation water, boron is required for certain metabolic activities in plants such as cellular multiplication, the metabolism of nucleic acids. Deficiency in boron levels will result in poor budding, excessive branching, and in general, inhibit plant growth. However, higher boron levels accelerate plants' decay and expiration. Different plants can withstand different boron levels. For example, the optimum boron concentration range is  $0.3\text{--}0.5\text{ mg L}^{-1}$  for citrus, grapes, and  $0.5\text{--}0.8\text{ mg L}^{-1}$  for corn. On the other hand, boron concentration in irrigation water which is only slightly higher than the minimum will be negative for plant growth and will exhibit signs of 'boron poisoning' with yellowish spots on the leaves and the fruit, accelerated decay, and ultimately plant expiration (Boncukcuoglu *et al.*, 2004). Therefore, removal of boron from water and wastewater is a crucial problem for environmental control. There is no easy method for removal of boric acid and borates from aqueous solution. As has already been stated in the literature, conventional sedimentation and biological treatment methods remove boron poorly from water. Also, coagulation-precipitation methods are not effective and not feasible for this purpose (Nadav, 1999). More recently, Kabay (2015) published a review on boron separation processes from geothermal water.

#### 6.6.1.1 Boron removal by solvent extraction

Extractants for boron are classified into three groups: (i) extractants of boric acid without any reactions (physical extraction); (ii) extractants of boric acid accompanying a reaction which forms a neutral ester; (iii) extractants of boric acid accompanying a reaction with tetrahydroxy borate to form a borate salt complex. In the case of physical extraction, high extractability is not attainable. The extractants belonging to groups (ii) and (iii) are suitable for extracting boron from acidic and alkaline solutions, respectively (Matsumoto *et al.*, 1997).

Boric acid/borate easily reacts with compounds having polyols like mannitol, giving anionic complexes at the neutral pH. With carbohydrates and most polyols possessing 1,2-diol systems, the borate ion forms anionic mono (1:1) and bis (1:2) diol-monoborate species. It was reported that the stability of the borate complex is strongly dependent on the type of diol, namely 1,2- or 1,3-diols (Geffen *et al.*, 2006).

#### 6.6.1.2 Boron removal by coagulation and electrocoagulation

As has already been stated in the literature, conventional co-precipitation methods are not very effective for boron removal from water. Also, coagulation-precipitation methods are not feasible (Nadav, 1999). In co-precipitation, the removal efficiency is about 90% using  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{Ca(OH)}_2$ . This method is not effective due to the sludge production at the end of the process. Electrocoagulation (EC) has been used for the removal of boron from thermal waters and the efficiency of boron removal from geothermal water was up to 95% at optimal conditions. Yilmaz *et al.* (2008) showed that boron removal efficiency increased from pH 4.0 to 8.0 and decreased at pH 10.0. Boron removal efficiency reached 95% with increasing current density but energy consumption also increased in this interval. At higher temperatures of solution, such as 313 and 333 K, boron removal efficiency increased (Yilmaz *et al.*, 2008).

#### 6.6.1.3 Boron removal by adsorption

Adsorption is comparatively more useful and economical at low pollutant concentration. The application of low cost and easily available materials in wastewater treatment has recently been widely investigated. Ooi *et al.* (1996) used some inorganic and organic adsorbents for boron removal in brine after salt production from seawater. Activated carbon, activated alumina, hydrous cerium oxide, and hydrous lanthanum oxide exhibited a high performance for boron among the inorganic adsorbents (Ooi *et al.*, 1996). Karahan *et al.* (2006) employed clays and chemically modified clays as adsorbents for the removal of boron from aqueous solutions. In addition, fly ashes (Ozturk and Kavak, 2005; Polat *et al.*, 2004), some natural adsorbent materials (Inukai *et al.*, 2004) and other inorganic adsorbents (Ay *et al.*, 2007; Ozturk and Kavak, 2004, 2008;

Seki *et al.*, 2006; Seyhan *et al.*, 2007; Yurdakoç *et al.*, 2005) were effective materials for boron removal from water. Polat *et al.* (2004) reported on boron removal from seawater by using different types of coal and fly ashes. Yurdakoç *et al.* (2005) investigated the boron sorption with Siral 5, 40, and 80. A chitosan resin derived with *N*-methyl-D-glucamine exhibited a high ability in boron sorption (Sabarudin *et al.*, 2005).

#### 6.6.1.4 Boron removal by ion-exchange

The use of boron-selective chelating ion-exchange resins seems to still be the most useful among several methods of boron removal. In the literature, it was reported that boron-selective resins based on macroporous polystyrene matrices with *N*-methyl-D-glucamine (NMDG) ligand are the best sorbent for boron removal (Badruk *et al.*, 1999a, 1999b; Bicak *et al.*, 2001; Kabay *et al.*, 2004a, 2004b, 2007, 2008a, 2009; Kunin and Preuss, 1964; Marston *et al.*, 2005; Okay *et al.*, 1985; Parshova *et al.*, 2007; Recepoglu and Beker, 1991; Senkal and Bicak, 2003; Simonnot *et al.*, 2000; Yilmaz *et al.*, 2007; Yilmaz-Ipek *et al.*, 2007, 2009, 2010; Yoshizuka *et al.*, 2010a).

The NMDG groups capture boron through a covalent attachment and an internal coordination complex formation (Marston *et al.*, 2005). It was reported that boron elution is relatively easy and completed at pH less than 1.0 (Marston *et al.*, 2005).

Badruk *et al.* (1999a, 1999b) reported on the preliminary results of batch-mode and column-mode studies for boron removal from the wastewaters of Kizildere geothermal power plant using commercially available boron-selective resins containing NMDG groups. The comparative results obtained using different *N*-glucamine-type resins (Purolite S108, Diaion CRB01, Diaion CRB 02) and column performances of these resins for boron removal from geothermal wastewater were reported elsewhere (Kabay *et al.*, 2004a). Column-mode removal of boron from geothermal wastewaters was performed using NMDG-type chelating resin by 10 cycles in the Kizildere geothermal field, Turkey (Kabay *et al.*, 2004b). Column-mode recovery of boron from acidic eluate solution was performed using a weak base ion-exchange resin (Kabay *et al.*, 2004b).

Elsewhere, fibrous sorbents based on polypropylene and viscose fibers grafted with polystyrene and glycidylmethacrylate and functionalized with *N*-methyl-D-glucamine were employed for boron removal. Fibrous sorbents exhibited much faster kinetics for boron sorption than that of boron-selective ion-exchange resins (Parshova *et al.*, 2007).

The synthesis of novel boron-selective resins with a high capacity, a high selectivity, and a high sorption rate is still of importance for boron removal from water. For this purpose, Wolska *et al.* (2011) prepared boron-selective polymer sorbents by reacting styrene-vinylbenzyl chloride and divinylbenzene with NMDG functional groups by the membrane emulsification method, followed by polymerization. The obtained NMDG-type resins exhibited a good performance for removal of boron from water (Wolska and Bryjak, 2011; Wolska *et al.*, 2010). Also, Samatya *et al.* (2010a) reported on boron removal performances of monodisperse-porous particles with dextran-based molecular brushes attached to the particles via 'click chemistry' and 'direct coupling'. These particles were found to be efficient for boron removal (Samatya *et al.*, 2010a). The monodisperse-porous poly (glycidyl methacrylate-co-ethylene methacrylate) particles carrying diol functionality were synthesized as potential boron-selective resins (Samatya *et al.*, 2010b). These resins were used for removal of boron from geothermal water and also its reverse osmosis permeate (Samatya *et al.*, 2012a). A novel sorbent having a high boron sorption capacity was also synthesized using monodisperse-porous poly (vinylbenzyl chloride-co-divinylbenzene) beads by a new 'modified seeded polymerization' technique (Samatya *et al.*, 2012b). The resultant chelating resins were successfully applied for the removal of boron from geothermal water and its reverse osmosis (RO) permeate (Samatya *et al.*, 2015a, b).

It was reported that polymer-supported core-shell type iminodipropylene glycol functions are very effective in chelation with boric acid and could be used for boron removal at trace levels. Yavuz *et al.* (2013a) performed the graft copolymerization of glycidyl methacrylate (GMA) onto dehydrochlorinated poly(vinyl chloride) (DHPVC) by ATRP method. Santander *et al.* (2013) synthesized a novel boron-selective resin using *N*-(4-vinylbenzyl)-*N*-methyl-D-glucamine as monomer and *N,N*-methylene-bis-acrylamide as the crosslinking agent. The resin exhibited a



Table 6.2. Experimental data for feed geothermal water during single and double membrane operation at pressures of 1.2 MPa and 1.5 MPa (adapted from Yavuz *et al.*, 2013b).

Feed geothermal water for single membrane operation							
$p$ [MPa]	$T$ [°C]	EC [ $\mu\text{S cm}^{-1}$ ]	pH	TDS [mg L <sup>-1</sup> ]	Salinity [‰]	$Q$ [L h <sup>-1</sup> ]	B [mg L <sup>-1</sup> ]
12	28.1	1725	7.25	863	0.7	290.15	9.03
15	27.8	1744	7.3	872	0.7	330.1	10.2
Feed geothermal water for double membrane operation							
$p$ [MPa]	$T$ [°C]	EC [ $\mu\text{S cm}^{-1}$ ]	pH	TDS [mg L <sup>-1</sup> ]	Salinity [‰]	$Q$ [L h <sup>-1</sup> ]	B [mg L <sup>-1</sup> ]
12	26.0	1744	7.35	859.5	0.7	396.35	9.15
15	30.2	1771	7.35	886.0	0.7	437.75	9.51

high performance for boron removal from geothermal water. The kinetics of boron sorption was very fast when compared to the commercially available boron-selective resin Diaion CRB02. It was reported that the synthesized sorbent can be useful for sorption in short-bed systems.

#### 6.6.1.5 Boron removal by membrane processes

According to the literature, the RO process could be efficiently used (with >95% rejection) for removal of boron from groundwater (Cengeloglu *et al.*, 2008). Also, Koseoglu *et al.* (2010) investigated boron removal from geothermal water using a different RO and nanofiltration (NF). It was reported that the RO process was very effective for desalination of geothermal water (Kabay, 2015; Koseoglu *et al.*, 2010).

Oner *et al.* (2011) used four different commercially available RO membranes (AG, AD, AK and BW-30) for boron and silica removal from geothermal water. It was concluded that boron rejection and permeate flux depended strongly on membrane type and operating pressure. The seawater RO (AD) membrane exhibited higher boron rejection. In addition, the significant influence of pH on boron rejection was observed.

Elsewhere, Tomaszewska and Bodzek (2013) investigated desalination of geothermal water by means of a hybrid ultrafiltration (UF)-RO process in a pilot plant. It was reported that a high-quality water may be obtained even after the first RO stage of desalination. However, the addition of a second step of RO processing by increasing pH was needed for boron removal from geothermal water.

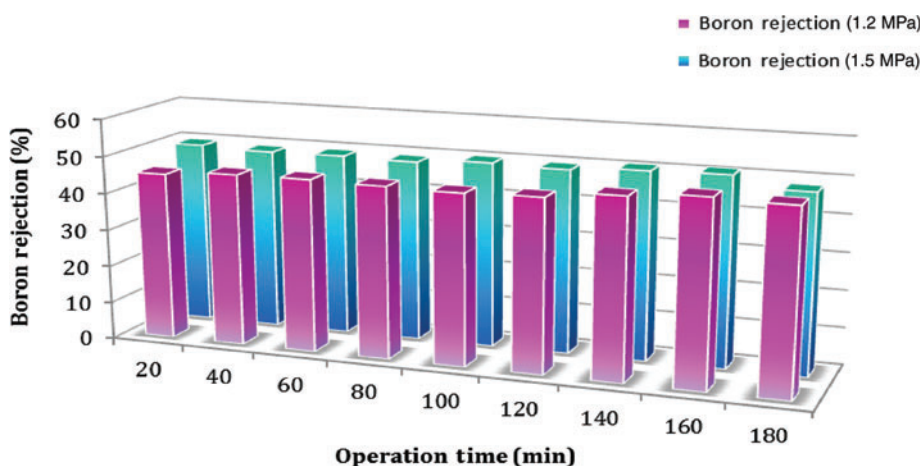
A case study was performed at a geothermal field by using a mini pilot-scale RO osmosis system containing Filmtech BW30 spiral-wound RO membranes. The pilot system contained two parallel mounted brackish water RO membranes. By means of this, desalination of geothermal water can occur for double and single membrane configurations. The desalination performance of RO systems was investigated as a function of applied pressure and numbers of membrane modules (Yavuz *et al.*, 2013b). The qualities of feed and product waters were examined by measuring electrical conductivity, Total dissolved solids (TDS), permeate recovery, permeate flux, salinity and boron concentration, as can be seen in Tables 6.2 and 6.3.

Desalination of geothermal water was influenced by applied pressure, which affects the boron rejection. As shown in Figure 6.2, average boron rejection is 47.0% for 1.2 MPa of operating pressure for single membrane operation. When operating pressure was 1.5 MPa, the respective value was 53.7%. As can be seen, if the operating pressure increases, the boron rejection percentage

Table 6.3. Experimental data for permeate for single and double membrane operation at pressure of 1.2 MPa and 1.5 MPa (adapted from Yavuz *et al.*, 2013b).

Permeate by single membrane operation									
$p$ [MPa]	$T^a$ [°C]	EC <sup>b</sup> [ $\mu\text{S cm}^{-1}$ ]	pH	TDS <sup>c</sup> [mg L <sup>-1</sup> ]	Sal <sup>d</sup> [‰]	$Q^e$ [L h <sup>-1</sup> ]	B [mg L <sup>-1</sup> ]	Flux [L m <sup>-2</sup> h <sup>-1</sup> ]	$Y^f$ [%]
12	29.7	24.295	5.35	12.225	0	101.1	4.79	38.85	46.55
15	28.9	19.835	5.43	9.9450	0	117.4	4.66	44.65	35.55
Permeate by double membrane operation									
$p$ [MPa]	$T^a$ [°C]	EC <sup>b</sup> [ $\mu\text{S cm}^{-1}$ ]	pH	TDS <sup>c</sup> [mg L <sup>-1</sup> ]	Sal <sup>d</sup> [‰]	$Q^e$ [L h <sup>-1</sup> ]	B [mg L <sup>-1</sup> ]	Flux [L m <sup>-2</sup> h <sup>-1</sup> ]	$Y^f$ [%]
12	26.88	30.4	5.45	15.3	0	184.5	5.84	35.5	46.55
15	30.64	26.3	5.40	13.2	0	236.8	5.40	45.5	54.05

<sup>a</sup>Temperature; <sup>b</sup>Electrical conductivity; <sup>c</sup>Total dissolved solids; <sup>d</sup>Salinity; <sup>e</sup>Flow rate; <sup>f</sup>Permeate recovery.

Figure 6.2. Effect of applied pressure on boron rejection for single membrane configuration (adapted from Yavuz *et al.*, 2013b).

increases. Boron rejection was 36.1% at 1.2 MPa of operating pressure and the respective value was 43.1% at 1.5 MPa of operating pressure for double membrane configuration, as shown in Figure 6.3.

Figure 6.4 shows the variations of permeate flux with respect to applied pressure for single membrane operation. Quality and quantity of product water is affected by the applied pressure. The flux values increase with increasing pressure. As seen in Figure 6.4, water flux across the membrane increased with increasing pressure. Although the osmotic pressure stayed constant, applied pressure increased. When 1.5 MPa of pressure was applied, the maximum flux 46% is obtained. As operating pressure increases the permeate flux values increase. While the water flux values are in the range of 35.5% for 1.2 MPa operating pressure, the respective value is 45.5% at 1.5 MPa for double membrane configuration, as shown in Figure 6.5.

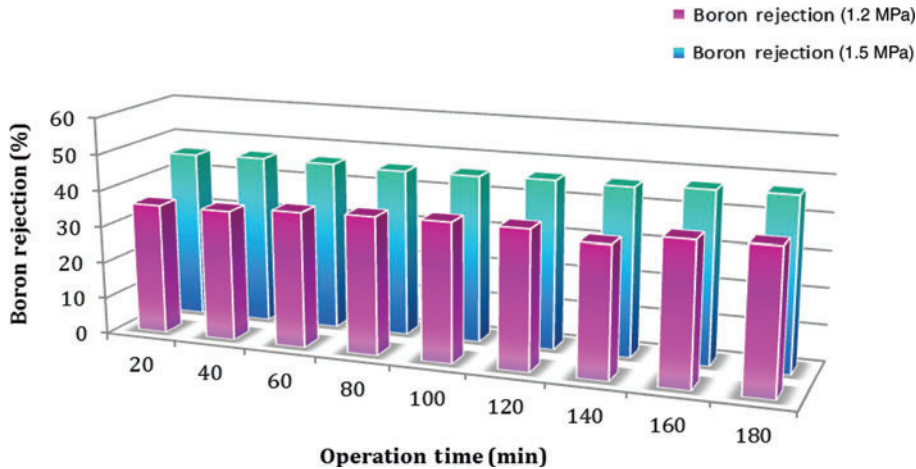


Figure 6.3. Effect of applied pressure on boron rejection for double membrane configuration (adapted from Yavuz *et al.*, 2013b).

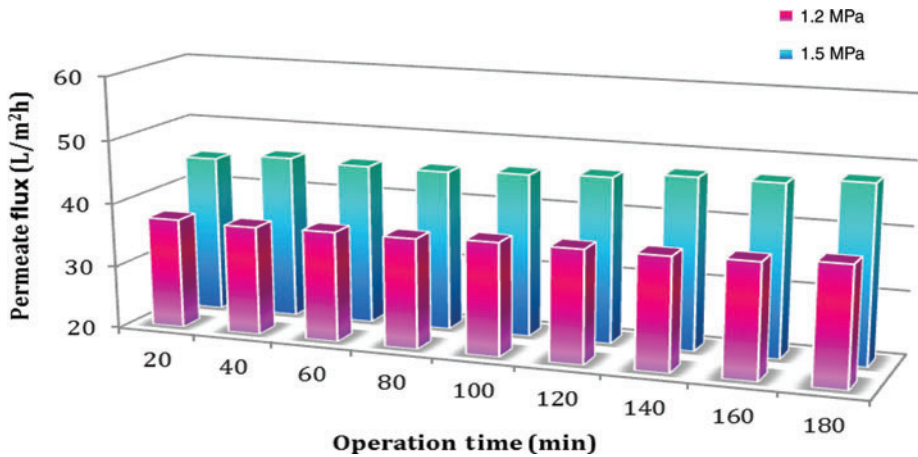


Figure 6.4. Effect of applied pressure on permeate flux for single membrane configuration (adapted from Yavuz *et al.*, 2013b).

According to the results obtained, it was concluded that product water quality depends on the operating pressure and membrane configuration. Increasing pressure resulted in higher permeate recoveries and permeate fluxes. Salt rejection also increased with increasing operating pressure. The maximum boron rejection obtained with single membrane configuration was 49% at 1.5 MPa of applied pressure. The minimum boron concentration in the product water was still  $4.7 \text{ mg L}^{-1}$  at this condition. Since the boron concentration in the permeate was higher than the acceptable limit for irrigation water, BWRO method employing geothermal water at natural pH and 1.5 MPa of operating pressure was found to be not suitable for eliminating boron from geothermal water.

As shown in Figure 6.6, the pH of geothermal water greatly influenced the boron removal from geothermal water for operations with both single and double membranes operation. At pH 10.5, for both single and double membranes configurations, boron level in the product water was less than  $1 \text{ mg L}^{-1}$  which is suitable level for irrigation (Yavuz *et al.*, 2013c). Another group of

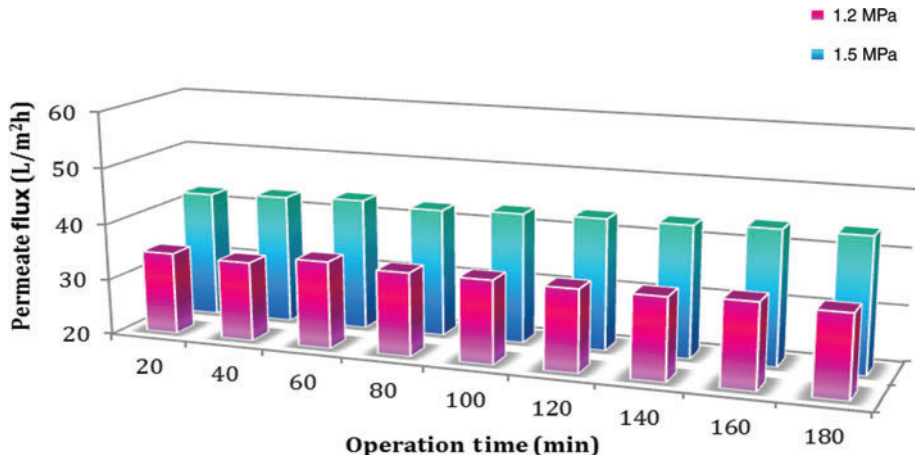


Figure 6.5. Effect of applied pressure on permeate flux for double membrane configuration (adapted from Yavuz *et al.*, 2013b).

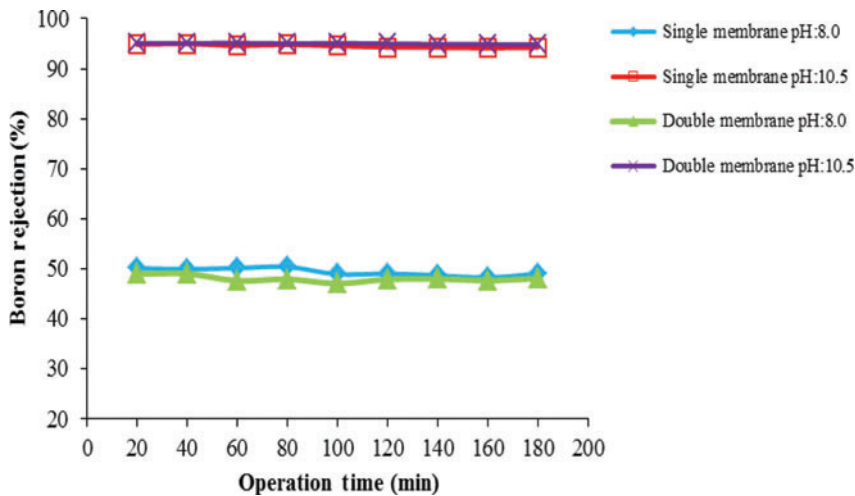


Figure 6.6. Effect of pH on boron rejection for single and double membrane operations (adapted from Yavuz *et al.*, 2013c).

researchers studied boron removal from geothermal water at a pilot plant by an integrated system combining ultrafiltration process and RO. They obtained similar results as those here in terms of high boron removal from geothermal water at high pH (Tomaszewska *et al.*, 2013).

As seen in Figure 6.7, for the seawater RO membrane (SW30-2540), the average boron rejection at 1.5 MPa was 77%. When the pressure increased further, the average boron rejection obtained at 4.0 MPa of operating pressure was 83%. In the case of the high-rejection seawater RO membrane (XUS-SW30XHR-2540), the corresponding average boron rejections at 1.5 and 4.0 MPa were 79.1 and 84.6%, respectively (Yavuz *et al.*, 2013d).

In the literature (Kabay *et al.*, 2015), other membrane processes which are applied in boron removal such as NF (Dydo *et al.*, 2005), polymer-enhanced ultrafiltration (Dilek *et al.*, 2002; Smith, 1995), electrodialysis (Melnik *et al.*, 1999, 2005; Oren *et al.*, 2006; Turek

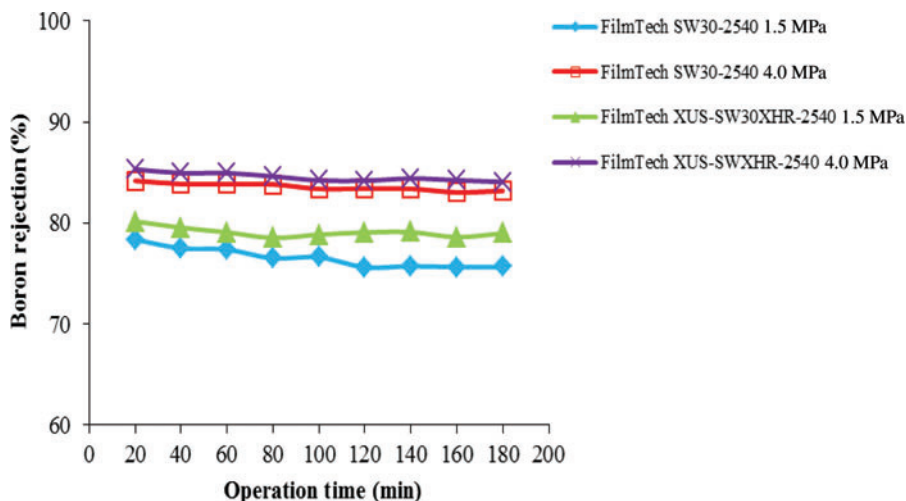


Figure 6.7. Effect of applied pressure on boron rejection by SWRO membranes (adapted from Yavuz *et al.*, 2013d).

*et al.*, 2005, 2007; Yazicigil and Oztekin, 2006), Donnan dialysis (Ayyildiz and Kara, 2005), electrodeionization (Wen *et al.*, 2005) were also reported.

Kabay *et al.* (2008b) studied boron removal by electrodialysis as a function of pH, applied voltage, feed flow rate and initial boron concentration in the feed. It was found that the highest boron transport occurred at pH 10.5 due to the formation of  $B(OH)_4^-$  ions in the solution at high pH. Similar results regarding better boron removal efficiency at high pH were also confirmed by Turek *et al.* (2008). Electrodialytic treatment of boron-containing wastewater with univalent permselective membranes was tested to obtain optimum boron removal conditions by Turek *et al.* (2007, 2008).

Elsewhere, the treatment of boron-containing wastewater by means of ED was examined using Neosepta AMX and CMX membranes by Turek *et al.* (2007). As a pre-treatment, the desalination of acidic leachate was first carried out to remove excess salinity. Then, at a high pH (9–10), it was possible to remove 97% of boron by ED. It was reported that  $OH^-$  ions were primarily transferred from the diffusion layer through the membrane (Turek *et al.*, 2007), but it was necessary to keep the required pH level in the diluate. Bandura-Zalska *et al.* (2009) also investigated the electrodialytic desalination of wastewater containing boron. Dydo (2012) predicted the rate of boric acid transport by ED and found that diffusive and convective mechanisms control the boric acid transport rate. In a separate work, Dydo and Turek (2013) reported that the electrical current efficiencies for borate transport are low because of low borate mobility, although the rate for borate transport in ED is high. Since borate ion exists only at high pH, there is a serious risk of membrane scaling due to the existence of calcium and magnesium ions in the solution. Therefore, it was recommended that the diluate solution be demineralized before borate removal by ED. Dydo (2013) investigated the effects of the ED process parameters, such as boric acid concentration in the diluate, membrane type, and ion type transferred across the membrane and electric current density on the boric acid transport rate from the diluate. An integrated membrane system was also studied by Dydo and Turek (2014) for boron removal, concentration and boric acid recovery. For that purpose, boron and polyol containing water was first treated by ED and then, after pH adjustment, concentrated by RO in a two-stage system.

ED was also found to be an effective method for separation of strong acids from boric acid. Bialek *et al.* (2014) proposed ED as a method for hydrochloric acid regeneration from the effluents

containing both hydrochloric acid and boric acid. The result obtained was that boric acid transport across the hydrochloric acid was much slower.

Shimada *et al.* (2007) examined the removal of boron from aqueous solution with polyvinyl alcohol membranes under the conditions where one side of the membrane was kept acidic and the other alkaline (pH 10). The borate ions formed a complex with the membrane, and the chemical potential gradient compelled borate transport (Shimada *et al.*, 2007). Donnan dialysis was investigated as a new method for regeneration of boron-selective resins (Bryjak *et al.*, 2007).

The electrodeionization (EDI) process is also very efficient for the production of high-purity water. Normally, weakly-ionized species, such as carbon dioxide, silica and boric acid are difficult to remove by means of RO and ED methods. The removal of silica and boron from ultra-pure water by EDI was performed by Wen *et al.* (2005). The EDI method was also employed for purification of the RO permeate of geothermal water by Arar *et al.* (2013a, 2013b, 2014). Boron and silica concentrations in the product water were highly reduced in optimized conditions (Arar *et al.*, 2013a).

### 6.6.2 Arsenic removal from geothermal water

An extensive literature review on arsenic removal from geothermal water was published by Yoshizuka *et al.* (2010a). According to the latter, the concentrations of arsenic in geothermal water show variations in different geothermal regions. It was noted that arsenic concentration is quite high, especially in hot springs. This is due to the differences in mineralogical, physical and chemical properties of rocks, soils and sediments in contact with this water. It was reported that arsenic is significantly leached from aquifers under conditions of high temperature and pressure. Geothermal waters may contain As(V) and As(III) forms, depending on oxidation-reduction conditions (Yoshizuka *et al.*, 2010a).

It is not easy to remove arsenic using only one treatment method because arsenic can be found in geothermal waters at different speciation. In addition, the physical and chemical characteristics of geothermal waters are not the same, and furthermore, extremely high temperature of geothermal water will affect the performance of the treatment method (Yoshizuka *et al.*, 2010a). Some factors affecting the cost and feasibility of treatment methods for arsenic removal from geothermal water were reported by Alaerts and Khouri (2004). It is necessary to lower the concentration of arsenic to  $10 \mu\text{g L}^{-1}$  or less if geothermal water is going to be used for drinking and cooking purposes. Geothermal waters with high arsenic content could be used to heat clean river water for greenhouses, indoor swimming pools and other facilities (Okada *et al.*, 2004). However, such geothermal waters can be directly utilized for drinking, agriculture and bathing after arsenic has been removed from geothermal water with a suitable treatment method (Gallup, 2007).

Okada *et al.* (2004) used a superconducting magnet for arsenic removal from geothermal waters in Japan. Before magnetic treatment, the arsenic in the water was oxidized to As(V) with hydrogen peroxide and then Fe(III) sulfate was added to the water at pH 4 to co-precipitate the As(V) with paramagnetic iron (oxy)(hydr)oxides. Yoshizuka *et al.* (2010b) were able to separate arsenic from geothermal water using granulated magnetite as an adsorbent.

Elsewhere, Koseoglu *et al.* (2011) investigated the arsenic removal performance of arsenic-selective ion-exchange resins, Lewatit FO 36 and ArsenX<sup>np</sup>, from geothermal water.

An integrated process combining membrane filtration and ion-exchange processes could be considered for simultaneous arsenic and boron separation from geothermal water. Most recently, Yanar (2015) suggested a flow scheme for this purpose (Fig. 6.8). As seen in this flow sheet, it is possible to separate boron and arsenic from geothermal water by a combination of membrane filtration and ionexchange processes. In addition, the concentrations of arsenic and boron could be reduced to permissible levels for drinking water and/or irrigation water at the same time.

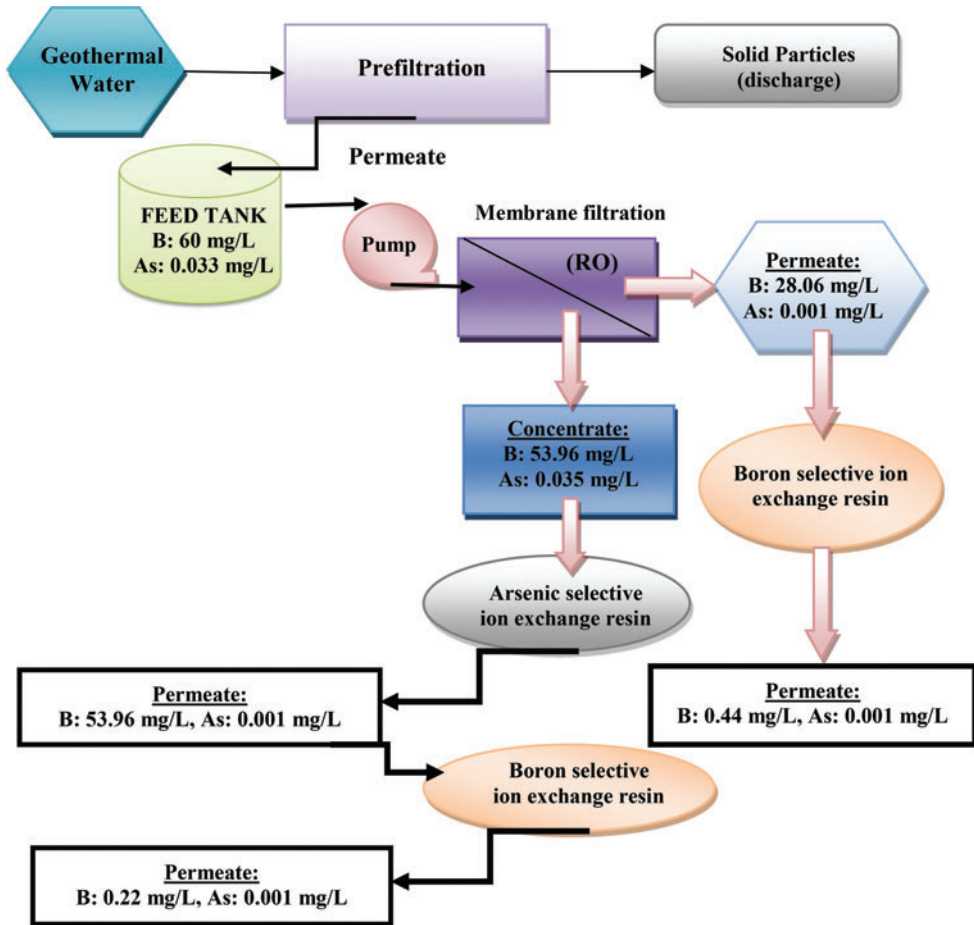


Figure 6.8. Process scheme for separation of arsenic and boron from geothermal water by an integrated process (adapted from Sözal-Yanar, 2015 by the kind permission of author).

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## CHAPTER 7

### Removal of boron and arsenic from geothermal water by ion-exchange

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#### 7.1 INTRODUCTION

In geothermal systems, geothermal water ascends to the surface by reacting with the wall rocks causing mineral dissolution. Mineral-fluid equilibria play an important role in determining the chemistry of the discharge fluids (Tyrovola *et al.*, 2006). The solute concentrations in geothermal water vary greatly due to variations in temperature, gas content, heat source, rock type, permeability, age of the hydrothermal system and fluid source or mixing with other water sources, such as seawater. Geothermal waters may contain various kinds of species such as  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{SiO}_2$ ,  $\text{NH}_3$ , noble gases, boron and arsenic (Barbier, 2002). Due to the high concentration of minerals in geothermal waters, pre-treatment is needed before using and discharging them into the environment. Yoshizuka *et al.* (2010a) reported that the concentrations of boron and arsenic in geothermal water are much higher than the permissible level for drinking water.

Boron is considered as one of the harmful elements present in geothermal waters. It is an important micronutrient for some plants but high amounts of boron in irrigation water causes toxic effects on others (Hilal *et al.*, 2011; Kabay *et al.*, 2010a, 2010b; Roessner *et al.*, 2006; Yoshizuka *et al.*, 2010a). The World Health Organization (WHO) kept the boron limit in drinking water at  $0.5 \text{ mg L}^{-1}$  for many years (WHO, 1998, 2003, 2009) but this value was revised to  $2.4 \text{ mg L}^{-1}$  in 2011 (WHO, 2011). However, the boron limit for irrigation water is still recommended to be  $0.5 \text{ mg L}^{-1}$ , bearing in mind the toxic effect of boron for some plants.

The presence of arsenic in natural water is related to the process of leaching from the arsenic-containing source rocks and sediments. It is generally associated with geochemical environments such as basin-fill deposits of alluvial-lacustrine origin, volcanic deposits, inputs from geothermal sources, mining wastes and landfills. Uncontrolled anthropogenic activities, such as smelting of metal ores, use of arsenical pesticides and wood preservative agents, may also release arsenic directly into the environment (Choong *et al.*, 2007; Kabay *et al.*, 2010a; Yoshizuka *et al.*, 2010a, 2010b). The toxic and carcinogenic effects of arsenic on living beings are well known. Therefore, a water treatment process is necessary before using and discharging geothermal waters containing boron and arsenic into the environment.

#### 7.2 REMOVAL OF BORON FROM GEOTHERMAL WATER BY ION-EXCHANGE

##### 7.2.1 Toxicity of boron

Boron has a marked effect on plants in terms of both nutrition and toxicity, and its over-dose or under-dose may cause toxicity or deficiency symptoms, respectively (Fujita *et al.*, 2005; Kabay *et al.*, 2015; Yoshizuka *et al.*, 2010a). Boron deficiency will result in poor budding, excessive branching, and in general inhibits plant growth. A minimum boron concentration in irrigation

water is required for certain metabolic activities of plants. A boron concentration in irrigation water which is only slightly higher than the minimum, has a negative impact on plant growth and causes boron poisoning, signified by yellowish spots on the leaves and the fruit, accelerated decay, and ultimately, plant expiration (Kabay *et al.*, 2015; Nadav, 1999). In geothermal fields, boron could be a problem if the geothermal brine is discharged to the environment without any treatment (Badruk *et al.*, 1999a, 1999b; Kabay *et al.*, 2015; Kluczka *et al.*, 2007; Okay *et al.*, 1985; Recepoglu and Beker, 1991; Waggott *et al.*, 1996).

On the other hand, it was most recently reported that boron is toxic to reproduction and development in experimental animals at high doses (Duydu *et al.*, 2015). The No Observed Adverse Effect Levels (NOAELs) for the developmental and reproductive adverse effects of boron are defined as 9.6 and 17.5 mg kg-bw<sup>-1</sup> day<sup>-1</sup>, respectively. According to Duydu *et al.* (2015), none of the adverse effects of boron observed in rats have been proven for humans in environmental and occupational epidemiology studies. Therefore, they reported that the developmental and reproductive effects of boric acid observed in animal experiments are invalid for humans based on the results of numerous independent human studies (Duydu *et al.*, 2015).

### 7.2.2 Boron removal methods

Due to the extensive use of boron by various industries such as glass, ceramic, cosmetics, nuclear and leather industries, its removal from industrial wastewaters has received much attention in recent years. The methods used for removing boron from aqueous solutions are quite complex. As has already been stated in the literature, conventional sedimentation and biological treatment remove little, if any, boron from sewage, and chemicals commonly used in the water treatment have nearly no effect on the boron levels in water (Sahin, 2002).

Various treatment processes such as coagulation, electro-coagulation (Yilmaz *et al.*, 2007), adsorption (Çengeloğlu *et al.*, 2007; Öztürk and Kavak, 2003, 2005; Polat *et al.*, 2004; Yurdakoc *et al.*, 2005), solvent extraction (Kwon *et al.*, 2005; Matsumoto *et al.*, 1997), ion-exchange (Badruk *et al.*, 1999a, 1999b; Bryjak *et al.*, 2008; Kabay *et al.*, 2004a, 2004b, 2006, 2008a, 2008b, 2008c, 2010b, 2013a, 2013b; Yilmaz *et al.*, 2006; Yilmaz-Ipek *et al.*, 2007a, 2007b, 2009) and membrane filtration (Arar *et al.*, 2013; Dydo and Turek, 2013, 2015; Guler *et al.*, 2011, 2015; Kabay, 2015; Kabay and Bryjak, 2015; Kabay *et al.*, 2015; Köseoğlu *et al.*, 2010; Melnik *et al.*, 1999; Oner *et al.*, 2011; Prats *et al.*, 2000; Redondo *et al.*, 2003; Sánchez *et al.*, 2013a; Turek *et al.*, 2005, 2007, 2008a, 2008b; Yavuz *et al.*, 2013a, 2013b, 2013c) have been employed for boron separation.

An ion-exchange method using boron-selective chelating resins has been considered as the best and most effective method to remove boron from water. It has been reported that the chelating resins containing polyol functional groups – in which the hydroxyl groups are in the cis-position – show a high selectivity for boron removal by forming a stable complex. The most widely studied chelating resins contain *N*-methyl-D-glucamine (NMDG) functional groups (Badruk *et al.*, 1999a, 1999b; Bryjak *et al.*, 2008; Inukai *et al.*, 2004; Kabay *et al.*, 2004a, 2004b, 2006, 2008a, 2008b; Kunin and Preuss, 1964; Li *et al.*, 2011; Sabarudin *et al.*, 2005; Yilmaz *et al.*, 2006; Yilmaz-Ipek *et al.*, 2007a, 2007b, 2009, 2010, 2011, 2013).

Boron contained in geothermal waters accumulates in the soil, especially when they are used as irrigation water, and this may cause a change in the characteristics of soil. Also, they can mix with underground waters by passing through the soil and form complexes with lead, copper, cadmium and nickel ions. The toxicities of these complexes are reported to be higher than those of the heavy metals alone (Çengeloğlu *et al.*, 2007). Considering these negative impacts, the removal of boron from geothermal water has become an important concern.

#### 7.2.2.1 Removal of boron by ion-exchange

The use of boron-selective chelating ion-exchange resins still seems to be the most important method for boron removal. According to the literature, the boron-selective ion-exchange resins having NMDG groups are the best sorbents for boron removal (Badruk *et al.*, 1999a, 1999b; Bicak *et al.*, 2001; Bryjak *et al.*, 2008; Inukai *et al.*, 2004; Kabay *et al.*, 2004a, 2004b, 2006,

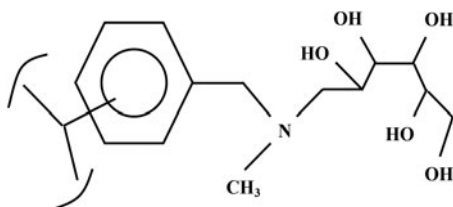


Figure 7.1. The structure of boron-selective chelating resin containing NMDG group (reproduced from Marston *et al.* (2005) with the kind permission of M. Busch).

2008a, 2008b, 2010a; Kunin and Preuss, 1964; Marston *et al.*, 2005; Okay *et al.*, 1985; Parshova *et al.*, 2007; Recepoglu and Beker, 1991; Simonnot *et al.*, 2000; Yilmaz *et al.*, 2006; Yilmaz-Ipek *et al.*, 2007a, 2007b, 2009, 2010, 2011) due to their high selectivity and reusability. Vicinal diol groups on the particles are regarded as the most efficient ligands for the chelation of boron. Commercially available boron-selective chelating ion-exchange resins are mostly prepared from macroporous poly(styrene-co-divinylbenzene) by functionalization with the NMDG group. The structure of this resin is shown in Figure 7.1.

It was reported that the NMDG groups capture boron through a covalent attachment and an internal coordination complex formation (Marston *et al.*, 2005). It was mentioned that stripping of boron from the resin is relatively easy at pH less than 1.0 and therefore, relatively high acid concentrations of acid are required for the complete and rapid elution of the boric acid from boron-selective resins (Marston *et al.*, 2005).

Maeda *et al.* (1995) reported that the macroporous poly(GMA) (glycidyl methacrylate) modified by 2-amino-2-(hydroxymethyl)-1,3-propanediol (HM) exhibited a high affinity for boron and bound boron selectively from the waste solutions of geothermal power stations. The uptake capacity, however, decreases markedly with an increase in the molar fraction of divinylbenzene (DVB) in the copolymer, poly(GMA-co-DVB).

Polyglycidyl methacrylate (GMA)-methyl methacrylate (MMA)-DVB (divinylbenzene) terpolymer beads have been prepared and used as an ideal support for preparation of boron-selective ion-exchange resins. The resulting resin was an efficient material for boron sorption (Bicak *et al.*, 2001). Elsewhere, polymer-supported iminodipropylene glycol functionalities have been shown to be efficient at chelating with boric acid and can be used for boron capture (Senkal and Bicak, 2003). The commercially available boron-specific resins are based on the copolymers of styrene and divinylbenzene. Badruk *et al.* (1999a, 1999b) reported on the preliminary results for boron removal from geothermal water using ion-exchange resins having NMDG groups. Kabay *et al.* (2004a, 2004b) and Yilmaz-Ipek *et al.* (2009, 2010, 2011, 2013) employed the commercially available NMDG-type chelating resins, such as Diaion CRB01, CRB02, and Purolite S 108, for the removal of boron from geothermal brine. Some field tests were performed using the boron-selective resin Diaion CRB02 for boron elimination from geothermal water (Kabay *et al.*, 2004b). For the selective separation of boron from an acidic eluate solution by the acid-retardation technique, a weak base anion-exchange resin, Diaion WA30, was used (Kabay *et al.*, 2004b).

Koseoglu *et al.* (2011) investigated the performance of two commercial boronselective ion-exchange resins with NMDG functional groups, Lewatit MK 51 and Diaion CRB03, for boron removal from geothermal water by batch- and column-mode tests. In addition, the efficiencies of a boron-selective composite fiber adsorbent (polyethylenecoated polypropylene fiber with NMDG functional groups) and a commercial boronselective fiber adsorbent (Smopex 248V, viscose fibers grafted with glycidyl methacrylate and functionalized with NMDG) were investigated for boron removal from geothermal water containing  $34.0 \text{ mg L}^{-1}$  of boron. As shown in Figure 7.2, the optimum amount of resin concentrations of Lewatit MK 51 and Diaion CRB03 were determined as  $5 \text{ g resin L}^{-1}$  of geothermal water for reducing the boron concentration below  $1 \text{ mg L}^{-1}$ , while the respective value was  $4 \text{ g resin L}^{-1}$  of geothermal water for the composite fiber adsorbent.



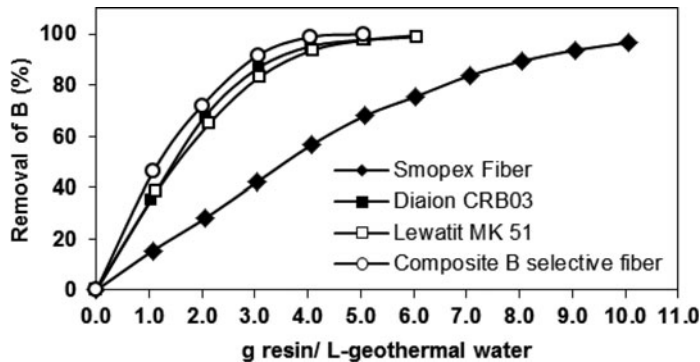


Figure 7.2. Effect of resin/fiber amount on boron removal from geothermal water (adapted from Koseoglu (2009) by kind permission of the author).

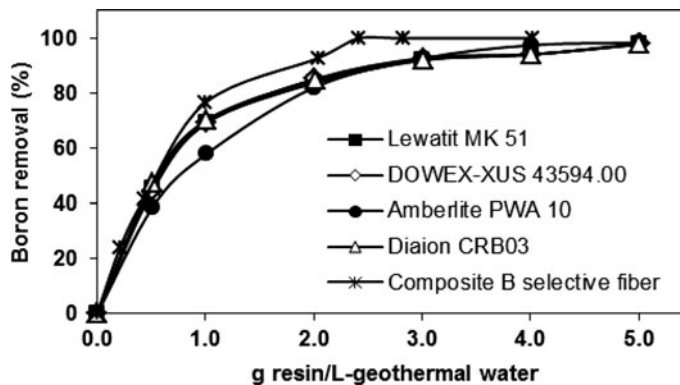


Figure 7.3. Effect of resin/fiber amount on boron removal from geothermal water (adapted from Koseoglu (2009) by kind permission of the author).

However, the boron concentration of the geothermal water could not be drawn below  $1.0 \text{ mg L}^{-1}$  even with  $10 \text{ g}$  of Smopex 248V fiber adsorbent per liter of geothermal water.

Elsewhere, the performances of boron-selective ion-exchange resins, Amberlite PWA10, Lewatit MK 51, Diaion CRB03 and Dowex 43594.00, and a composite boron-selective fiber which is composed of a polyethylene coated polypropylene fiber with *N*-methylglucamine functional groups, were compared for boron removal from geothermal water (Koseoglu, 2009). For all of the boron-selective resins employed, the optimum resin amount was determined as  $3.0 \text{ g L}^{-1}$  of geothermal water, whereas for the composite fiber it was  $2.0 \text{ g L}^{-1}$  of geothermal water (Fig. 7.3).

The breakthrough profiles of Lewatit MK 51, Diaion CRB03 and Smopex 248V were also compared using column studies. It was determined that Diaion CRB03 had the best column performance with the highest breakthrough and total capacities, as shown in Figure 7.4. Elution of boron from the resins and fibers were performed completely by  $5\% \text{ H}_2\text{SO}_4$  solution, as shown in Figure 7.5.

#### 7.2.2.2 Removal of boron by sorption-membrane filtration hybrid method

Recently, the interest in hybrid processes has increased substantially. These have been developed to address the need for overall process optimization and/or cost reduction. The hybrid process combining sorption and membrane filtration have recently been introduced as an effective method for water treatment. It allows the removal and/or recovery of some species that can exist in water

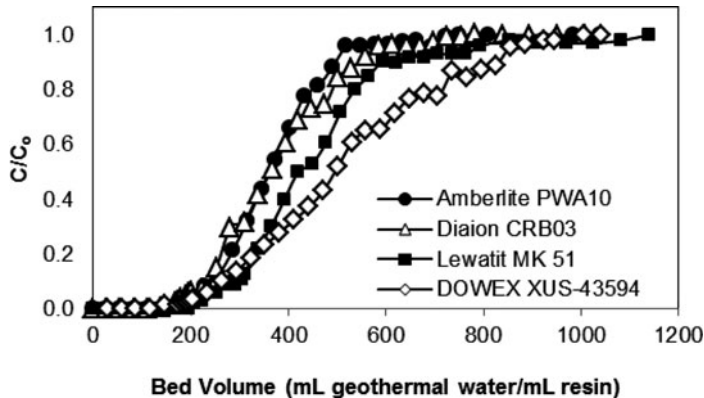


Figure 7.4. Breakthrough profiles of boron by ion-exchange resins (adapted from Koseoglu (2009) by kind permission of the author).

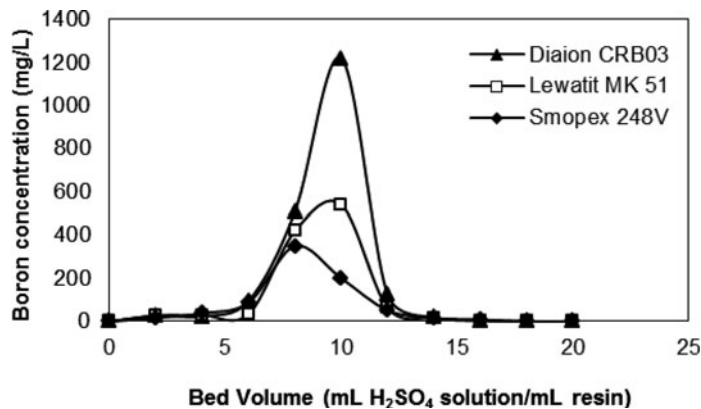


Figure 7.5. Elution profiles of boron (adapted from Koseoglu (2009) by kind permission of the author).

at just trace amounts (Koltuniewicz *et al.*, 2004). Combination of the advanced sorbents with their separation on membranes reveals many advantages compared with conventionally used fixed bed systems. The main advantage of this separation method is the high efficiency and lower costs of the process compared with classical sorption in a fixed bed. The sorbents can be used as very fine particles that increase the surface area. In consequence, sorbents show higher uptakes and enhance the kinetic rate of the seeded ultrafiltration process.

In the first step of the hybrid process, the target component is bound to the coupling agent and, as a large complex, it is retained by the membrane. The complex is decomposed in the second step by using a suitable eluting agent.

Novel sorbents and binding agents, such as organic and inorganic sorbents, chelating and ion-exchange resins, molecularly imprinted polymers and coordinating agents, micelles and colloids with a size of few nanometers to dozens of micrometers, could be employed in the hybrid processes for selective separations (Kabay and Bryjak, 2013).

The commercially available chelating ion-exchange resins generally exhibit slow kinetics due to the diffusion-controlled rate limiting processes, although they have a high selectivity. Due to their poor kinetics, the utilization of chelating ion-exchange resins in water treatment applications is limited (Sengupta and Sengupta, 2002). In ion-exchange operations, particle diameter in a

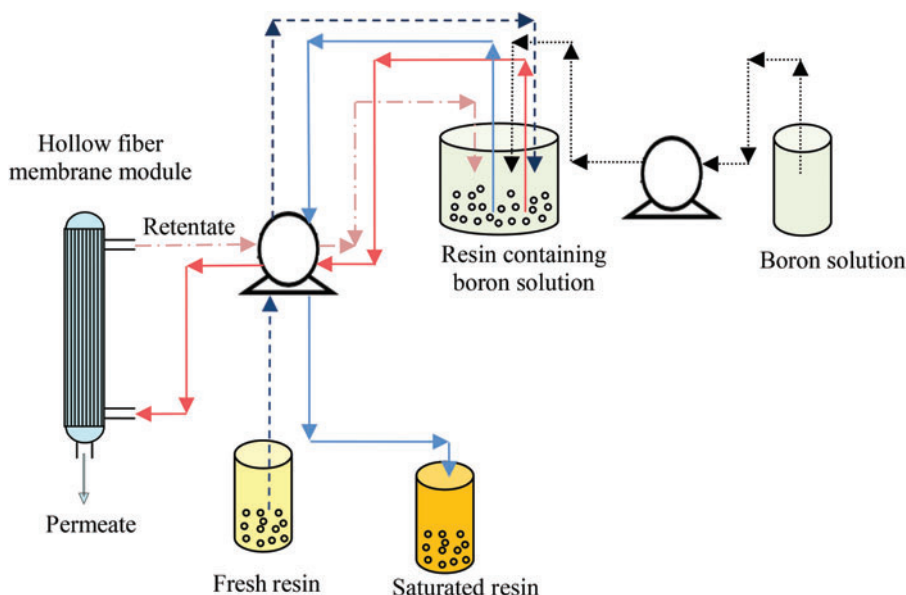


Figure 7.6. Experimental set-up of sorption-submerged membrane filtration hybrid system (adapted from Yilmaz-Ipek (2009) by kind permission of the author).

packed bed influences pressure drop and the kinetics of ion-exchange. The pressure drop is inversely proportional to the particle diameter. This is why smaller diameter particles cannot be used in a packed bed (Bird *et al.*, 1960). On the other hand, integrating an ion-exchange process with a membrane filtration in a hybrid process was considered to have much higher efficiency and lower process cost when compared with the fixed bed sorption method. A high efficiency in the process could be reached with sorbent beads with small particle sizes due to the increased surface area and enhanced kinetics (Bird *et al.*, 1960; Kabay and Bryjak, 2013; Koltuniewicz *et al.*, 2004; Sengupta and Sengupta, 2002).

A sorption-membrane filtration hybrid method was extensively tested for boron removal from geothermal water and seawater (Blahušiak *et al.*, 2009, 2015; Bryjak and Kabay, 2015; Bryjak *et al.*, 2008, 2009; Kabay *et al.*, 2006, 2008, 2009, 2013a, 2013b; Guler *et al.*, 2011; Onderková *et al.*, 2009; Samatya *et al.*, 2015b; Yilmaz *et al.*, 2006). Boron sorption was carried out using commercially available boron-selective chelating ion-exchange resins that had been ground to a powder. During the process, the boron-loaded resin was filtered through submerged micro-filtration or ultrafiltration membranes. A schematic system arrangement of one of the hybrid systems is illustrated in Figure 7.6. Geothermal water was passed through the submerged membrane module along with boron-selective ion-exchange resins for 2 h. Boron was sorbed by selective ion-exchange resins. Subsequently, the treated water penetrated into a hollow-fiber membrane module including 50 polypropylene membranes with a diameter of 0.5 mm, thickness 200  $\mu\text{m}$ , pore diameter 0.4  $\mu\text{m}$ , and a length of 40 cm, by providing a vacuum inside. To obtain constant fresh resin concentration in the system, the fresh suspension of boron-selective resins was fed to the membrane module. Simultaneously, in order for the system to avoid accumulation of resin in the suspension loop, boron-saturated resin was withdrawn from the system at the same flow rate as the fresh resin. At predetermined time intervals, permeate samples were taken from the system.

As seen in Figure 7.7, resin particle size has an apparent influence on boron removal from geothermal water by the sorption-membrane hybrid method in which the boron-selective ion-exchange resin Diaion CRB02 was used as the sorbent. The kinetics of the resin improved greatly

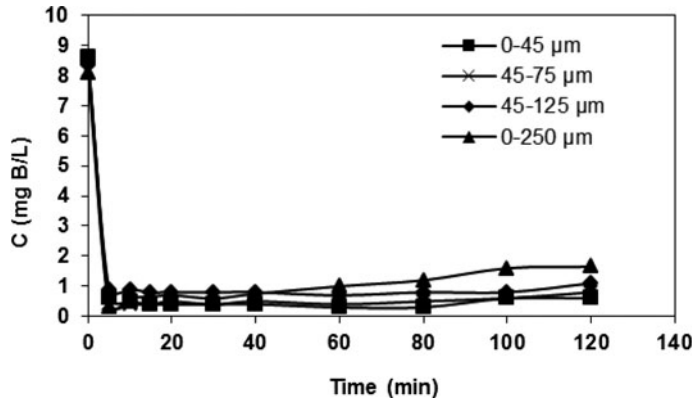


Figure 7.7. Effect of resin particle size on boron removal from geothermal water (resin concentration:  $2 \text{ g L}^{-1}$ ; Resin replacement rate:  $1 \text{ mL min}^{-1}$ ) (adapted from Yilmaz-Ipek (2009) by kind permission of the author).

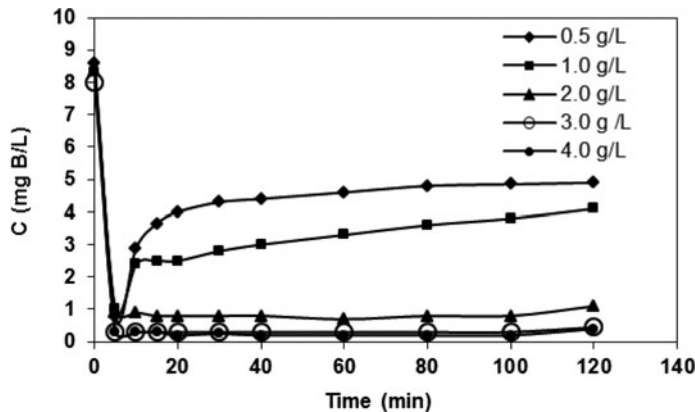


Figure 7.8. Effect of resin concentration on boron removal from geothermal water (Particle size range:  $45\text{--}125 \text{ }\mu\text{m}$ ; resin replacement rate:  $1 \text{ mL min}^{-1}$ ) (adapted from Yilmaz-Ipek (2009) by kind permission of the author).

with a decrease in the particle size. As the resin size range decreased, boron removal efficiency improved by decreasing the boron concentration to lower levels, since the ability of boron to reach the binding sites of the resin increased due to the increased effective surface area. It is noteworthy that it was also possible to reduce the boron concentration below  $1 \text{ mg L}^{-1}$  of boron during two hours of operation with Diaion CRB02 resin with various particle size ranges.

As shown in Figure 7.8, an increase of resin concentration was also effective for boron removal from geothermal water. Optimum resin concentration was found to be  $2.0 \text{ g L}^{-1}$  to decrease the boron concentration below  $1.0 \text{ mg L}^{-1}$  which is the permissible level of boron in irrigation water in Turkey. Figure 7.9 shows that the concentration of boron in the permeate increased at higher resin replacement rates for fresh and saturated resins due to the shorter contact time. The optimum replacement flow rate was found to be at  $0.5\text{--}1.0 \text{ mL min}^{-1}$  to decrease the boron concentration below permissible levels of boron in irrigation water.

According to the experimental results obtained, it was proven that a sorption-membrane filtration hybrid system could be an alternative method to the more commonly used fixed bed column-mode operation. Fine particles of resins remove boron very quickly from the geothermal

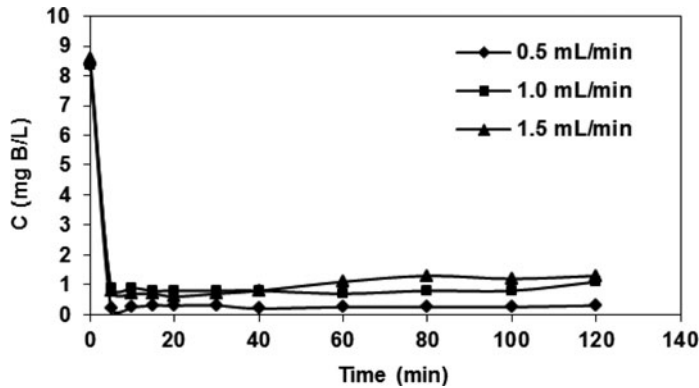


Figure 7.9. Effect of resin replacement flow rate on boron removal from geothermal water (particle size range: 45–125  $\mu\text{m}$ ; resin concentration: 2 g  $\text{L}^{-1}$ ) (adapted from Yilmaz-Ipek (2009) by kind permission of the author).

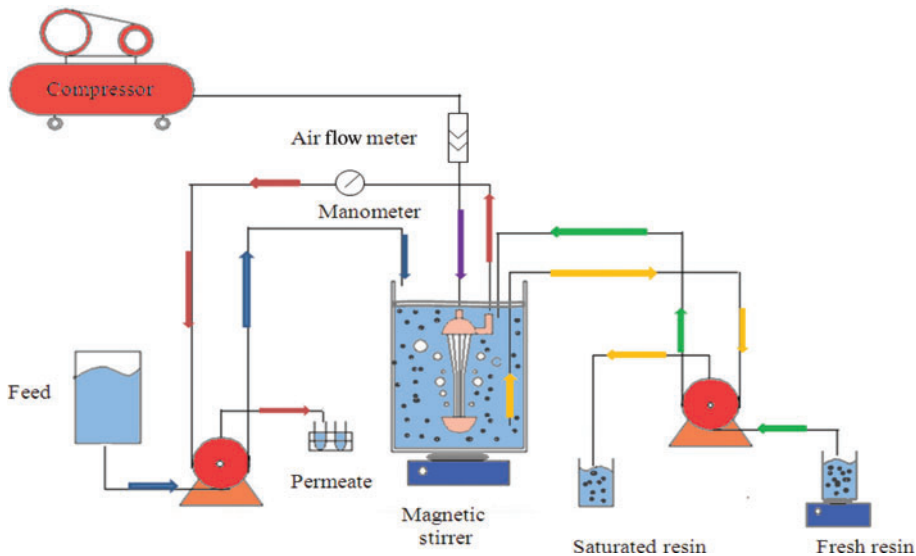


Figure 7.10. Flow sheet of sorption-membrane hybrid system (adapted from Kabay *et al.*, 2013a, 2013b).

water due to their highly available surface areas. To control the boron concentration in the permeate of a submerged membrane module, the following points should be taken into consideration:

1. Size of the resin particle
2. Flow rate of permeate
3. Replacement flow rate of resin suspension
4. Resin content in the suspension.

Kabay *et al.* (2013a 2013b) also employed Dowex XUS-43594.00, with an average particle diameter of 20  $\mu\text{m}$  and a submerged hollow-fiber type ultrafiltration (UF) membrane module (ZW-1, GE) in a submerged membrane–ion-exchange hybrid system for boron removal from geothermal water and the reverse osmosis (RO) permeate of geothermal water. The flow sheet of the system is shown in Figure 7.10.

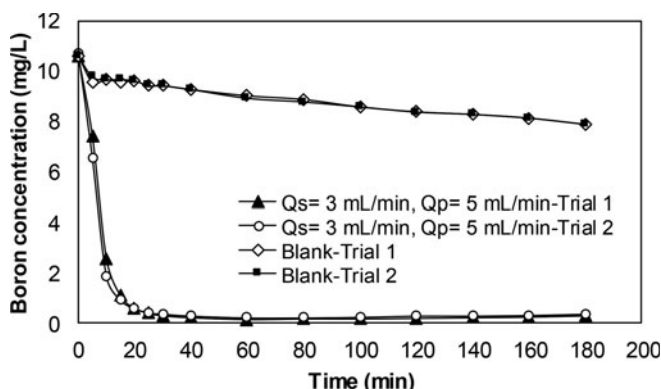


Figure 7.11. Boron concentration of the permeate versus time (adapted from Kabay *et al.*, 2013b).

The concentration of boron in the geothermal water permeate could be lowered below  $1.0 \text{ mg L}^{-1}$  in 15 min by keeping the concentration of ion-exchange resin in the suspension at  $3 \text{ g resin L}^{-1}$  of geothermal water, the replacement rates of fresh and saturated resins at  $3 \text{ mL min}^{-1}$ , and the flow rate of permeate at  $5 \text{ mL min}^{-1}$  (Fig. 7.11). According to Kabay *et al.* (2013b), the recycle performance of the hybrid system could be improved by eliminating the resin loss during washing and regeneration stages and improving elution conditions.

Abdulgader *et al.* (2013) suggested that the reason for the limited use of hybrid systems is a shortage of fine sorbents and the cost of their regeneration. Some attempts to synthesize small particles are described in the next section and the manufacturing of such sorbents appears not to be too difficult. The cost of regeneration can be reduced by the use of less expensive chemicals or by integrating the hybrid systems with other processes. As examples one can point to the electro-dialytical recycling of acid solution from the post-regeneration step (Turek *et al.*, 2008b), or the use of RO concentrate brine as an eluting agent in sorbent regeneration by Donnan dialysis (Bryjak *et al.*, 2007).

#### 7.2.2.3 Novel sorbents for boron removal from geothermal water

In the published literature, it was reported that the commercially available boron-selective ion-exchange resin beads were ground before they were employed in the hybrid process, since the particle size of commercially available boron-selective resins ranged from 0.2 to 1.0 mm. When the ion-exchange resin beads were ground to an average particle size of  $20 \mu\text{m}$  this may have caused some heterogeneity and irregularly shaped particles, and thus process sustainability might have been negatively influenced.

The synthesis of novel boron-selective sorbents with high capacity, high selectivity, and a high sorption rate prompted great interest for boron removal and recovery from natural waters and wastewater. Wolska *et al.* (2010, 2011) prepared boron-selective small particles ( $25 \mu\text{m}$ ) by reacting NMG with styrene-vinyl benzyl chloride-divinylbenzene using a membrane emulsification method followed by polymerization. The resulting chelating resins showed good performance in an adsorption-membrane filtration hybrid system used for removal of boron from water (Wolska and Bryjak, 2011, 2013; Wolska *et al.*, 2010). Monodispersed polymer particles can give advantages over conventional ion-exchange particles, such as kinetics and boron removal performance (Alexandratos, 2007).

Samatya *et al.* (2010a) reported on boron removal performances of monodispersed porous particles with dextran-based molecular brushes attached to the particles via click chemistry and direct coupling. They implied that these particles were efficient in boron removal from aqueous solutions. Monodispersed porous poly(glycidyl methacrylate-co-ethylene methacrylate) particles

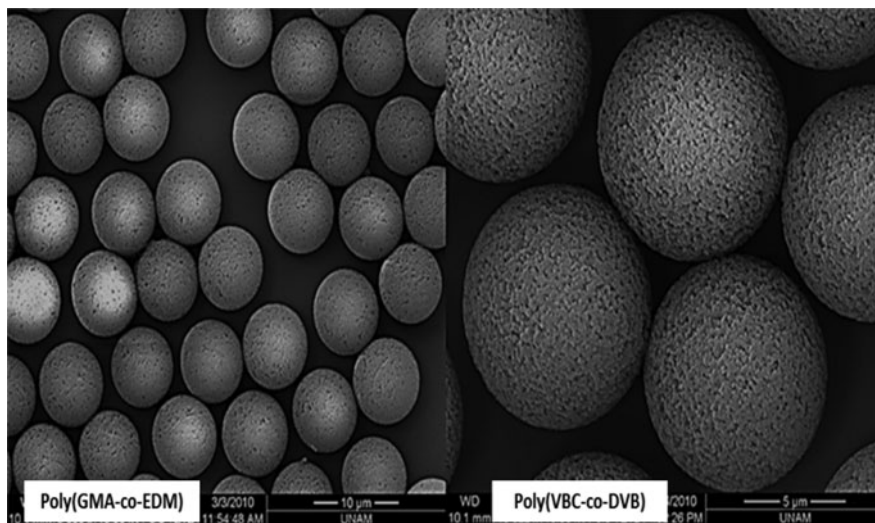


Figure 7.12. SEM photos of poly(GMA-co-EDM) and poly(VBC-co-DVB) particles (adapted from Samatya *et al.*, 2010b, 2012a, 2015a).

carrying a diol functionality were reported to have potential as boron-selective resins (Samatya *et al.*, 2010b). Samatya *et al.* (2012a) also produced new boron-selective sorbents based on monodispersed porous poly(vinylbenzyl chloride-co-divinylbenzene) by a new ‘modified seeded polymerization’ technique. By using a chloromethyl functionality, the beads were derivatized by a simple, direct reaction with a boron-selective ligand, NMDG. These resins were used for the removal of boron from geothermal water and also from its RO permeate (Samatya *et al.*, 2012b, 2015a).

The SEM photos given in Figure 7.12 show the surface morphology of the poly(GMA-co-EDM) and poly(VBC-co-DVB) particles. These photos indicate that monodispersed porous particles have a predominantly highly porous surface and include macropores. Based on the scanning electron microscopy (SEM) evaluation, the average size and the polydispersity indices were  $9\text{ }\mu\text{m}$  and 4.6%, respectively, for poly(GMA-co-EDM), and  $8.5\text{ }\mu\text{m}$  and 5.0%, respectively, for poly(VBC-co-DVB) particles. The specific surface areas of poly(GMA-co-EDM) and poly(VBC-co-DVB) particles were measured as  $31.2\text{ m}^2\text{ g}^{-1}$  and  $35.0\text{ m}^2\text{ g}^{-1}$ , respectively.

Monodispersed nanoporous poly(GMA-co-EDM) and poly(VBC-co-DVB) beads functionalized with NMDG groups were also employed in a submerged membrane-ion-exchange hybrid system for boron removal from geothermal water (Samatya *et al.*, 2015b). The boron concentration could be reduced from 11.0 to  $\leq 1\text{ mg L}^{-1}$  in 20 min using poly(GMA-co-EDM)-NMDG beads with  $4\text{ g resin L}^{-1}$  of geothermal water, compared to 30 min for poly(VBC-co-DVB) beads with the same resin concentration (Fig. 7.13).

Yavuz *et al.* (2013d) developed a polymer-supported core-shell type iminodipropylene glycol function capable of chelating with boron. The graft copolymerization of glycidyl methacrylate (GMA) onto dehydrochlorinated poly(vinyl chloride) (DHPVC) was performed by atom transfer radical polymerization (ATRP) to give iminopropylene glycol functions of sorbent.

Elsewhere, Santander *et al.* (2013) reported the synthesis of a novel boron-selective resin prepared from *N*-(4-vinylbenzyl)-*N*-methyl-D-glucamine as the monomer and *N,N*-methylenebis-acrylamide as a crosslinking agent.

More recently, Zerze *et al.* (2015) reported an iminobis-alkylene diol functionality as an alternative boron-chelating group and its incorporation into various polymer topologies for the removal of boron via direct sorption and polymer-enhanced ultrafiltration (PEU). Sánchez *et al.* (2013a)

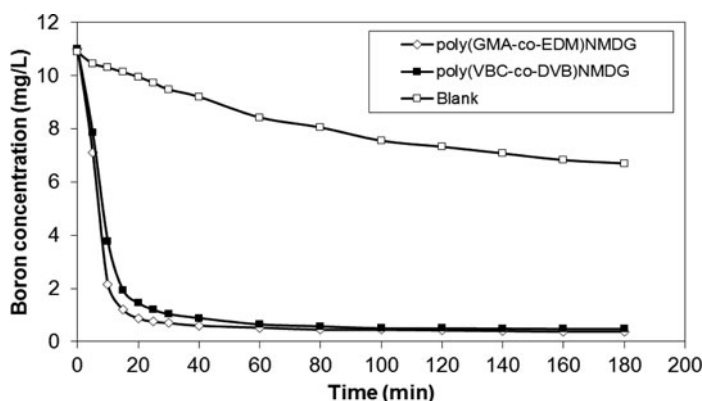


Figure 7.13. Boron concentration in the permeate versus time (resin concentration: 4 g resin L<sup>-1</sup> of geothermal water) (adapted from Samatya *et al.*, 2015b).

also used the liquid-phase polymer-based retention (LPR) technique based on the complexation of borate by poly(glycidylmethacrylate-*N*-methyl-D-glucamine), followed by separation of the formed complexes on UF membranes.

### 7.3 REMOVAL OF ARSENIC FROM GEOTHERMAL WATER BY ION-EXCHANGE

#### 7.3.1 Toxicity of arsenic

Arsenic has several oxidation states (+III, +V, 0, -III) and a variety of inorganic and organic forms (Leermakers *et al.*, 2006). Two forms are common in natural water: arsenite and arsenate, referred to as As(III) and As(V). As(III) and As(V) predominate in moderately reducing anaerobic environments, such as groundwater- and oxygen-rich aerobic environments, respectively (Mohan and Pittman, 2007).

The toxicology of arsenic is classified into acute and chronic types. Acute arsenic poisoning usually occurs through ingestion of contaminated food or drink. The major early manifestation of acute arsenic poisoning includes burning and dryness of the mouth and throat, dysphasia, colicky abdominal pain, projectile vomiting, profuse diarrhea, hematuria, muscular cramps, facial edema and cardiac abnormalities, and shock. Chronic arsenic poisoning may cause melanosis (darkening of the skin), edema (swelling of hands and feet), keratosis (hardening of skin nodules), and enlargement of liver, kidneys and spleen. Some more serious health problems of chronic arsenic exposure are gangrene and skin, lung or bladder cancer (Choong *et al.*, 2007).

Extensive toxicity studies of arsenic have shown that different forms exhibited different toxicities. Inorganic arsenic species are more toxic than the organic compounds. With the exception of the tetramethylarsonium ion, acute toxicity generally decreases with an increasing degree of methylation (Leermakers *et al.*, 2006).

#### 7.3.2 Methods of arsenic removal

The toxic and carcinogenic effects of arsenic on living beings are well documented. Therefore, a water treatment process is necessary before the utilization and discharge of a geothermal water (Altundogan *et al.*, 2002). The efficient removal of arsenic would provide direct usage of water for the purposes of recreation, agriculture, washing and even drinking (Gallup, 2007).

In conventional techniques, arsenic removal is performed by the oxidation of soluble As(III) to As(V), followed by the separation of As(V) by exploiting any of the physicochemical

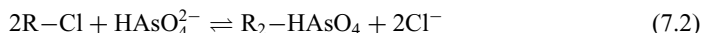
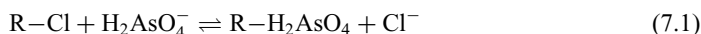


properties, such as coagulation-precipitation, adsorption, ion-exchange, RO, and electrodialysis. The conversion of As(III) to As(V) is done by using oxidizing chemical agents such as chlorine and potassium permanganate (Mondal *et al.*, 2006). Addition of chemicals in the oxidation step increases the cost of these techniques. Alternative methods like ozone oxidation, bioremediation and electrochemical treatments are also used in the removal of As from aqueous media (Choong *et al.*, 2007).

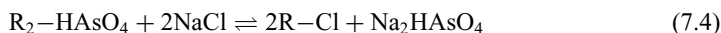
### 7.3.2.1 Removal of arsenic by ion-exchange

Ion-exchange is one of the techniques recommended by the US Environmental Protection Agency (EPA) for remediation of As with the capability of efficient removal from water containing  $<120 \text{ mg L}^{-1}$  sulfate ( $\text{SO}_4^{2-}$ ) and  $<500 \text{ mg L}^{-1}$  total dissolved solids (Clifford and Ghurye, 2002).

Strong-base anion-exchange resins in  $\text{Cl}^-$  form are used for As(V) removal from aqueous medium using ion-exchange. The As(V) ions exchange with the  $\text{Cl}^-$  ions and, eventually, the resin becomes exhausted when all or most of the exchange sites are loaded with As(V) or other anions (Choong *et al.*, 2007). The As(V) ions are exchanged according to the following reactions (Korngold *et al.*, 2001):



Regeneration of the exhausted resin, which returns the resin to the  $\text{Cl}^-$  form, can be carried out by NaCl solution:



Strong-base anion-exchange resins, such as poly(styrene-co-divinylbenzene), containing quaternary trimethyl amine (Type 1) or dimethylethanolamine (Type 2) functional groups are preferred for As(V) removal. If resistance to organic fouling is necessary, then polyacrylic divinylbenzene resins with triethylamine functional groups can also be used as ion-exchange beads to remove As(V) (Clifford and Ghurye, 2002; Greenleaf *et al.*, 2006).

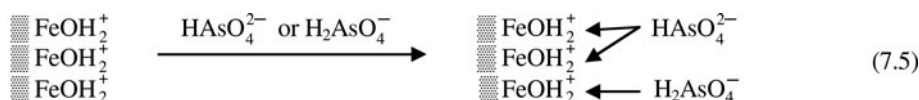
In some cases, because of its ease of handling and sludge-free operation, ion-exchange can be employed rather than adsorption for arsenic removal in small-scale and point-of-entry systems. However, it is difficult to remove As(III) directly with the ion-exchange method due to the fact that As(III) is found predominantly as a neutral species ( $\text{H}_3\text{AsO}_3$ ) in water with a pH value below 9.0. Therefore, oxidation of the As(III) to As(V) is necessary prior to ion-exchange separation. On the other hand, the predominant species of As(V),  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$ , are negatively charged at those pH values. Thus, the removal of the ionic form of the As(V) is easier than As(III). Another parameter influencing arsenic removal by ion-exchange is the presence of competing ions. When water is contaminated with arsenic, it also often contains high concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$  and  $\text{SiO}_4^{4-}$  ions and the competition between these anions decreases the efficiency of the removal of arsenic (Korngold *et al.*, 2001; Malik *et al.*, 2009). Korngold *et al.* (2001) carried out selective removal of As(V) from drinking water with strong-base anion-exchange resins. The influences of the parameters such as types of anion-exchange resin and water composition on the efficiency of the process were investigated. Two types of strong-base anion-exchange resins were used: Purolite A-505 and Relite A-490. Purolite A-505 belongs to Type 1 with trimethyl ammonium group, whereas Relite A-490 was designed for selective  $\text{NO}_3^-$  removal and has other strong-base groups. It was observed that when  $\text{SO}_4^{2-}$  and other anions were present in the water in high concentrations, the process was not efficient and a sharp decrease in arsenic removal was observed for both of the ion-exchange resins used.

A wide variety of sorbents for arsenic removal from aqueous media was presented in the literature. Some of these sorbents include zeolites (Xu *et al.*, 2002), goethite ( $\alpha\text{-FeOOH}$ )

(Hao *et al.*, 2014), clay (Lin and Puls, 2000), kaolinites (Cornu *et al.*, 1999), fly ash (Goswami and Das, 2000), red mud (Altundogan *et al.*, 2002) and akaganéite nanocrystal ( $\beta$ -FeOOH) (Deliyanni *et al.*, 2003).

Lackovic *et al.* (2000) evaluated a novel technology for the removal of arsenic by using zero-valent iron (ZVI) (iron filings). The experimental studies using ZVI succeeded in the removal of both As(III) and As(V) below  $5 \mu\text{g L}^{-1}$ . Other advantages of ZVI included its low cost and nontoxic nature. Tyrovola *et al.* (2006) performed a field study for arsenic removal from geothermal water by ZVI. The pilot consisted of an arsenic removal reactor followed by an iron removal reactor. In addition, the effects of temperature,  $\text{PO}_4^{3-}$  and  $\text{NO}_3^-$  ions were investigated by batch sorption tests. The presence of  $\text{PO}_4^{3-}$  and  $\text{NO}_3^-$  ions decreased the rates of arsenic removal and the temperature of the water was an important parameter for the kinetics.

Different types of iron products, like silica containing iron (III) oxide (Zeng, 2003), iron oxide impregnated activated carbon (Reed *et al.*, 2000) and iron oxide polymeric materials (Katsoyiannis and Zouboulis, 2002) were also used for removal of As. It is well known from the literature that the hydrated oxides of polyvalent metals, like Fe(III), Al(III), Ti(IV) and Zr(IV), exhibit ligand sorption properties by forming innersphere complexes. It has also been reported that these metal oxides provide sorption of a wide variety of anionic ligands and transition metal cations when dispersed within a polymeric host material. Freshly precipitated hydrated Fe(III) oxide (HFO) particle surfaces are considered to be a diprotic acid with two dissociation constants. At neutral pH,  $\text{FeOH}_2^+$  and  $\text{FeOH}$  are the predominant species which can selectively bind both As(III) and As(V) through the formation of bidentate and/or monodentate innersphere complexes. The Fe(III) ion serves as an electron-pair acceptor or Lewis acid (Sarkar *et al.*, 2008):



where shaded lines represent the solid phase.

Sarkar *et al.* (2007) investigated arsenic removal by a hybrid anion exchanger, which is essentially a spherical anion-exchange resin bead containing dispersed nanoparticles of HFO and commercially available as ArsenX<sup>np</sup>. The field performances of well-head arsenic removal units using ArsenX<sup>np</sup> demonstrated that such units could effectively produce arsenic-safe water for more than 20,000 bed volumes. In another study, batch-mode and column-mode experiments were performed for As(V) removal to evaluate the effect of pH and silica on the arsenic removal capacity of two HFO-based hybrid media, ArsenX<sup>np</sup> and npRio. From the data obtained, it was determined that an increase in the pH and silica content had an adverse impact on arsenic capacity for both ArsenX<sup>np</sup> and npRio. Although both ArsenX<sup>np</sup> and npRio had similar hybrid iron oxide media, the decrease in arsenic capacity caused by increased pH and silica levels was less significant for ArsenX<sup>np</sup>. This situation was caused by differences in the physical form of the hydrous iron oxide on the beads and the physical effects of silica-coating pores of the resin substrate. ArsenX<sup>np</sup> was a macroporous resin, whereas npRio was microporous, and so the arsenic capacity of npRio decreased more by silica-coating (Möller and Sylvester, 2008). Beker *et al.* (2010) prepared a magnetically active hybrid sorbent material by dispersing colloid-like HFO particles in the outer periphery of a macroporous ion-exchange resin (Amberlite XAD-2) and examined its adsorption-desorption behavior. The new sorbent material could simultaneously remove both As(V) and 2,6-dichlorophenol from aqueous solutions at around neutral pH. Elsewhere, hybrid ion-exchange fibers that contain dispersed HFO nanoparticles were synthesized and used for both arsenic removal and water softening (Greenleaf *et al.*, 2006).

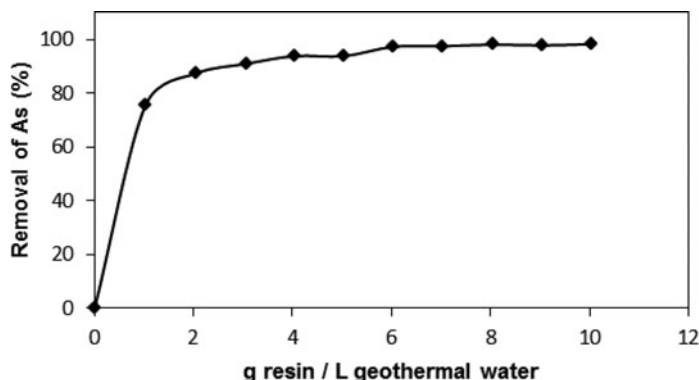


Figure 7.14. Arsenic removal from geothermal water by Lewatit FO 36 (adapted from Koseoglu *et al.*, 2011).

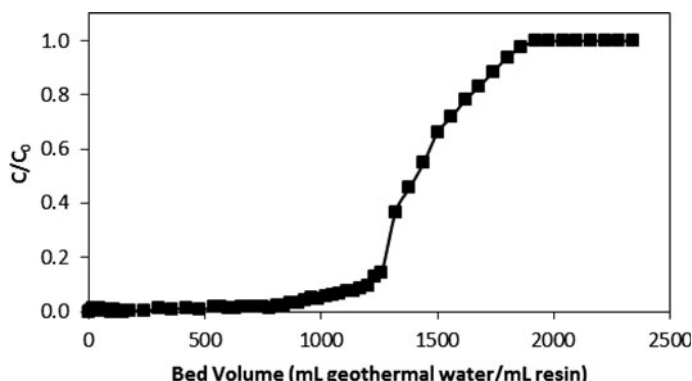


Figure 7.15. Breakthrough profile of arsenic by Lewatit FO 36 (adapted from Koseoglu *et al.*, 2011).

Yoshizuka *et al.* (2010a 2010b) prepared and characterized a magnetite-type adsorbent for the treatment of geothermal waters from sites in Kyushu, Japan. The maximum adsorption for arsenic was achieved at pH 7, which was suitable for usage with geothermal waters (pH 3–9). The linear regression based on the Langmuir adsorption equation indicated that the adsorption process was via the adsorption of a single adsorbate onto a corresponding site on the surface of the adsorbent. This magnetite-type adsorbent could bind  $0.95 \text{ mmol g}^{-1}$  of As.

Koseoglu *et al.* (2011) investigated the arsenic removal performance of two types of commercial As selective ion-exchange resins – Lewatit FO 36 and ArsenX<sup>np</sup> – from geothermal water by batch- and column-mode sorption tests. Both of the arsenic-selective resins had a polymer matrix of crosslinked polystyrene and  $\text{FeO}(\text{OH})$  as arsenic-selective functional group in their structures. Lewatit FO 36 was found to be more effective with a higher breakthrough and total capacity. Figure 7.14 shows the results of batch-mode studies carried out with Lewatit FO 36 for arsenic removal from Hachoubaru (in Japan) geothermal water containing  $3.23 \text{ mg L}^{-1}$  of As. It was possible to remove 97% of arsenic from geothermal water by using 6 g resin per liter of geothermal water.

In the column-mode study performed with Hachoubaru geothermal water, arsenic-selective chelating resin, Lewatit FO 36, was used for arsenic removal. For Lewatit FO 36, breakthrough and total capacity were calculated as 1.74 and  $4.67 \text{ mg As mL}^{-1}$  of resin, respectively, by accepting the breakthrough point as the one just before the concentration reached  $0.01 \text{ mg As L}^{-1}$ . Figure 7.15 illustrates the breakthrough profile of arsenic.

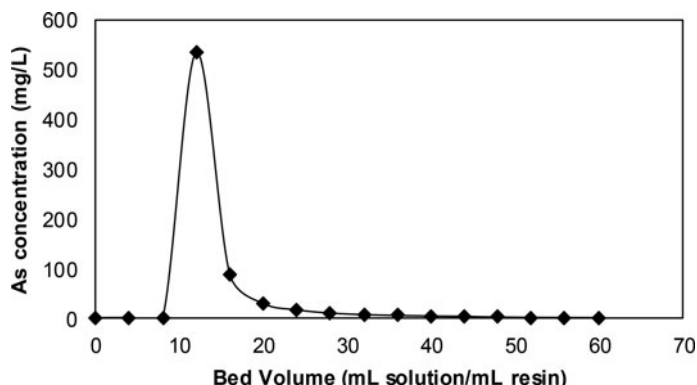


Figure 7.16. Elution profile of arsenic from Lewatit FO 36 (adapted from Koseoglu *et al.*, 2011).

For column-mode elution of arsenic from the resin, an aqueous solution of 2% NaOH-3% NaCl mixture was employed. The elution profile of arsenic is shown in Figure 7.16.

According to Koseoglu *et al.* (2011), Lewatit FO 36 is a monodispersed resin with a diameter of 0.35 mm. Due to better packing of the bed and the higher mass transfer area, the column performance of Lewatit FO 36 for arsenic removal was better than that of ArsenX<sup>np</sup>.

There are also other hybrid techniques, such as the LPR method, for arsenic removal using some ion-exchange polymers forming complexes with arsenic, followed by ultrafiltration. The performances of some polymers in removing arsenic species in solution by the LPR method were intensively studied in the literature (Rivas and Aguirre, 2007; Rivas *et al.*, 2007a, 2007b; Sánchez *et al.*, 2013b).

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## CHAPTER 8

### Membrane techniques in the treatment of geothermal water for fresh and potable water production

Michał Bodzek & Krystyna Konieczny

#### 8.1 INTRODUCTION

More than 70% of the earth is covered with water, of which 97% is saltwater with salt content above  $1 \text{ g L}^{-1}$ . Among the remaining 2.5% of water sources, 69% is glacier and permafrost ice, while less than 1% of total freshwater sources, that is, around 0.01% of total water, is available for humans and ecosystems (Bodzek and Konieczny, 2005). The disproportional distribution of water sources on earth accompanied by the exacerbation of its quality is one of the most significant factors affecting the growth and development of society. Water is a very important feedstock, resources of which are said to be renewable, but on the other hand limited. The recovery of water resources is additionally slowed down or constrained by anthropogenic activity. The limited access to freshwater is mainly caused by (Bodzek and Konieczny, 2011):

- pollution of the environment (including natural waters) by industrial and agricultural activities as well as direct deposition of municipal wastewaters into the environment in some inhabited regions;
- local and global increases in human population accompanied by higher standards of living;
- regional climate changes responsible for the decrease in water resources.

The requirements stated for the technology of water treatment depend on its type. Groundwater may be simply treated before its distribution to the water system, while surface water and other water types, due to the presence or the possibility of presence of dangerous contaminants, must undergo complex treatment comprising many unit operations. A partial solution to the problem of water contamination and lack of potable water is the development and introduction of new technologies (Sozański *et al.*, 2009). Hence, technological systems of water treatment are constantly broadened or modernized with additional, modern unit processes, which enable the removal of a wide range of contaminants present in ground and surface waters as well as in wastewaters. Water treatment systems should be extended with advanced processes where the application of membrane separation techniques is also highly recommended (Bodzek and Konieczny, 2010).

The intensive exploitation of freshwater sources, together with huge usage, generates a need for alternative water sources. One of the solutions to the problem is desalination of saltwater from various sources, which could be used for social and industrial purposes. Thus, the main reason for the development of water desalination techniques is the lack of freshwater resources in many countries all around the world.

Desalination of seawater and salty groundwater is a common method of potable and industrial water production and has become the main water treatment technique in regions with a dry climate, especially in Middle Eastern countries. Two-thirds or, according to others, half of desalination installations operated around the world are located in the Middle East. Next are North America (19%), Europe (13%), Asia (12%) and Africa (6%) (Bodzek and Konieczny, 2011). Those regions are characterized by very poor surface water resources; thus, groundwater is there the main source for potable water production. As groundwater is known to be highly mineralized, it is not the best source of drinking water. Despite the fact that the number of sea and groundwater desalination

installations is fast increasing and they produce large amounts of usable water, the price of the product is still quite high for most people. In the 1980s desalinated water costs were high in comparison with fresh surface water treated using conventional methods. However, it was still a cheaper solution than, for example, long-distance water transport (Ghaffour *et al.*, 2013; Subramani *et al.*, 2011). The development of water desalination methods has also been caused by the increase in costs of water treatment using conventional methods, thanks to the decrease in freshwater sources and difficulties in building and costs of water tanks, as well as the problematic uptake of water from deep ground sources and increasing contamination of ground and surface waters. Nowadays, the investment costs of large water desalination installations are comparable with the costs of modern, conventional drinking water treatment plants (Bodzek and Konieczny, 2011).

Desalination market is driven by a limited drinking water supply of the people, and increasing demand for water, caused by population growth and changes in their style of life. The decrease in water desalination costs caused by the constant technology development is also important. When the technology started to be applied, it was dedicated only to water production in countries with cheap energy sources (Bodzek and Konieczny, 2011; Ghaffour *et al.*, 2013). Nowadays, due to technological and economic progress, it is a common method of potable water production. The economic improvement in the technology has directly resulted in the development of membrane processes, especially reverse osmosis (RO), which has become the most popular desalination technology. In the Persian Gulf countries, thermal methods are also quite popular as a result of the historical background, and the composition of seawater is complex and difficult to desalinate. In this region, the production of drinking water from seawater has been used for nearly 150 years (Bodzek and Konieczny, 2011). In the 1950s electrodialysis was developed on an industrial scale, and in the 1960s the reverse osmosis method was developed (Bodzek and Konieczny, 2011).

It has been found that around 30% of the human population suffers from potable water deficit; thus the main aim of desalination technologies is to supply people with fresh drinking water. The total capacity of all desalination installations operated nowadays is 66.4 M (million) m<sup>3</sup> day<sup>-1</sup> and in 2015 it is predicted to reach 100 Mm<sup>3</sup> day<sup>-1</sup> (Ghaffour *et al.*, 2013). The number of desalination installations constantly increases not only in the Middle East or Northern Africa, but also in regions in which one would not expect to be able to apply the method, for example Spain and Australia (i.e. dry and semi-dry areas) (Ghaffour *et al.*, 2013). Globally, 63.7% of water produced via desalination is obtained using membrane processes and 34.1% by means of thermal methods (Fig. 8.1). The main desalination feed is seawater (58.9%), then brackish groundwater (21.2%), and the rest are surface and wastewater. However, these data are very unreliable due to the dynamics of the desalination market. The increase in seawater desalination capacity is now ca. 55% per year<sup>-1</sup>.

The value of the desalination market is expected to reach 31 billion US\$ in 2015 (Table 8.1) (Bodzek and Konieczny, 2010). More than 50% of all investments are dedicated to seawater reverse osmosis (SWRO), due to the lower costs of both investment and total water production in comparison with other methods. Nevertheless, thermal processes will still be used, especially in regions where the cost of energy is sufficiently low. However, the trend is towards exchanging the multi-stage flash distillation (MSF) method with multi-effect distillation (MED) and towards competition between MED and SWRO in cases when the raw water is very contaminated and of high salinity. Thermal processes are already known to be reliable and successful at co-generation of energy and water. However, the flexibility and simplicity of design, together with the positive economic aspect, means that the SWRO plants located at new power plants do not involve thermal systems.

Seawater is an unlimited source of the feed water in desalination processes; thus it represents the highest share in desalinated water production. On the other hand, brackish water, most often collected from groundwater, is also an important source of raw water. In Table 8.2 the range of salinity estimated for sea and brackish water is presented (Ann, 2004). The salt concentration in seawater varies from 24,000 to 42,000 mg L<sup>-1</sup> (average 35,000 mg L<sup>-1</sup>), depending on

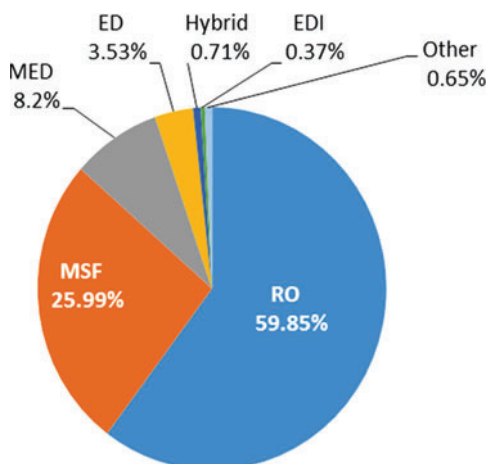


Figure 8.1. Capacity of the desalination processes installed in the first quarter of 2012, according to the technology (RO: reverse osmosis; MSF: Multi-stage flash distillation; MED: Multi-effect distillation; ED: Electrodialysis; EDI: Electrodeionization) (Ghaffour *et al.*, 2013).

Table 8.1. Development and prediction of the desalination market (Bodzek and Konieczny, 2010).

Type of installation	2006–2010 [billion US\$]	2011–2015 [billion US\$]
RO – seawater	9.92	15.48
MED – seawater	3.03	4.04
MSF – seawater	8.39	7.07
Small thermal plants	2.06	2.33
RO – brackish water	1.43	2.18
RO – ultrapure water	0.21	0.30
Total	25.04	31.40

Table 8.2. Salinity of seawater and brackish water (Ann, 2004).

Water	Total salinity [g m <sup>-3</sup> ]
Baltic Sea	7000
Oceans	35000
Mediterranean Sea	38000
Red Sea	41000
Persian Gulf	45000
Aral Sea	29000
Low saline brackish water	1000–5000
Highly saline brackish water	5000–15000

the location. The concentration of salts in brackish water is much lower and varies from 2000 to 5000 mg L<sup>-1</sup>. The standards of salt content established for potable water are usually equal to 250 mg L<sup>-1</sup>.

Problem of access to high-quality water reaches also the area of the European continent, which due to its climate, generally is not considered to be scarce in this field. In Poland, for example, the problem is quite significant as the average water sources established for the region are three times

lower than average values established for Europe and are equal to  $1580 \text{ m}^3 \text{ citizen}^{-1} \text{ year}^{-1}$  (during dry periods the value is even lower, in the range of  $1000\text{--}1100 \text{ m}^3 \text{ citizen}^{-1} \text{ year}^{-1}$ ) (Tomaszewska and Bodzek, 2013). Recently, a very clear tendency of changes in average and extreme river water flows and levels and lake water and groundwater levels, that is, the main sources of freshwater, has been observed. The specific hydrogeological conditions of southern Poland make an actual water deficit problem for local communities (Kundzewicz and Kowalczak, 2008). Thus, geothermal water may become an important resource for freshwater production in this region.

The management of geothermal water resources requires proper and environmentally safe methods of their utilization. The available thermal waters exploited nowadays in Poland have been classified as fresh, brackish or brine with mineralization level reaching even up to  $100 \text{ g L}^{-1}$  (Bujakowski and Barbacki, 2004; Bujakowski *et al.*, 2008; Kępinska, 2003; Tomaszewska, 2011), while the main method of their utilization is the deposition to surface waters. The increased salinity and the presence of microelements, that is, boron, barium, strontium, fluorides, bromides and heavy metals, generate significant limits for the deposition method used in geothermal water utilization. Due to the deficit of proper quality fresh groundwater (including that of potable water purity grade) in many regions of Poland, studies on the desalination of cooled, brackish geothermal water for freshwater production have been undertaken. Most trends in the research are directed to the production of potable water (Bonte *et al.*, 2013; Gallup, 2007; Kępinska, 2003; Tomaszewska, 2011, 2012) and supplemental water for energy industry purposes. The former trend is additionally adjusted by the use of thermal water heat in heat exchange systems (Bujakowski *et al.*, 2008; Tomaszewska and Pająk, 2013). Moreover, the use of desalinated geothermal water in agriculture and other branches of industry is also mentioned (Gallup, 2007).

## 8.2 DESALINATION METHODS

The desalination process relies on the production of desalted water from sea or brackish water. The desalted water can then be used as freshwater, while the concentrated streams, that is, brine, are deposited into the sea, brackish water reservoirs, or evaporated in ponds. The typical diagram of the process including mass and energy balance is shown in Figure 8.2 (Bodzek and Konieczny, 2011). Energy is always required for the process, while the desalination itself can be performed using different methods classified according to the phase change and type of energy consumed (Bodzek and Konieczny, 2011; Subramani *et al.*, 2011). Thus, the following processes can be distinguished:

1. Due to the phase change:
  - without the phase change – reverse osmosis (RO) and electrodialysis (ED);
  - with the phase change – distillation and freeze drying.
2. Due to the type of energy required:
  - heat energy – distillation processes;
  - mechanical energy – reverse osmosis;
  - electrical energy – electrodialysis.

In terms of drinking and potable water production for industrial purposes, the desalination processes based on thermal and membrane methods are found to be the most important (Bodzek and Konieczny, 2011). The membrane processes are found to be the main ones involved in the technology due to the lower energy consumption in comparison with thermal methods (Al-Karaghoul and Kazmerski, 2013; Rahimi *et al.*, 2014; Subramani *et al.*, 2011).

The membrane desalination is usually based on reverse osmosis or electrodialysis, in which ion-exchange membranes are used for ion separation (Bodzek and Konieczny, 2011). The history of desalination by means of the membrane process is already more than 100 hundred years old (Younos and Tulou, 2005). The latest research shows the possibility of membrane distillation or forward osmosis use for desalination purposes (Gryta, 2012; Linares *et al.*, 2015; Low, 2009;

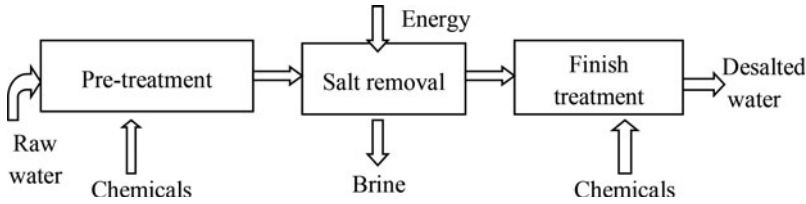


Figure 8.2. Scheme of desalination process (Bodzek and Konieczny, 2011).

Table 8.3. Comparison of the operating parameters of thermal and membrane desalination methods (Fritzmann *et al.*, 2007).

Parameter	MSF	RO	ED
Consumption of thermal energy [ $\text{kWh m}^{-3}$ ]	12	–	–
Consumption of electrical energy [ $\text{kWh m}^{-3}$ ]	35	0.4–0.7	1
Typical salinity of raw water [ $\text{g L}^{-1}$ ]	30–100	1–45	0.1–3
Quality of desalted water [ $\text{mg L}^{-1}$ TDS]	<10	<500	<500

Subramani *et al.*, 2011; Wang and Chung, 2015). In Table 8.3 the most important operational parameters of thermal and membrane methods are compared (Fritzmann *et al.*, 2007).

The main desalination methods are freeze drying, air humidification/dehumidification, processes involving sun or wind energy, and ion-exchange (Al-Karaghoul and Kazmerski, 2013). However, except for ion-exchange, the mentioned techniques have not yet been commercially applied, but may be useful in specific conditions or after further development and improvement (Bodzek and Konieczny, 2011).

### 8.2.1 Thermal methods

The most important thermal processes cover flash distillation, that is, evaporation of the heated liquid by decompression and/or multi-effect boiling. The evaporation-based group of processes is multi-stage flash distillation (MSF), multi-effect distillation-evaporation (MED) and single-stage vapor compression, which includes mechanical vapor compression (MVC) and thermal vapor compression (TVC) (Al-Karaghoul and Kazmerski, 2013; Bodzek and Konieczny, 2011; Van der Bruggen and Vandecasteele, 2002).

Multi-stage flash distillation (MSF) was introduced to commercial use in the 1960s and immediately became the most popular process for seawater desalination for the next few decades due to its simplicity and effectiveness (Al-Wazzan and Al-Modaf, 2001; Borsani and Rebagliati, 2005; Van der Bruggen and Vandecasteele, 2002). The operation of MSF is based on the generation of vapor from the saline raw water in a series of decompression chambers at stepwise pressure decrease. MSF units are characterized by capacity of  $10,000$  to  $35,000 \text{ m}^3 \text{ day}^{-1}$  and are composed of between four and 40 chambers of continuously lower temperature and pressure. Such a system configuration causes the immediate vaporization of the saltwater, followed by vapor condensation to freshwater and the use of the condensation energy to heat up the raw water. The heated water is then introduced to a series of chambers operated at stepwise decreasing pressure in which the portion of evaporated water decreases from one chamber to another and the vapor is continuously taken out of the system. Next, the gaseous product is condensed and collected as freshwater. The raw water flows through a series of heat exchangers, in which the vapor condensation simultaneously occurs, which ensures a partial energy recovery and decreases the overall energy demand of the process, that is, the energy required for raw water heating and vapor cooling (Fig. 8.3) (Al-Karaghoul and Kazmerski, 2013; Bodzek and Konieczny, 2011).



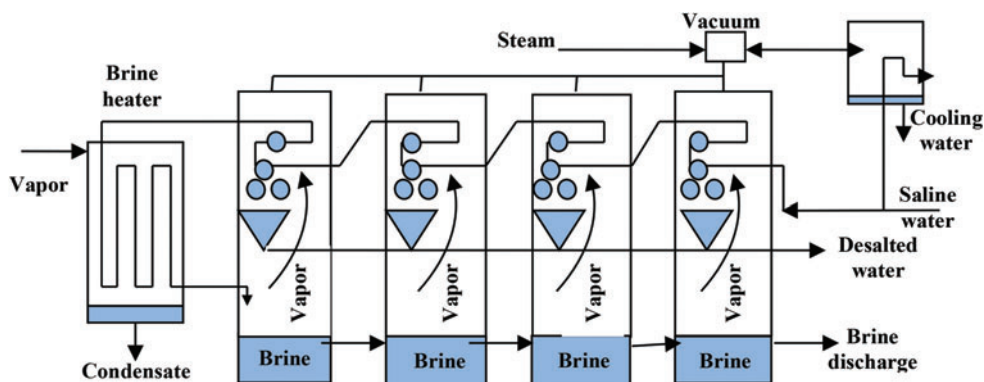


Figure 8.3. Scheme of the multi-stage flash distillation (MSF) process (Al-Karaghoul and Kazmerski, 2013; Bodzek and Konieczny, 2011).

Nevertheless, MSF is an energy-consuming process, which requires the supply of heat and electrical energy. The heat for raw water heating is usually supplied as low-pressure steam (0.1 to 0.3 MPa), while medium-pressure steam is used in the injector in order to obtain vacuum conditions in particular sections of the device. The electrical energy drives recycling pumps of cooled water, distillate, brine, condensate, and dosing chemicals. The external heat is obtained from fossil fuel-heated boilers, which can be power plant waste heat, from nuclear reactors, renewable energy resources, and other energy systems, and is used to heat up the raw water to the temperature of 90 to 110°C. The brine formed during the process is partially recycled to the system in order to increase the water recovery rate and the rest is deposited outside the system. The main advantages of MSF systems are reliability and simplicity of exploitation. Additionally, heat exchangers used in the process have no direct contact with raw water and thus the scaling phenomenon is also limited. However, scaling may occur inside MSF chambers and on pipes; hence periodical cleaning and deposits removal is required. However, in order to maximize the operational periods, acidic additives, anti-scalants and optimal brine temperature below 110°C are used (Van der Bruggen and Vandecasteele, 2002). Moreover, in order to prevent the growth of microorganisms in system devices, biocides are also applied. The MSF process is found to be insensitive to initial salt concentration and colloids content in the raw water. The concentration of soluble substances in the final product does not usually exceed 50 mg L<sup>-1</sup> (Van der Bruggen and Vandecasteele, 2002). In comparison with MED systems it is easier to control corrosion in MSF devices due to their simpler construction. The most significant disadvantage of MSF technology is the high energy demand, which makes it less economically attractive than MED. Hence, it is widely applied in regions with low energy costs (Van der Bruggen and Vandecasteele, 2002). Despite all the facts, MSF is still the most popular thermal seawater desalination process after RO; however, MED technology has become a serious competitor to MSF in the desalination trends (Al-Karaghoul and Kazmerski, 2013).

Multi-effect distillation (MED) is the oldest technique of seawater desalination (Al-Karaghoul and Kazmerski, 2013; Bodzek and Konieczny, 2011; Grater, 1998; Rahimi *et al.*, 2014). The technology is based on the transport of heat to sea or brackish water obtained from the condensation of steam in a series of evaporators/heat exchangers (Fig. 8.4) (Bodzek and Konieczny, 2011).

Vapor compression (VC) processes rely on the generation of heat by the compression of steam in a mechanical or thermal compressor, partially evaporation of water and then condensation of steam in the pipe heat exchanger, from which the energy is used for heating the raw water (Fig. 8.5) (Al-Karaghoul and Kazmerski, 2013; Bodzek and Konieczny, 2011; Borsani and Rebagliati, 2005). In the first heat exchanger, the initial steam stream undergoes condensation, which results

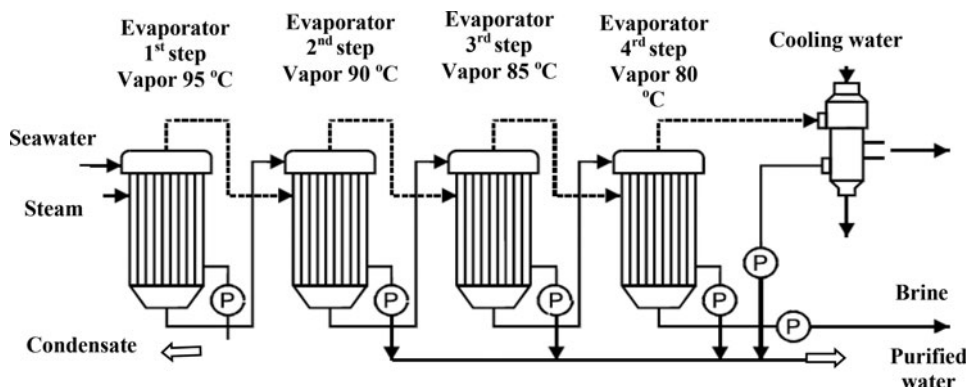


Figure 8.4. The principle of the multi-effect distillation (MED) process (Bodzek and Konieczny, 2011).

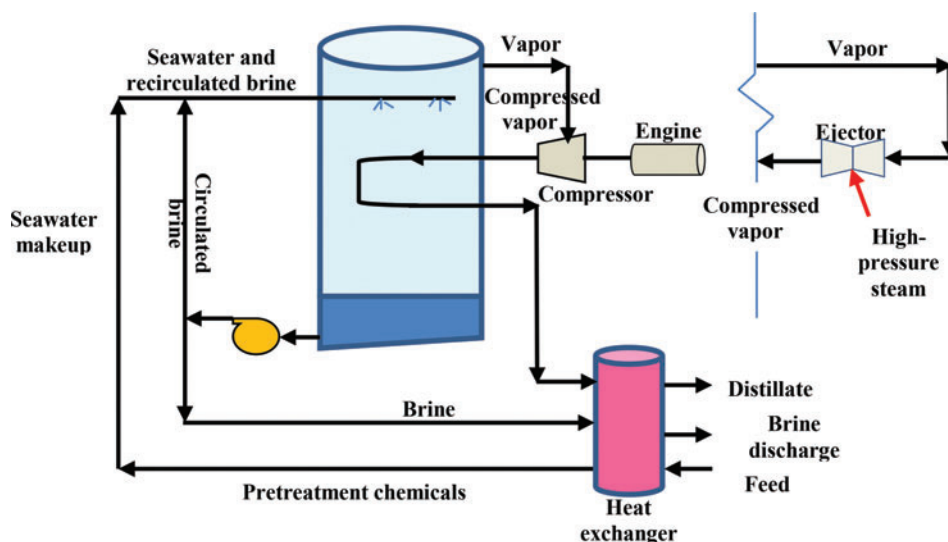


Figure 8.5. Vapor compression (VC) scheme (Al-Karaghoul and Kazmerski, 2013; Bodzek and Konieczny, 2011; Borsani and Rebagliati, 2005).

in the preliminary evaporation of heated raw water. The formed secondary steam stream is then introduced to the second heat exchanger operated at slightly lower temperature and pressure conditions, while the condensate from the first heat exchanger is recycled to the steam generator. The capacity of a typical MED unit usually varies from 600 to 30,000 m<sup>3</sup> day<sup>-1</sup>, and its construction is based on two main technological designs. The former consists of vertical pipes in which the thin film of raw water boils during the flow inside the pipe, while the vapors condense on the external walls of the exchanger pipes. The latter solution is based on horizontal pipes, on the external surface of which the raw water is sprayed, while the steam flows inside the pipes, where it condenses, resulting in the production of purified water (Al-Karaghoul and Kazmerski, 2013). The application of such systems results in an efficient rate of heat transport and thus the effective running of the evaporation and condensation stages (Bodzek and Konieczny, 2011; Van der Bruggen and Vandecasteele, 2002). However, the exploitation of MED systems is accompanied by corrosion and scaling caused by the precipitation of deposits, for example CaSO<sub>4</sub> from oversaturated brine solutions. The ratio of the produced water to steam consumption in MED is

Table 8.4. Comparison of energy consumption of thermal desalination processes (Ghaffour *et al.*, 2013; Wilf, 2007).

Parameter	MED	MSF	VC
Thermal energy [ $\text{kWh m}^{-3}$ ]	4–7	7–12	–
Consumption of electrical energy [ $\text{kWh m}^{-3}$ ]	1.2–2.0	2.5–5	8.5
Equivalent of total energy consumption [ $\text{kWh m}^{-3}$ ]	5.5–9	10–18	8.5

very high and depends on the number of heat exchangers. On the other hand, the number of heat exchangers is limited by the initial temperature in the first device of the series, which must not exceed  $120^{\circ}\text{C}$  due to the scaling risk, and the minimal temperature in the last device, which should enable the sufficient heating of the raw water. Additionally, the minimum temperature difference between particular devices must be  $5^{\circ}\text{C}$ . The number of heat exchangers is hence usually between eight and 16 (Bodzek and Konieczny, 2011; Van der Bruggen and Vandecasteele, 2002).

The raw water is introduced to the VC process by a heat exchanger, while the steam generated in the evaporator is compressed by means of mechanical (MVC) or thermal (TVC) methods. The condensation of steam increases the temperature of raw water, while the flash decompression enables the separation of salts from the liquid. The process is additionally enhanced by the differences in molecular weights of particular salts and water. The concentrated brine is taken out of the devices using recirculation pumps and is separated into two parts, from which one is mixed with the feed water and recycled to the system, while the second is the deposited liquid waste stream. VC units are usually designed as small- or medium-capacity systems of daily production rates, in the case of MVC equal to 100 to  $3000 \text{ m}^3 \text{ day}^{-1}$ , while in the case of TVC the range is from 10,000 to  $30,000 \text{ m}^3 \text{ day}^{-1}$  (Al-Karaghoul and Kazmerski, 2013). Distillation-based desalination methods, that is, MED and MSF, involve steam for raw water heating, but they also require electrical energy for pump operation. In the case of MVC the electrical energy is the only one required, while TVC systems utilize steam in thermal compressors.

In Table 8.4, the energy demands for all the discussed evaporation methods of desalination are compared (Ghaffour *et al.*, 2013; Wilf, 2007).

The developments and improvements in the operation of thermal processes, which significantly influenced the cost effectiveness of those methods, relied on the following:

- an increase in installation capacities up to  $90,000 \text{ m}^3 \text{ day}^{-1}$  for MSF,  $23,000 \text{ m}^3 \text{ day}^{-1}$  for MED and  $4000 \text{ m}^3 \text{ day}^{-1}$  for VC;
- the undertaking of actions devoted to energy and heat consumption reduction;
- the application of novel building and construction materials (also of lower costs);
- the introduction of hybrid systems (thermo-thermal or thermo-other technology combinations), that is, multi-effect evaporation (MEE)-TVC, MSF-RO, MSF-MEE, and the addition of membrane techniques as water-softening method.

### 8.2.2 Reverse osmosis (RO)

The desalination of brackish water was the first successful commercial application of reverse osmosis (Van der Bruggen and Vandecasteele, 2002), and became part of regular industrial practice in the 1960s. In the next decade, membranes based on relatively high permeability material, suitable for desalination of seawater, appeared on the market. In the 1980s RO became a serious player in the desalination market and a successful competitor in distillation-based processes. In the following decade, desalination by seawater reverse osmosis (SWRO) and brackish water reverse osmosis (BWRO) became a commonly applied method of freshwater production from salty water at costs comparable to other freshwater production methods (Malaeb and Ayoub, 2011). Nowadays, more than 90% of RO installations are involved in the production of drinking and

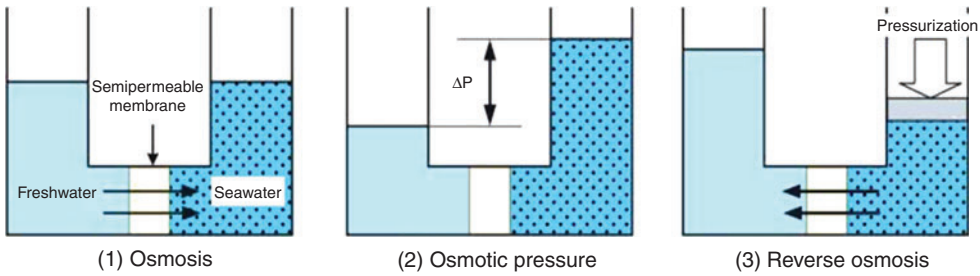


Figure 8.6. The principles of forward osmosis and reverse osmosis (Bodzek and Konieczny, 2011).

potable water as well as treatment of water for energy, semiconductor etc. industries. Hence, a lot of research and development projects focused on the topic are devoted to the reduction of energy consumption during the process, minimization of membrane scaling and fouling and improvement and production of high-capacity membranes (Peñate and García-Rodríguez, 2012).

#### 8.2.2.1 The basis of the RO process

Reverse osmosis is a membrane separation process, in which the membrane is permeable to freshwater while being resistant to soluble salts permeation, which is assured by the use of pressure higher than the osmotic pressure of sea- or brackish water. During the process two fractions are obtained: pure water (permeate) and concentrated salts solution (retentate or concentrate). The basis of RO can be found in the natural osmosis process. If the membrane separates the solution from the solvent of two solutions of various concentrations, then a spontaneous flow of the solvent to the solution of higher concentration occurs. The pressure that equalizes the osmotic flow is called the osmotic pressure ( $\pi$ ). If the hydrostatic pressure at the solution side is higher than the osmotic pressure then the solvent flow is in the direction from the solution side to the solvent side; thus the direction reverses to the natural osmosis direction (Fig. 8.6) (Bodzek and Konieczny, 2011). The required transmembrane pressure value may reach up to 12 MPa (met in the first commercial RO systems), but the modern units are usually operated at the pressure of 5 MPa for seawater and 2 MPa for brackish water. The effectiveness of the process depends on operational parameters, membrane properties, and raw water characteristics.

With the assumption that the dissolved substance does not permeate through the osmotic membrane (ideal membrane), the dependence of the permeate flux ( $J_v$ ) on the pressure ( $\Delta p$ ) can be described by Equation (8.1) (Bodzek and Konieczny, 2011):

$$J_v = L(\Delta p - \Delta \pi) \quad (8.1)$$

In practice, however, part of the dissolved substances passes through the membrane, and thus Equation (8.2) is applied:

$$J_v = L(\Delta p - \sigma \Delta \pi) \quad (8.2)$$

$\sigma$  is the so-called reflection coefficient, referring to this part of the membrane which is impermeable to the dissolved substances and it describes the deviation of selectivity of real membrane from ideal membrane. The value of membrane permeability ( $L$ ) depends on the solubility of substance permeating through the membrane and on its diffusion coefficient. For RO membranes, the value of  $L$  parameter is within the range of  $10^{-6}$ – $10^{-8} \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1} \text{ Pa}^{-1}$ . The dissolved substance mass flux ( $J_s$ ) that passes through the membrane depends only on the concentration of the substance at both membrane sides:

$$J_s = L_s(C_s - C_p) \quad (8.3)$$

where:

- $L_s$ : permeability of the membrane compared with the dissolved substance
- $C_s$ : concentration of the substance in the feed solution
- $C_p$ : concentration of the substance in the permeate.

Introducing the equations describing permeate flux and the dissolved substance flux to the retention coefficient equation and considering the dependence shown in Equation (8.4):

$$C_p = J_s/J_v \quad (8.4)$$

one can obtain:

$$R = 1 - \frac{C_p}{C_s} = \frac{L(\Delta P - \Delta \pi)}{L(\Delta P - \Delta \pi + L_s)} \quad (8.5)$$

which clearly shows that the retention coefficient increases with the transmembrane pressure increase.

Mass transport models applied in the RO process may be divided into three main groups (Malaeb and Ayoub, 2011):

- models based on irreversible thermodynamics;
- porous models, which assume that the transport through membrane pores is both diffusion and convection;
- non-porous or homogeneous models (solution-diffusion models), which assume that the transport through the membranes occurs in free spaces between polymer chains or modules, usually by means of diffusion.

Irreversible thermodynamic models regard the membrane as the black box, in which sufficiently slow processes run at the border of equilibrium state, and the fluxes of dissolved substances and solvent are directly connected with the difference in chemical potential between both sides of the membrane (Hassan *et al.*, 2007). The porous models concept is based on the combination of several mechanisms, including size and charge exclusion as well as dielectric exclusion (Yaroshchuk and Staude, 1992). The neutral dissolved substances are excluded by the sieving effect or spherical barriers, that is, substances of higher molecular weight are retained by the membrane. The transport of uncharged substances through the membrane is additionally enhanced by the convection caused by pressure difference and by the diffusion due to concentration gradient. On the other hand, in the case of charged substances the transport mechanisms are controlled by electrostatic repulsion of the Donnan effect, which results in interaction between the charged particles and the constant electric charge of the membrane material matrix (Yaroshchuk and Staude, 1992).

The choice of membrane for the RO process is based on the affinity of the solvent (water) to the membrane material, while the pore size plays a much less significant role, as the separation mechanism is of solution-diffusion type. Hence, RO membranes should be characterized by high affinity to water and, simultaneously, no affinity to dissolved substances. Most RO membranes are polymeric membranes, composite with thin separation film and several supported layers of weak separation properties (Bodzek and Konieczny, 2005, 2011). Commercially available modules are of spiral-wound or hollow-fiber configuration. The latter type are characterized by high packing density, that is, high capacity, but they are less fouling resistant. The membranes may be asymmetric of one polymer layer or composite comprising two or more layers. Functional groups introduced to the polymer structure are responsible for the charge of the membrane, while the rate of adsorption of dissolved substances is defined using membrane hydrophobicity, charge, and surface roughness (Malaeb and Ayoub, 2011). Recently available spiral-wound modules of high membrane surface have enabled a decrease in both the installation dimensions and number of pressure tanks (Malaeb and Ayoub, 2011; Peñate and García-Rodríguez, 2012).

Reverse osmosis is widely used on an industrial scale, mainly in desalination of water for potable water production. Additionally, the process is used in desalination of wastewater and other solutions as well as water recovery from many industrial wastewater and municipal landfill

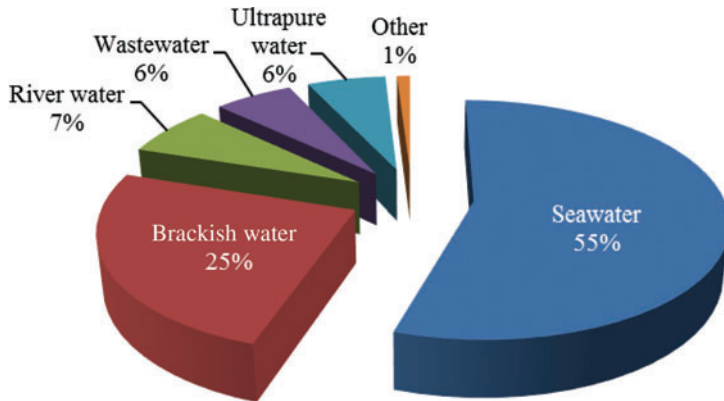


Figure 8.7. Performance of desalination installations according to the type of feed (Bodzek and Konieczny, 2011).

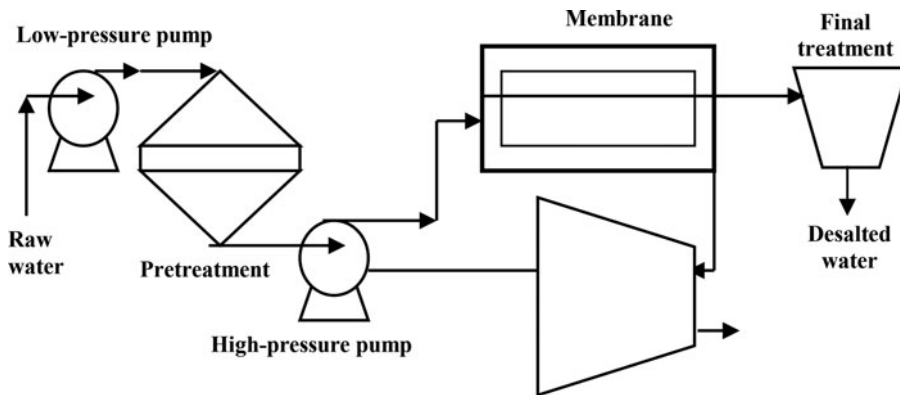


Figure 8.8. A simplified diagram of RO water desalination with energy recovery from retentate (Al-Karaghoul and Kazmerski, 2013; Bodzek and Konieczny, 2011; Eltawil *et al.*, 2009; Wilf, 2007).

leachates (Bodzek *et al.*, 2004; Malaeb and Ayoub, 2011). RO installations may be found at such industrial plants as semiconductor production, food processing, pharmaceuticals production, biotechnological facilities, tanneries, textiles and paper production, mine water treatment plants, crude oil and crude gas plants, and many others (Häyrynen *et al.*, 2008; Juang *et al.*, 2008; Maragliano and Moss, 2005; Vourch *et al.*, 2008; Zhang *et al.*, 2008). The process is also used for industrial-grade water production, for example in heat and power energy production plants. In Figure 8.7, the percentage share of RO installation capacities used in different types of water and wastewater treatment is shown (Bodzek and Konieczny, 2011).

#### 8.2.2.2 Water desalination by means of RO

The scheme of a typical installation for water desalination by means of RO is shown in Figure 8.8.

It is divided into several sections involved in the production of potable water (Al-Karaghoul and Kazmerski, 2013; Bodzek and Konieczny, 2011), that is:

- section of water collection and pressure pumps
- section of raw water pretreatment
- section of membrane modules with energy recovery from retentate
- section of treated water preparation to distribution.

The advantage of reverse osmosis application is the relatively low cost of the produced water, which varies in the range of 0.50–0.70 US\$ m<sup>-3</sup>, while in the case of MSF and MED it is 1.0–1.4 US\$ m<sup>-3</sup>, depending on the energy price (Al-Karaghoul and Kazmerski, 2013; Bodzek and Konieczny, 2011; Ghaffour *et al.*, 2013; Reddy and Ghaffour, 2007; Tomaszewska and Bodzek, 2013). The energy demand is much lower than in the case of distillation-based processes; however, the costs of raw water pumping are still significant. Nowadays, due to the significant decrease in operational costs in the last 20 years, RO has become the commonly used method for sea and brackish water desalination, and the economic effect has been obtained due to improvement in the process and the application of renewable energy sources. The overall capacity of seawater desalination by means of RO continuously increases, even in the Gulf State region, where the energy is quite cheap. According to the quality of raw water, RO requires the use of a pretreatment process, the efficiency of which is vary variable, in order to protect the membranes from fouling and biofouling (Gallup, 2007). The total capacity of all RO installations used in water desalination is the highest among all processes (Fig. 8.7). The significant economic improvement of the process has made it possible for many countries to implement the technology in potable and municipal water production from seawater, and even in some cases in the preparation of water for agriculture needs, for example in Spain (Tomaszewska and Pająk, 2013).

The main exploitation problem connected with RO capacity is the irreversible change in membrane permeability caused by fouling, a phenomenon which is the result of many factors. Fouling is the deposition of substances present in the feed solution on the membrane surface and/or inside membrane pores, which affect its permeability. Fouling may be caused by many factors, among which growth of microorganisms (biofouling), deposition of mineral salts on the membrane surface (scaling), and formation of filtration cake by dissolved or suspended substances present in the solution are of the highest importance (Bodzek and Konieczny, 2011; Gryta, 2012). In order to limit the impact of these undesired phenomena on the process capacity the pretreatment of raw water and improvement in operational conditions are crucial for the proper performance of the RO module. Fouling may also reveal a reversible character, if the deposit formed on the membrane surface can be totally removed and the initial capacity of the membrane can be restored. The form of irreversible fouling is found to appear when coating/contamination of the membrane takes place inside the membrane pores and thus neither mechanical nor chemical cleaning are sufficient to recover the initial process efficiency (Bodzek and Konieczny, 2005, 2011). Many studies have already shown that the membrane surface smoothness as well as hydrophilic character of the membrane material may significantly increase the membrane resistance to fouling (Malaeb and Ayoub, 2011; Płatkowska-Siwiec and Bodzek, 2011; Vrijenhoek *et al.*, 2001).

The form of fouling connected with the growth of microorganisms on the membrane surface, that is, biofouling, is one of the most dangerous for both RO and other membrane processes. The bacteria immobilized on the membrane surface form a kind of biofilm, which comprises their cells and external polymers produced by microorganisms, which are very difficult to remove (Ivnitskya *et al.*, 2005; Matin *et al.*, 2011). Membranes used in desalination of seawater are especially exposed to this phenomenon. The most severe effects of biofouling are the increased hydraulic resistance of the membrane, decreased permeability, enhanced concentration polarization impact and decreased retention of salts. The significant lowering of RO membranes' capacity and efficiency, and thus of the whole system, results in the increase in exploitation costs as more frequent cleaning and exchange of membranes must be done. The growth of bacteria can be limited by chlorine addition to the treated water. However, the presence of free chlorine may also affect the membrane performance; thus chloramines are preferably used for that purpose (Malaeb and Ayoub, 2011). On the other hand, the recently developed polysulfone osmotic membranes have turned out to be resistant to free chlorine (Park *et al.*, 2008). Other prevention actions taken against biofouling cover pretreatment of raw water, addition of biocides other than chlorine and the most promising one, the modification of membrane surface.

The second exploitation problem observed during the operation of the RO process is the formation of membrane scale, that is, scaling, which usually comprises CaCO<sub>3</sub>, CaSO<sub>4</sub> and BaSO<sub>4</sub>, whereby the severity of the phenomenon depends on the volumetric ratio of the permeate to

the raw water. Scaling causes a decrease in both membrane capacity and permeate quality. The phenomenon occurs at high concentration of calcium, phosphate, carbonate, silica and other ions and it becomes critical when the concentration equilibrium of dissolved substances exceeds the solubility equilibrium expressed by saturation indices, which in this case are  $>1$  (Antony *et al.*, 2011). Nevertheless, the phenomenon may be controlled by the addition of anti-scalants and decrease in both solution pH and permeate recovery rate. The addition of anti-scalants is found to be an effective method with a volumetric permeate recovery rate equal to 50% (Bodzek and Konieczny, 2005, 2011). However, the main disadvantages of the method are the high cost of chemicals, the increase of brine amount and the enhancement of the phenomena in the case of an overdose of the agent. The affinity to membrane scale formation has been determined by a number of studies, the results of which enable the proper anti-scalant to be chosen individually for the given process, as the agents have already been found to reveal selective properties. Hence, if there is a mixture of scale-forming substances in the raw water, then a mixture of anti-scalants should be applied (Antony *et al.*, 2011).

In recent years, a series of studies focused on the prevention of membranes fouling and scaling has been undertaken (Bonnelye *et al.*, 2004; Chesters, 2009; Den and Wang, 2008; Goosen *et al.*, 2004; Pontie *et al.*, 2005; Qin *et al.*, 2005a, 2005b; Shi and Benjamin, 2009; Shon *et al.*, 2009; Yang *et al.*, 2008). These have been mostly devoted to:

- membrane cleaning by means of novel anti-scalants and the prevention of fouling and scaling using various chemicals other than anti-scalants;
- pretreatment of the raw water with the use of low-pressure driven membrane filtration and nanofiltration;
- application of electrocoagulation as a pretreatment method for silica removal;
- modernization of classical pretreatment of the raw water with coagulation and filtration or powdered activated carbon (PAC) adsorption, as well as the application of ozone;
- use of flotation with dissolved air and double direct filtration – the efficient method of pretreatment of seawater of high and unstable turbidity and algal bloom.

#### 8.2.2.3 The pretreatment of raw water for RO desalination

The proper pretreatment of raw water is the key factor determining either success or failure of a desalination process. It is especially important in the case of process performance with RO use (Bodzek and Konieczny, 2005, 2011; Jamaly *et al.*, 2014), but also in the case of other desalination techniques.

The range of preliminary treatment of water for desalination depends mainly on the quality and type of the raw water (i.e. surface water, brackish water, seawater, salted industrial water) as well as on the type of the membrane module applied. For example, surface water is characterized by high turbidity and natural organic matter (NOM) content compared with, for example, groundwater (wells), which on the other hand contain significant silica, iron, and manganese concentration. Thus, the required pretreatment technology may be quite simple, involving only non-enhanced filtration, that is, in the case of groundwater, or it may be more complex, that is, in the case of surface water (Bodzek and Konieczny, 2011; Jamaly *et al.*, 2014). Generally, the main aim of the raw water pretreatment is the prevention or limitation of membrane fouling and scaling. It should mainly assure the removal of suspended substances (suspensions, colloids), scale-forming compounds, and dissolved substances able to precipitate at membrane system operational conditions. The conventional preliminary treatment system may comprise all or a selection of the following (Bodzek, 1999; Bodzek and Konieczny, 2005, 2006; Jamaly *et al.*, 2014; Peñate and García-Rodríguez, 2012):

- removal of high molecular weight particles by means of sieving;
- chlorination used for raw water disinfection;
- oxidation and deep filtration for iron removal;
- alkalinity decrease by pH control;



- addition of anti-scalants in the form of complexing compounds, e.g. sodium hexamethaphosphate (SHMP) or EDTA and other anti-scalants;
- removal of chlorine from water using copper (II) sulfate or sodium hydrosulfite ( $\text{NaHSO}_3$ ), which eliminates the possibility of membrane damage with  $\text{Cl}_2$ ;
- active carbon adsorption in order to remove organic substances;
- disinfection using UV or ozone;
- final filtration directly before RO modules based on sand filters of gravitational type with various grain size or immersed type of small screen size.

The amount of the required chemicals depends on the composition of the raw water. In determining the water pretreatment technology, one should also consider: membrane material, module configuration, raw water quality, permeate recovery rate, and permeate quality (Bodzek and Konieczny, 2011).

It has already been accepted that fouling and scaling phenomena affect the membrane performance. In order to determine the severity of fouling caused by organic substances present in water, the silt density index (SDI) test is performed (Bodzek and Konieczny, 2005, 2011; Fritzmann *et al.*, 2007). The SDI test is based on the measurement of the time during which the membrane filter of pore size  $0.45\ \mu\text{m}$  becomes blocked while filtrating the investigated water at the pressure of 210 kPa. The most commonly used filters are those supplied by Millipore. The measurement comprises two stages, that is, the determination of time  $t_1$  necessary to collect  $500\ \text{cm}^3$  of the permeate, and the determination of time  $t_2$  necessary to collect the next  $500\ \text{cm}^3$  (or  $100\ \text{cm}^3$ ) portion of the permeate; the second measurement starts 15 min after the previous measurement ends. The SDI index is then calculated using the following relation:

$$\text{SDI} = \frac{1 - t_1/t_2}{t} \quad (8.6)$$

The SDI indicates the percentage permeate flux decrease at the unit of time. Its performance with a 15 min break (SDI 15) usually results in the value range 0–6.67 and it is a common indicator of colloidal substance content in waters (Bodzek and Konieczny, 2011). Some membrane producers, in order to guarantee proper membrane performance, strictly establish the permissible SDI value for the raw water. It can be found that hollow-fiber modules can be used for the treatment of water with SDI below 2, while for spiral-wound ones the value may reach up to 4 (Bodzek and Konieczny, 2005).

Recently, it has been shown that low-pressure driven membrane processes, that is, ultrafiltration (UF) and microfiltration (MF), are reliable methods of removal of suspended substances, and some organic and microbiological contaminants, including pathogens (Ebrahim *et al.*, 1997; Halpern *et al.*, 2005; Van der Bruggen and Vandecasteele, 2002; Van Hoof *et al.*, 1999). The use of MF/UF as a method of pretreatment of water before RO desalination enables a decrease in investment costs of 20% and 12.5% respectively for brackish and seawater desalination, compared with the cost of the systems based on conventional solutions. Moreover, traditional pretreatment methods require higher chemical doses and greater space as well as resulting in generation of poorer quality wastewater. Substantial savings can also be obtained in operating costs (Jamaly *et al.*, 2014; Van der Bruggen and Vandecasteele, 2002).

Microfiltration is known to effectively remove suspended substances, and thus it may be used to decrease SDI value. The energy demand of the MF process is relatively low; thus the cost of the method is comparable with that of groundwater pretreatment (Ebrahim *et al.*, 1997), while the cost of conventional surface water pretreatment is usually twice as high. MF permeate is characterized by satisfactory quality, low COD/BOD<sub>5</sub> ratio and low SDI index, compared with raw water parameters; however the permeate quality still strongly depends on the feed water properties. Seawater of good quality may undergo RO desalination at minimum pretreatment by means of MF and at sufficiently low costs (Bodzek and Konieczny, 2011). Dey *et al.* (2013) described the process of water desalination carried out in a pilot test at the Arabian Sea, in which tubular ceramic MF membranes (of pore size  $0.1\ \mu\text{m}$ ) of 19-channel configuration were used as a pretreatment before RO. The results showed an increase in the permeate flux to  $350\text{--}370\ \text{L m}^{-2}\text{h}^{-1}$ , decrease

in turbidity and SDI to 1.0 and  $<3$ , respectively, at the same transmembrane pressure of 0.12 MPa and feed preparation by pressurized sand filter filtration. Corral *et al.* (2014) ran competitive studies on the use of MF and a sand filter filtration as a pretreatment for RO desalination. They concluded that the MF filtrate SDI index was below 3, which significantly improved the RO membranes' performance over a long exploitation period. Despite the similar costs of MF and conventional filtration, the former technique is preferred due to the stability of filtrate quality and process capacity.

The quality of RO feed may be further improved by the replacement of microfiltration with ultrafiltration. UF membranes are found to remove not only suspended compounds, pathogens and bacteria, but also dissolved high molecular organic compounds, colloids and viruses. It requires the use of higher transmembrane pressures from 100–500 kPa; thus it also generates higher costs. Nevertheless, it has been shown that the use of UF as a pretreatment method still generates 10% savings in comparison with conventional techniques (Van Hoof *et al.*, 1999). The benefits may be further improved if one considers the quality of UF filtrate, that is, the RO feed. The obtained SDI values are always far below 2 and the ratio of COD/BOD<sub>5</sub> is improved due to the partial removal of dissolved organic substances (Van der Bruggen and Vandecasteele, 2002). As an example of the effective use of UF in water pretreatment before desalination, the results of pilot studies obtained during the North Sea water desalination should be examined (Murrer and Rosberg, 1998). The installation was equipped with a capillary UF module (capillary diameter 0.8 mm) by Norit and RO modules by FluidSystems Co., USA. The quality of UF permeate was as follows: turbidity  $<0.16$  NTU, dissolved organic carbon content  $0.7 \text{ mg L}^{-1}$ , dissolved substance content  $36,200 \text{ mg L}^{-1}$  and colloids content  $<15 \text{ mg L}^{-1}$ . The SDI index determined for the seawater was 5.5–6.2, while for UF permeate it was 2.8–3.3 (Dey *et al.*, 2013). The microbiological analyses showed the efficient removal of microorganisms via UF; thus the biofouling of RO membranes was also limited. The integrated system of UF-RO was also used to prepare water from seawater for Wangtan power plant, China. The quality of water after the UF pretreatment was as follows: NTU $<1$ , SDI $<3$ , at the filtrate recovery rate of 95% (Busch *et al.*, 2009a). Additionally, the frequency of RO membrane cleaning was also modified and the obtained permeate flux was in the range of  $9.5$  to  $16.5 \text{ L m}^{-2} \text{ h}^{-1}$ . Van Hoof *et al.* (1999) used a UF-RO system to perform water renovation from wastewater. The obtained results show that SDI after UF was equal to 1.8 at permeate flux  $22\text{--}25 \text{ L m}^{-2} \text{ h}^{-1}$  and the water recovery rate was 70%.

The technology of UF pretreatment may be improved by its combination with coagulation or adsorption on activated carbon. The results obtained for hybrid systems comprising coagulation and UF/MF compared with those obtained for direct membrane filtration showed that the latter method enabled the removal of organic substances at the level of 20%, while in the case of the former system it was 80–90% depending on the type of substance (Bodzek, 2013). The removal rate was found to be the function of coagulant dose, coagulant type, pH, temperature and mixing time and speed. The organic contaminants are adsorbed on the coagulant's flocks, which are then retained by the UF membrane. Chatkaew *et al.* (2011) found that a combination of PAC adsorption with UF membrane filtration was a sufficient method for feed preparation in RO desalination as it improves both the removal of organic substances (up to 70%) and permeate flux. Other studies show that the backflushing of PAC/UF systems was a very efficient method of permeate flux decline prevention and assured the production of high-quality RO feed, but at PAC doses not higher than  $20 \text{ mg L}^{-1}$  (Tomaszewska and Mozia, 2002).

The application of MF and UF improves investing and exploitation costs of the preliminary treatment system and widens the range of raw water types that can be further desalinated by means of RO (Bodzek and Konieczny, 2011; Jamaly *et al.*, 2014). The studies on the economic evaluation of UF application as a raw water pretreatment clearly show that the costs could be decreased, but only for long-period operations, as the membrane lifetime increased by 20–30% (Jamaly *et al.*, 2014). Voutchkov (2010) also showed that the use of UF and MF in water desalination systems significantly decrease the SDI index; thus RO membrane biofouling and cleaning frequencies were decreased to one or two per year, and thus membrane conservation costs were also lower (Pearce, 2008). However, conventional pretreatment systems may still be more attractive than non-conventional ones due to the costs and energy demand (Table 8.5) (Den and Wang, 2008).

Table 8.5. A comparison of the pretreatment costs using UF and conventional methods for water desalination plants with a capacity of RO 90,000 m<sup>3</sup> day<sup>-1</sup> (Den and Wang, 2008).

Type of cost	Method of pretreatment [US\$ m <sup>-3</sup> ]	
	Conventional	Ultrafiltration
Investment	0.22	0.23
Operational (O&M)	0.07	0.09
Energy	0.16	0.16
Chemicals	0.05	0.03
Operational variable	0.22	0.20
Total	0.51	0.52

Conventional systems turn out to be cheaper due to overall, unit and employment costs. However, the capacity of RO membranes to produce good quality water when preceded by conventional pretreatments is still limited. Generally, the preliminary raw water treatment based on UF/MF systems is strongly recommended for small- and medium-capacity plants (Peñate and García-Rodríguez, 2012).

Many studies show the reasonableness of the use of Nanofiltration (NF) as a pretreatment method applied to RO feed preparation in the desalination process, while the scaling up from pilot installations to commercial/industrial ones is now taking place (Abou-Elfetouh *et al.*, 2011; Al-Amoudi and Farooque, 2005; Al-Hajouri *et al.*, 2013; Al-Sofi *et al.*, 1998; Hassan *et al.*, 2000; Jamaly *et al.*, 2014; Peñate and García-Rodríguez, 2012). A detailed description of such a solution is presented in Section 8.4.2.

To sum up the various possibilities of RO desalination feed preparation, it must be noted that low investment costs and overall costs of water production will still favor the use of conventional solutions, while in regions of limited space access and high salt concentration in raw water the use of membrane technologies (UF/MF) will be recommended. The benefits of the exploitation of RO desalination combined with various pretreatment methods may be summarized as follows (Jamaly *et al.*, 2014):

- The use of raw water pretreatment favors the elongation of RO membranes' lifetime, increases their capacity, enables the production of better quality water and minimizes the membranes' chemical cleaning frequency. Non-conventional pretreatment methods improve operational costs due to the reduction in the amount of required chemicals and lower costs of continuous system operation.
- In order to produce good quality water from raw water of high salinity ( $>35,000$  mg L<sup>-1</sup>), membrane pretreatment methods (UF/NF) seem to be more effective than conventional techniques due to the efficient organic, colloidal and biological fouling limitation and lower pressure drop in the RO system, i.e. lower energy costs.
- MF is used to prepare water for RO desalination; however, significantly high pore size range of between 0.1 and 10 µm minimizes its efficiency in biofouling prevention and colloidal substances removal.
- The use of integrated UF-RO systems enables improvement in the quality of feed introduced to reverse osmosis, especially regarding the turbidity ( $<0.1$  NTU) and SDI ( $<1$  mg L<sup>-1</sup>), as well as microbiological parameters (bacteria, cysts, viruses).
- NF membranes can be used as a pretreatment method that offers a unique selectivity due to bivalent ions and medium molecular weight organic substances.
- Conventional pretreatment systems are characterized by lower operational costs than non-conventional techniques in the case of treatment of water of low-salinity. The quality of the water produced by RO combined with conventional methods is poorer than that obtained in combination with other membrane processes.

#### 8.2.2.4 Membranes

The progress in water desalination by means of RO is mainly expected in the field of the development of novel membrane materials, improvement of the existing systems and introduction of novel solutions in process performance as well as in the use of cheaper material for the construction of membrane modules (Geise *et al.*, 2014; Lee *et al.*, 2011; Peñate and García-Rodríguez, 2012; Subramani *et al.*, 2011; Xu *et al.*, 2013). The studies focused on these topics intend to bring profits to the desalination industry by the lowering of energy cost and required membrane area, simplification of preliminary treatment and supplying membrane that will be cheaper in production and exploitation (Lee *et al.*, 2011). The prospects of novel multifunctional membrane materials offering higher permeability, improved retention of ions and organic contaminants and operational reliability are considered.

Reverse osmosis has been the first membrane process to be applied in industrial-scale conditions. In the late 1950s, Reid and Breton (1959) stated that thin, symmetric, Cellulose Acetate (CA) membranes obtained by means of the phase inversion method could effectively retain particles of salts with the retention rate of 98%, but at extremely low permeate flux, that is, below  $10 \text{ mL m}^{-2} \text{ h}^{-1}$ . Next, in the 1960s, Loeb and Sourirajan (1961) first produced acetylcellulose asymmetric membranes which could be practically applied in RO and were characterized by 99% retention of NaCl and volumetric permeate flux level of  $0.35 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$ . The first non-cellulose-based asymmetric membrane developed by Hoehn and Richter (1980) was the Aromatic Polyamide (PA) membrane in the form of hollow fiber, supplied by DuPont under the trade name B-9 Permassep® for brackish water desalination. Despite relatively low fluxes given by this membrane, its commercial success has been possible due to the high packing density of the fibers, which have resulted in the satisfactory capacity of the whole module. Another breakthrough in commercial RO application has been the development of the procedure for composite membrane preparation by Cadotte (1977). Nowadays around 90% of all operated membranes are composite membranes (Matsuura, 2001). The production of this type of membranes is a multi-stage process, that is:

- separated production of the support layer;
- the preparation of the skin (active) layer made of different membrane material by means of *in situ* method based on:
  - the immersion of the support layer in the polymer solution (or spraying of the active polymer) followed by drying;
  - the direct polymerization on the support layer.

The present RO membranes market is dominated by composite membranes of polyamide (thin-film composite, TFC), comprising three layers: polyester support layer (thickness 120–150  $\mu\text{m}$ ), microporous transient layer, that is, polysulfone ultrafiltration membrane (40  $\mu\text{m}$ ), and a very thin active layer (skin thickness – 0.2  $\mu\text{m}$ ) (Lee *et al.*, 2011). The polyester used as a support cannot be directly bonded with the active layer due to the high irregularity and porosity. Hence, between skin and support layers the transient, polysulfone, microporous layer is introduced in order to ensure the resistance of the ultrathin skin layer to high pressures involved in the process. The formation of the skin layer relies on the coating of the transient layer with hydrophilic monomer (polyethyleneimine, PEI, 1,3-phenylenediamine or other) and immersing the material in hydrophobic monomer (toluenediisocyanate, benzo-1,3-carboxylic acid chloride or other) (Bodzek and Konieczny, 2011; Matsuura, 2001). Next, on the phase border polymerization process take place due to which this polymeric film is formed on the membrane surface. The extreme thickness of the active layer aims to minimize the hydraulic resistance during permeate transport and the size of the “pores” does not usually exceed 0.6 nm, which enables a high retention of salts (above 99%) to be obtained. Composite membranes are more chemically, mechanically and biologically resistant than cellulose acetate ones and are characterized by high independence of presence of contaminants, increased durability and easy cleaning (Fritzmann *et al.*, 2007; Lee *et al.*, 2011).

Many studies carried out over the last few decades have resulted in significant improvements in the properties and materials used in membrane production (Lee *et al.*, 2011). There are still many efforts devoted to the upgrading of RO membranes' morphology and structure, their functionality (permeability and selectivity) and resistance (mechanical, chemical and biological stability) (Geise *et al.*, 2014; Lee *et al.*, 2011). A significant improvement in the field of salt retention and permeability of RO membranes used to highly salted water desalination has been observed in recent years. In the 1980s RO systems used to seawater desalination required more than  $26 \text{ kWh m}^{-3}$  of energy. Nowadays, the average energy demand of such systems is only  $3.4 \text{ kWh m}^{-3}$  (Subramani *et al.*, 2011). Hence, there are still possibilities to upgrade RO membrane permeability by using novel materials even if they reveal increased salt permeation rate. The reduction in the costs of water production may in this case be found in energy savings, as there are lower exploitation pressures or increases in capacity and the installations operate at higher fluxes and water recovery rates. Moreover, membrane producers are still working on the development of membranes with high boron retention due to the need for a decrease in boron concentration in permeate, which results from the latest standards in this field (Bodzek, 2015). The most selective membranes reveal the stable retention of boron at the level of 90% and are suitable to be operated as a single-stage RO system.

New-generation membranes should be characterized by permeability twice as high as that of the osmotic membranes used nowadays (Subramani *et al.*, 2011), and the requirements for raw water pressure should be decreased at unchanged salt retention rate. Recent studies run on nanostructure osmotic membranes have revealed that they are characterized by an attractive permeability and many scientists find nanotechnology to be a method enabling revolutionary progress in the water desalination industry (Lee *et al.*, 2011; Subramani *et al.*, 2011). So far, such membranes are in the R&D phase and there are still many problems to be solved. To the main challenges may be included the high costs of nanomaterials and difficulties in procedures of commercially available nanomembranes. Moreover, the health and safety aspects of nanomembrane introduction to water production must be included due to the presence of nanoparticles. New-generation osmotic membranes can be divided into nanocomposite, nanotube and biomimetic types (Lee *et al.*, 2011; Subramani *et al.*, 2011).

The skin layer of nanocomposite RO membranes is formed by means of dispersion of zeolite or titanium dioxide nanoparticles in a conventional thin polyamide layer (Hoek and Ghosh, 2014; Jeong *et al.*, 2007; Lee *et al.*, 2011). The introduction of zeolite nanoparticles to the polymeric matrix doubles the permeate flux of RO membranes in seawater desalination compared with conventional membranes' capacity at the same salt retention level of 99.7%. The application of RO membranes based on nanocomposites also results in ca. 20% lower energy consumption (Subramani *et al.*, 2011). Despite the fact that nanocomposite RO membranes require much lower raw water transmembrane pressure than presently used membranes, long-term operation data for their use are not yet available. There are also no data on the chemical stability of zeolite particles in the polyamide matrix nor on boron retention (Subramani *et al.*, 2011). Nanocomposite-based membrane technology can now be found in the commercial testing phase.

The application of carbon nanotubes to desalination also leads to lower energy consumption than in the case of conventional systems of seawater desalination by means of RO (Corry, 2008; Lee *et al.*, 2011; Subramani *et al.*, 2011). The transport of water and ions passes through membranes formed of carbon nanotubes of diameter  $<2 \text{ nm}$ , which enables the desired salt retention to be obtained and even up to a tenfold increase in membrane permeability. This should result in 30–50% energy savings. The modeling of the process has shown that boron nitride nanotubes reveal even higher affinity to water transport than carbon nanotubes and may enable even up to 100% salt retention (Hilder *et al.*, 2009). As in the case of nanocomposite membranes, data on the long-term operation, scaling-up procedure and chemical and mechanical stability are unavailable for nanotube-based membranes.

Novel solutions in water desalination may also result in the use of biomimetic membranes (Bowen, 2006; Subramani *et al.*, 2011). Such membranes copy highly selective transport through natural cell membranes. The proteins involved in artificial membrane formation are called

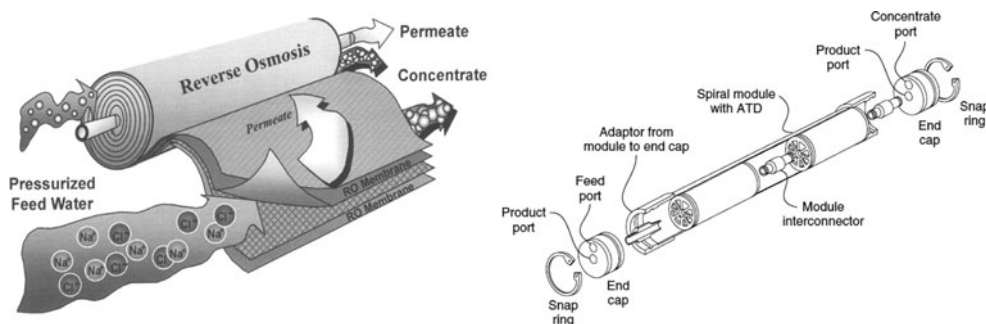


Figure 8.9. Spiral-wound module design (Al-Karaghoul and Kazmerski, 2013; Halpern *et al.*, 2005).

aquaporins, which reveal high and selective permeability of water, while the transport of ions is limited due to electrostatic repulsions that occur inside the channel (Subramani *et al.*, 2011). It is found that aquaporin-based membranes are a hundred times more water permeable than commercial RO membranes, which can lead to energy savings of up to 70% in the case of their commercial usage (Subramani *et al.*, 2011). It has been shown that highly permeable and selective membranes based on the introduction of functional aquaporin Z protein to novel triple block copolymer possess much higher water permeability than the conventional RO membranes (Subramani *et al.*, 2011). However, the particular difficulty of biomimetic membranes is connected to their damage affinity at high operational pressure conditions.

Nanocomposite membranes based on the zeolite films have lower water flux when compared with carbon nanotubes and aquaporin-based membranes. The latter show more potential due to their similarity to the RO membranes applied commercially at present. However, the economics of the process, covering the complicated synthesis procedure and additional energy demand of the introduction of nanoparticles to the skin layer, may be a problem. There exists a need for further R&D studies which will cover optimization of size and dose of nanoparticles, elimination of crystal defects and simplification of nanoparticles synthesis.

#### 8.2.2.5 Membrane modules

In RO systems used to brackish and seawater desalination, hollow fibers or spiral-wound membrane modules of cellulose acetate, aromatic polyamides or composite membrane are used (Al-Karaghoul and Kazmerski, 2013; Ivnitskya *et al.*, 2005). In the initial stage of membrane water desalination, hollow-fiber modules supplied by DuPont, and nowadays also by Japanese company Toyobo, have been used (Corry, 2008; Fritzmann *et al.*, 2007). An important event in the development of membrane-based water desalination was the replacement of widely used hollow-fiber modules with spiral-wound modules of high capacity in the 1970s and 1980s (Bodzek and Konieczny, 2005, 2011; Fritzmann *et al.*, 2007; Wilf, 2007). Most of the presently operated RO water desalination installations are based on spiral-wound membrane modules (Fig. 8.9) (Al-Karaghoul and Kazmerski, 2013; Halpern *et al.*, 2005). They are characterized by a better set of parameters, such as the ratio of permeability to packing density, fouling control and exploitation procedure, as well as easy scaling up, cheap costs of exchange, and, most importantly, the cheapest configuration of TFC membrane-based modules (Baker, 2001; Wilf, 2007). Usually six to eight identical modules are organized in a series mode using central pipes for permeate outflow, which are placed in a cylindrical pressurized vessel (Fritzmann *et al.*, 2007). Even though the spiral-wound configuration of membranes was developed several dozen years ago, improvement works are still being carried out, especially in the fields of spacer size, feed inflow channels and tanks exchange, construction materials and module joints, which all lead to a decrease in process fouling. Polyamide membranes in spiral-wound modules are the dominant player in the NF/RO market with a share of 91% (Lee *et al.*, 2011).

Table 8.6. Membranes and modules for RO available on the world market (Lee *et al.*, 2011).

Membrane module name	Membrane material and module type	Permeate flux [m <sup>3</sup> day <sup>-1</sup> ]	Salt rejection [%]	Specific energy consumption <sup>d</sup> [kWh m <sup>-3</sup> ]
Dow Filmtec <sup>TM</sup> 8-in. SW30HRLE	TFC cross-linked fully aromatic polyamide spiral-wound	28.0 <sup>a</sup>	99.6–99.75 <sup>a</sup>	3.40
Hydranautics 8-in. SWC4+	TFC cross-linked fully aromatic polyamide spiral-wound	26.4 <sup>b</sup>	99.7–99.8 <sup>b</sup>	4.17
Toray 8-in. TM820C	TFC cross-linked fully aromatic polyamide spiral-wound	19.7–24.6 <sup>a</sup>	99.5–99.75 <sup>a</sup>	4.35
Toyobo 16-in. HB10255	Asymmetric cellulose triacetate hollow-fiber	60–67 <sup>c</sup>	99.4–99.6 <sup>d</sup>	5.00

<sup>a</sup>test condition: 32 g L<sup>-1</sup> NaCl; 5.5 MPa; pH = 8; 8% recovery; <sup>b</sup>test condition: as in (a) but pH = 7; 10% recovery; <sup>c</sup>test condition: as in (a) but 30% recovery; <sup>d</sup>different operation parameters.

There are four main companies that supply RO membrane modules to industrial seawater desalination plants, that is, DOW, Toray, Hydranautics and Toyobo. Their characteristics are given in Table 8.6.

Recent studies on the innovation and improvements in construction of spiral-wound module elements concentrate on the assurance of larger filtration at unchanged module volume and on optimization of hydrodynamics to minimize concentration polarization effects. Such elements are characterized by increased capacity accompanied by higher salts retention (Panete and García-Rodríguez, 2012). Another purpose of all studies and actions undertaken in the field of RO membrane module improvements is energy saving. The most significant actions are the design, creation and configuration of systems dedicated to membrane modules (large-diameter spiral-wound modules, number and type of membranes and modules in one pressurized tank, improved feed/permeate spacers), upgrades in two-stage desalination systems, high quality of involved pumps and energy recovery.

Membrane modules of 8 inches in diameter are the standard RO/NF systems elements involved in water desalination and renovation. In industrial-scale RO desalination plants, where such modules are used, costs of desalination are high, as the number of elements, pressurized tanks, piping and joints must directly increase with the desired capacity increase. Hence, the consortium of membrane suppliers, that is, Dow Filmtec<sup>TM</sup>, Hydranautics, Toray America and Trisep, have run research and evaluation works on novel RO modules of diameter larger than the standard 8 inches. Hydranautics and Dow (Filmtec<sup>TM</sup>) have developed new modules of 16 inches diameter, application of which reduces investment and exploitation costs of RO water desalination installation by 20% (Ng *et al.*, 2008; Panete and García-Rodríguez, 2012; Yun *et al.*, 2006). Modules of 16 inch diameter possess a large active membrane area and capacity even 4.3 times greater than standard SWRO modules. Recently the Koch company has even introduced 18 inch diameter modules under the trade name MegaMagnum®, and this diameter size is defined by the company as the optimum one (Lee *et al.*, 2011; Panete and García-Rodríguez, 2012). The appearance of new-size membrane modules has caused the commercial developments of elements and pressurized tanks dedicated to two sizes of systems (Panete and García-Rodríguez, 2012). Gottberg (2004) estimates that a typical desalination system of capacity 3789 m<sup>3</sup> day<sup>-1</sup> equipped with 8-inch modules must comprise 25 pressurized tanks and 175 other elements, whereas the same capacity system based on an 18-inch module requires only five tanks and 25 elements. The number of elements with “o-ring” type sealing is decreased 14 times, which significantly reduces the number of outages caused by failures of this equipment. The special requirements for 18-inch systems are ca. 50% smaller compared with 8-inch devices. Additionally, the lower number of joints and the module size itself assures the reduction of capital costs.

The design and configuration of membrane modules have a significant impact on the process capacity and economics of a water RO desalination plant (Subramani *et al.*, 2011; Wilf and Bartels, 2005). The conventional membrane modules in water desalination are usually configured as a two-stage system of six elements placed in one pressurized tank. Such solutions are characterized by high raw water and concentrate flows, which avoids the severity of concentration polarization, but at increased raw water pressure, which must be used to compensate pressure drop within the modules. The innovations also focus on the use of single-stage systems to desalinate water of high salinity rate, or, in some cases, to introduce seven or eight modules to one pressurized tank (Petry *et al.*, 2007; Wilf and Bartels, 2005). Such proposals result in an energy demand decrease of 2.5% (Wilf and Bartels, 2005). A reverse osmosis system based on the six-elements configuration requires 34% more pressurized tank than eight-elements configuration, considering the same separation area (Wilf and Bartels, 2005). Additionally, the extended system possesses other benefits, for example, higher concentrate flow rate accompanied by lower concentration polarization effect and higher capacity and, thus, a smaller number of tanks and 8% decrease in investment costs (Panete and García-Rodríguez, 2012).

Another modification in RO system design is the use of membranes of different properties in the same pressurized tank (Panete and García-Rodríguez, 2012). Usually membranes supplied by one producer are involved in a system; however, there exists the possibility of designing several-stage RO systems in which membranes supplied by different producers are used in one pressurized tank. The application of such a solution in conventional RO desalination plants enhances the performance and conservation of the system as well as giving 5–8% of capital cost savings, but with the highest share of membranes supplied by the main producers (Busch *et al.*, 2009b; García-Molina *et al.*, 2009; Panete and García-Rodríguez, 2011, 2012). Examples of plants involving such a system configuration are SWRO Jubail (Panete and García-Rodríguez, 2012) or SWRO Las Palmas III (Panete and García-Rodríguez, 2011). However, the disadvantage of the multi-type membrane system is that not all producers apply the same joints to the connection of particular elements.

A decrease in fouling severity as well as exploitation at the higher critical flux (Winters, 1997) may be obtained when the proper construction of spacers at the feed side is applied. It results in an increase in the raw water and concentrate flows, minimizes the pressure drop within the module and enables more efficient cleaning of membranes. Hence, spacers of thickness ranging from 0.66 to 0.86 mm are used, which increases the feed channel in comparison with separating elements of conventional size. The larger spacers are usually applied in the treatment of brackish surface water, which contains significant amounts of colloids and is prone to biofouling. Feed side spaces, used in most spiral-wound modules, are made of polyolefin-based materials of high quality, which are tolerable to high pressure and low pH used during module cleaning (Panete and García-Rodríguez, 2012). Recently, polypropylene spacing elements have been tested due to the high chemical stability, low costs and specific properties of the material (Escobar, 2009). There are also some studies devoted to the modification of surface of conventional spacer material. The exploitation of spiral-wound modules of low fouling affinity decreases cleaning costs as well as operational and total costs of the installation (Schwinge *et al.*, 2004).

As the demands on the quality of desalinated water are very restricted, mainly due to the boron concentration, the use of multi-stage RO systems (Sauvet-Goichon, 2007) results in a decrease in overall energy demand (Panete and García-Rodríguez, 2012; Subramani *et al.*, 2011). In such installations, the second stage of the filtration is used to polish the permeate obtained in the first stage (Panete and García-Rodríguez, 2012). The usage of modules of high capacity in the first stage of the treatment means that the raw water pressure, as well as the energy demand, may be significantly decreased. According to the lower contaminant retention revealed by such a module type, compared with a standard desalination module, the requirements of the second-stage membranes may be sharpened. However, the benefits obtained at the first stage easily compensate those additional capital costs. Another solution is based on the partial introduction of the first stage permeate to the second-stage polishing (Zhu *et al.*, 2009a). In the conventional system, the total volume of the purified stream obtained in the first stage is directed to the second



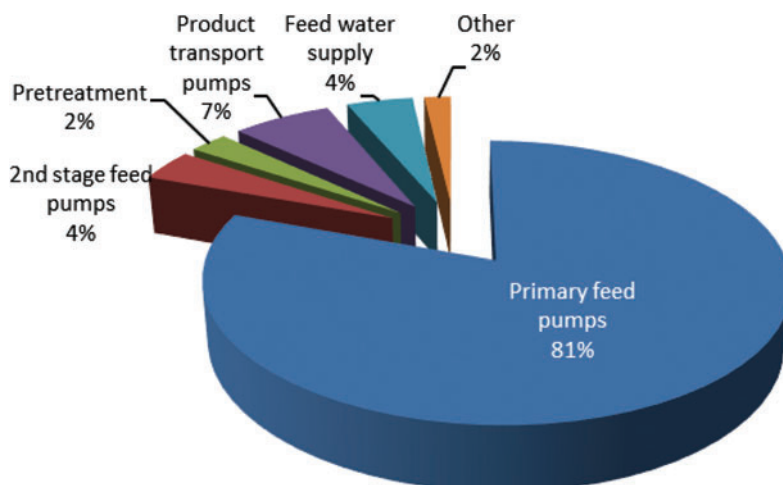


Figure 8.10. Distribution of energy consumption in two-stage desalination system using RO (Wilf and Bartels, 2005).

stage, which, due to the already decreased salt content, requires lower pressures. The decrease in energy demand by RO desalination systems may also be obtained using two-stage hybrid systems with concentrate staging (Subramani *et al.*, 2011; Zhu *et al.*, 2009b). The first stage of such a system is equipped with membranes of high retention dedicated to brackish or seawater desalination, while the second stage involves only membranes for seawater desalination. Such a system design results in the application of lower transmembrane pressures due to the lower hydraulic resistance of the membrane (Subramani *et al.*, 2011). The two-stage configuration may also be made using nanofiltration (NF), which also significantly improves the energy efficiency (Subramani *et al.*, 2011). The energy demand established for the two-stage system with NF has been estimated at  $2.06 \text{ kWh m}^{-3}$ , while for the two-stage RO system with partial permeate polishing it is  $2.32 \text{ kWh m}^{-3}$ , which corresponds to a lower energy demand of 12% and 5%, respectively (Subramani *et al.*, 2011).

Most of the energy required by the RO desalination system is used by feed pumps, in preliminary treatment of the raw water, produced water and chemical transport and purified water distribution. The usage of energy in the two-stage seawater desalination system is shown in Figure 8.10. It can be seen that more than 80% of the energy is consumed by the basic feed pump (Wilf and Bartels, 2005). Even though the flows and pumping system philosophy are clarified in the specification of an RO system project, the choice and the exploitation of pumps and other system elements play a very important role in overall energy demand reduction in the plant. In order to obtain the highest capacity of pumps, one should check the energy efficiency and savings of the pumping system operation and use the motors and drives of variable frequency (Manth *et al.*, 2003). Energy-saving operation is obtained by using the optimum pump rotary speed application for the highest capacity (Subramani *et al.*, 2011) by introducing a pump electrical motor with a variable-frequency drive (Torre, 2008). All the abovementioned solutions may be applied to improve the device's efficiency and energy consumption.

#### 8.2.2.6 Energy recovery

In modern installations for water desalination it is possible to recover 30–40% of the energy of high-pressure retentate by means of special mechanical devices (Fig. 8.11) (Andrews and Laker, 2001; Fritzmann *et al.*, 2007; Subramani *et al.*, 2011; Wang *et al.*, 2004). Such an energy recovery system is the main way of reducing the costs of desalted water and makes this method a serious

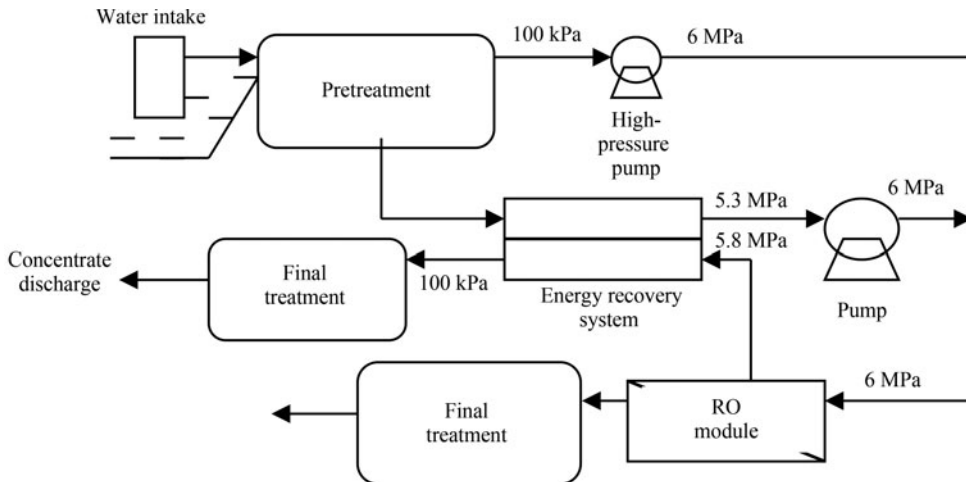


Figure 8.11. The idea of energy recovery in the installation of desalination with RO method (Andrews and Laker, 2001; Fritzmann *et al.*, 2007; Subramani *et al.*, 2011; Wang *et al.*, 2004).

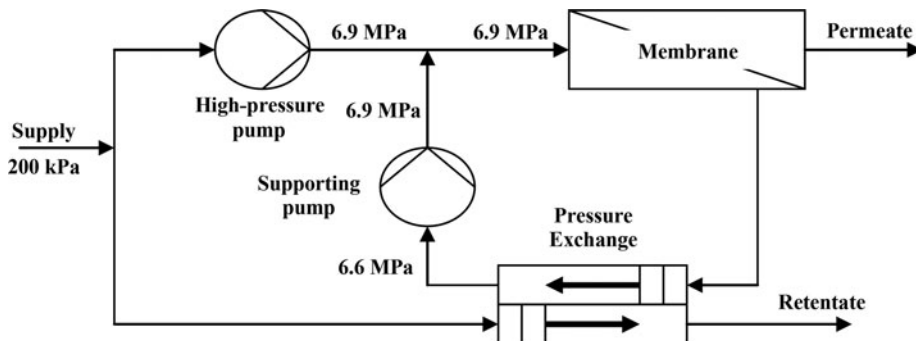


Figure 8.12. Diagram of the direct exchange of the retentate pressure on mechanical energy (Fritzmann *et al.*, 2007; Greenlee *et al.*, 2009).

alternative for conventionally used solutions. The idea has also resulted in the development of special mechanical systems dedicated to the transport of energy present in the retentate to the RO feed water. Before the concentrate is removed from the system, its pressure is recovered by its direction to the energy recovery system. In solutions with energy recovery systems it is possible to decrease the overall energy demand to  $2\text{--}4\text{ kWh m}^{-3}$  in the case of seawater desalination, and to  $<1\text{ kWh m}^{-3}$  for brackish water treatment systems (Fritzmann *et al.*, 2007; Subramani *et al.*, 2011). The amount of the recovered energy depends on the equipment type and efficiency.

Systems used in energy recovery from retentate applied in an RO desalination plant may be divided into two groups (Andrews and Laker, 2001; Fritzmann *et al.*, 2007). The first one includes rotary devices (efficiency of 96–98%), in which the hydraulic energy of the retentate is directly transformed into mechanical energy used in pressure pumps (Fig. 8.12) (Fritzmann *et al.*, 2007; Greenlee *et al.*, 2009).

In those solutions, only part of the raw water has to be compressed in the high-pressure pump, whereas the additional pump is required before the raw water entrance to the system, as there are pressure drops occurring in the RO system itself and in pipes. Most seawater desalination facilities are already equipped with class I devices (Subramani *et al.*, 2011).

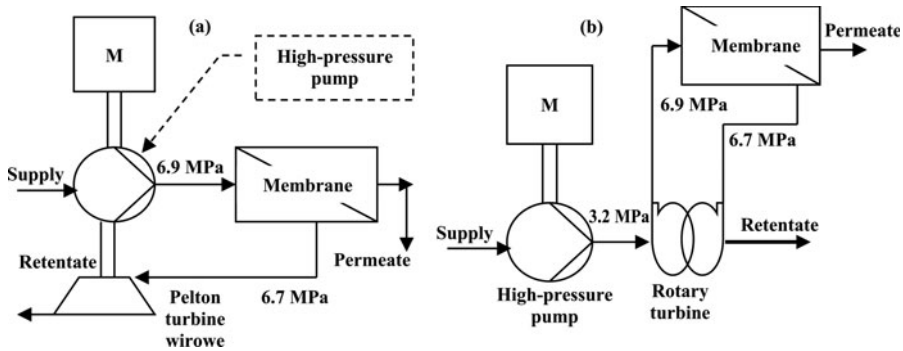


Figure 8.13. Diagram of retentate pressure exchange on mechanical energy using (a) Pelton turbine, (b) rotary turbine (Fritzmann *et al.*, 2007).

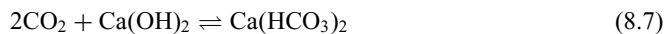
Class II devices use the hydraulic energy of RO concentrate in the two-stage process, in which firstly the energy is converted into centrifugal mechanical force, and then transformed again to hydraulic energy (Greenlee *et al.*, 2009). In this solution, Pelton or rotary turbines are used (Fig. 8.13) (Fritzmann *et al.*, 2007).

In Pelton's turbine, the high-pressure stream (concentrate) is introduced to the turbine by the nozzle, which speeds up the rotor, and then transports the rotary force to the shaft which connects the turbine and the high-pressure pump (Fig. 8.13a). The rotary turbine comprises the pump and the turbine connected in one device by means of the rotor (Fritzmann *et al.*, 2007). The turbine rotor transforms the retentate energy into mechanical energy present in the feed solution (Fig. 8.13b). The centrifugal recovery systems of class II are characterized by limited capacity (Fritzmann *et al.*, 2007). The commercially available Pelton's turbine efficiency may reach up to 90%, while the overall mechanical efficiency of conjugated turbine pumps varies from 75 to 85% (Stover, 2007).

#### 8.2.2.7 Final treatment of desalinated water

The treatment of water after desalination depends on its further use. The crude permeate obtained from RO does not meet the standards on drinking water established in Poland and in the European Union (RMZ, 2015), especially due to the low dissolved-substances content, which makes it highly corrosive and dangerous for human health (Fritzmann *et al.*, 2007). The final treatment of water after RO is a very important part of the desalination facility.

Water dedicated to human consumption and to municipal purposes should be degassed (decarbonized) and should undergo pH improvement and chlorination (Subramani *et al.*, 2011). In order to obtain the proper alkalinity of water, calcium hydroxide solution is added and it is then dissolved with the use of carbon dioxide according to the following reaction (Fritzmann *et al.*, 2007; Subramani *et al.*, 2011):



Another solution is the use of limestone for increasing water remineralization and alkalinity, dissolution of which is also enhanced by means of  $\text{CO}_2$  (Fig. 8.14). Hence, the water is mineralized according to the following reaction:



Unbounded carbon dioxide must be neutralized by the addition of NaOH or  $\text{Na}_2\text{CO}_3$ , which simultaneously enables the proper pH and alkalinity of the desalted water to be obtained.

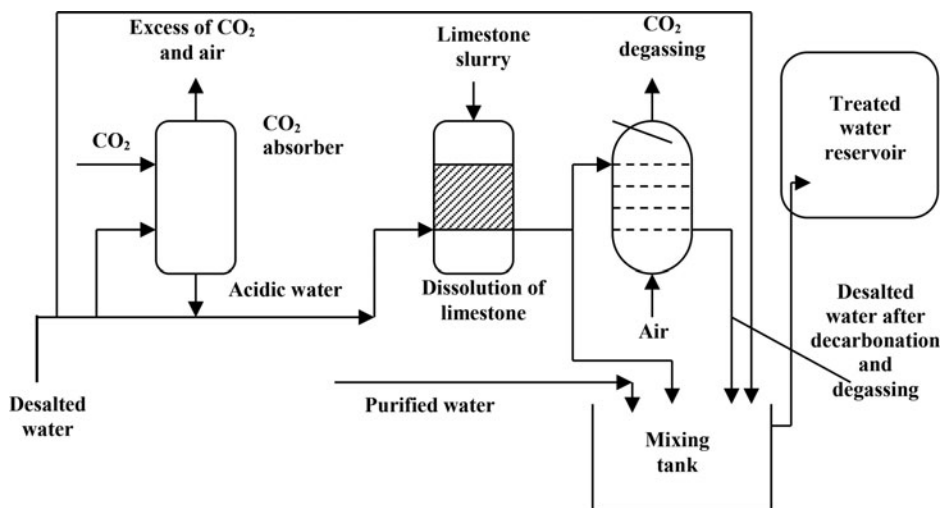


Figure 8.14. Final treatment of desalted water using limestone (Fritzmann *et al.*, 2007).

The final stage of the water preparation is its disinfection. The most common method used for that purpose is chlorination, which aims to prevent the growth of microorganisms in the water during its distribution or storage (Fritzmann *et al.*, 2007).

### 8.2.3 Electrodialysis

Another membrane technique that can be used in brackish and seawater desalination is electrodialysis (ED) and electrodialysis reversal (EDR) (Fritzmann *et al.*, 2007). Electrodialysis was developed in the 1950s and was mainly applied to brackish water desalination. In the process, ion-exchange membranes (cation exchange and anion exchange) placed in an electric field are used. They aim to limit the transport of cations or anions (Bodzek and Konieczny, 2011) present in the salted water.

Ion-exchange membranes are semipermeable barriers obtained from spatially cross-linked polymers with ion-exchange functional groups built within the polymeric structure. Cation exchange membranes contain negatively charged groups (e.g.  $\text{SO}_3^{2-}$ ) strongly bonded to the polymeric network, while anion exchange membranes possess positively charged groups (e.g.  $\text{NH}_3^+$ ). Ion-exchange membranes should reveal high selectivity in comparison with only one type of ion, low electric resistance, high mechanical (shape) and chemical resistance as well as large exchange capacity (Strathmann, 2004).

Electrodialysis is used to separate the components present in liquid solutions and the transport of ions through the membranes occurs at the influence of the external electrical field (Bodzek and Konieczny, 2011; Narębska, 1997; Strathmann, 2004; Wiśniewski, 2001). In the electrodialysis process an electrodialytic pile (electrodialyzer) comprised of several hundred cation and anion exchange membranes installed in parallel is used (Fig. 8.15). Membranes are separated by means of spacers, and the overall system is placed in stretching frames. The idea of the ED process relies on the directed ions flow at the constant electric field. Electrolyte ions easily pass through the membranes, while heavy colloids of greater particle sizes are retained on the membrane surface. Due to the electric current flow, differentiation of the solution composition in the electrodialyzer chambers occurs. Membrane, that is, cation exchange (enabling only cations flow) and anion exchange (also enabling anions flow), barriers placed alternately in the electrodialyzer separate the device into desalination chambers (dialysate chambers) and concentrated

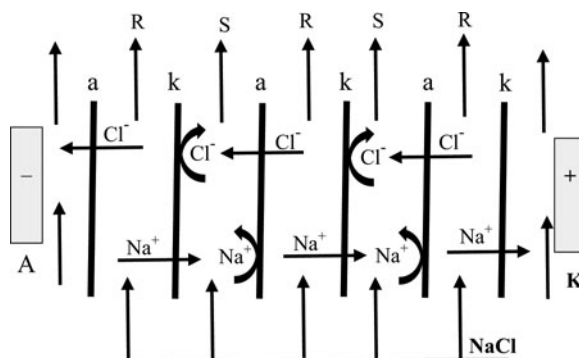


Figure 8.15. Principle of conventional electrodialysis of the sodium chloride solution: a: anion-selective membrane; k: cation-selective membrane; R: desalted solution (diluted); S: solution (Wiśniewski 2001).

solution chambers (concentrate chambers) (Bodzek and Konieczny, 2011). The transport of the electrolyte occurs only in the direction from the diluted solution to the concentrated solution. Ions migrate to proper electrodes through membranes, which are able to stop or permeate them, and thus the concentrate containing concentrated salts and salt-free product are obtained in alternated electro-dialyzer chambers. Feeds introduced to every chamber (including electrode chambers) are circulated in order to equalize concentration, and thus to limit the impact of concentration polarization.

As a result of ions flow during the process, a drop in dialysate conductivity may be observed, due to which the stepwise decrease of current intensity accompanied with a process efficiency decrease is observed. The increase of the voltage on the electrodes assures the proper current intensity, but it also causes an energy consumption increase. The effectiveness of desalination and the concentration of the aqueous inorganic salts solution is described by means of the following indicators: process selectivity, current efficiency and unit costs. Electrodialysis selectivity is mainly determined by properties of the applied ion-exchange membranes. The quantitative measure of membrane selectivity is the number of counter ions transported, that is, the ions of the charge opposite to one of the functional groups present in the polymeric matrix of the membrane (Narębska, 1997). The current efficiency describes the part of the current flowing through the electrodialyzer which is used to transport ions from diluate to concentrate. It is defined as the ratio of the number of moles of a substance which is transported out of the desalinated solution by ion-exchange membrane to the number of moles calculated using Faraday's law (Narębska, 1997; Strathmann, 2004; Wiśniewski, 2001).

In Figure 8.16 the scheme of the installation for the electro dialysis process is shown (Bodzek and Konieczny, 2011). ED installation comprises the device for preliminary water preparation, the membrane pile, a low-pressure circulation pump, a constant current source and a final water treatment section. In order to assure the supply of electrical current to the electrodes, rectifiers are usually used. The final water treatment section includes water stabilization by means of degassing and pH correction and the section for water preparation to distribution. The capacity of a typical electro dialysis plant varies from 2 to 145,000 m<sup>3</sup> day<sup>-1</sup> (Al-Karaghoul and Kazmierski, 2013). The main advantages of ED are: decreased number of unit operations, elimination of additional reagents used, limitation of product losses and minimization of environmental dangerous side streams. There are also some disadvantages, including the non-ideal selectivity of membranes and the need for preliminary treatment of the raw water. The latter operation aims to prevent membrane blockage with higher molecular weight ions as well as the precipitation of carbonates and sulfides and the removal of non-ionized substances (silica, bacteria and insoluble organic compounds). However, the preliminary treatment is also not run in a perfect way; thus the periodic removal

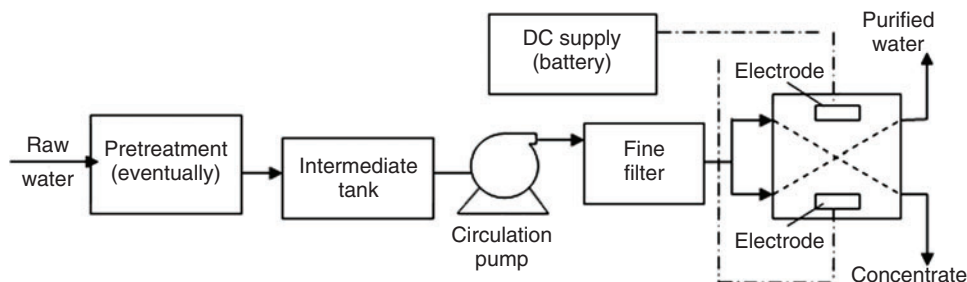


Figure 8.16. Diagram of an installation for the electrodialysis process (Bodzek and Konieczny, 2011).

of deposits from the ED system must be carried out. An alternative solution for ED considering fouling and scaling may be electrodialysis reversal (EDR), in which the direction of current flow is periodically switched (which results in the elongation of the membrane lifetime and hence costs reduction). EDR assures the removal of colloids and eventually freshly precipitated deposits, and thus it prevents membrane blockage. The electrical energy is the only type of energy required in the ED process, including DC used for the electrodes and AC for the pumps. In the case of raw water of low-salinity level ( $<2500 \text{ mg L}^{-1}$ ) the energy demand revealed by the ED unit varies from  $0.7$  to  $2.5 \text{ kWh m}^{-3}$ , while at salt concentration between  $2500$  and  $5000 \text{ mg L}^{-1}$  the range is  $2.64$ – $5.5 \text{ kWh m}^{-3}$  (Al-Karaghoul and Kazmierski, 2013).

The ED position on the market has been assured by the company Ionics after it developed a process with changeable polarization, that is, electrodialysis reversal (EDR) (Narebska, 1997; Strathmann, 2004; Wiśniewski, 2001). In this method, the current flow direction is changed 3–4 times per hour, which causes a change in direction of ions flow, and thus the diluate chambers become concentrate chambers and the concentrate chambers become timely diluate chambers. Such a system operation assures the removal of colloids and deposited precipitates, and thus it prevents membrane blockage and enables the process to be run at high oversaturation with calcium sulfates and calcium carbonate without the need for addition of chemicals to improve the solubility of those compounds. EDR widens the range of ED use to waters of higher contamination with inorganic and organic compounds, elongating the membrane lifetime and reducing costs.

The main field of use of ED with monopolar membranes is the desalination of brackish waters (Bodzek and Konieczny, 2011; Kim, 2011; Ortiz *et al.*, 2005; Tsiakis and Papageorgiou, 2005) containing  $1000$ – $5000 \text{ mg L}^{-1}$  for potable water production. If the concentration of salts in raw water remains in the range of  $1000$ – $2000 \text{ mg L}^{-1}$ , it is thus possible to produce desirably purified water by means of a single-stage system at a water recovery rate of up to  $85\%$  (Tsiakis and Papageorgiou, 2005). The highest number of installations of brackish water desalination by means of ED can be found in the USA, Japan and China (Wiśniewski, 2001). In those installations, the water desalination is run on the basis of EDR, which allows fouling and scaling to be prevented in the electrodialyzer's chambers. In the USA, there are several dozens of installations for production of drinking water from brackish water by means of the EDR method with a total capacity of  $150,000 \text{ m}^3 \text{ day}^{-1}$  (Leitner and Leitner-Murnay, 1977). The ED process is one of the main methods used in Japan for potable water production from brackish water. One of the largest installations has been operated since 1990 in Oshima, Tokyo (Leitner and Leitner-Murnay, 1977). Raw water of salinity  $1600 \text{ mg L}^{-1}$  is treated via a two-stage ED system. The capacity of the installation is established at  $1850 \text{ m}^3 \text{ day}^{-1}$  of usable water of final salt concentration ca.  $420 \text{ mg L}^{-1}$  and the water recovery rate obtained in the process reaches up to  $86\%$  (Hamada, 1995). The EDR process has already been successfully used for 30 years in China for desalination of brackish water with sufficiently high sulfate hardness (Song *et al.*, 1995). There are several dozen installations operating in the country with total capacity of up to several thousand  $\text{m}^3 \text{ day}^{-1}$ , which are used to produce industrial-grade desalinated water.

The electrodialysis process can also be used in seawater desalination, but in this case the multi-stage process configuration enabling usable water production (including potable water) of salinity ca.  $700 \text{ mg L}^{-1}$  at raw water salt content of  $35,000 \text{ mg L}^{-1}$  must be used (Bodzek and Konieczny, 2011). The costs of the process are higher, as the energy demand increases and it is proportional to the amount of salt transported through the membranes. Nevertheless, the two-stage configuration of electrodialysis is one of the most economically attractive desalination processes in which raw water of high salinity level (i.e. seawater) is used and the energy demand level is acceptable (Ryabtsev *et al.*, 2001, 2002). In the first process stage at optimal membrane load, most of the salt is removed (ca. 70% or more) and brine solution of boundary concentration (i.e. of conductivity 70–80% higher than raw water of salinity  $20\text{--}40 \text{ g L}^{-1}$ ) and diluate solution of salt concentration  $4\text{--}6 \text{ g L}^{-1}$  are obtained. The dialyzate is demineralized during the second stage of the process, which, contrary to conventional ED, enables the production of potable water using the electrodialysis method (Ryabtsev *et al.*, 2002). Such a solution results in the reduction of investment and operational costs and a decrease in unit raw water usage. This type of installation with capacity of  $200 \text{ m}^3 \text{ day}^{-1}$  is operated in Xisha islands, China. In the installation, 10 electrodialyzers operating in series, containing 200 to 300 chamber pairs each, are used (Xiujuan *et al.*, 1995). The cost of the water production is equal to  $0.5 \text{ US\$ m}^{-3}$  and it is five times lower than the cost of water transportation using sea transport.

There have also been some studies on the possibility of using ED in brackish industrial wastewater desalination, salt production and recovery of organic acids from salty waste solutions (Kim, 2011).

It should be noted that the costs of production of usable water in plants equipped with the EDR technique are comparable with costs obtained for the RO method. The main advantage of EDR over RO is the possibility of direct water production of sufficient salinity water and higher water recovery rates (Thompson *et al.*, 1977). The process is uneconomic at high salt concentrations, but it becomes cost-attractive in the case of brackish water (i.e. of salt concentration below  $6000 \text{ mg L}^{-1}$ ) desalination. At low concentration of salts in water ED/EDR is more profitable than RO and it is usually used in the chemical and petrochemical industries for desalination of diluted solutions and streams containing organic substances (Fritzmann *et al.*, 2007; Van der Bruggen and Vandecasteele, 2002). The process can also be used in desalination of water containing  $3\text{--}8$  ( $10$ )  $\text{g L}^{-1}$  of salts, but it is not recommended for seawater desalination (Strathmann, 2004).

Studies on the possibility of an increase in ED/EDR effectiveness during water desalination have been run by Turek (2002a, 2002b, 2004) and Turek and Dydo (2003a), in which they have analyzed phenomena occurring in adjacent hooding dilute and concentrate chambers depending on the solution concentration difference and distance between membranes. They have proposed countercurrent power of electrodialyzer chambers and the use of a net of thickness  $0.19 \text{ mm}$  made by means of weaving techniques as a spacer. The study has shown that the use of this type of spacer enables an increase to be obtained in boundary current density in comparison with a conventional spacer of the same thickness (Turek and Dydo, 2003a), and the hydraulic resistances observed within the electrodialyzer are smaller. The developed spacer has been used in studies of electrodialytic desalination of seawater using a two-stage system equipped with two electrodialyzers of countercurrent power. The study has shown that it is possible to produce diluate of salt concentration  $0.45 \text{ g L}^{-1}$  at unit power consumption of  $6.6\text{--}8.7 \text{ kWh m}^{-3}$ , that is, much lower than in a conventional ED system ( $16\text{--}24.3 \text{ kWh m}^{-3}$ ). The cost of the desalination has been estimated at  $1.05 \text{ US\$ m}^{-3}$ . It is comparable with that of RO and distillation. Hence, it has been revealed that, in terms of costs, ED used in water production from seawater in small- and medium-scale plants may soon become a serious alternative to RO and evaporation systems (Turek, 2002a).

#### 8.2.4 Membrane distillation

Membrane distillation (MD) is a relatively new, promising separation technique, on which the first patents and publications already appeared in the 1960s (Tomaszewska, 2009). An increase

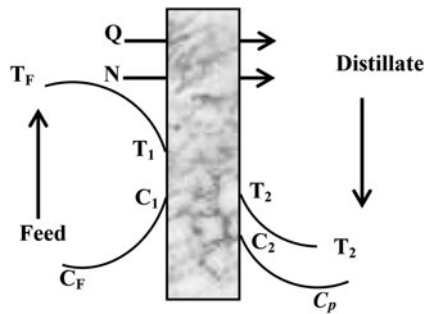


Figure 8.17. The principle of direct contact membrane distillation (D: distillate, N: feed, C: concentration,  $T$ : temperature,  $p$ : vapor pressure,  $Q$ : heat).

in interest in MD started in the 1980s, and was accompanied by membrane production developments and improvements in construction of membrane modules. Many advantages of membrane distillation have been highlighted, especially the possibility of low parameter heat and sun and geothermal energy use (Tomaszewska, 2009). Despite a wide interest in this technique so far MD has not yet reached commercial application to water desalination, mainly due to the lack of proper membranes and negative opinions on the economics of the process (Tomaszewska, 2009).

Membrane distillation (MD) is the process of evaporation through porous, lyophobic membrane, which acts only as a non-selective physical barrier (Alkhudhiri *et al.*, 2012; Gryta, 2012; Khayet and Matsuura, 2011; Tomaszewska, 1996, 2014; Wang and Chung, 2015). The feed solution is in direct contact with the membrane surface, which separates aqueous solutions of various temperatures and compositions (Fig. 8.17) (Bodzek and Konieczny, 2011). Vapor particles diffuse through membrane pores and then, independently of the MD module configuration, their condensation on another membrane side occurs or permeate in the gaseous form is taken out of the device and the condensation is carried out outside the module. The driving force of the process is the difference in vapor pressures, which results in temperature difference at both membrane sides, whereas the transport direction is from the warmer side to the colder side.

The collection of permeate obtained in the MD process can be made in different ways, (Fig. 8.18) (Alkhudhiri *et al.*, 2012; Khayet and Matsuura, 2011; Wang and Chung, 2015). In direct contact membrane distillation (DCMD) (Fig. 8.18a) the vapor passing through the membrane undergoes condensation directly in the distillate, which is also in contact with the membrane surface. In air-gap membrane distillation (AGMD) the permeate condensates at the surface of a plate cooled with water, which is separated from the membrane by means of an air gap (Fig. 8.18b) and the condensed permeate has no direct contact with the membrane surface.

In sweeping gas membrane distillation (SGMD) (Fig. 8.18c), permeate is taken out of the module by means of sweeping gas and its condensation is run outside the module. In vacuum membrane distillation (VMD) (Fig. 8.18d), the vacuum is created at the permeate side of the membrane and the permeate condensation is carried out outside the module.

One of the available membrane distillation configurations is also osmotic membrane distillation, known also as osmotic distillation or isothermal membrane distillation, in which the transport through a hydrophobic membrane is caused by the difference in vapor pressures resulting in a difference in solution concentration at both membrane sides. In this technique the vapor collection of permeate is made by the use of a saturated solution of salts and nonionic compounds, for example glycols or glycerin (Tomaszewska, 2009). All the abovementioned process configurations are characterized by specific advantages and disadvantages. However, due to its simple construction, direct contact membrane distillation (DCMD) is most often investigated.

The mechanism of mass transport during MD can be divided into three basic stages: water vaporization at phase boundary between warm feed and gas in membrane pores, diffusion of vapor particles through hydrophobic membrane pores and condensation of permeate vapors in cold



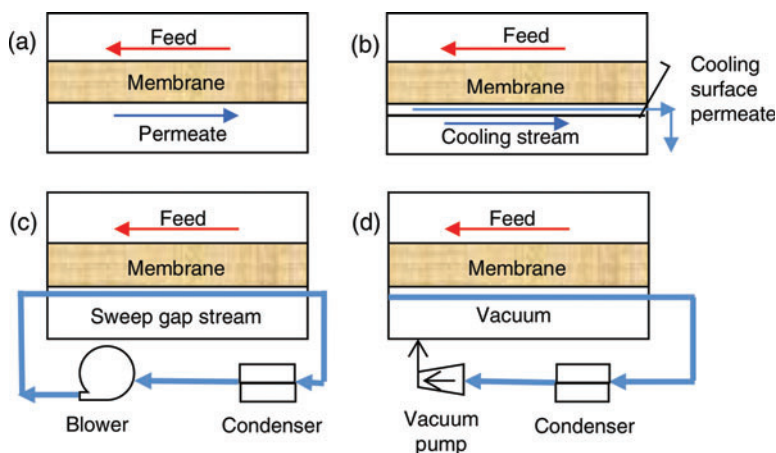


Figure 8.18. Configurations of membrane distillation: (a) direct contact membrane distillation; (b) air-gap membrane distillation; (c) sweeping gas membrane distillation; (d) vacuum membrane distillation (Alkhudhiri *et al.*, 2012; Khayet and Matsuura, 2011; Wang and Chung, 2015).

distillate stream (Tomaszewska, 1996, 2014). The wetting of a membrane causes non-selective flux and the process stops. The composition of permeate, and thus MD selectivity, depends on vapor pressures of particular components of a feed solution, which are in equilibrium with the aqueous phase of the feed at actual concentration and temperature conditions (Tomaszewska, 1996, 2014). This means that the feed component with higher vapor pressure diffuses more quickly through hydrophobic membrane pores. In the case of inorganic salt water solutions, for example NaCl, the vapor pressure of the salt is assumed to be equal to zero and it is only water vapor that is in equilibrium with the salt solution. In the case of water solutions of other non-volatile substances, the retention of dissolved substances is practically equal to 100% regardless of their concentration in the feed (Tomaszewska, 1996). Moreover, the presence of the membrane prevents the entrainment of liquid droplets as is observed in conventional distillation; thus the purity of permeate is very high.

In membrane distillation, asymmetric or composite membranes formed of polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF) or polypropylene (PP) are used (Tomaszewska, 1996). The presence of more narrow pores in the active layer of a membrane prevents the moistening of membrane pores. MD membranes are supposed to be characterized by high chemical and thermal stability. Recently a lot of publications on the production of membranes for membrane distillation have appeared in the literature (Tomaszewska, 1996). Composite, porous hydrophobic/hydrophilic MD membranes of a new generation are characterized by higher permeability and enable heat losses caused by the heat conduction through the membrane polymer to be minimized (Qtaishat *et al.*, 2009a, 2009b; Su *et al.*, 2010; Tomaszewska, 2014). There are high hopes associated with the ceramic membranes with hydrophobic polymer coating (e.g. fluoroalkylsilanes, perfluoroalkylsilanes). Ceramic membranes, however, have higher coefficients of heat transport and there is a higher temperature polarization effect and, as a result, smaller permeate flux compared with polymer membranes. Membranes applied nowadays in membrane distillation are also used in modules dedicated to other processes, mainly microfiltration. These involve hollow-fiber, frame-plate and spiral-wound module configurations (Tomaszewska, 2014).

Membrane distillation may be a competitive technique to reverse osmosis, especially in the case of production of water for municipal purposes. Due to the required feed temperature, which is much lower than boiling temperature, the feed heating may be done using energy carriers from other processes, including also waste heat sources present in many branches of the industry. The operational conditions of membrane distillation also enable the use of sun or geothermal

energy (Tomaszewska, 1996, 2014). MD does not require the use of significant pressures; only a low-pressure application is needed for solution recirculation, which simplifies the construction of modules. The advantages of MD enable the process to be successfully used in pure water production and wastewater utilization, especially for their concentration, which would enable the recovery of clean water and valuable or, on the other hand, environmentally dangerous compounds from them (Tomaszewska, 1996, 2014). There are also some limitations of the MD process, among which the requirement for the feed to be the water solution is the most important one. The presence of surfactants or even small amounts of organics in the feed may cause wetting of the membrane surface. Permeate fluxes obtained in MD are relatively low in comparison with pressure-driven membrane processes, for example RO. Additionally, concentration and temperature polarization phenomena, which affect the process capacity, can be encountered. Membrane fouling in the case of water desalination by means of membrane distillation is less significant than in other processes, due to the fact that the membrane pores are much wider than those in RO or UF (Gryta, 2003; Tomaszewska, 1996). However, in order to assure the proper performance of MD installation, preliminary water treatment should be applied.

The wetting of the membrane during long-term MD operation has already been mentioned as an important process disadvantage and limitation (Bodzek and Konieczny, 2011). The studies carried out on the topic show that after several thousand hours of process runs its capacity, due to the membrane wetting, may decrease even by 50%. The highest decrease in capacity is noted within the first several hours of module exploitation. Moreover, it has been shown that the formation of deposits on the membrane surface speeds up the membrane wetting (Bodzek and Konieczny, 2011).

The retention rate of non-volatile compound equal to almost 100% observed for membrane distillation has enabled the process to be used for demineralized water production from salty water (Alkhudhiri *et al.*, 2012; Gryta, 2012; Khayet and Matsuura, 2011; Tomaszewska, 1996, 2014; Wang and Chung, 2015). The quality of feed water has almost no impact on the quality of distillate (i.e. desalted water), the measured specific conductivity of which usually varies within  $0.2\text{--}0.9\ \mu\text{S cm}^{-1}$  (Tomaszewska, 2014).

The first studies on membrane distillation have already mentioned the high costs of the process, which have been estimated at several US\$ per cubic meter of water with the use of polytetrafluoroethylene (PTFE) membrane available in the 1980s. The estimated costs of one cubic meter of water produced via large-scale MD installation in 1987 were equal to 2 US\$ (Gryta, 2003). The progress in hydrophobic membrane production methods and in MD module construction techniques has significantly improved the process economics. One of the methods said to be unquestionably applied to the process is the recovery of permeate condensation heat. The optimization of module operation and the proper membrane choice (thickness, porosity, pore size) are also necessary for cost improvement. An understanding of the dependence of the permeate flux and water production costs on the applied module construction and operational parameters (membrane area, feed temperature, feed and permeate flow rates) as well as on the heat exchanger dimensions is also extremely important (Gryta, 2003). If all of the abovementioned methods are involved in the process, the cost of  $1\ \text{m}^3$  of water produced by means of MD can be established at  $0.26\text{--}0.56\ \text{US\$}$  (Al-Obaidani *et al.*, 2008).

The high energy consumption of the MD process makes the produced water costs strongly dependent on supplied energy costs and, simultaneously, on process temperature. The total cost of energy (vapor) used in the process depends also on the effectiveness of heat recovery from the distillate and its reuse in the feed solution heating. The exploitation costs of MD may also be decreased by the application of low-energetic energy sources, that is, waste energy sources. For example, the feeding of membrane modules with hot solutions outflowing from evaporation installation used in distilled water production have increased the MD capacity by 7.5% and improved the energy use effectiveness by 10% (De Andres *et al.*, 1998). The use of cheap energy sources in MD makes it a competitive technique even for RO (Bodzek and Konieczny, 2011). The combination of sun distiller with MD installations causes an increase in capacity by several times (Banat *et al.*, 2002; Tomaszewska, 2014).

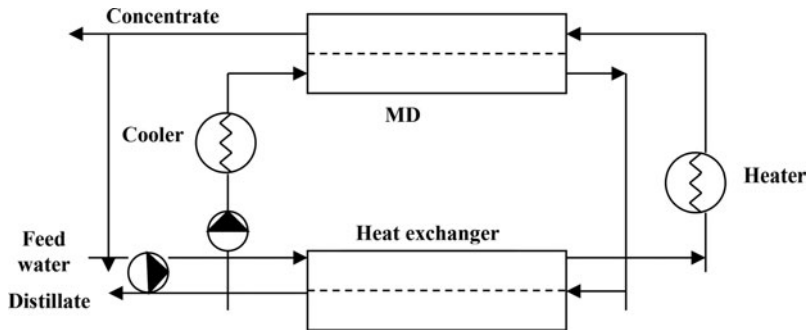


Figure 8.19. Scheme of MD installation with heat recovery (Bodzek and Konieczny, 2011).

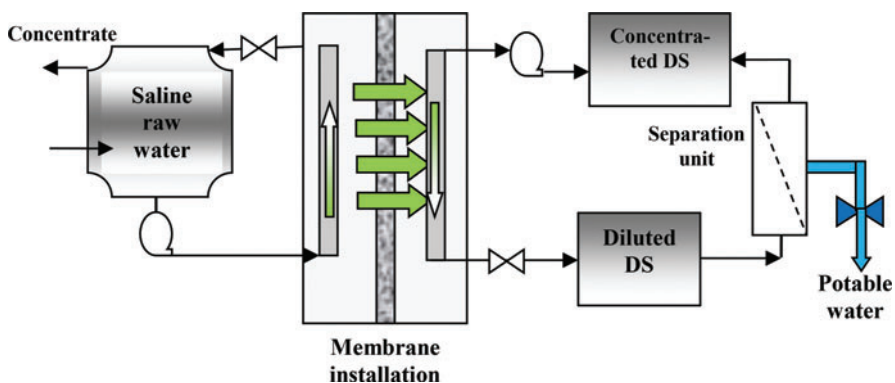


Figure 8.20. Diagram of water desalination using forward osmosis method (Liu *et al.*, 2009).

The most appropriate performance of water desalination by means of MD is the one with an external heat exchanger introduced to the process (Fig. 8.19) (Bodzek and Konieczny, 2011). The evaporation of 1 m<sup>3</sup> of water in an MD installation requires ca. 600–690 kWh of energy (Gryta, 2003; Zakrzewska-Trznadel *et al.*, 1999). The use of modules with heat recovery decreases the external energy demand to 150–180 kWh (Zakrzewska-Trznadel *et al.*, 1999). The transport of heat to the cooler membrane side increases the temperature of the liquid flowing at this part of the MD cell. Hence, the heat in the preliminary heating of the feed solution may be recovered, which decreases the energy consumption of the process.

### 8.2.5 Forward osmosis

Forward osmosis (FO) is a type of membrane process in which, due to the osmotic pressure gradient, the spontaneous transport of water through semipermeable membrane in the direction from the feed (of low osmotic pressure) to the solution of high osmotic pressure (draw solution) (Fig. 8.6, left) takes place (Cath *et al.*, 2006; Zhao *et al.*, 2012). The osmotic pressure gradient at both membrane sides is caused by the difference in concentration of soluble substances (Cath *et al.*, 2006). In Figure 8.20, the scheme of process stream flows in water desalination by means of FO is shown (Liu *et al.*, 2009).

The concentrated solution (draw solution) on the permeate side is the source of the driving force for the FO process. The draw solution usually comprises a gaseous mixture of ammonia and carbon dioxide (McCutcheon *et al.*, 2006a), but also solutions of salts and sugars, and recently magnetic

nanoparticles (Cath *et al.*, 2006; Chung *et al.*, 2012). The factors influencing the choice of the draw solution type are: high osmotic pressure, non-toxicity, easy recovery and simple permeate separation as well as chemical stability and low costs (Chung *et al.*, 2012). The recovery of the draw solution components can be made by means of stripping in the case of volatile and gaseous components, decomposition or precipitation in the case of salts and the action of magnetic field or ultrafiltration in the case of nanoparticles (Chung *et al.*, 2012; Liu *et al.*, 2009).

FO membranes are significantly different from RO membranes, especially in resistance to pressure compression and specificity of the active layer. RO membranes must be resistant to high pressures as hydraulic pressure is the driving force of the process, while in FO osmotic pressure difference is involved and thus membranes do not need to be significantly mechanically stable (Liu *et al.*, 2009). In FO a cellulose acetate membrane is produced via phase inversion method and composite TFC polyamide membranes with porous polysulfone or polyethersulfone layer in a hollow-fiber flat sheet configuration are also used (Zhao *et al.*, 2012). Most of the methods used in FO asymmetric membrane preparation, including those of cellulose acetate and TFC, are exactly the same as in the case of conventional RO membranes, that is, phase inversion and thermal modification or phase inversions and interphase polymerization. The support of the TFC membrane produced by means of phase inversion method determines the volumetric water flux during FO, while the active layer is responsible for salts retention. The transient layer in FO membranes should be characterized by high porosity and hydrophilicity, while the active layer should reveal high salts retention and minimum backward diffusion of dissolved substances (Liu *et al.*, 2009). In laboratory-scale studies of FO, hollow-fiber or flat sheet membranes are used. In larger-scale applications there are also plate-frame, spiral-wound, tubular or hollow-fiber modules (Cath *et al.*, 2006), as with RO.

The main advantage of the FO process is low, if any, hydraulic pressure, which corresponds to low energy consumption in water production (Cath *et al.*, 2006; McCutcheon *et al.*, 2006a). Other benefits are: high retention of a wide range of contaminants, smaller affinity to fouling in comparison with pressure-driven processes (Choi *et al.*, 2009) as a result of no hydraulic pressure applied and the use of special composite membranes (Mi and Elimelech, 2010). The slight overpressure observed in forward osmosis at the feed side is a result of flow resistances generated in a membrane module, while the equipment used is very simple and membrane supporting parts have no impact on the module exploitation. In the case of processing substances from the food or pharmaceutical industries, forward osmosis possesses one crucial feature, that is, it concentrates the feed solution with no need for high pressure or temperature application, which could be harmful to the product.

However, the significant limitation of FO is the lack of high-capacity membranes, reducing external and internal concentration polarization (ECP and ICP) (Fig. 8.21) and fouling, as well as backward diffusion of dissolved substances (McCutcheon *et al.*, 2006a; Zhao *et al.*, 2012).

Concentration polarization is a common and inevitable phenomenon observed in both pressure-driven and osmotic membrane processes (Cath *et al.*, 2006; McCutcheon *et al.*, 2006b; Zhao *et al.*, 2012). In the case of osmotic processes, concentration polarization is caused by the difference in concentration of the feed and draw solutions (Zhao *et al.*, 2012). Generally, ECP occurs at the skin layer surface of asymmetric membranes, while ICP appears in the porous membrane layer.

There have been several patents granted on various methods and systems of water desalination by means of forward osmosis (Cath *et al.*, 2006). Among them can be distinguished two FO water desalination routes: direct and indirect FO (Figs. 8.19 and 8.21) (Li *et al.*, 2014). The concept of direct FO desalination is similar to conventional membrane desalination processes (e.g. RO or NF), in which the desalted water is produced directly from salted water (seawater or brackish water). In direct FO desalination, the salted water is the feed solution (FS), while permeate (pure water) dilutes the draw solution (DS), which is osmotic salt solution (e.g. NaCl) or a volatile substance mixture (e.g.  $\text{NH}_3/\text{CO}_2$ ) (Linares *et al.*, 2015). The process requires an additional stage dedicated to the separation of osmotic solution and desalted water (Fig. 8.20) (Linares *et al.*, 2015; McCutcheon and Elimelech, 2006b). In indirect desalination, highly salted waters are used as a draw solution, while wastewaters or urban rainfall waters are used as a feed (Li *et al.*, 2014;

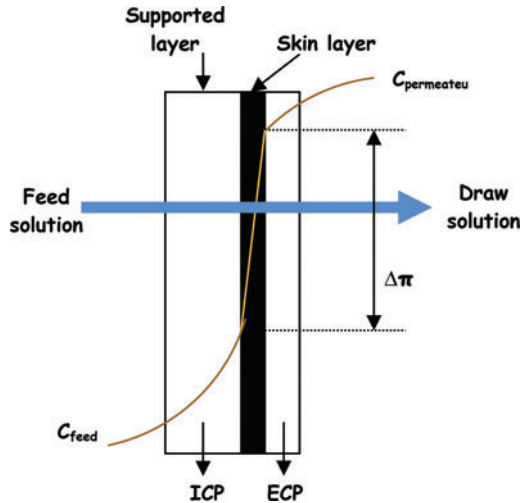


Figure 8.21. Concentration polarization in forward osmosis when using asymmetric membranes (McCutcheon *et al.*, 2006a; Zhao *et al.*, 2012).

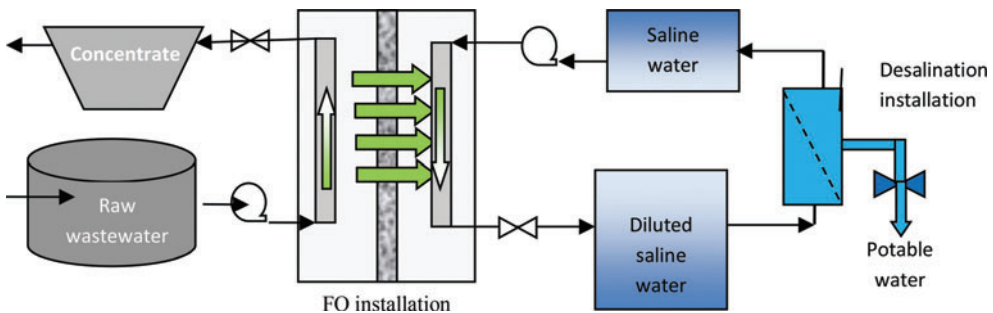


Figure 8.22. Indirect scheme of water desalination with forward osmosis (Linares *et al.*, 2015).

Linares *et al.*, 2015). Seawater and brackish water are potential draw solutions used in such cases (Fig. 8.22) (Linares *et al.*, 2015).

The attractiveness of such a solution is that the pure water may be recovered by means of osmotic energy use only. Additionally, the diluted salted solution (used as a draw solution) may be desalinated using low-pressure driven reverse osmosis or any thermal desalination technique, which results in reduction of the overall desalination process costs. All experience gained so far on the exploitation of forward osmosis as an alternative water desalination process has revealed two main already mentioned limitations of the technique: the lack of proper membranes and effective draw solution recovery methods. However, the combination of forward osmosis with RO results in higher fluxes than those obtained in single forward osmosis, and thus the energy consumption is lower (Choi *et al.*, 2009).

Even though FO is characterized by promising features in terms of fouling and scaling, the retention of specific contaminants such as boron, which is crucial in the evaluation of seawater desalination effectiveness by means of RO performance, is still unknown. Moreover, the regeneration of draw solution requires sufficient amount of energy and if there is no waste heat available for regeneration procedure, then FO is less attractive than RO (Semiati, 2008; Subramani

Table 8.7. The chemical composition of raw seawater and brine from Dekhelia (Cyprus) (Fritzmann, 2007).

Analysis	Raw seawater [mg L <sup>-1</sup> ]	Brine [mg L <sup>-1</sup> ]	Ratio (brine/raw water)
Ca <sup>2+</sup>	450	891	1.98
Mg <sup>2+</sup>	1452	2878	1.98
Na <sup>+</sup>	12480	24650	1.975
K <sup>+</sup>	450	888	1.973
HCO <sub>3</sub> <sup>-</sup>	160	315	1.97
CO <sub>3</sub> <sup>2-</sup>	0.2	0.4	2
SO <sub>4</sub> <sup>2-</sup>	3406	6745	1.98
Cl <sup>-</sup>	22099	43660	1.98
TDS	40500	80030	1.98
pH	8.1	7.7	

*et al.*, 2011). Studies have been carried out on the improvement of FO applied membrane properties (Yang *et al.*, 2009); however, long-term operational data are not yet available and only laboratory-scale results published in the literature can be used as a basis. With regard to seawater desalination, especially with a high water recovery rate demand, forward osmosis can be applied, but only in the case where the draw solution is characterized by very high osmotic pressure.

### 8.3 CONCENTRATE UTILIZATION

Except for energy consumption, one of the most crucial parameters of all desalination technology evaluation is the amount and the composition of concentrate formed during the process and methods of its utilization or neutralization (Kim, 2011; Perez-Gonzalez *et al.*, 2012; Subramani and Jacangelo, 2014). The volume of the concentrate is especially important in the case of installations located far away from oceans (Subramani and Jacangelo, 2014).

The side streams formed during the process may reveal a negative environmental impact (Bodzek and Konieczny, 2011; Tsiourtis, 2001; Van der Bruggen and Vandecasteele, 2002). The most problematic stream is brine, that is, concentrate formed during desalination, mainly in RO. It is an aqueous solution of high concentration of salts, deposition of which to the environment may cause some problems, especially in terms of: (i) stream temperature, (ii) stream salinity and (iii) amount of external additives used in the process (Van der Bruggen and Vandecasteele, 2002). The increased temperature as well as high salinity of the concentrate affects the amount of oxygen dissolved in natural water reservoirs. The introduction of warm brine to surface waters causes a decrease in the amount of oxygen, which has a negative impact on water ecosystems. The temperature of RO brine is more or less the same as the temperature of the feed, while in the case of thermal processes its temperature may be 10°C higher than that of raw water (Bodzek and Konieczny, 2011).

In the case of seawater desalination by means of RO, the amount of salts in the brine is almost twice as high as in seawater (Table 8.7) (Fritzmann, 2007), while in the case of thermal processes, the concentration is ca. 10% higher (Bodzek and Konieczny, 2011).

Hence, the effect of salinity in brine deposition reservoirs is much greater in the case of RO. Brine may be deposited into inland waters (surface water), deep wells or special evaporation lagoons or it may be drained directly to soil or to a sea (Bodzek and Konieczny, 2011; Kim, 2011; Perez-Gonzalez *et al.*, 2012; Subramani and Jacangelo, 2014). The deposition options for surface water reservoirs also include rivers, bays, flowing lakes, brine water channels or oceans (Subramani and Jacangelo, 2014). The applied deposition method is specific for every desalination plant and depends on the amount and on the quality of the concentrate. The costs of the utilization are also very important and must be carefully considered before the method is

chosen (Ahmed *et al.*, 2001; Al-Wazzan and Al-Modaf, 2001; Arnal *et al.*, 2005). Nevertheless, in all cases the impact of the brine on freshwater or soil must be limited as much as possible (Bodzek and Konieczny, 2011). Due to the high costs, some facilities avoid the deposition of brine into the environment and consider other available solutions such as dilution or mixing with wastewaters. Concentrate mixed with industrial or municipal wastewater is further treated in a wastewater treatment plant (Subramani and Jacangelo, 2014). The deposition into deep dwelling wells also enables the introduction of the concentrate to underground, porous rock located from several to several thousands of meters below the ground level, depending on the geological conditions of the deposition location (Perez-Gonzalez *et al.*, 2012). Evaporation in special lagoons is another option for brine utilization, suitable in the case of small amounts of the stream and for plants located in a warm and dry climate zone with low earth surface exploitation costs (Subramani and Jacangelo, 2014). The deposition of brine into sea does not generally cause environmental problems, as brine contains salts usually present in seawater and some negligible amounts of additives, that is, chemicals used in membrane cleaning, anti-scalants and anticorrosive compounds. The deposition of brine into inland water reservoirs is not a recommended method, as it may cause serious environmental damage. In the case where such a solution is the only reasonable option, detailed research on the results of brine deposition into the environment and on the minimization of its impact must be carried out. In the case of brackish water desalination, the need for concentrate may be eliminated by mixing raw seawater into it before its introduction to RO desalination (Glueckstern and Priel, 1996).

Another group of contaminants present in the brine consists of chemicals used in the desalination process. They may be divided into four main groups: (i) chemicals from membrane cleaning, (ii) biocides used in all desalination processes, (iii) anti-scalant used in RO and distillation methods and (iv) antifoam compounds used in distillation (Van der Bruggen and Vandecasteele, 2002). Nowadays the chemicals are said to be environmentally friendly, that is, easily biodegradable in natural conditions. As an example, polymers based on maleic acid anhydride of low eutrophication potential or biodegradable antifoam compounds of reduced toxicity can be mentioned (Bodzek and Konieczny, 2011). However, harmful biocides are still used and it is difficult to replace them with substances of lower environmental hazard.

Another option for utilization and deposition of desalination concentrates is processing them with the use of unit operations (Kim, 2011; Perez-Gonzalez *et al.*, 2012; Subramani and Jacangelo, 2014). Among the available methods, reverse osmosis and thermal methods or their combination are mentioned, as well as processes based on ion-exchange membranes, membrane distillation and forward osmosis (Kim, 2011; Perez-Gonzalez *et al.*, 2012; Subramani and Jacangelo, 2014). The removal of dissolved substances from concentrate is most commonly performed by means of membrane-based technologies. However, before the use of these methods it is important to establish the preliminary treatment actions, that is, the removal of substances responsible for membrane scaling and fouling as well as solution foaming (Perez-Gonzalez *et al.*, 2012). The main criteria for the choice between membrane and thermal methods are the content of total dissolved substances (TDS) in the concentrate. In the case of RO the pressure limit is established at 8.2 MPa due to the construction of pressurized tanks used in spiral-wound module systems. At high TDS ( $>40,000 \text{ mg L}^{-1}$ ) in concentrate, the required pressure exceeds the limit value, that is, 8.2 MPa, and such a high value is needed to overcome osmotic pressure and assure efficient water flux. Hence, when using concentrates of high TDS content, minimization of the stream amount and maximum reduction of the environmental impact should be made by means of thermal processes. The recovery of trading products is the final aim of concentrates use regardless of their source. If valuable substances are recovered from concentrates a double benefit is obtained: the reduced environmental impact resulting from the concentrate use and global improvement of the desalination economics. Hence, concentration by means of RO or other methods is followed by final water evaporation combined with salts crystallization (Perez-Gonzalez *et al.*, 2012).

In the case of reverse osmosis, the zero liquid discharge process is used. It relies on two-stage RO, whereby the concentrate obtained in the first stage undergoes preliminary removal of scaling and fouling precursors (preliminary softening) and then the second RO stage is run

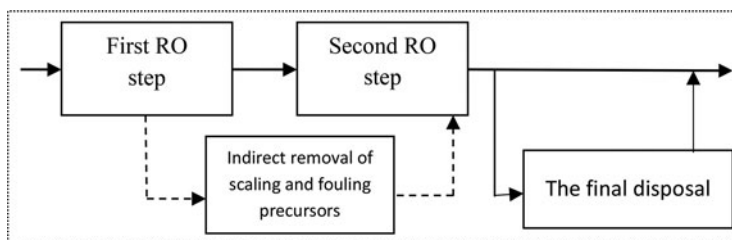


Figure 8.23. General scheme of RO concentrate treatment (Perez-Gonzalez *et al.*, 2012).

(Fig. 8.23) (Gabelich *et al.*, 2007, 2010; Perez-Gonzalez *et al.*, 2012; Wangnick, 2000). This treatment configuration enables the recovery of more than 95% of water. Complete concentrate utilization may be obtained via final application of the evaporation/crystallization system (Perez-Gonzalez *et al.*, 2012).

The removal of scaling precursors from desalination concentrates can be made using several methods, including chemical softening with calcium oxide or softening in crystallizers (e.g. fluidized bed crystallizers) with crystallization precursors (Kim, 2011; Perez-Gonzalez *et al.*, 2012; Subramani and Jacangelo, 2014). The use of calcium hydroxide ( $\text{Ca(OH)}_2$ ) requires the addition of flocculants in order to increase the water recovery rate up to 95% (Ordóñez *et al.*, 2012). The alternative for calcium compounds application is the addition of sodium hydroxide or sodium carbonate, which aims to increase pH. The choice of the chemical depends on concentrate composition and current chemical prices. The advantage of conventional chemical softening methods is the removal of ions responsible for scaling, while the disadvantage is the formation of additional deposits and problematic pH control (Gabelich *et al.*, 2010).

Electrocoagulation is an alternative process for bivalent and metal ions removal from concentrate. The method is based on the electrochemical production of coagulants introduced to the solution by means of aluminum or iron electrodes (Baudequin *et al.*, 2011), which leads to the coagulation of contaminants present in the concentrate. The dissolution of the metal anode is accompanied by the formation of hydrogen on the cathode, which enhances flotation of flocks. Subramani *et al.* (2012) have used electrocoagulation in concentrate treatment, during which they have obtained over 90% barium, magnesium, strontium and silica removal, while the water recovery rate obtained within the two-stage reverse osmosis has been established at 93% (Baudequin *et al.*, 2011). The advantage of the use of electrocoagulation in RO concentrate processing is the smaller amount of waste deposits in comparison with the conventional softening technique, as well as the higher removal rates of ions responsible for membrane scaling and other metals. The main limitations of the method are high exploitation and conservation costs as a result of the need for electrode replacement, high energy demand and a lack of references in industrial-scale systems.

An interesting solution is the combination of several unit operations such as RO, ion-exchange and chemical softening, which limits membrane fouling and scaling and produces a high water recovery rate. In Figure 8.24, the scheme of the HERO process (Cob *et al.*, 2012; Jun *et al.*, 2004; Subramani and Jacangelo, 2014) is presented. In this technology, the chemical softening precedes the first stage of RO, which is preceded by ion-exchange and followed by second-stage membrane polishing, while the final step involves evaporation/crystallization.

The biological removal of sulfates with the use of microorganisms reducing those ions to sulfides is also proposed as a method of concentrate treatment, as this improves the water recovery rate during further RO treatment (Subramani and Jacangelo, 2014). Sulfides and carbonates formed during the process are then removed by aeration of the solution at acidic conditions. The removal of sulfates may also be obtained by means of chemical oxidation methods, which are widely used in the decomposition of organic contaminants (Subramani and Jacangelo, 2014).



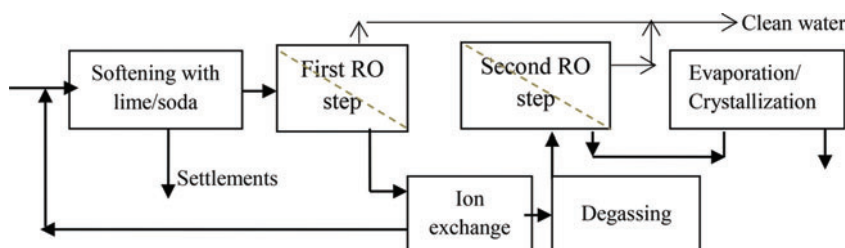


Figure 8.24. Hybrid scheme of treatment of RO concentrate (HERO process) (Subramani and Jacangelo, 2014).

At relatively low-salinity level, the use of desalination concentrate, except in RO, may be also carried out using electrodialysis (ED) or electrodialysis reversal (EDR) (Subramani and Jacangelo, 2014; Zhang *et al.*, 2012, 2011). Zhang *et al.* (2012) have discussed the concentration of RO retentate of conductivity  $3.90\text{--}4.14\text{ mS cm}^{-1}$  generated at a wastewater treatment plant. They have obtained a water recovery rate equal to 97.5% at optimum current density  $3050\text{ A m}^{-2}$ . The main disadvantage of ED application in the use of desalination concentrate is the formation of barely soluble precipitates, which limits the effectiveness of the process. Similarly, as in the case of RO, the preliminary removal of bivalent ions via chemical softening (Tran *et al.*, 2012), and crystallization in reactors (Kongold *et al.*, 2009) is applied, which assures a water recovery rate of up to 98%. An improvement in the water recovery amount up to 99% can be obtained by the use of ion-exchange or biological active filters before the EDR process (Subramani and Jacangelo, 2014). The secondary concentrate from the EDS system may be used in ion-exchange bed regeneration or brine utilization by means of gypsum crystallization (Subramani and Jacangelo, 2014). The use of concentrate generated in surface water desalination can be also conducted by means of ED with bipolar membranes. In this case mixtures of acids and bases suitable to be used in the regeneration of ion-exchange beds are obtained. The method has also been applied in the utilization of RO concentrates generated at wastewater treatment plants (Perez-Gonzalez *et al.*, 2012).

Conventional thermal methods that can potentially be applied in the use of desalination concentrate are multi-effect distillation (MED), thermal vapor compression (TVC) or mechanical vapor compression (MVC). Among those three techniques, the MVC method is the most efficient according to energy consumption and it also leads to zero liquid discharge (Fig. 8.25) (Subramani and Jacangelo, 2014). The process requires the addition of anti-scalants in order to prevent the formation of insoluble salts on the heat exchanger walls. During the MVC process the distillate and the concentrate are obtained and the latter stream, through the equalization tank, undergoes thermal evaporation (Subramani and Jacangelo, 2014). MVC systems are efficient at the concentration of dissolved substances present in RO concentrate at energy (electricity) consumption equal to  $7\text{--}12\text{ kWh m}^{-3}$  or  $22\text{--}25\text{ kWh m}^{-3}$  depending on the information source (Subramani and Jacangelo, 2014). The MVC system is widely applied due to its low energy consumption, relatively short retention time and low exploitation costs. Even though the investment cost usually exceeds that required for MED, studies have been carried out to improve this economic parameter of MVC (Subramani and Jacangelo, 2014). Nevertheless, the MED process with water recovery rate of 93%, as well as an integrated RO-MED system (99% recovery rate), is also used in RO concentrate utilization (Kim, 2011). This requires preliminary concentrate treatment due to a decrease in silica content, which prevents the formation of silica stone on the heat exchanger walls.

Novel technologies that have been recently introduced to RO concentrate utilization are forward osmosis (FO) and membrane distillation, but liquid-liquid extraction as well as electrodialysis with bipolar membranes can be used (Kim, 2011).

Forward osmosis (FO) is a membrane process which can also be applied to desalination concentrate, especially to one generated during an RO-based process. Tang and Ng (2008) have used

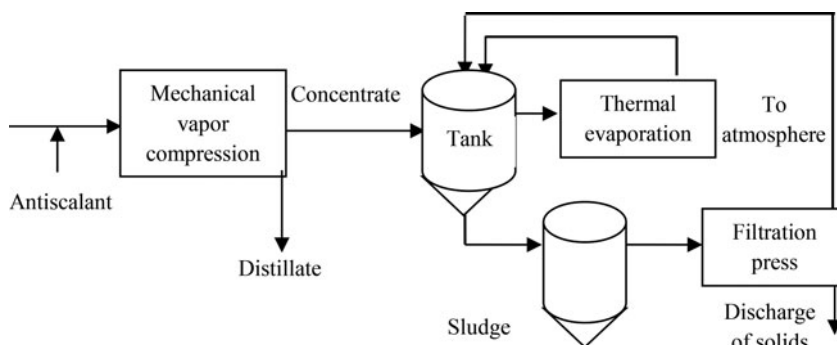


Figure 8.25. Scheme of utilization of RO concentrate using MVC and thermal evaporation processes (Subramani and Jacangelo, 2014).

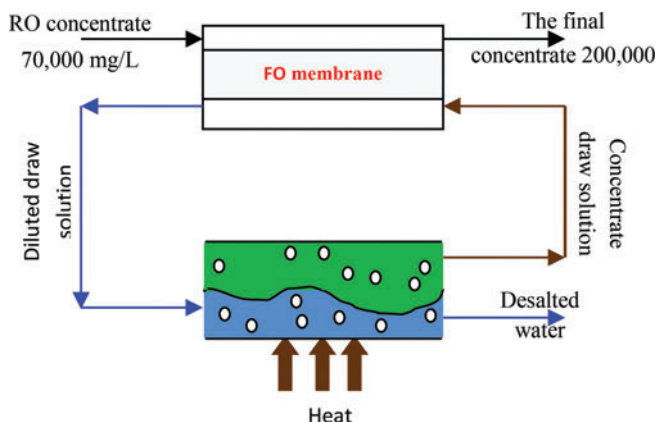


Figure 8.26. Diagram showing utilization of RO concentrate with FO process (Subramani and Jacangelo, 2014).

fructose (5–6 M) as a draw solution and cellulose acetate membrane to utilize RO concentrate (1-M NaCl), but they have obtained only 76% of water recovery and capacity equal to  $8.2 \text{ L m}^{-2} \text{ h}^{-1}$ . McGinnis *et al.* (2012) have run studies on the use of highly salted (TDS ca.  $73,000 \text{ mg L}^{-1}$ ) concentrate with the use of  $\text{NH}_3/\text{CO}_2$  mixture as the draw solution and FO (TFC) composite membranes obtaining average membrane flux of ca.  $2.6 \text{ L m}^{-2} \text{ h}^{-1}$  and water recovery rate level of  $64 \pm 2.2\%$ . TDS content in the produced water ( $<300 \text{ mg L}^{-1}$ ) has met the standards for its deposition to the environment and the energy consumption is lower by 42% in comparison with a conventional mechanical vapor compression (MVC) system (McGinnis *et al.*, 2012). Hickenbottom *et al.* (2012) have involved Cellulose Triacetate (TCA) and 26% NaCl solution as a draw solution in their studies. The capacity of the process has reached  $5\text{--}7 \text{ L m}^{-2} \text{ h}^{-1}$  at 50% water recovery rate. Recently, the forward osmosis process has been used to concentrate solution from  $70,000$  to  $225,000 \text{ mg L}^{-1}$  TDS (Fig. 8.26) (Subramani and Jacangelo, 2014), with a water recovery rate equal to 60% and the permeate flux within  $2\text{--}4 \text{ L m}^{-2} \text{ h}^{-1}$ . This system has enabled US Environmental Protection Agency standards to be met for metals, radionuclides, chlorides and TDS established for treated wastewater as well as for boron ( $<0.05 \text{ mg L}^{-1}$ ). The main advantage of the FO process in RO concentrate utilization is the low energy consumption, as additional, external pressure is not required (Zhao *et al.*, 2012). The FO process also reveals lower affinity to fouling than pressure-driven membrane techniques and the eventual phenomenon is of

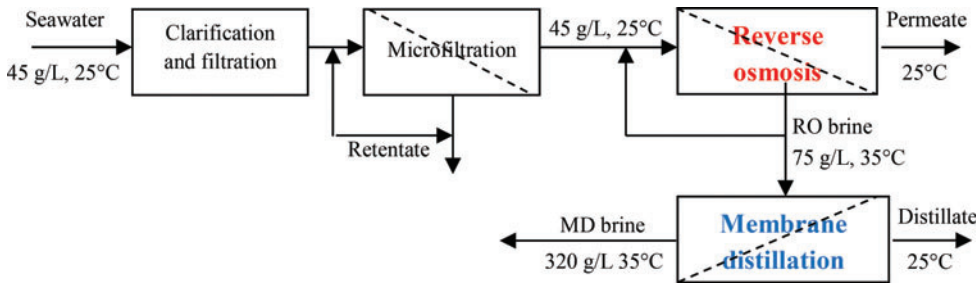


Figure 8.27. Scheme of water desalination using integrated RO and MD method (Drioli *et al.*, 1999, 2002).

Table 8.8. The volume of production and the costs of desalinated water in membrane and hybrid systems (Drioli *et al.*, 1999).

Process	Ratio of desalinated water to feed	Cost of water production [US\$ m <sup>-3</sup> ]
Reverse osmosis (RO)	0.391	1.25
Membrane distillation (MD)	0.856	1.32
Hybrid system: RO + MD	0.856	1.25

reversible character and may be easily minimized by the process of hydrodynamics optimization (Li *et al.*, 2014).

The utilization of NF/RO desalination concentrates, but also of streams generated during other desalination processes, may also be done by integrated processes involving MD (Ji *et al.*, 2010; Mericq *et al.*, 2010; Susanto, 2011; Tun and Groth, 2011). Studies on hybrid systems comprising MD and RO have been performed by Drioli *et al.* (1999, 2002) (Fig. 8.27).

The feed in the process is seawater of salt content 45 g L<sup>-1</sup> and temperature of 25°C. The water recovery rate obtained for RO is equal to 40%, while for membrane distillation it is 77%, that is, an overall process recovery rate of 87.5%. The brine obtained during MD is saturate solution of concentration 320 g L<sup>-1</sup>. As MD effectiveness is independent of feed composition, the production of a higher amount of pure water is possible and simultaneously the amount of RO concentrate can be proportionally decreased. A comparison of the costs of RO, MD and RO + MD systems show that the use of the hybrid system results in production of higher amounts of water than in the case of RO at the same costs, while in the case of MD the amount of water is comparable to the hybrid system, but the costs are 5% higher (Table 8.8) (Drioli *et al.*, 1999).

The membrane distillation shown in Figure 8.28 can be operated as a membrane crystallizer system. It is the modern device used in the production of crystals from oversaturated solutions. Its operation relies on the use of membrane distillation for oversaturated salt solution production and direction of the concentrate to the crystallizers, in which the metastable solution undergoes crystal nucleation and formation (Bodzek and Konieczny, 2011; Drioli *et al.*, 2002).

Tun and Groth (2011) have used MD with a crystallizer to use RO concentrate (of conductivity ca. 1.5 mS cm<sup>-1</sup>) generated during industrial wastewater treatment and they have obtained fluxes within 3–5 L m<sup>-2</sup> h<sup>-1</sup> and overall water recovery rate at the level of 95%. In brine treatment coming from RO sea water desalination system, the initial permeate flux has been 1.44 L m<sup>-2</sup> h<sup>-1</sup> and a 90% water recovery rate accompanied by NaCl crystals formation has been obtained (Tun and Groth, 2011). Nevertheless, the already low initial flux has been decreasing during the process run due to membrane fouling with natural organic matter (NOM). The presence of NOM in RO concentrates affects the kinetics of NaCl crystallization due to a decrease in the nucleating

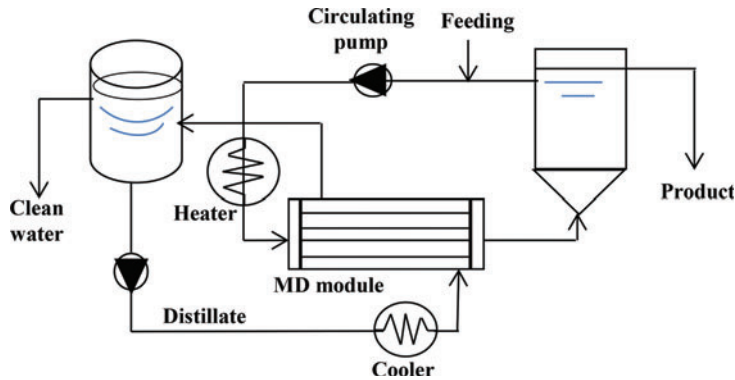


Figure 8.28. Diagram of membrane crystallizer (Drioli *et al.*, 2002).

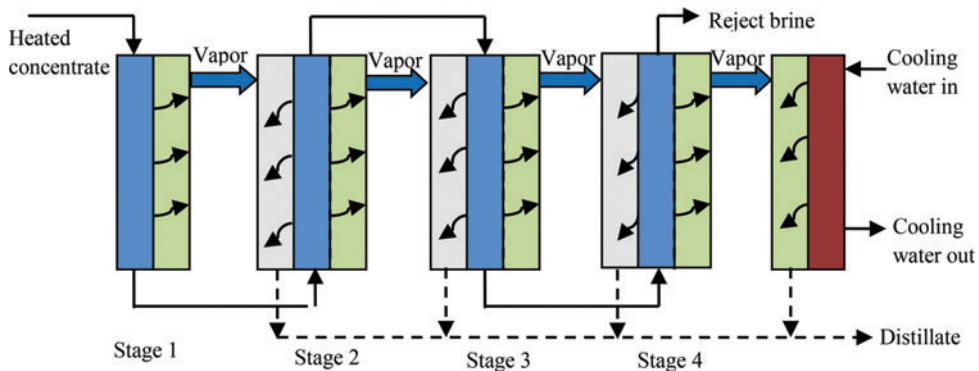


Figure 8.29. Diagram of membrane crystallizer (Subramani and Jacangelo, 2014).

solution density and effectiveness of crystals growth (Ji *et al.*, 2010). An integrated system of gas-liquid membrane contractor and conventional and membrane crystallizer has also been used in the utilization of NF concentrate. Calcium carbonate has been removed by 89% and 36 kg of NaCl and 8 kg of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  have been produced per  $\text{m}^3$  of nanofiltration retentate. Additionally, the amount of water condensed at the distillate side of the membrane crystallizer has improved the water recovery rate of NF from 64 to 95% (Drioli *et al.*, 2004).

The combination of NF/RO with MD enables an increase in the water recovery rate, in some cases even up to more than 90%. Criscuoli and Drioli (1999) have performed a detailed energy and exergy analysis of the integrated NF/RO/MD system, which has revealed an energy consumption level of  $13 \text{ kWh m}^{-3}$ , but with the possibility of a decrease to  $2.6 \text{ kWh m}^{-3}$  in the case of waste heat availability.

The four-stage vacuum membrane distillation (VMD) system used in the utilization of concentrate from thermal seawater desalination ( $\text{TDS} = 100,000 \text{ mg L}^{-1}$ ) is characterized by higher water recovery rate (Fig. 8.29) and permeate flux of  $5.2 \text{ L m}^{-2} \text{ h}^{-1}$  (Subramani and Jacangelo, 2014). Even though the value is lower than that obtained for direct MD, the V-MEMD system's energy consumption is lower due to the use of waste heat to increase the concentrate temperature and a serial configuration of membranes. Mericq *et al.* (2010) have used VMD to treat concentrate from RO seawater desalination with a capacity of 7 to  $17 \text{ L m}^{-2} \text{ h}^{-1}$ , and the obtained water recovery level has reached 89%. Nevertheless, the precipitations of calcium carbonate and sulfate have affected the membrane performance exhibited by the membrane flux decrease.

## 8.4 INTEGRATED DESALINATION SYSTEMS

Modern desalination systems operating nowadays are mostly configured into integrated (hybrid) units, among which four main trends can be distinguished (Ang *et al.*, 2015; Bodzek and Konieczny, 2011; Hamed, 2005; Helal, 2009):

- The integration of reverse osmosis with thermal methods;
- The use of nanofiltration for desalination technology with the aim to prevent scaling;
- The replacement of conventional pretreatment with UF, MF or NF;
- The combination of reverse osmosis with ion-exchange (electrodeionization) in the production of deeply deionized water.

### 8.4.1 *Integration of reverse osmosis with thermal methods*

The concept of hybrid desalination is based on the combination of the benefits of different technologies and the maximum elimination of their disadvantages. The following systems can be found (Ang *et al.*, 2015; Awerbuch, 2005; Fazle-Mahbub *et al.*, 2009; Fritzmann *et al.*, 2007; Hamed, 2005; Helal, 2009):

- simple hybrid systems in which every method is exploited separately;
- integrated hybrid systems, in which there are commonly exploited sections (e.g. raw water intake, raw water preliminary treatment system, etc.);
- hybrid systems combining both electricity and desalinated water production.

Within the second group of systems, particular technologies are combined by means of sharing some common elements or processes (e.g. raw water intake and its preliminary treatment, mixing of RO and MSF products, final treatment of desalinated water, etc.). The combination of the raw seawater intake undergoing RO, as well as MSF desalination, as well as integration of water pretreatment results in the reduction of investment costs in comparison with the use of separate systems (Awerbuch, 2005). The mixing and common final treatment of water distributed outside the desalination plant enables the exploitation of the RO installation at relatively high content of dissolved substance in the permeate, which elongates the membranes' lifetime and reduces the costs of their exchange (Ang *et al.*, 2015), as well as decreasing energy consumption due to the possibility of a higher water recovery rate (Fazle-Mahbub *et al.*, 2009). In the case where the membrane exploitation period is elongated from three to five years, the annual amortization costs can be reduced by almost 40% (Awerbuch, 2005). The mixing of thermal and membrane desalination products additionally enables the use of a single-stage RO system instead of a two-stage configuration, which is usually applied at conventional RO-based plants (Fazle-Mahbub *et al.*, 2009; Fritzmann *et al.*, 2007; Helal, 2009). In this way, the problem of boron appearance in the treated water is also eliminated for plants operating on a hybrid system. Integrated, hybrid MSF/RO installations additionally enable the use of waste heat in RO installations, which is derived by cooling water from MSF installations as well as the use of pressure energy of the RO retentate in the MSF process. Low-pressure water vapor can be involved in the degassing and deaeration of RO-treated raw water in order to minimize corrosion, which enables the use of lower quality, but more economically attractive steel construction materials for RO installation elements. The next advantage is the maintenance of the raw water temperature at a satisfactory level, which results in the high permeate fluxes obtained during the process. This is especially important during the winter season, when the seawater temperature usually reaches 15°C, while its increase by only 1°C results in a water production capacity increase of 1.5–3% (Awerbuch, 2005). The overall stream of raw water undergoing desalination may also be decreased. The experiments run in this field have shown that the production capacity obtained for an RO system operated at 33°C raw water is 42–48% higher in comparison with an isolated RO system used to desalination of seawater at 15°C (Awerbuch, 2005; Helal, 2009).

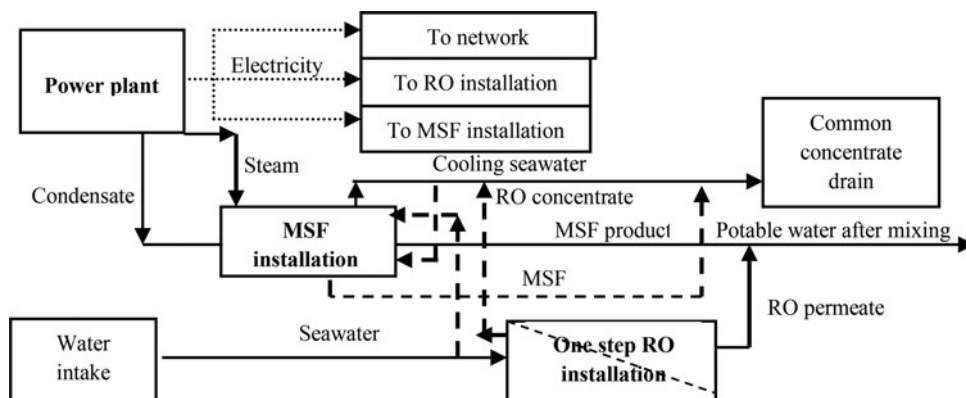


Figure 8.30. Simple hybrid three-step system power plant/desalination RO/desalination MSF (Bodzek and Konieczny, 2011).

Hybrid desalination systems combining thermal and membrane salt removal from water with an electricity production system are found to be a technically and economically satisfying alternative for desalination and energy management (Awerbuch, 2005). Such hybrid configurations (RO installation/thermal installation/power plant) are characterized by exploitation flexibility, lower energy consumption and investment costs, higher accessibility of installations and better water and power management (water, contrary to electricity, is a storable product) (Fazle-Mahbub *et al.*, 2009; Ghaffour *et al.*, 2013). Nowadays, most seawater desalination plants with multi-stage flash distillation (MSF) or hybrid MSF/RO systems operate on the block system of double desalination, that is, production of both desalinated water and electricity. Moreover, the sharing of seawater intake, its common preliminary treatment, the mixing of RO permeate with MSF distillate and its final preparation for distribution results in a significant decrease in investment and exploitation costs (Awerbuch, 2005; Fazle-Mahbub *et al.*, 2009). MSF, MED and VC as well as nanofiltration (NF) can also be used with RO in hybrid systems (Ghaffour *et al.*, 2013). In Figure 8.30, the scheme of the triple hybridization: electricity-MSF-SWRO system is shown (Bodzek and Konieczny, 2011). The use of hybrid seawater desalination systems (co-generation of energy production MSF with SWRO installation) is highly beneficial in cases where significant disturbances in water and energy demand are observed (Ghaffour *et al.*, 2013). The combination of desalination processes with energy production also improves the efficiency of fuel energy use as well as the electricity production. The use of power plant energy during periods of decreased energy consumption for the production of water, which can be stored and applied in an increased consumption period, improves the efficiency of the system as well as the economic effect (Ghaffour *et al.*, 2013; Maliva *et al.*, 2006). For example, in the case of a plant producing 150,000 m<sup>3</sup> of water per day operating at the optimum ratio of SWRO to MSF/MED = 2 (i.e. 100,000 m<sup>3</sup> day<sup>-1</sup> RO and 50,000 m<sup>3</sup> day<sup>-1</sup> MSF/MED), the cost of water production decreases by 0.064 US\$ m<sup>-3</sup>, which results in annual savings equal to 3.4 million US\$ (Ghaffour *et al.*, 2013).

The third solution integrating RO and thermal methods is the following combined set: RO – thermal method – NaCl crystallization (Fig. 8.31) (Bodzek and Konieczny, 2005). It is used to treat highly salted inland waters. The main aim of desalination is the elimination of salts accompanied by the production of valuable products. In this technology, the RO retentate is concentrated using the thermal method with simultaneous water recovery and selective NaCl crystallization.

A hybrid system integrating MSF and RO desalination, in which the MSF installation is fed with RO retentate, has also been proposed (Hamed, 2005). In this solution, MSF is used as a second-stage treatment for the increase of purified water volume compared with single-stage reverse

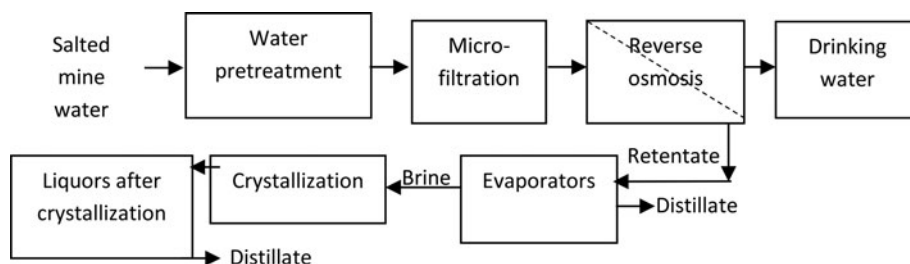


Figure 8.31. Scheme of hybrid installation linking RO and thermal methods (Bodzek and Konieczny, 2005).

osmosis. The reduction in the system dimensions and the limitation of preliminary treatment unit operations means that a reduction in exploitation and operational costs is obtained. Moreover, the use of cheaper membranes and an improvement in the effectiveness of the thermal co-generation installation are possible. The RO permeate and MSF distillate can be mixed, which enables the use of membranes of lower salt retention rate.

#### 8.4.2 Hybrid systems with nanofiltration

Considering the benefits resulting from the use of hybrid systems, it is important to compare the basic desalination techniques by an assessment of the factor, that in each of them limits the obtaining of high concentration of salts in the concentrated stream, that is, the decrease in vapor pressure for thermal methods, the increase in osmotic pressure in reverse osmosis and the increase in electromotive force of the concentration cell with no transport in the case of electrodialysis (Turek and Dydo, 2003b). Such an analysis, as well as a comparison of the technological parameters of RO and thermal installations reveals that the use of RO for treatment of water of salinity above  $70 \text{ g L}^{-1}$  and the production of concentrate of salinity above  $90 \text{ g L}^{-1}$  is unadjusted (Magdziorz and Seweryński, 2004). Hence, the introduction of nanofiltration before reverse osmosis is a breakthrough in the latter method, or even in the distillation-based method, as it enables the process to be carried out up to a brine concentration level equal to  $150 \text{ g L}^{-1}$ . In this solution, NF permeate undergoes desalination, what allows a high water recovery rate to be obtained as it avoids crystallization of calcium sulfate in the concentrated stream, due to the nanofiltration removal of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions. NF membranes eliminate hardness and part of the dissolved substances, and almost totally remove the multi-valent metal salts, while in the case of monovalent metals their NF retention reaches 10–50% depending on the NF membrane type. It significantly decreases the osmotic pressure of water undergoing RO, in comparison with raw water (e.g. seawater), and thus RO membranes can be operated at a lower pressure (lower energy consumption) and at higher permeate recovery rate (Magdziorz and Seweryński, 2004). Additionally, the process becomes more environmentally friendly as the amount of additional chemicals (anti-scalants, acids) is reduced. Moreover, the need for second-stage RO water polishing can be omitted, as permeate obtained in the first stage is already characterized by a TDS concentration of  $200 \text{ mg L}^{-1}$ . It causes the desalted water to be cheaper by 30% compared with the price of water produced by a conventional RO system (Magdziorz and Seweryński, 2004). Some interesting studies in the field have been performed by Drioli *et al.* (2002). The introduction of nanofiltration to seawater or other salty water desalination is especially favored in the case of increased bivalent ions content. In Table 8.9, the composition of process streams obtained in the system of nanofiltration/RO treatment, that is, raw water, NF permeate and RO permeate, is presented (Drioli *et al.*, 2002).

Desalination by means of the system NF-evaporator-crystallizer or NF-RO-evaporator-crystallizer is also proposed (Turek and Dydo, 2003b). Hence, the use of NF membranes of relatively high retention of NaCl (e.g. 40%) is suggested in order to improve the water recovery

Table 8.9. The composition of the process streams for NF/RO hybrid system (Drioli *et al.*, 2002).

Component	Raw water [mg L <sup>-1</sup> ]	Permeate after NF [mg L <sup>-1</sup> ]	Permeate after RO [mg L <sup>-1</sup> ]
HCO <sub>3</sub> <sup>-</sup>	140	53.2	2.2
Na <sup>+</sup>	10500	8190	114
Cl <sup>-</sup>	19100	16700	200
SO <sub>4</sub> <sup>2-</sup>	2650	265	9.8
Ca <sup>2+</sup>	400	46.4	1.3
Mg <sup>2+</sup>	1270	140	5.6

rate of the RO process, which precedes thermal evaporation. It is accepted that if the vapor pressure, that is, the effectiveness of evaporation methods, does not strongly depend on salts concentration there is no need to decrease Cl<sup>-</sup> concentration (and therefore the salts at all). Additionally, the concentrate produced during desalination may be concentrated until market-grade salt is obtained, and thus due to the production of two valuable products (purified water and salt), overall process costs may be decreased. The desalination of seawater by means of the proposed system may result in a water recovery rate equal to 77.3%, that is, much higher than that obtained in evaporation or RO methods. The ecological effect of the solution is also very important as a greater amount of salt (ca. 85%) is utilized and due to the use of NF the amount of additional chemicals is reduced.

An interesting option for the use of nanofiltration in hybrid desalination systems is the filtration of brackish mine water with simultaneous sulfate salts crystallization. In order to prevent crystallization of salts forming membrane scale, NF is run for oversaturated solutions and crystallization seedings are also introduced to the cycle (Juby *et al.*, 2000; Magdziorz and Seweryński, 2002; Turek, 2002c). It enables the production of concentrate of salt content much higher than 70 g L<sup>-1</sup>, that is, 150–160 g L<sup>-1</sup>, and with membrane processes at low costs. A study on seeding technique use has been run by the Resources Conservation Company (RCC) in Norway (Magdziorz and Seweryński, 2004). The study has been carried out on a pilot-scale installation equipped with tubular RO modules by Osmonics (Type 520) made of cellulose acetate. The installation has been used for desalination of brackish water (of mineralization rate 3 g L<sup>-1</sup>) at water recovery rate above 90%, which corresponds to oversaturation of the solution with calcium sulfate. During the blockage neither membrane fouling nor scaling were observed (Magdziorz and Seweryński, 2002). Laboratory and pilot-scale studies (of capacity 140–170 L h<sup>-1</sup> of treated brine) on the use of NF and seeding technique have also been realized with the use of brackish waters of characteristic similar to the majority of mine waters in Poland (Konieczny and Bodzek, 2003; Magdziorz and Seweryński, 2002, 2004; Magdziorz and Thorsen, 1995; Bodzek and Konieczny, 2011 (Fig. 8.32)). The mineralization has reached 70–100 g L<sup>-1</sup>, with calcium ions, magnesium ions and sulfate content of 60–120, 80–140 and 40–130 mmol L<sup>-1</sup>, respectively.

Nanofiltration of raw seawater used in hybrid systems power plant/MSF or power plant/RO/MSF (Fig. 8.30) results in feed water softening and removal of 90% of ions responsible for scaling, mainly sulfates, carbohydrates, calcium and magnesium (Awerbuch, 2005; Helal, 2009), whereat the retention of chlorides does not reach 50%. The high removal of bivalent ions during NF enables an increase in the water recovery rate during RO desalination and eliminates the risk of scale formation on the membrane surface or heat exchanger walls. It also reduces the required dose of anti-scalant and enables the operation of an MSF unit with brine at an upper limit temperature, that is, 130°C. The distillation capacity may be increased from 15 to 45% at a temperature increase from 90–110°C to 120–125°C (Awerbuch, 2005; Helal, 2009). The hybrid, pilot-scale MSF installation described in Hamed (2005) has been successively operated at brine temperature of 130°C, and the product recovery rate has reached 70%, while for the conventional MSF system it has been established at 35%. The mixture of NF permeate and raw seawater has been used as a feed to MSF in the investigated system.



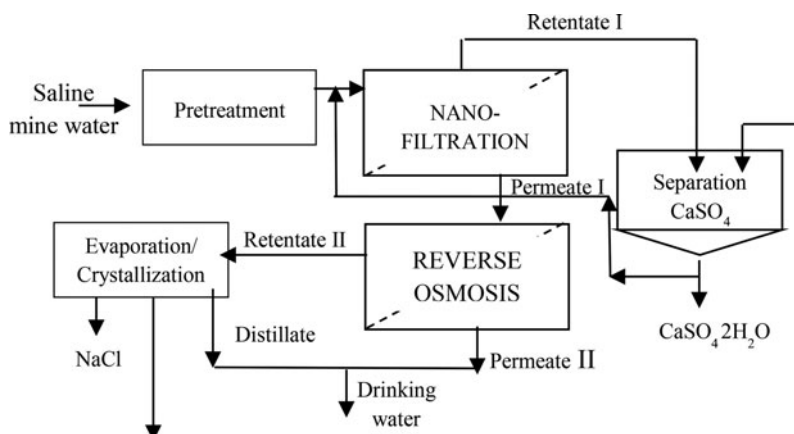


Figure 8.32. Installation scheme of mine water concentration using nanofiltration and reverse osmosis with an initial crystallization of calcium sulfate (Bodzek and Konieczny, 2011).

In the pilot-scale studies carried out at the Saline Water Conversion Corporation (SWCC) laboratories in Saudi Arabia, the effectiveness of triple hybrid systems of capacity  $20 \text{ m}^3 \text{ day}^{-1}$ , that is, conventional filtration on double filters-NF-SWRO, double filtration-NF-MSF and double filtration-NF-concentrate SWRO-MSF, has been tested (Awerbuch, 2005; Hassan *et al.*, 1998; Helal, 2009). The use of NF has resulted in a decrease in  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$  ions by 89.6, 94.0, 97.8 and 76.6%, respectively, and the total hardness content by 93.3%, reducing the energy demand by 17%. The use of NF also causes a reduction in  $\text{Cl}^-$ ,  $\text{Na}^+$  and  $\text{K}^+$  by 40.3% and TDS removal from seawater by 57.7%. The integration of NF with the MSF process has caused the MSF section to operate efficiently for 1200 hours (50 days) with no need for the addition of anti-scalants or antifoaming compounds and at a feed temperature of  $130^\circ\text{C}$ . During the exploitation, the product recovery rate increased from 35% (the value usually obtained for conventional MSF systems) to 70%. In the second experiment the MSF feed was totally composed of RO retentate. The MSF section of the trihybrid system has worked sufficiently for 976 hours (41 days) at a feed water temperature of  $130^\circ\text{C}$ . The introduction of NF has significantly improved water production by more than 60% as well as the costs of pilot-scale MSF and SWRO installations, which have decreased by 30% (Al-Sofi, 2001). The successful results obtained during pilot-scale studies have resulted in the construction of an industrial-scale NF/RO/MSF system in Umm Lujj, Saudi Arabia (Fig. 8.33) (Bodzek, 2015).

#### 8.4.3 Hybrid systems with ion-exchange/electrodeionization

The access to a relatively cheap raw water source is the crucial parameter taken into account when considering the location of an industrial plant. There is a trend to avoid the use of municipal water in industrial purposes. Hence, technologies enabling the reuse of wastewaters (e.g. treated wastewaters from municipal mechanical-biological treatment, industrial wastewaters, waste cooling waters or surface waters, etc.) are desired. Such a need also results in an increase in raw water salinity, a higher demand for demineralized water, and an increase in chemical prices and costs of deposition of wastewater after regeneration of ion-exchange beds (Ali *et al.*, 1989; Cuda *et al.*, 2006; Fendri *et al.*, 2011; Tsiourtis, 2001).

In the last several years a change in demineralized water production issues has been observed. Membrane processes are becoming very popular methods used in the production of water for power and also other industrial purposes, enabling the solution of many problems that usually appear during conventional demineralized water production techniques and water treatment (Bodzek and

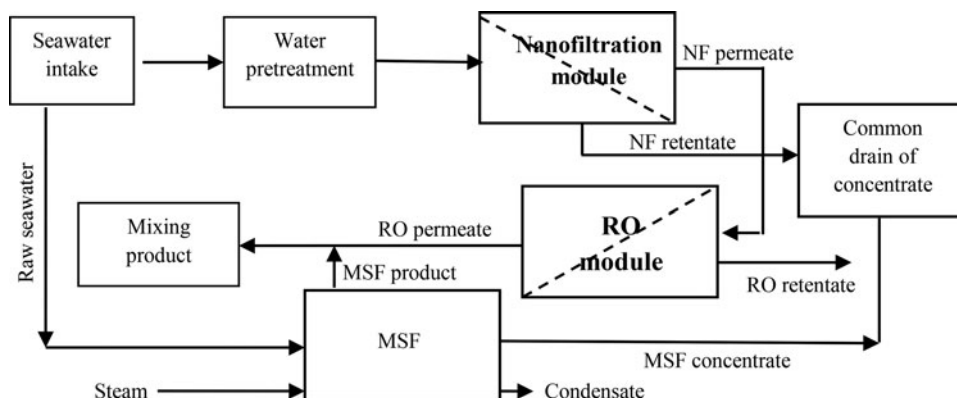


Figure 8.33. Hybrid desalination system NF/RO/MSF (Bodzek, 2015).

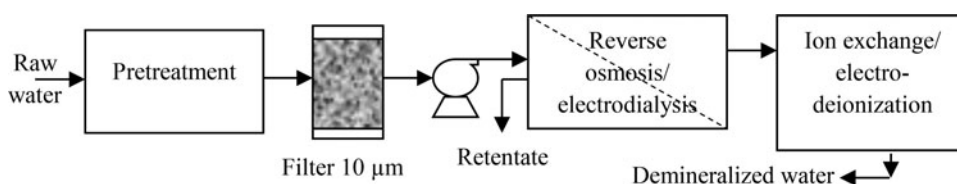


Figure 8.34. Diagram of typical installation of water demineralization by reverse osmosis (Bodzek and Konieczny, 2005).

Konieczny, 2005, 2007). For deep demineralization (steam boilers, electronic systems) hybrid systems – reverse osmosis with ion exchange/electrodeionization – are usually applied (Fig. 8.34) (Bodzek and Konieczny, 2005, 2007).

In some systems, RO is replaced either by electrodialysis (ED) or by electrodialysis reversal (EDR). The preliminary treatment of raw water in the RO process (usually comprising coagulation-flocculation-sedimentation, but also MF/UF) is a crucial factor, and the technology of the pretreatment depends on the contamination rate of the raw water.

The EDR system is less sensitive to raw water contamination than processes based on reverse osmosis and ion-exchange, which enables the use of raw surface waters of SDI value ranging within 5 to 6. The EDS technique also assures a high water recovery rate of 85–95%. The RO/EDR system results in the removal of 99.5% of total dissolved solids. The method is especially beneficial in the case of high salinity of raw water, that is,  $>350\text{--}450\text{ mg L}^{-1}$  NaCl. Fendri *et al.* (2011) have tested several conventional and alternative demineralization technologies including the two-stage RO system and ion-exchange on mixed bed. In the membrane process, BW30LE-440 and BW30-400 membranes by Filmtec were used in the first and second stages respectively. The concentrate from the second stage was recirculated and mixed with the feed (raw Black Sea water) for the first stage. The permeate from the second stage of TDS concentration  $9\text{ mg L}^{-1}$  was introduced to the ion-exchange bed, which was a mixture of strongly acidic cationite (Dowex Monosphere 650C) and strongly basic anionites (Dowex Monosphere 550A). The TDS content in the product obtained after the process did not exceed  $0.019\text{ mg L}^{-1}$ . The water stream produced was dedicated to energy production purposes.

The introduction of RO to demineralization does not eliminate all the disadvantages of ion-exchange, especially the need for regeneration of beds with chemicals. In the latest solutions, conventional ion-exchange is replaced with electrodeionization (EDI) (Bodzek and Konieczny, 2005; Fendri *et al.*, 2011). Electrodeionization is a process combining electrodialysis

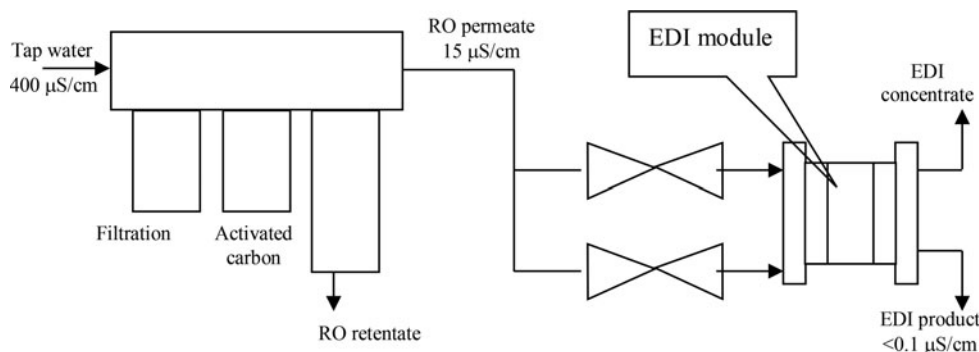


Figure 8.35. Diagram of RO-EDI process for water demineralization (Bodzek and Konieczny, 2011).

and ion-exchange, in which the regeneration of ionites is not required (Bodzek and Konieczny, 2011).

Both electrodialysis (ED) and ion-exchange are used for the separation and removal of metal ions and their mixtures. However, during electrodialysis the electrical resistance increases with time as ions are removed from the diluted solution chamber to the concentrate chamber. It results in higher energy consumption and lower efficiency of ion removal. One of the solutions to the problem may be the use of electrodeionization (EDI), in which the diluate chamber is filled with conductive material (ion-exchanger). Electrodeionization is a combination of electrodialysis and ion-exchange (Bodzek and Konieczny, 2005). The technique involves the use of conventional ion-exchange resin, but the voltage applied causes the transport of ions to proper electrodes, and thus to the concentrate stream. The second action of the constant current voltage is dissociation of the water into  $\text{H}^+$  and  $\text{OH}^-$ , which reacts with the ion-exchange groups of the resin, and thus causes their regeneration. Chambers supplied by the ion-exchanger are fed with the contaminated water, and from those chambers the purified water is taken out. The ion-exchanging chambers and concentrate chambers are separated with ion-exchanging membranes. Hence, the need for chemical regeneration of the ion-exchange bed is avoided. Studies on the EDI process have revealed that it comprises two stages. The first is the diffusion of ions from the solution to the ion-exchange resin material, while the second stage covers the electrical conduction to the membrane surface due to the presence of the solid state and electric field (Yeon *et al.*, 2003). Moreover, the solid phase keeps conductivity in the diluate chamber and enhances ion exchange, as the *in situ* regeneration of the bed takes place during EDI (Gabelich *et al.*, 2010).

In Figure 8.35, the scheme of the system of water demineralization via integrated RO-EDI method is shown. RO permeate of conductivity  $15\ \mu\text{S}\ \text{cm}^{-1}$  directly feeds the EDI module with no further treatment. The EDI unit operates at recovery capacity of 75–90%. Such a process configuration results in production of water of conductivity below  $0.1\ \mu\text{S}\ \text{cm}^{-1}$  (Bodzek and Konieczny, 2011).

As an example of a hybrid installation based on RO-EDI, the system for production of water for gas-steam block turbine supply operated in EC Plant Wrotków/Lublin may be mentioned (Table 8.10) (Bodzek and Konieczny, 2005, 2011). The system comprises conventional preliminary treatment (chlorination, decarbonization, multi-stage filtration including active carbon, softening and detail filtration at  $5\ \mu\text{m}$ ), two-stage reverse osmosis and EDI.

## 8.5 THE CONSIDERATION OF ENERGY ISSUES IN WATER DESALINATION

Desalination processes are characterized by significant energy consumption required for the separation of salts from water, which in rapid desalinated water demand creates a series of problems, among which issues of energy consumption and environmental pollution resulting

Table 8.10. Analysis of the raw and demineralized water for RO-EDI system at EC Wrotków (Bodzek and Konieczny, 2005, 2011).

Parameter	Raw water	Permeate after RO	Water after EDI
Conductivity [ $\mu\text{S cm}^{-1}$ ]	499	8.2	0.06
Chlorides [ $\text{mg L}^{-1}$ ]	14.2	0.04	<0.03
Sulfates [ $\text{mg L}^{-1}$ ]	24.9	0.1	<0.1
Silica [ $\text{mg L}^{-1}$ ]	24.2	0.055	0.006
Organic carbon [ $\text{mg L}^{-1}$ ]	9.0	<0.2	<0.2
Ba [ $\text{mg L}^{-1}$ ]	0.055	0	0
Ca [ $\text{mg L}^{-1}$ ]	91.3	0.007	0
Fe [ $\text{mg L}^{-1}$ ]	0.003	0.001	0.001

fossil fuel use are of the highest importance. The costs of energy are 25–45% of the total costs of the desalination process (Tsiourtis, 2001). An analysis of energy demand shows that thermal processes involve more energy (electricity and heat) than RO (it requires only electric power) as well as requiring more additional chemicals for scaling, corrosion and prevention of foam formation (Ghaffour *et al.*, 2013).

#### 8.5.1 Energy consumption

In distillation-based processes (MSF, MED and TVC) there are two types of energy involved: low-temperature heat for water evaporation generated by low- and medium-pressure turbines and electric energy for pump operation, with heat being the dominant one (Al-Karaghoul and Kazmierski, 2013). The MVC process, on the other hand, requires only the supply of electrical energy. All thermal units are equipped with tubular condensers and complex pumping systems including raw water intake pump, distillate, brine and chemical dosing pumps. The simplest distillation technique, that is, single-stage evaporation, requires the supply of huge amounts of energy, as the water evaporation process uses  $650 \text{ kWh m}^{-3}$  of energy, depending on the temperature, but regardless of the salt content in the raw water (Al-Karaghoul and Kazmierski, 2013). MSF and MED processes decrease the energy consumption by the use of a multi-stage configuration. The heat efficiency of the thermal process is usually evaluated on the basis of ratio of distillate mass (kg) to the inlet stream mass (GOR) or of the distillate mass to 2326 kJ of heat (Al-Karaghoul and Kazmierski, 2013). The use of heat in an MSF plant varies from  $190 \text{ MJ m}^{-3}$  ( $\text{GOR} = 12$ ) to  $282 \text{ MJ m}^{-3}$  ( $\text{GOR} = 8$ ), for which the equivalent electrical energy use is  $15.83$  and  $23.5 \text{ kWh m}^{-3}$ , which gives a total energy consumption of  $19.58$ – $27.25 \text{ kWh m}^{-3}$  (Al-Karaghoul and Kazmierski, 2013). For the MED process the energy demand is  $14.45$ – $21.35 \text{ kWh m}^{-3}$  depending on the GOR value, for MVC it is  $7$ – $12 \text{ kWh m}^{-3}$  and for TVC  $16.26 \text{ kWh m}^{-3}$  (Semiati, 2008). The advantages of thermal processes include better quality distillate than permeate from RO process. In addition, thermal processes can be supplied with water of lower quality (higher salinity), without extensive pretreatment (Bodzek and Konieczny, 2011).

In the case of membrane processes the only energy that needs to be applied is the electrical energy. In the RO process an alternating current is used for pumps, while in ED the direct current is used for electrodes and AC or DC for pumps. The energy consumption in RO depends mainly on raw water salinity and permeate recovery rate. The osmotic pressure is strictly connected to the content of total dissolved solids in the raw water, and thus the desalination of water of high salinity requires the supply of higher amounts of energy. The size of installation also impacts the energy demand; nevertheless the average energy consumption varies from  $3.7$  to  $8 \text{ kWh m}^{-3}$  depending on the installation capacity (Al-Karaghoul and Kazmierski, 2013; Avlonitis *et al.*, 2003; Semiati, 2008). For a typical RO unit dedicated to seawater desalination (Avlonitis SWRO) of  $24,000 \text{ m}^3 \text{ day}^{-1}$  capacity, the energy consumption range is  $4$  to  $6 \text{ kWh m}^{-3}$ , including the

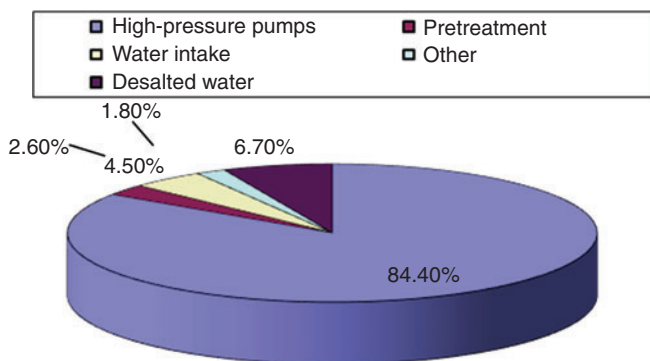


Figure 8.36. Energy consumption at different stages of RO desalination process (Fritzmman *et al.*, 2007).

recovery of energy from retentate. In Figure 8.36, the energy consumption at particular stages of water desalination by means of RO is shown (Fritzmman *et al.*, 2007).

In the case of brackish water desalination, lower transmembrane pressure is required and thus the energy consumption is also lower. Brackish water reverse osmosis (BWRO) is characterized by energy use from 1.5 to 2.5 kWh m<sup>-3</sup> (Al-Karaghoul and Kazmierski, 2013; Avlonitis *et al.*, 2003; Semiat, 2008). In general, the RO process requires less energy than MSF or MED as heating of the raw water is not required and the energy consumption is a function of water salinity (raw water osmotic pressure) (Tsiourtis, 2001; Van der Bruggen and Vandecasteele, 2002). In ED with water of low-salinity (<2500 mg L<sup>-1</sup>) the use of electrical energy varies from 0.7 to 2.5 kWh m<sup>-3</sup>, whereas for waters of salinity 2500 to 5000 mg L<sup>-1</sup> it is 2.64 to 5.5 kWh m<sup>-3</sup>, respectively (Adiga *et al.*, 1987; Kuroda *et al.*, 1987).

To sum up, the energy consumption in desalination processes depends on installation capacity, type of process, construction materials and raw water quality. It should also be considered that energy demand in distillation processes (MSF, MED, TVC) is independent of raw water salinity, which is contrary to membrane processes (RO and ED). If the energy consumption of the most popular methods of seawater desalination (MSF, MED, RO) is compared it can be noticed that distillation processes (MSF and MED) require more energy than RO. This is due to two main reasons: high water evaporation heat and continuous improvement of RO technology, including the field of energy requirement. Brackish water desalination is most often carried out with the use of RO or ED. It is generally known that RO is the cheaper at raw water TDS > 5000 mg L<sup>-1</sup>, while the use of ED is more profitable for raw waters of <5000 mg L<sup>-1</sup> of TDS. In Table 8.11, the energy consumption of the most popular desalination methods is presented (Al-Karaghoul and Kazmierski, 2013).

The relatively high energy consumption in desalination makes the processes still economic in the case of cheap energy supply, which can be met in many countries of the Middle East. However, in other regions, where the access to fuels is limited, water production by means of desalination may be quite expensive. Technological progress in heat exchange, membrane processes, energy recovery equipment, chemical prices and a combination of methods or processes leads to a reduction of energy consumption in desalination and thus reduces the process of freshwater production (Van der Bruggen and Vandecasteele, 2002). There are two main pathways to achieve a decrease in energy use during water desalination (Van der Bruggen and Vandecasteele, 2002):

- optimization and minimization of energy use during desalination,
- the use of alternative energy sources.

In desalination of seawater by means of RO there has been a fivefold decrease in energy use from 20 kWh m<sup>-3</sup> at the end of the 1970s to below 4.0 kWh m<sup>-3</sup> reached nowadays (Al-Karaghoul and

Table 8.11. Energy consumption of desalination processes <sup>(1)</sup> with energy recovery; <sup>(2)</sup> for low TDS) (Al-Karaghoul and Kazmierski, 2013).

Parameter	MSF	MED	MVC	TVC	SWRO	BWRO	ED
Size of installation [m <sup>3</sup> day <sup>-1</sup> ]	50000–70000	5000–15000	100–3000	10000–30000	To 128000	To 98000	2–145000
Electricity [kWh m <sup>-3</sup> ]	2.5–5	2–2.5	7–12	1.8–1.6	4–6 <sup>(1)</sup>	1.5–2.5	2.64–5.5
Heat [MJ m <sup>-3</sup> ]	190–282	145–230	None	227	None	None	None
Total energy consumption [kWh m <sup>-3</sup> ]	19.58–27.25	14.45–21.35	7–12	16.26	4–6	1.5–2.5	2.64–5.5, 07–25 <sup>(2)</sup>
Quality of water [mg L <sup>-1</sup> ]	~10	~10	~10	~10	400–500	200–500	150–500

Kazmierski, 2013; Fritzmann *et al.*, 2007). In the case of brackish water, the energy demand is lower and nowadays it is established below 1.5 kWh m<sup>-3</sup> (Al-Karaghoul and Kazmierski, 2013). Many reports and analyses performed by non-profit organizations and consulting companies have shown that if proper materials and devices for energy recovery are used, then freshwater may be produced from seawater at energy consumption of 1.58 kWh m<sup>-3</sup> (Fritzmann *et al.*, 2007). Similar tendencies are also observed for other desalination methods.

The new trend for the further reduction of investment costs as well as energy consumption is the idea of hybrid desalination systems with the use of membrane techniques, which were discussed in the previous chapter. In those solutions, the coproduction of electricity and desalinated water, mainly via systems with MSF distillation and reverse osmosis (Van der Bruggen and Vandecasteele, 2002) is possible. Coproduction of water and electrical energy by means of thermal processes enables the reuse of waste heat from a power plant in the form of low-pressure vapor used as a heat source for MSF or MED (Tsiourtis, 2001).

The exemplary changes in the design of conventional systems can be found in the replacement of steam turbines with gas turbines, improvement in exploitation and construction of condensers and cooling towers, compared with those used at the beginning of MED use (Dvornikov, 2000), and in energy recovery systems applied to RO (Harris, 1999). In the last case, the use of pressure exchange systems, in which the energy present in the brine is transferred to raw water by means of a hydraulic system, as an alternative for mechanical energy recovery via turbines, should be mentioned (Geisler *et al.*, 2001).

### 8.5.2 The use of renewable energy sources

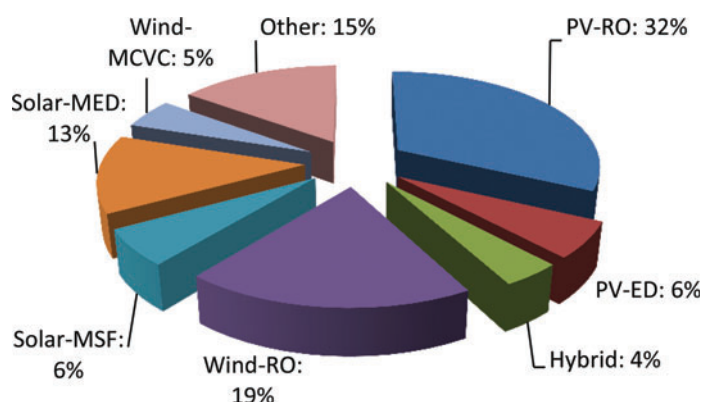
Renewable energy sources are energy sources, the use of which does not lead to the long-term deficit of the feedstock, as it recovers in a relatively short time. Systems based on renewable energy use energy from sources which are available in nature. Such sources are wind, sun radiation, waterfalls, sea tides, sea waves or geothermal. Their main advantage is that they are environmentally friendly, that is, their use is not related to the production of environmentally hazardous wastes. In contrast, non-renewable energy sources are those that renew very slowly or not at all, such as crude oil, coal, natural gas or uranium. The use of fossil fuels in energy production increases the emission of greenhouse gases. Due to this aspect, the studies on the use of alternative and renewable energy sources lead to their future use in water desalination processes (Tsiourtis, 2001; Van der Bruggen and Vandecasteele, 2002).

The use of three types of renewable energy is considered for desalination purposes, that is, geothermal, wind and sun energy. These forms of energy, however, are characterized by some

Table 8.12. General combinations of renewable energy technologies and desalination methods (Eltawil *et al.*, 2009).

Source of energy							
Solar				Wind		Geothermal	
PV	Solar thermal			Shaft	Electricity	Electricity	Heat
	Heat	Shaft	Electricity				
RO	RO	MVC	ED	MVC	RO	RO	TVC
ED	MED	RO	RO	RO	ED	ED	MED
MVC	MSF		MVC		MVC	MVC	MSF

MED: multi-effect distillation; MSF: multi-stage flash distillation; TVC: thermal vapor compression; MVC: mechanical vapor compression; RO: reverse osmosis; ED: electrodialysis.

Figure 8.37. Distribution of renewable energy in desalination process (Eltawil *et al.*, 2009).

limits compared with the desalination process, and thus their application as the only energy source is also limited. On the other hand, the production of water for municipal purposes by means of desalination supplied by renewable energy is found to be the solution for water deficit in areas of limited access to conventional energy sources (heat and electrical energy). Although the desalination of water with the use of renewable energy is not yet a competitive alternative to conventional systems considering economic aspects, such systems are, however, already applied in some regions and may become more popular in the near future (Tsiourtis, 2001).

There are many combinations of renewable energy sources and desalination processes, which can be tested within innovative research programs (AbKadir *et al.*, 2010; Eltawil *et al.*, 2009; Kalogirou, 2005). The energy can be mainly generated in the form of heat, electricity or mechanical energy. In Table 8.12 and Figure 8.37, the possible desalination systems supplied by renewable energy are shown (Eltawil *et al.*, 2009). The costs of energy in the desalination process are 50 to 70% of total desalination costs, which is the reason why many desalination plants are located near power plants or other industrial facilities with waste energy to be disposed of (Eltawil *et al.*, 2009).

#### 8.5.2.1 Wind energy

Wind energy is produced with the use of wind turbines in which it is converted to mechanical or electrical energy, which can be further used in water desalination. As reverse osmosis is

found to be the water desalination process with the lowest energy demand and coastal regions are characterized by high wind energy potential, the use of this type of energy is one of the most promising and preferable alternatives for the renewable energy introduction to desalination (Eltawil *et al.*, 2009; García-Rodríguez *et al.*, 2001; Kalogirou, 2005; Liu *et al.*, 2007; Pestana *et al.*, 2004). There have been a series of studies on the combination of wind energy and the RO process. Several facilities have been installed and tested all over the world; however, the technology is said to be still in the R&D phase.

There are several methods of desalination system integration with wind energy. The first is the installation of a wind turbine and its connection to the energy distribution systems, from which the desalination plant is supplied with energy. The second option relies on the direct conjunction of wind turbine and desalination system. However, in this case the desalination process is at risk of power disturbances and breaks in energy supply resulting from the nature of the source (wind). The solution to the problem is the integration of the desalination plant with supporting energy systems, for example, batteries, diesel generators or flywheels.

Small-scale desalination installations supplied by wind energy have been constructed mainly on islands (wind accessibility) (Tsiourtis, 2001). An example of a wind energy-based RO system is the installation located at Gran Canaria, Spain (García-Rodríguez *et al.*, 2001). Other examples are the RO plant operating at Split in Dalmatia (Croatia) (Vujčić and Krneta, 2000) or on the Norwegian Utsira islands (Enercon project) (Paulsen and Hensel, 2005, 2007). There is also a wind-supplied RO installation started in 1995 located in Trapani, Achaia, near Petra (Greece) (Kalogirou, 2005). Since 1998 the European Union has funded many studies and carried out many programs and demonstration projects on desalination systems supplied by wind energy, that is (European Commission, 1998):

- Suderoog island (Germany, North Sea) – capacity  $6\text{--}9\text{ m}^3\text{ day}^{-1}$ ;
- Ile du Planier (France, Mediterranean Sea) – capacity  $0.5\text{ m}^3\text{ h}^{-1}$ ;
- Helgoland (Germany, Germany) –  $2.4\text{ m}^3\text{ h}^{-1}$ ;
- St. Nicolas islands (France, Atlantic) – hybrid system of wind and diesel;
- Drenec island (France, Atlantic) – wind energy converter of 10 kW power.

Moreover, at Oahu island (Hawaii), a wind-based RO plant for brackish water desalination of capacity  $13\text{ L min}^{-1}$  and wind velocity  $5\text{ m s}^{-1}$  has been analyzed (Kalogirou, 2005) and the wind turbine is directly connected to a high-pressure pump. Such installations are also constructed in Australia (Robinson *et al.*, 1992) or in the Middle East, where in 1986 a system of capacity  $25\text{ m}^3\text{ day}^{-1}$  based on hybrid energy supply, that is, wind diesel, was started up (Kalogirou, 2005).

An ED-based brackish water desalination system supplied by wind energy is also taken into consideration as it may be adapted to changeable wind energy. Experimental studies of such a system of a capacity of  $192\text{--}72\text{ m}^3\text{ day}^{-1}$  located at Gran Canaria, Spain have been discussed in several publications (Kalogirou, 2005).

The advantage of a wind-supplied desalination system is the lower cost of production compared with water transport to islands or the use of fossil fuels for energy production. The use of wind energy may result in a reduction in the unit price of water produced by means of RO by 20%, assuming average wind velocity exceeds  $5\text{ m s}^{-1}$  (Kiranoudis *et al.*, 1997). García-Rodríguez *et al.* (2001) have analyzed the impact of climate conditions, nominal power of wind turbine, salt concentration in sea or brackish water, operational conditions, plant production capacity, RO module costs and wind turbine costs on desalinated water costs. The results of their studies reveal the need for further technological improvements of wind turbine exploitation economics. The disadvantage of such a system is wind force instability, which may cause power supply breaks, and thus desalinated water supply disturbances. According to changes in wind velocity, proper precautions for the control of the power inlet to the desalination system must be used. The control system is found to be the crucial element in wind-supplied RO desalination design.



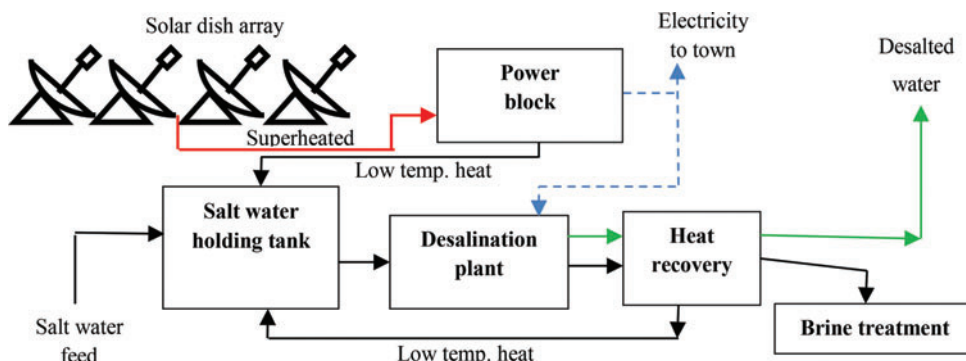


Figure 8.38. Combination of thermal solar energy with desalination (thermal or RO) (modified from Eltawil *et al.*, 2009).

#### 8.5.2.2 Solar energy

Solar energy may be converted into heat or electricity. The heat is obtained with the use of solar panels or direct solar distillation systems. Electricity may be produced using photovoltaic (PV) solar batteries or solar power plants (Al-Karaghoul and Kazmerski, 2013). However, solar energy available in several countries is characterized by high investment costs (Tsiourtis, 2001; Van der Bruggen and Vandecasteele, 2002).

In water desalination installations, solar energy may be used for feed water preheating or for vapor production. The technology of direct solar water desalination has already been used for many years and is based on the greenhouse effect. It relies on covering the water tank with a cover permeable to sun radiation, under which the seawater evaporates and after condensation is collected in special collectors (Al-Karaghoul and Kazmerski, 2013; Van der Bruggen and Vandecasteele, 2002). The method, however, is economically unattractive as the capacity is established at  $3 \text{ L m}^{-2}$  of the heated area, which corresponds to average daily capacity of distillation devices equal to 4 to  $6 \text{ L m}^{-2}$ . On the other hand, recent studies have revealed that solar distillation of seawater may become an efficient method if there is an improvement in materials and modernization in system design (Al-Karaghoul and Kazmerski, 2013; Al-Karaghoul *et al.*, 2009; Hummel, 1997). Nevertheless, solar systems are used for freshwater supply in some agricultural regions located in dry, distant areas, where there is the need for small amounts of drinking water (Al-Karaghoul *et al.*, 2009; El-Sebaei *et al.*, 2012; Qiblawey and Banat, 2008).

Solar energy is also used in direct solar distillation (solar ponds), or combined systems for electricity and desalinated water production by means of MED or hybrid MED/RO method (Fig. 8.38) (Glueckstern, 1995).

Low-temperature waste heat is used to heat up the feed water, which results in a decrease in RO energy demand. However, the feed water may be heated up only to the level limited by the membrane material and other operational parameters. The modification of the solution relies on the use of vapor for steam turbine supply and electrical energy production as well as supporting the pump drive (at lower pressure and temperature) (Eltawil *et al.*, 2009; Kalogirou, 2005).

The connection of RO with solar photovoltaic (PV) cells enables the conversion of thermal energy into mechanical, which seems to be more complicated than a distillation process based on conventional energy sources. However, due to the low energy consumption in RO the use of solar energy in this option seems to be profitable in regions of high solarization (Voros *et al.*, 1998). There are two types of membrane system supplied by PV: reverse osmosis (RO) and electrodialysis (ED). There are commercial systems of RO or ED equipped with PV dedicated to water desalination in remote areas (Kalogirou, 2005).

Several installations combining photovoltaic cells with reverse osmosis of capacity  $1 \text{ m}^3 \text{ day}^{-1}$  have been installed in Gran Canaria in Spain (Herold and Neskakis, 2001), in distant areas of

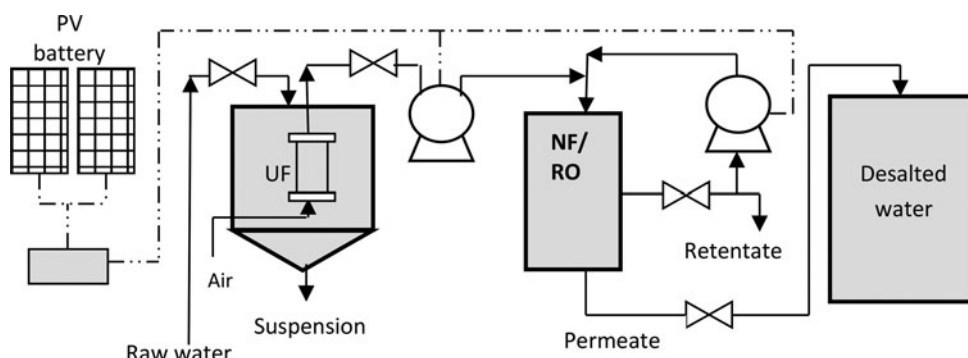


Figure 8.39. Diagram desalination system PV-UF/NF (Richards and Schäfer, 2002).

Table 8.13. Selected brackish water RO desalination installations powered with PV (Eltawil *et al.*, 2009).

Location	TDS concentration in raw water [mg L <sup>-1</sup> ]	Performance [m <sup>3</sup> day <sup>-1</sup> ]	PV [kW]	Battery [kWh]
Sadous Riyadh (Saudi Arabia)	5800	15	10	264
Haifa (Israel)	5000	3	3.5 + 0.6	36
Elhamrawie (Egypt)	3500	53	wind	200
Heelat ar Rakah (Oman)	1000	5	18	9.6
White Cliffs (Australia)	3500	0.5	3.25	None
Solarflow (Australia)	5000	0.4	0.34	None

Egyptian deserts (Ahmad and Schmid, 2002), and in agricultural areas of Jordan (Gocht *et al.*, 1998) and Sicily (Pretner and Iannelli, 2002; Scrivani, 2005), where they operate without problem. Kalogirou (2001), Tzen *et al.* (1998) and Bouguecha *et al.* (2005) have analyzed the economics of PV-RO desalination systems, while Al Suleimani *et al.* (2000) have discussed in detail the economics of the system installed in Heelat ar Rakah, Oman. An especially interesting prototype of an installation dedicated to water production from contaminated surface water or brackish water based on ultrafiltration and NF/RO desalination supplied by solar energy has been developed in Australia (Fig. 8.39) (Richards and Schäfer, 2002, 2003; Schäfer and Broeckmann, 2005; Schäfer and Richards, 2005). The system is designed to produce 1000 L of drinking water per day at energy consumption of 5 Wh L<sup>-1</sup>. The membranes are operated at pressure above 0.7 MPa. The system is fully autonomic as it requires just the raw water source.

In Table 8.13, several systems of brackish water RO desalination supplied by PV are presented (Eltawil *et al.*, 2009).

The main problem of PV desalination technology is the high cost of photovoltaic cells and their accessibility (Bodzek and Konieczny, 2011). The competitiveness of the RO-PV system compared with conventional systems depends mainly on the production capacity and concentration of salts in raw water (García-Rodríguez, 2003). Many initial demonstrations of PV-RO systems have generally been standard RO systems designed to be supplied by diesel engines or batteries charged with PV. Such a solution requires a large PV area due to the low effectiveness of standard RO systems as well as batteries. Additionally, large PV areas and regular replacement of batteries generate high costs of such systems.

Photovoltaic cells may also be combined with electrodialysis (Van der Bruggen and Vandecasteele, 2002). The use of PV cells for ED is attractive for regions of high and stable

solarization. Lundstorm (1979) was the first to describe a small installation for water desalination by means of ED supplied by PV batteries. Ishimaru (1994) has investigated the reliability of an integrated PV-ED system used in Japan for the treatment of water of  $1500 \text{ mg L}^{-1}$  TDS. The unit of capacity of  $200 \text{ m}^3 \text{ day}^{-1}$  has produced drinking water of satisfactory purity grade for two years. Al Madani (2003) has investigated ED devices combined with photovoltaic batteries determining the impact of process parameters (flow rate, temperature) on the installation effectiveness in the treatment of simulated NaCl solutions as well as natural groundwater of medium salinity level. The retention of salt has been equal to 95% for groundwater and 99% for simulated water and it has been obtained at low product flow rates. ED requires a direct current source for electrodes supply and this can be assured by a PV system. Additionally, ED pumps are of low-pressure type and can be powered with DC or AC current (Al-Karaghoul and Kazmerski, 2013). A PV-ED system is an interesting alternative for brackish water desalination ( $<2500 \text{ mg L}^{-1}$ ).

#### 8.5.2.3 Hybrid systems of wind and solar energy

Complementary features of wind and energy enable the design of desalination systems supplied by both these types of energy. Hybrid systems of RO-solar energy PV-wind energy have been developed and implemented for water desalination in, for example, agricultural regions of Oman (Al Malki *et al.*, 1998), Israel (Weiner *et al.*, 2001), northern Mexico, several small German islands in the North Sea (Petersen *et al.*, 1981), the southern part of Tunis (Houcine *et al.*, 1999), and in Argentino (Sicily) (Pretner and Iannelli, 2002). Mohamed and Papadakis (2004) and Mohamed *et al.* (2006) have presented a hybrid, autonomic seawater RO desalination system based on wind and PV energy supply. The calculated cost of the produced water has been established at  $5.2 \text{ € m}^{-3}$ , while the energy savings have reached 50% in comparison with other solutions. The analysis of the effectiveness and costs of seawater RO desalination using wind and solar radiation as renewable energy sources has shown the energy consumption level as  $2.33 \text{ kWh m}^{-3}$  in east African climate conditions and water production capacity of  $35 \text{ m}^3 \text{ day}^{-1}$ , which is a much lower value than that calculated for other projects (Charcosset, 2009). Weiner *et al.* (2001) have investigated experimentally and numerically the autonomic installations for desalination of capacity  $9 \text{ m}^3 \text{ day}^{-1}$  supplied by wind and photovoltaics. On the basis of this study an installation combining wind and solar energy use with no additional energy support, for example batteries or diesel engine, has been designed. Kershman *et al.* (2002) have investigated seawater desalination by means of RO (SWRO) supplied by a renewable energy source (hybrid system of PV/wind/grid/RO) dedicated for use in small-scale installations in Libya ( $300 \text{ m}^3 \text{ day}^{-1}$ ). The expected nominal power for the system operation has been established for RO desalination at 70 kW (net power after the energy recovery from concentrate), for a PV solar system at up to 50 kW and for a wind system at up to 200 kW. The main aim of the study was to reduce conventional energy use by 40%.

#### 8.5.2.4 Geothermal energy

Geothermal energy refers to the internal heat of the earth, which accumulates in a hydrothermal system, while “thermal water” is the groundwater, the temperature of which at the outflow of the spring is not lower than  $20^\circ\text{C}$  (Bujakowski *et al.*, 2008; Goosen *et al.*, 2010; Tomaszewska and Pająk, 2013). It is known that the earth’s temperature below a certain level is constant all year (Goosen *et al.*, 2010). Depending on the temperature, geothermal water of low ( $<100^\circ\text{C}$ ), medium ( $100\text{--}150^\circ\text{C}$ ) and high ( $>150^\circ\text{C}$ ) temperature may be distinguished (Popiel *et al.*, 2001). Water desalination plants may be supplied directly with the geothermal energy for raw water heating in MED distillation units or directly, when the geothermal energy is converted into electric energy used to supply RO systems (Goosen *et al.*, 2010). In general, geothermal water sources of high temperature are the most sought after for the commercial production of electricity, which is further used in reverse osmosis (Goosen *et al.*, 2010). The direct use of geothermal waters of low and medium temperature is suitable in the application of thermal desalination technologies. High-pressure geothermal springs enable the direct use of energy to supply mechanical desalination techniques, while high-temperature geothermal water can be used to direct production of

electricity to supply RO, ED and MVC (Al-Karaghoul and Kazmerski, 2013). Thermal distillation processes based on direct geothermal heating are the most commonly chosen for water desalination. Ophir (1982) has presented an economic analysis of desalination fed with geothermal water of temperature range 110–130°C, while Karytsas (1996) has performed technical and economic considerations on the possibility of use of geothermal resources of temperature 75 and 90°C to feed various distillation systems. Bourouni *et al.* (1999, 2001) have described installations in which humidification and drying processes make use of polypropylene evaporators and condensers at 60–90°C. Moreover, the recent progress in membrane distillation technologies enables the use of geothermal brine of temperature 60°C (Bourouni *et al.*, 1999). Geothermal energy of low enthalpy ( $T > 60^\circ\text{C}$ ) can be effectively used in sea or brackish water desalination in order to produce drinking or irrigating water. The most effective method of seawater desalination is the direct supply of geothermal heat to the plant based on multi-effect distillation (MED). The MED process supplied by geothermal energy is profitable due to the lower energy demand in comparison with other seawater desalination techniques. The MED method is based on the heat transport to sea or brackish water during condensation of vapor in a series of evaporators, or heat exchangers. The advantage of the process is that the internal walls of the heat exchanger are always covered with a thin layer of feed water, which significantly prevents the formation of scale.

The first plant for water desalination supplied by geothermal energy was built in 1972 in the USA, and subsequent installations have been constructed in France, Tunisia and Greece. In the 1990s a project for seawater desalination on Kimolos Island, Greece, was developed, involving the use of low enthalpy geothermal energy in the process (Goosen *et al.*, 2010; Karytsas, 1996). The flow rate of geothermal water was equal to  $60\text{ m}^3\text{ h}^{-1}$ , its temperature was in the range of 61–62°C and it was collected from a well of 188 m depth. The pilot installation produced freshwater and it was supposed to assure the water autonomy of the island. The MED method with vacuum distillation was used as the desalination technique configured in the two-stage system (D-TU-2-1200 – ALFA LAVAL DESALT). The production capacity of the installation was equal to  $80\text{ m}^3\text{ day}^{-1}$ . The cost of the produced water was established at  $1.6\text{ € m}^{-3}$  (including annual exploitation costs), which was the level suitable for small plants, whereas the cost was said to be reduced in the case of the system scaling up and further geothermal energy application.

#### 8.5.2.5 The comparison of various desalination technologies supplied by renewable energy

The comparison of different desalination technologies based on renewable energy, considering costs (implementation, operation, conservation) and exploitation (water recovery, fluxes) is very difficult. Prices of materials and services are significantly dependent on location and period of the project development. In Figure 8.40, it can be seen that the most popular technique is the use of photovoltaic cells combined with reverse osmosis (Tzen and Morris, 2003), while in Table 8.14 a review of recommended desalination processes based on renewable energy depending on the inlet parameters is presented (Mathioulakis *et al.*, 2007).

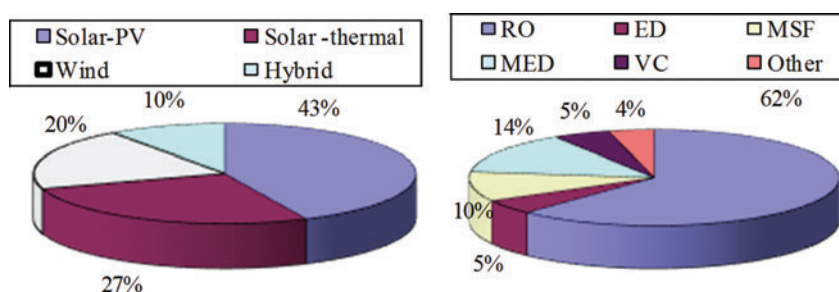


Figure 8.40. Desalination processes powered with renewable energy sources and renewable energy sources used in desalination (Tzen and Morris, 2003).

Table 8.14. Recommended combinations of desalination and renewable energy sources (Mathioulakis *et al.*, 2007).

Raw water	Desalted water	Renewable energy source	Size of the installation			The right combination
			Small	Medium	Large	
Brackish water	Distillate	Solar	*			Solar distillation
	Drinking water	Solar	*			PV-RO
	Drinking water	Wind	*	*		Wind-RO
	Drinking water	Wind	*	*		Wind-ED
Seawater	Distillate	Solar	*			Solar distillation
	Distillate	Solar			*	Thermal solar-MED
	Drinking water	Solar	*			PV-RO
	Drinking water	Solar	*			PV-ED
	Drinking water	Wind	*	*		Wind-RO
	Drinking water	Wind	*	*		Wind-ED
	Drinking water	Wind		*	*	Wind-VC
	Drinking water	Geothermal		*	*	Geothermal-MED

Photovoltaic cells (PV) are a suggested solution for small plants located in sunny climates. For large units, wind energy seems to be more attractive, as it requires only a suitable location. Such conditions are met on an island where there are proper wind conditions and harshness of the terrain.

## 8.6 ECONOMIC ANALYSES OF DESALINATION PROCESSES

The methods commonly used in water desalination, that is, multi-effect distillation (MED), multi-stage flash distillation (MSF), reverse osmosis (RO) and electrodialysis/electrodialysis reversal (ED/EDR) have significantly improved – initially they were regarded as cost- and energy-demanding technologies, while nowadays they are competitive methods of drinking water production (Van der Bruggen and Vandecasteele, 2002). In the past, due to high costs, desalination was not regarded as the best process for drinking and industrial-grade water production (Tsiourtis, 2001). The technological progress within the last 30–40 years has caused a significant improvement in water desalination economics, due to a decrease in the processing of materials, a reduction in energy consumption and easier access (know-how) to various water treatment technologies. Progress can mainly be found in multi-stage flash distillation (MSF) (materials and process) and reverse osmosis (RO), due to improvements in membrane construction and materials and use of energy recovery devices.

The growth of the desalination market has attracted many organizations and companies which have focused on the improvement of seawater desalination due to the reduction in costs. The combination of technological maturity, systems integration and competition has caused a decrease in desalinated water costs over recent decades, establishing it at 0.50 US\$ m<sup>-3</sup> (Ghaffour *et al.*, 2013) for large SWRO installations and specific regional conditions and below 1.00 US\$ m<sup>-3</sup> for MSF systems. Thus, it should be noted that seawater desalination costs decreased from 1.7 US\$ m<sup>-3</sup> in 1988 to 0.55–0.80 US\$ m<sup>-3</sup> of desalinated water at the beginning of the 21st century in the case of systems of capacity above 50,000 m<sup>3</sup> day<sup>-1</sup>. For installations of capacity 10,000–50,000 m<sup>3</sup> day<sup>-1</sup> the present cost of water is established at 0.68–0.81 US\$ m<sup>-3</sup> of desalinated water (Bodzek and Konieczny, 2011; Ghaffour *et al.*, 2013). The range in costs is the result of regional conditions at the installation locations (taxes, environmental use fees, etc.).

The technological progress in design and integration of membrane processes observed over the last two decades has also caused a reduction in brackish water desalination costs of more than a

Table 8.15. The cost of energy and water (average values) for commercial large-scale desalination processes (Eltawil *et al.*, 2009; Kalogirou, 2005).

Process	Heat [kWh m <sup>-3</sup> ]	Electricity [kWh m <sup>-3</sup> ]	Total [kWh m <sup>-3</sup> ]	Investment costs [US\$ m <sup>-3</sup> day <sup>-1</sup> ]	Total cost of water [US\$ m <sup>-3</sup> ]
MSF	7.5–12	2.5–4	10–16	1200–2500	(0.8–1.5) <sup>a</sup>
MED	4–7	1.5–2	5.5–9	900–2000	0.7–1.2
SWRO	–	(3–4) <sup>b</sup>	3–4	900–2500	0.5–1.2
BWRO	–	0.5–2.5	0.5–2.5	300–1200	0.2–0.4

<sup>a</sup> Including grants (fuel price); <sup>b</sup>Including energy recovery system.

half and in some cases even by 64% (Ghaffour *et al.*, 2013). The establishment of rigid costs for brackish water desalination is a difficult issue due to the instability of its composition (Arras *et al.*, 2009). In general, the cost of brackish water desalination is always lower than seawater treatment, due to the lower concentration of salts in raw water, that is, lower required transmembrane pressure and higher water recovery rates. It also results in lower energy consumption and much lower investment costs. The low cost of drinking water produced from brackish water may be also obtained in the case of EDR. A very large installation of total capacity 200,000 m<sup>3</sup> day<sup>-1</sup> for brackish water desalination has been constructed in Barcelona, Spain (Ghaffour *et al.*, 2013). EDR is usually preferred over RO in the case of raw waters of high ratio of sulfates to chlorides. The costs of brackish water desalination have decreased from 0.50–0.80 US\$ m<sup>-3</sup> in the 1980s to 0.20–0.35 US\$ m<sup>-3</sup> nowadays. The costs of desalination of brackish water of significant mineralization (33,000 mg L<sup>-1</sup>) are established at 0.25–0.28 US\$ m<sup>-3</sup> of desalted water in the case of conventional preliminary treatment, high-capacity membranes and installation capacity of 15,000 m<sup>3</sup> day<sup>-1</sup> (Abdelmajid and Fethi, 2002; Bodzek and Konieczny, 2011).

The present desalination costs are competitive with the transport costs of water over long distances, and RO process is found to be the optimal solution for desalination of low-salinity raw waters, regardless of installation capacity. It is predicted that desalination costs will continue to decrease due to the further improvement of technologies and the use of renewable energy sources. The automation of the process and progress in operation control systems may also prevent the eventual increase of process cost due to the stability of operational parameters (Pestana *et al.*, 2004).

It is difficult to make a detailed comparison of different desalination plants as actual costs depend on many variables, which are specific for every investment (Tsiourtis, 2001). The costs of desalination mainly depend on the following (Bodzek and Konieczny, 2011; Ghaffour *et al.*, 2013):

- Raw water quality – low TDS concentration in raw water (e.g. brackish water) results in lower energy demand in comparison with raw water of high TDS level (seawater). The desalination costs also depend on temperature and poor quality of raw water (suspension, turbidity), which causes severe RO membrane fouling, corrosion of devices and, in the case of MSF, other exploitation problems (Ghaffour *et al.*, 2013).
- Installation configuration and capacity – this influences the size and number of particular basic elements of installation and also additional equipment (e.g. pumps, water tanks, water distribution system, etc). High-capacity installations require significant investment costs compared with low-capacity systems. Nevertheless, due to the advantages of scaling up, savings in unit production costs can still be found (Eltawil *et al.*, 2009; Kalogirou, 2005). The investment costs obtained for various commercial technologies are different (Table 8.15). Thermal processes of comparable capacity require proper space and area as well as the use of more expensive materials and more sophisticated equipment than in the case of SWRO (which requires only electrical energy supply) and also higher amounts of additional chemicals for the prevention

Table 8.16. The costs of water desalination for a variety of the latest large-scale projects (Ghaffour *et al.*, 2013).

Place	Year run	Performance [m <sup>3</sup> day <sup>-1</sup> ]	Capital costs [US\$]	Water costs [US\$ m <sup>-3</sup> ]
Fujairah 2 MED/SWRO	2011	460000/136000	616 M/190 M	
Adelaide SWRO 2-pass	2011	273000	1.79 B	
Sydney SWRO 2-pass	2010	250000	933 M	
Hadera SWRO	2010	347900	425 M	0.63
Shuaiba MSF	2010	880000	2.4 B	0.95
Barka 2 SWRO 2-pass	2009	123500	800 M	
Marafiq MED-TVC	2009	800000	3.4 B	0.83
Skikda SWRO	2008	100000	110 M	0.73
Ras Laffan B MSF	2008	272500	900 M	0.80
Oxnard BWRO (1.38 g L <sup>-1</sup> )	2008	28400	25 M	0.31
Alicante 2 SWRO	2008	65000	89 M	
Hamma SWRO	2008	200000	250 M	0.82
El Paso BWRO (2.55 g L <sup>-1</sup> )	2007	55670	87 M	0.41
Perth SWRO 2-pass	2007	143700	347 M	1.20
Palmachim SWRO	2007	110000	110 M	0.78
Rabigh MED-TVC	2005	25000	–	1.15

of scaling, corrosion and foaming. On the other hand, distillate from thermal processes is of better quality than the RO product. Additionally, thermal processes are independent of initial parameters of raw water (salinity), and thus significant simplifications in the preliminary treatment system can be made.

- The accessibility and price of electrical energy – if the plant is to be supplied by electrical energy produced at a distance from the plant, RO is economically more favorable than thermal or hybrid processes. The minimization or reduction in energy demand also has a significant impact on the unit processing cost of the water produced.
- Location of the investment – the accessibility of the area and its condition and proximity to the water source and concentrate disposal place need to be considered when establishing costs of water production. The costs of pumping and pipelines resulting from the raw water transportation and concentrate disposal will be much lower if the raw water source and concentrate collector are located near the plant.
- Costs connected with raw water intake, preliminary and final treatment – these can be decreased if the installation is an extension of the existing water treatment plant, not a new facility. The final treatment of water mainly requires improvement in pH and minerals content for the produced water to meet the standards on drinking water quality (Gacem *et al.*, 2012).
  - Concentrate utilization – the latest regulations for environmental production obligate designers and constructors of the installation to develop and apply advanced methods of concentrate utilization (Lattemann and Höpner, 2008). Hence, salinity, temperature (in the case of thermal processes) and chemical waste issues must be resolved (Hoepner and Lattemann, 2002; Lattemann and Höpner, 2008).
- Requirements resulting from local/national permissions and the law (Sadhukhan *et al.*, 1999).

Currently there are trials on the analysis of existing and recently started water desalination installations based on various technologies, which can provide more detailed information on the process economics (Table 8.16). Significant differences can be noted in the total costs estimated for installations of comparable capacity and design. In some plants, the price of water is high due to special conditions and requirements of the process, that is, complex preliminary water treatment line or restricted environmental regulations, which increase permission and construction costs.

Table 8.17. The percentage distribution of individual cost elements for RO (Eltawil *et al.*, 2009).

Type of cost	Brackish water [%]	Seawater [%]
Fixed costs	54	37
Electricity	11	44
Labor	9	4
Membrane replacement	7	5
Maintenance and parts	9	7
Chemical substances	10	3

The total costs generated in a desalination plant can be divided into investment/capital costs and operational and management (O&M) costs. The total costs are defined as the sum of investment and operational costs established for 1 m<sup>3</sup> of produced water. Investment costs cover all expenses related to the realization of a given desalination project starting from the concept, through design, permissions, financing, construction, start up and final acceptance of operation (Wilf, 2007). All these types of costs can be divided into direct and indirect. Direct costs cover land exploitation costs, water intake, equipment, supporting devices, plant infrastructure and concentrate disposal (type of desalination method, plant production capacity, the destination of waste streams and environmental regulations). Indirect costs are percentage costs of the direct expenses. They can also include transport and its eventual insurance and other unpredicted costs. The O&M costs can also be divided into direct and indirect costs. Direct costs cover insurance and amortization. The usual insurance costs are established at 0.5% of total capital, while the amortization ranges from 5–10%. Main indirect costs are salaries, energy, chemicals and conservation expenses. The latter costs together with spare parts are usually less than 2% of annual capital costs (Eltawil *et al.*, 2009). In Table 8.17, the percentage share of particular costs generated during seawater and brackish water desalination by means of RO is presented (Eltawil *et al.*, 2009). It should be noted that:

- direct costs are the main ones for both types of desalination processes, considering the origin of the raw water;
- the main difference between brackish and seawater desalination can be found in energy consumption, whereas other costs decrease proportionally;
- costs related to membrane replacement, conservation, spare parts and exploitation materials are relatively low and depend on the technology level, while their impact on the total water desalination economics is negligible.

Thermal methods are found to be more expensive due to the amount of energy required for water evaporation. Membrane processes are more economically profitable in the case of brackish waters (3–10 g L<sup>-1</sup>), whereas in the case of seawater desalination (30 g L<sup>-1</sup>) membrane separation is not recommended due to the need for frequent membrane replacement. In Table 8.15 the investment and total costs of seawater desalination by means of thermal and RO methods are compared, while in Table 8.18 an analysis of particular water production costs using thermal methods compared with the RO method for installation capacity of 30,000 m<sup>3</sup> day<sup>-1</sup>, with electrical energy price 0.085 US\$ kWh<sup>-1</sup>, 7% outturn and 20 years of operation is shown (Banat, 2007). The total costs for industrial-scale thermal devices range from 0.80 to 1.50 US\$, 0.70 to 1.20 US\$ and 0.60 to 1.00 US\$, all per 1 m<sup>3</sup>, for MSF, MED and VC, respectively (Table 8.15) (Borsani and Rebagliati, 2005; Ghaffour *et al.*, 2013; Reddy and Ghaffour, 2007; Sommariva *et al.*, 2003).

The important parameter in desalination costs evaluation is the energy consumption, which is four times higher than the minimal energy required for production of drinking water from freshwater. Thermodynamic demand on energy for usual seawater desalination (35 g L<sup>-1</sup>) is equal to 0.78 kWh m<sup>-3</sup> for 0% recovery and 1.2 kWh m<sup>-3</sup> for 50% recovery, which is similar to RO energy demand (Ghaffour *et al.*, 2013). It should be noted that the total energy consumption



Table 8.18. Analysis of the individual component cost (relative to the costs of the RO process (100)) of desalinated water production by thermal methods compared with the costs obtained in RO (Banat, 2007).

Type of cost	MSF	MED	VC	RO
Investment	120	114	118	100
Energy consumption	215	175	140	100
Membrane replacement	—	—	—	100
Other costs	103	89	100	100
Production of desalinated water (total)	114	109	107	100

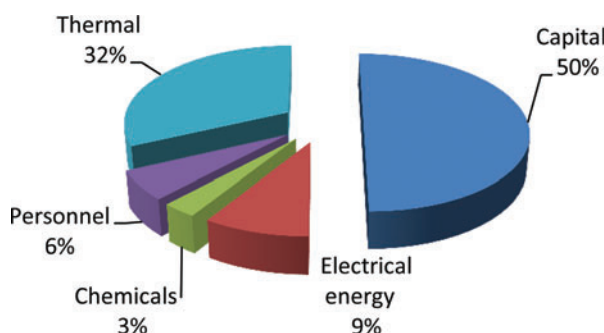


Figure 8.41. Typical cost structure for large thermal desalination installation for seawater (Eltawil *et al.*, 2009).

estimated for particular technologies is the clearest parameter for desalination costs evaluation, as in most cases the energy (especially heat) is highly refunded by governments, especially in countries of easy and cheap energy access. Hence, the costs of installations operating in different regions may not always be compared.

The data on costs and energy demand of desalination processes have been estimated by many authors and generally they can be summarized as follows (Eltawil *et al.*, 2009):

- Recent improvements in solar distillation technology make it the ideal method for remote, isolated areas of water demand lower than  $50 \text{ m}^3 \text{ day}^{-1}$ . In other sources, it is said that it can be even  $200 \text{ m}^3 \text{ day}^{-1}$ . All other technologies are found to be uneconomic for such small-scale systems.
- Reverse osmosis is the dominant process, which is characterized by energy consumption of  $6\text{--}10 \text{ kWh m}^{-3}$  of water and investment costs ranging from  $600$  to  $2000 \text{ US\$ m}^{-3}$  of production capacity (Kalogirou, 2005).
- RO-based systems combined with energy recovery are characterized by the lowest energy demand for seawater desalination ( $4\text{--}6 \text{ kWh m}^{-3}$ ) in comparison with other processes. In the case of brackish water desalination, the energy demand revealed by RO is much lower and varies from  $0.5\text{--}2.5 \text{ kWh m}^{-3}$ .
- For typical large-scale installations based on thermal processes, energy costs are usually 59% of total costs, and the next significant part of the costs are capital costs (Fig. 8.41) (Eltawil *et al.*, 2009). It seems that the most effective way to reduce the costs of thermal water desalination may be the use of alternative heat and energy sources. Moreover, the development of cheaper and less corrosive heat exchanging materials may also result in a decrease in capital and energy costs (Eltawil *et al.*, 2009).

Table 8.19. The costs of water desalination by thermal methods (Karagiannis and Soldatos, 2008).

Water type	Installation size [ $\text{m}^3 \text{ day}^{-1}$ ]	Cost [ $\text{€ m}^{-3}$ ]
MED	<100	2–8
	12000–55000	0.76–1.56
	>91000	0.42–0.81
MSF	23000–528000	0.42–1.40
VC	1000–1200	1.61–2.13

Table 8.20. The costs of water desalination by RO method (Karagiannis and Soldatos, 2008).

Water type	Installation size [ $\text{m}^3 \text{ day}^{-1}$ ]	Cost [ $\text{€ m}^{-3}$ ]
Brackish	<20	4.5–10.3
	20–120	0.62–1.06
	40000–4000	0.21–0.43
Sea	<100	1.2–15
	250–1000	1–3.14
	1000–4800	0.56–1.38
	15000–60000	0.38–1.30
	100000–320000	0.36–0.53

Table 8.21. Water desalination costs depending on the type of energy (Karagiannis and Soldatos, 2008).

Water type	Type of energy	Cost [ $\text{€ m}^{-3}$ ]
Brackish	Conventional	0.21–1.06
	Photovoltaic cells	4.50–10.32
	Geothermal	2.00
Sea	Conventional	0.35–2.70
	Wind	1.00–5.00
	Photovoltaic cells	3.14–9.00
	Solar collectors	3.50–8.00

Another parameter affecting desalination costs is the installation capacity. The RO method is widely used in large installations of daily capacity up to 320,000  $\text{m}^3$  of water. For an installation of capacity 40,000  $\text{m}^3 \text{ day}^{-1}$  desalination costs are established at 0.21–0.43  $\text{€ m}^{-3}$  (Karagiannis and Soldatos, 2008). In large systems, RO is the attractive system even for seawater desalination. At daily production ranging from 100,000–320,000  $\text{m}^3$  the costs vary from 0.36 to 0.53  $\text{€ m}^{-3}$ . In Tables 8.19 to 8.21 the effects of the installation capacity, desalination process type and applied energy origin on the unit price of desalinated water are presented (Karagiannis and Soldatos, 2008).

Finally, it may be concluded that reverse osmosis is a cheaper solution for high-capacity plants in comparison with other technologies. However, it should be remembered that production costs are strongly dependent on location; thus the economic comparison of different plants is not always clear and should be carefully considered individually. Thermal solar systems may become a dominant player in the desalination market as an example of clean energy-based systems for the 21st century. The solar energy-based technologies seem to be most appropriate to achieve a significant reduction in global  $\text{CO}_2$  emission. The time of return of solar power plant investment

is about half a year, while its lifetime reaches 25 years. The emission of greenhouse gases is very low and varies from  $0.010\text{--}0.015\text{ kg kWh}^{-1}$ , which is almost negligible when compared with gas ( $0.500\text{ kg kWh}^{-1}$ ) or coal ( $0.900\text{ kg kWh}^{-1}$ ) power plants (Eltawil *et al.*, 2009).

## 8.7 FINAL REMARKS

Over the past several years, desalting of seawater has become a method for the production of water at a cost comparable to the cost of freshwater production by other methods. The dominant techniques used on a large scale are RO and MSF, but MED and ED constantly extend the range of applications, although ED/EDR has limited use, in practice only for brackish water. Recently, research on new desalination techniques has been carried out, especially membrane distillation and forward osmosis. Significant improvements in technology and process design, the availability of alternative sources of energy, and the possibility of pretreatment and new materials has meant that the desalination process has become an ecologically friendly source of freshwater in many regions of the world, especially in those where their sources are limited. Reduction in the cost of desalination is associated with improvements in the production of membranes, higher efficiency of energy recovery, higher efficiency of pumps, better control of the formation of membrane scaling and improvements in the desalination process itself. There are numerous studies in the field of desalination related to reducing investment costs, reduction in energy demand and improvement in the exploitation. These have led to the achievement of hybrid installations combining electricity production and water desalination, which, thanks to the use of waste heat, are more economical.

An important issue in desalination is environmental hazards. Desalting mimics nature and is part of the natural circulation of water in it. Seawater and other types of natural waters evaporate naturally, thanks to solar energy and the chemical and physical properties of the Earth, desalting and purifying it, adapting it for use by all organisms on earth. Desalination processes mimic part of the hydrological cycle, using renewable and non-renewable sources of energy, chemicals made by man and his knowledge.

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## CHAPTER 9

### Review of direct discharge and recovery of reverse osmosis concentrates

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#### 9.1 INTRODUCTION

Water scarcity has been a worldwide problem throughout human evolution and will become a crucial challenge in the 21st century with the explosion of the global population within 5–6 decades (Jiang *et al.*, 2014). According to forecasts, by 2025 two-thirds of the world's population will live in regions with water scarcity (Drioli and Macedonio, 2012). The growth in demand for freshwater is partially satisfied by desalination plants that increasingly use membrane technologies and, among them, reverse osmosis (RO), to produce purified water. Operating with water recoveries from 35% to 85%, RO plants generate huge volumes of concentrates in the waste stream, containing compounds that are commonly discharged to water bodies and constitute a potentially serious threat to receiving ecosystems. These concentrates, also called brines or retentates, are a source of inorganic and organic compounds that can be recovered using appropriate procedures. There is an urgent need for sustainable management options regarding RO concentrates.

#### 9.2 GLOBAL DESALINATION OVERVIEW

Seawater desalination offers a seemingly unlimited, steady supply of high-quality water, without impairing natural freshwater ecosystems. The desalination of brackish groundwater provides another option towards increasing water supplies for inland regions (Elimelech and Phillip, 2011). Efficient utilization of concentrates and on-site energy resources could result in the production of both water and high-value minerals for beneficial use (Hickenbottom and Cath, 2014; Pérez-González *et al.*, 2012).

Membrane engineering plays a dominant role in water desalination and municipal water treatment. The 20th IDA Worldwide Desalting Plant Inventory (IDA, 2007) indicated that the production capacity of all desalination plants worldwide was around 44.1 million cubic meters per day ( $\text{Mm}^3 \text{ day}^{-1}$ ) by the year 2007. Worldwide, the installed desalination capacity grew at a compound average rate of 12% a year over 2002–2007, and the rate of capacity growth was expected to increase even further. Based upon country-by-country analyses involving desalination projects and official data on water supply and demand from agencies around the world, the total worldwide installed desalination capacity in 2015 was around 100 million  $\text{m}^3 \text{ day}^{-1}$ .

Seawater desalination continues to represent the largest percentage of global capacity at 59%, followed by brackish water at 22%, river water at 9%, and wastewater and pure water at 5% each (Fig. 9.1). North America is the only region where brackish water desalination is the dominant process used. The production capacity is  $3 \text{ Mm}^3 \text{ day}^{-1}$ , which represents more than one-third (36%) of the global brackish water desalination capacity. Overall, 21% of the production from brackish water sources takes place in the Gulf countries ( $1.7 \text{ Mm}^3 \text{ day}^{-1}$ ) and 13% ( $1.1 \text{ Mm}^3 \text{ day}^{-1}$ ) in Southern Europe (Lattemann *et al.*, 2010).



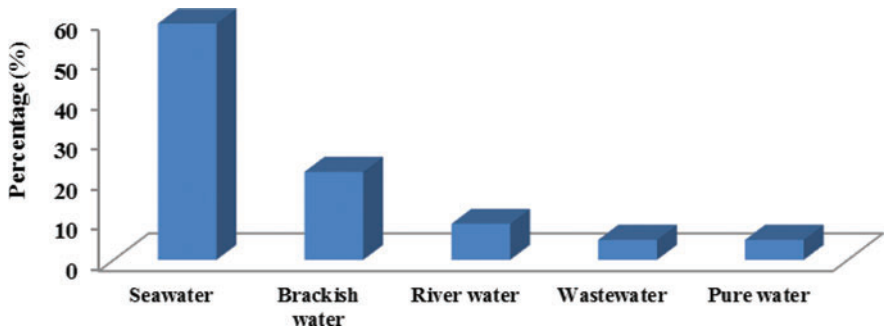


Figure 9.1. Distribution of desalination capacity according to water source (Lattemann *et al.*, 2010).

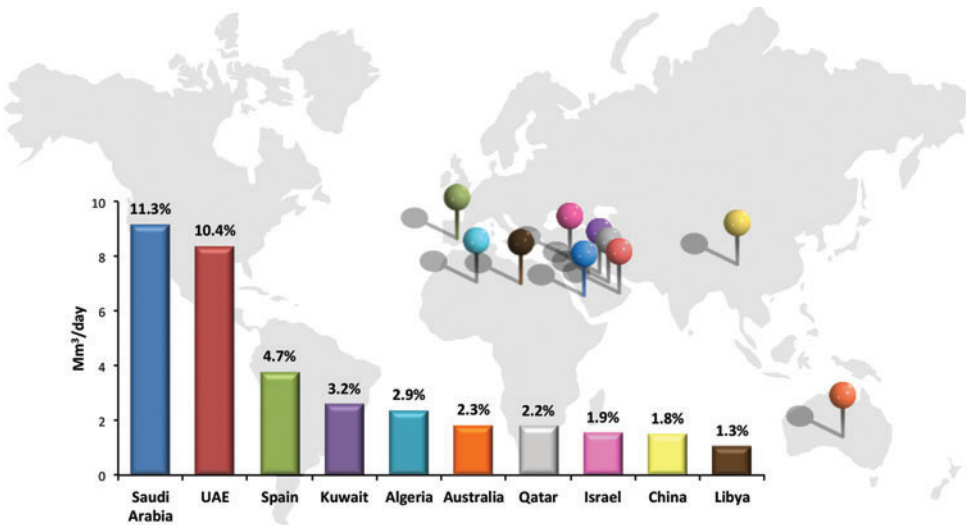


Figure 9.2. Top ten countries by their seawater desalination capacity. Bar chart represents the desalination capacity per country in  $\text{Mm}^3 \text{ day}^{-1}$  and the bar percentage is calculated with respect to the 2013 global desalination capacity of  $80.9 \text{ Mm}^3 \text{ day}^{-1}$  (IDA, 2013).

The top ten countries by their seawater desalination capacity are represented in Figure 9.2. Three enclosed sea areas account for the largest portion of the global seawater desalination capacity: the Gulf, the Red Sea, and the Mediterranean Sea (Lattemann *et al.*, 2010). The markets that were expected to see the fastest growth in desalination over 2013–2018 are South Africa, Jordan, Mexico, Libya, Chile, India, and China, all of which were expected to more than double their desalination capacity (IDA, 2013). In Spain, the production of desalinated seawater has been increasing, especially in the Mediterranean coastal areas. The temporal irregularity in river flows and the excessive exploitation and pollution of underground waters (by agricultural activities and seawater intrusion) have made it necessary to search for alternative water sources (Palomar and Losada, 2010).

An increasing proportion of desalination growth is occurring in the industrial sector. Production processes utilize water either as a cleaning agent, solvent, or as part of the final product, and process utilities, such as cooling towers, boilers and air handling units, utilize water to carry out

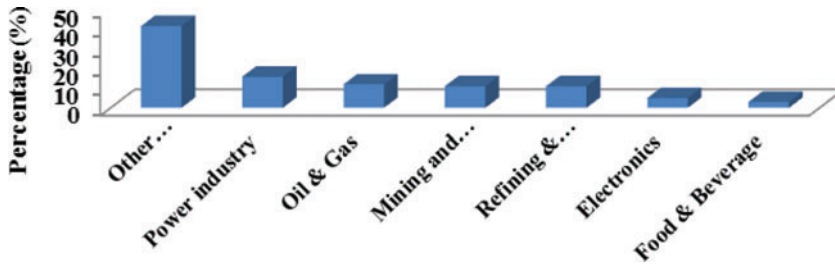


Figure 9.3. Distribution of desalination capacity according to industrial application (IDA, 2013).

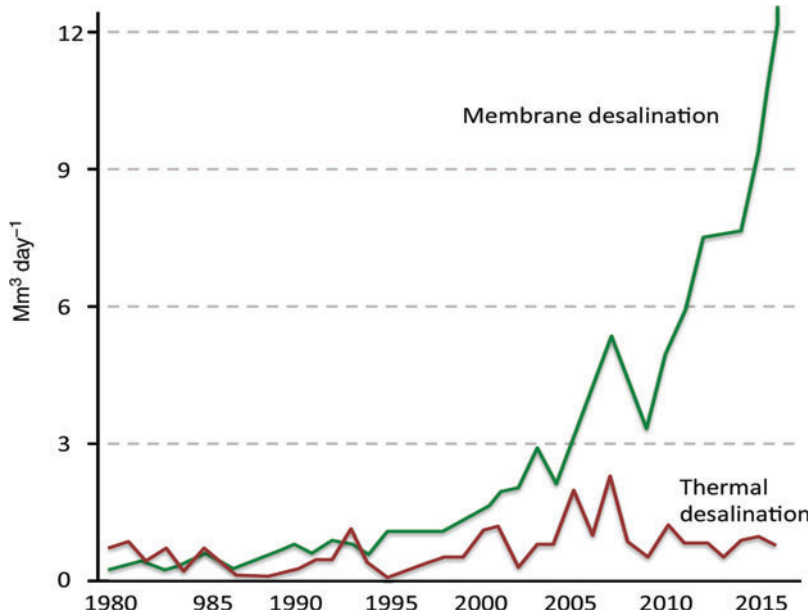


Figure 9.4. Annual new contracted capacity: thermal versus membrane. Source: DesalData/Desalination Markets (2010).

heat transfer, steam production and to make-up water loss due to evaporation. Since water is vital to many manufacturing processes and activities, its efficient use should be a priority in order to ensure that water scarcity and increasing water tariffs will have minimal effects on production (Agana *et al.*, 2013). Industrial applications for desalination increased to  $7.6 \text{ Mm}^3 \text{ day}^{-1}$  for 2010–2013, compared with  $5.9 \text{ Mm}^3 \text{ day}^{-1}$  for 2006–2009 (IDA, 2013). The distribution of desalination capacity according industrial application is described in Figure 9.3.

The development of desalination capacity by membrane and thermal processes shows that, by 1980, thermal distillation methods accounted for up to 75% of the cumulative installed capacity.

The vast majority of desalination plants constructed during the past two decades, as well as future planned facilities, are based on RO technology (Elimelech and Phillip, 2011), as indicated in Figure 9.4. Considering the desalination technologies currently used, RO possesses some inherent benefits, including lower costs, process simplicity and minimal environmental impacts (Greenlee *et al.*, 2009).

### 9.3 RO DESALINATION: CHARACTERISTICS AND DRAWBACKS

RO is a membrane technology widely applied in water desalination, the production of potable water, and more recently in tertiary wastewater treatment. The technology has the advantages of membrane processes, such as a modular construction and small footprint, which allows its combination with other treatment processes (Chelme-Ayala *et al.*, 2009). RO technology employs semi-permeable membranes that allow a solution to be separated into two streams: permeate (containing the purified water that passes through the membrane) and concentrate (the portion that contains salts and retained compounds). The driving force of the process is the pressure difference applied at the feed side to overcome the counteracting osmotic pressure and force the water to permeate through the membrane. The operating pressure for seawater desalination typically amounts from 5.5 to 6.8 MPa. For brackish water, the applied pressures are lower due to a lower osmotic pressure (Tarnacki *et al.*, 2012).

At present, RO is the most energy-efficient technology for seawater desalination and is the benchmark used to analyze any new desalination technologies (Fernandez-Gonzalez *et al.*, 2015). Decreases in energy consumption are attributed to continual technological improvements, including more highly permeable membranes, the installation of energy recovery devices, and the use of more efficient pumps (Elimelech and Phillip, 2011; Peñate and García-Rodríguez, 2012). Current state-of-the-art of RO plants consume between 2.2 and 5 kWh m<sup>-3</sup> and emit between 1.4 and 1.8 kg CO<sub>2</sub> per cubic meter of produced water (Fritzmann *et al.*, 2007; Likhachev and Li, 2013; Meerganz von Medeazza, 2005).

The main impacts of RO desalination processes on the environment are their energy consumption and the disposal of concentrate into the sea (Palomar and Losada, 2011). There is a high potential to reduce the environmental load of RO drastically when it is combined with renewable energies, such as wind energy and photovoltaic. There are some seawater RO (SWRO) plants coupled with renewable energies on the Canary Islands (photovoltaic and wind), and islands of Croatia and Norway (wind energy); there are also similar projects in Jordan, the Egyptian desert, Australia, and Saudi Arabia among others (Tarnacki *et al.*, 2012).

Apart from energy consumption, a key factor to consider in implementing RO technology is the volume of concentrate produced during the process. The volume of concentrate generated is most critical for inland RO plants that are located far away from the ocean (Subramani and Jacangelo, 2014). Concentrate disposal is a major economic factor and is affected by several factors, including site characteristics (geologic features, soil conditions, proximity to potential disposal site), regulatory requirements, public approval, and the type of concentrate disposal method. Based on these limitations, concentrate disposal costs can range from 5% to 33% of the produced water cost (Einav *et al.*, 2002; Tsiourtis, 2001).

### 9.4 RO CONCENTRATES: INFLUENCE OF PRODUCTION SITE

The characteristics of the RO concentrates depend on the quality of the feed water, the quality of the produced water (recovery varies from 35% to 85%), the pre-treatment method (added chemicals), and cleaning procedures (Chelme-Ayala *et al.*, 2009; Greenlee *et al.*, 2009; Palomar and Losada, 2011).

In addition to the high levels of salts, constituents in the concentrates are generally found at double (or higher) concentrations than in the feed water (Chelme-Ayala *et al.*, 2009); the RO concentrates also contain various chemicals used in the pre-treatment stage of desalination, including various de-fouling materials, as shown in Table 9.1 (Einav *et al.*, 2002; Waly *et al.*, 2011).

The quantity of concentrate is largely a function of a plant's recovery levels, which in turn are proportional to the total dissolved solids (TDS) concentration. Seawater desalination plant recovery levels are typically limited to 40% to 65% and the TDS levels of concentrate from those

Table 9.1. Main chemicals used in the pre-treatment of seawater desalination.

Compound	Purpose
NaOCl or free chlorine	Chlorination, preventing biological growth (antifouling)
FeCl <sub>3</sub> or AlCl <sub>3</sub>	Flocculation and removal of suspended matter from the water
H <sub>2</sub> SO <sub>4</sub> or HCl	pH adjustment to avoid precipitation of calcium carbonate
Sodium hexametaphosphate (SHMP) = (NaPO <sub>3</sub> ) <sub>6</sub> and similar materials	Prevention of scale formation on the pipes and on the membranes
NaHSO <sub>3</sub>	Neutralization of any remains of chlorine in the feed water

plants are usually in the range of 50,000–85,000 mg L<sup>-1</sup> (Voutchkov, 2011). Table 9.2 displays the average chemical characteristics of representative RO concentrates from seawater desalination plants.

The considerably lower salt concentrations of brackish groundwater and municipal wastewater tend to allow for much greater fractional recoveries. Brackish groundwater RO plants typically operate at recovery levels of 75–90%, corresponding to a concentration factor of 4–10. Wastewater treatment plants typically achieve recoveries of 70–85% for RO (concentration factors 3.3–6.7) (Voutchkov, 2011). For concentrates generated from the desalination of brackish groundwater (Table 9.3), the primary constituents of concern are calcium, silica and sulfate. The presence of high concentrations of calcium and sulfate result in exceeding the saturation limits of calcium carbonate (CaCO<sub>3</sub>) and calcium sulfate (CaSO<sub>4</sub>), thereby restricting the feed water recovery of the RO process (Subramani and Jacangelo, 2014).

When concentrates from wastewater treatment plants (WWTPs) are utilized (Table 9.4 and Table 9.5), scaling due to calcium phosphate (CaPO<sub>4</sub>) restrict the feed water recovery. Sulfate levels in concentrates from WWTPs are similar to the chloride content, while in concentrates from desalination plants, sulfate concentrations are 2–8 times lower than the chloride levels (Pérez-González *et al.*, 2012). Conductivity, TDS and chloride concentrations present significantly higher values in RO concentrates from desalination plants than in RO concentrates from WWTPs. However, concentrates from WWTPs present higher organic pollutant loads, but lower salinities, than desalination plant RO concentrates. Thus, treatment technologies must be adapted to the source of the RO concentrates, to eliminate problems associated with their composition.

The water quality of RO concentrates from industrial sites can be quite different depending on the industrial process (Table 9.6). For example, mine contaminated groundwater treatment sites may present a high concentration of calcium (1000 mg L<sup>-1</sup>) and sulfate (4400 mg L<sup>-1</sup>), in addition to metals (Subramani *et al.*, 2012). RO concentrates from textile effluents (Praneeth *et al.*, 2014) usually present similar conductivity, TDS and chloride concentrations to those from desalination processes. In the RO concentrates from a petrochemical plant, organic pollutant charge was found (Zhou, M. *et al.*, 2011) and fluctuations of chemical oxygen demand (COD) and total organic carbon (TOC) in the concentrate were observed over a research period of several months. RO concentrates from the steel industry in Tianjin, China, presented pH values close to neutral, and possessed a very high conductivity (mainly Cl<sup>-</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>) and low COD content (Zhou, M. *et al.*, 2011).

The composition of each type of concentrate clearly shows that the chemical characterization of RO concentrates is dependent on the feed water source. RO concentrate composition will define the adverse environmental impacts of the direct discharge of these effluents. Most importantly, chemical characterization of RO concentrates is essential to define the most adequate treatment technology, which should be in selected in accordance with the pursued objective: reducing concentrate volume, reducing concentrate pollutant load or recovering valuable compounds from RO concentrates.

Table 9.2. Characterization of RO concentrates from seawater desalination.

Parameters	Ji <i>et al.</i> (2010)	Melián-Martel <i>et al.</i> (2011)	Petersková <i>et al.</i> (2012)	Reig <i>et al.</i> (2014)	Sadhwani <i>et al.</i> (2005)	Waly <i>et al.</i> (2011)	Waly <i>et al.</i> (2012)	Yang <i>et al.</i> (2014)
pH	—	7.5	—	—	—	—	—	—
TDS [mg L <sup>-1</sup> ]	50200	79660	—	—	68764	51894	78034	—
Conductivity [ $\mu$ S cm <sup>-1</sup> ]	—	85200	—	—	—	—	—	—
SiO <sub>2</sub> [mg L <sup>-1</sup> ]	—	—	—	<1	—	0.9	0.26	—
B [mg L <sup>-1</sup> ]	—	8	4.5	—	—	7	—	2.9
Cations [mg L <sup>-1</sup> ]								
Na <sup>+</sup>	15500	25237	27521	20800	20657	16166	24489	15120
Mg <sup>2+</sup>	2020	2867	2450	2640	2751	1833	2711	2010
K <sup>+</sup>	—	782	554	750	814	616	868	452
Ca <sup>2+</sup>	625	960	—	830	814	583	948	714
Fe <sup>2+</sup>	—	—	—	0.2	—	—	—	—
Mn <sup>2+</sup>	—	—	—	0.01	—	—	—	—
Sr <sup>2+</sup>	—	14.6	—	0.02	—	12	—	—
Ba <sup>2+</sup>	—	0.02	—	<0.2	—	—	—	—
Anions [mg L <sup>-1</sup> ]								
Cl <sup>-</sup>	28800	41890	—	38800	37639	28166	43070	23400
SO <sub>4</sub> <sup>2-</sup>	3060	6050	—	5410	5628	4251	5544	3810
PO <sub>4</sub> <sup>3-</sup>	—	—	—	—	—	—	0.5	—
HCO <sub>3</sub> <sup>-</sup>	199	1829	—	—	452	256	293	—

Table 9.3. Characterization of RO concentrates from seawater desalination.

Parameters	Ahmed <i>et al.</i> (2003) <sup>(1)</sup>	Hajbi <i>et al.</i> (2010)	Korngold <i>et al.</i> (2009)	Macedonio <i>et al.</i> (2011)	Martinetti <i>et al.</i> (2009)	McCool <i>et al.</i> (2013)	Shane Walker <i>et al.</i> (2014)	Subramani <i>et al.</i> (2012)	Xu <i>et al.</i> (2013)
pH	6.2	7.2	—	4	8	7.6	—	7.9	7.9
TDS [mg L <sup>-1</sup> ]	17124	28000	—	—	—	19910	7890	5080	10860
Conductivity [ $\mu$ S cm <sup>-1</sup> ]	25984	33000	—	13500	—	21370	11500	—	—
Alkalinity [mg L <sup>-1</sup> ] as CaCO <sub>3</sub>	345	—	—	—	142	—	—	914	350
SiO <sub>2</sub> [mg L <sup>-1</sup> ]	15.6	—	103	56	72	72	—	254	152
Cations [mg L <sup>-1</sup> ]									
Na <sup>+</sup>	4160	5120	—	2084	5130	—	879	4828	2491
Mg <sup>2+</sup>	370	770	468	245	386	879	515	660	177
K <sup>+</sup>	134	—	—	79	—	13.8	—	125	122
Ca <sup>2+</sup>	1537	2080	1020	540	819	897	1030	895	717
Anions [mg L <sup>-1</sup> ]									
Cl <sup>-</sup>	8369	14170	6710	4068	8960	4440	3346	9333	5056
SO <sub>4</sub> <sup>2-</sup>	2334	5920	2688	2160	1920	12400	991	1920	1263
NO <sub>3</sub> <sup>-</sup>	14.6	—	—	—	—	—	87	—	20
PO <sub>4</sub> <sup>3-</sup>	—	—	—	0.04	2	—	—	—	61
HCO <sub>3</sub> <sup>-</sup>	421	—	—	—	223	491	1030	732	—

<sup>(1)</sup>Average composition of RO concentrates from desalination plants of Bahja, Rima, Nimr and Marmul of Petroleum Development Oman.

Table 9.4. Characterization of RO concentrates from wastewater treatment plants (I).

Parameters	Badruzzaman <i>et al.</i> (2009)	Bagastyo <i>et al.</i> (2011)	Chaplin <i>et al.</i> (2010)	Choi and Lee (2015) <sup>(1)</sup>	Ersever <i>et al.</i> (2007) <sup>(1)</sup>	Ersever <i>et al.</i> (2014)	Hwang and Shin (2013)	Justo <i>et al.</i> (2013)	Lee <i>et al.</i> (2009a)	Lee <i>et al.</i> (2009b) <sup>(1)</sup>
DOC [mg L <sup>-1</sup> ]	—	58	19.2	—	—	—	30.9	—	—	—
COD [mg L <sup>-1</sup> ]	—	173	—	365	—	—	22.6	77	64.6	—
TOC [mg L <sup>-1</sup> ]	25	—	—	—	40	8.4	—	28	18.4	24.5
TKN [mg L <sup>-1</sup> ]	—	—	—	—	—	3.8	31.7	23	—	—
NH <sub>4</sub> <sup>+</sup> [mg L <sup>-1</sup> ]	—	—	—	16.2	80	0	—	3.2	—	—
pH	—	8	—	—	—	—	—	8.3	7.2	7.5
TDS [mg L <sup>-1</sup> ]	2950	—	—	8470	3965	4440	11685	—	1218	1276
Conductivity [ $\mu$ S cm <sup>-1</sup> ]	3600	5020	4450	—	—	—	—	5960	1972	1990
Cations [mg L <sup>-1</sup> ]										
Mg <sup>2+</sup>	9.7	—	122	318	—	—	288	145	7.1	11.5
K <sup>+</sup>	88	—	22.6	—	—	—	—	135	65.3	38.4
Ca <sup>2+</sup>	96	—	306	1656	—	—	1437	477	110.1	63.8
Anions [mg L <sup>-1</sup> ]										
SO <sub>4</sub> <sup>2-</sup>	468	821	1584	—	1240	—	1512	569	218.4	159.1
NO <sub>3</sub> <sup>-</sup>	296	11.5	3.1	—	—	—	—	84	88.5	60.2
NO <sub>2</sub> <sup>-</sup>	—	0.4	—	—	—	—	—	—	8.3	—
PO <sub>4</sub> <sup>3-</sup>	10	—	—	—	20	20	—	4	34.7	21.3

<sup>(1)</sup>Average composition.

Table 9.5. Characterization of RO concentrates from wastewater treatment plants (II).

Parameters	Hao Lin and Li (2014)	Lu <i>et al.</i> (2013)	Malamis <i>et al.</i> (2012) <sup>(1)</sup>	Miralles-Cuevas <i>et al.</i> (2014c) <sup>(1)</sup>	Pérez <i>et al.</i> (2010) <sup>(1)</sup>	Radjenovic <i>et al.</i> (2011) <sup>(1)</sup>	Van Hege <i>et al.</i> (2002)	Van Hege <i>et al.</i> (2004) <sup>(1)</sup>	Westerhoff <i>et al.</i> (2009)	M. Zhou <i>et al.</i> (2011) <sup>(1)</sup>
DOC [mg L <sup>-1</sup> ]	25	47.5	—	50	23.3	57.2	—	—	40	—
COD [mg L <sup>-1</sup> ]	60	220	35	113	—	—	158	184	138	60
TOC [mg L <sup>-1</sup> ]	—	—	—	—	—	—	—	—	—	18
TKN [mg L <sup>-1</sup> ]	10	24.5	—	95	—	—	—	—	—	10
NH <sub>4</sub> <sup>+</sup> [mg L <sup>-1</sup> ]	—	—	0.5	110	121.8	—	—	—	—	—
pH	6.9	8.2	—	8.3	7.8	7.6	8.2	8.3	7	6.9
TDS [mg L <sup>-1</sup> ]	1129	10020	1073	—	—	—	—	—	5560	1129
Conductivity [ $\mu$ S cm <sup>-1</sup> ]	1705	—	—	6500	3250	4110	3990	4340	10000	1705
Cations [mg L <sup>-1</sup> ]										
Na <sup>+</sup>	203	—	269	650	—	—	—	—	—	203
Mg <sup>2+</sup>	7	—	28	195	—	—	—	32	—	7
K <sup>+</sup>	62	—	40	150	—	—	—	—	—	62
Ca <sup>2+</sup>	65	—	167	185	—	—	—	159	—	65
Anions [mg L <sup>-1</sup> ]										
Cl <sup>-</sup>	256	5200	—	1300	479	1.4	592.9	700	—	256
SO <sub>4</sub> <sup>2-</sup>	217	—	—	1000	443	240	—	—	—	217
NO <sub>3</sub> <sup>-</sup>	91	—	—	10	—	—	—	—	—	91
NO <sub>2</sub> <sup>-</sup>	2	—	75	16	—	—	—	—	—	2
PO <sub>4</sub> <sup>3-</sup>	39	—	—	—	—	—	—	—	—	39

<sup>(1)</sup>Average composition.



Table 9.6. Characterization of RO concentrates from different industrial processes.

	Praneeth <i>et al.</i> (2014)	Subramani <i>et al.</i> (2012)	C. Zhao <i>et al.</i> (2013) <sup>(1)</sup>	M. Zhou <i>et al.</i> (2011)
Industrial process	Textile	Mining	Petrochemical	Steel plant
Turbidity [NTU]	—	1.5	—	0.6
DOC [mg L <sup>-1</sup> ]	—	—	28	—
COD [mg L <sup>-1</sup> ]	—	—	102	160
TOC [mg L <sup>-1</sup> ]	—	—	—	31
TKN [mg L <sup>-1</sup> ]	—	19	—	—
NH <sub>4</sub> <sup>+</sup> [mg L <sup>-1</sup> ]	—	13	—	—
pH	8.8	4.1	7.8	8.3
TDS [mg L <sup>-1</sup> ]	47000	6100	2149	14745
Conductivity [μS cm <sup>-1</sup> ]	62600	—	3700	22300
Cations [mg L <sup>-1</sup> ]				
Mg <sup>2+</sup>	1650	270	71	332
K <sup>+</sup>	1085	26	—	—
Ca <sup>2+</sup>	1195	1000	134	272
Fe <sup>2+</sup>	—	0.1	—	—
Mn <sup>2+</sup>	—	150	—	—
Anions [mg L <sup>-1</sup> ]				
SO <sub>4</sub> <sup>2-</sup>	2750	4400	501	—
NO <sub>3</sub> <sup>-</sup>	—	36	—	—
NO <sub>2</sub> <sup>-</sup>	—	5.5	—	—

<sup>(1)</sup>Average composition.

## 9.5 ADVERSE EFFECTS OF CURRENT RO CONCENTRATE MANAGEMENT OPTIONS

Traditional management options for RO concentrates from desalination plants are dependent on the location of the plant. In coastal desalination plants, RO concentrates are directly discharged to sea, while in inland plants the traditional option consists of reducing the concentrate volume prior to disposal (Tang and Ng, 2008). Evaporation techniques have been widely applied to reduce the volume of concentrates, which produce a solid waste that is easier to manage than the original waste and a decontaminated liquid that can be directly discharged or even reused (Arnal *et al.*, 2005). Due to the adverse effects of concentrate disposal and the associated costs, current research is focused on reducing the impact of RO concentrates by reducing the volume and/or pollutant load of the concentrates. Besides this, there has also been research into the beneficial use of concentrate by-products, including analyzing the technical feasibility of isolating salts of a required morphology and purity (Stanford *et al.*, 2010). Recovering commercial by-products from RO concentrates is an optimum treatment option, as it solves the environmental problem of concentrate disposal and improves the economic profitability of RO at the same time (Pérez-González *et al.*, 2012).

Concentrate disposal in coastal desalination plants generally occurs by direct discharge to sea. The global installed desalination capacity is estimated at 86.6 Mm<sup>3</sup> per day in 2015 (IDA, n.d.). In RO desalination plants, the generated concentrate is about 55% of the collected seawater (Meneses *et al.*, 2010). Thus, approximately 33.3 Mm<sup>3</sup> of concentrate are discharge daily to sea and surface waters.

The first acknowledgment that concentrate and chemical discharges of desalination plants may pose a risk to the marine environment occurred in 1979; the study called for a thorough investigation of both the physical and biological components of the environment prior to construction and

on a regular basis during operation (Winters *et al.*, 1979). Roberts *et al.* (2010) reviewed the literature on the ecological impacts of desalination plants and concluded that there is a widespread belief and recognition that concentrate discharges pose a potentially serious threat to marine ecosystems. Laboratory-based experiments, toxicological investigations and manipulative field experiments clearly demonstrate the potential for concentrates and their constituents to illicit adverse impacts on aquatic organisms when present at sufficient concentrations. Furthermore, during pre- and post-treatment processes, a variety of chemical agents are added to enhance flocculation, prevent foaming or to avoid membrane deterioration (Meerganz von Medeazza, 2005). Research on the development of effective anti-scalants with no biological effects may assist in the production of less toxic concentrates in the future (Roberts *et al.*, 2010). However, with the traditional direct release of concentrates to the sea, their toxic components are discharged, including certain metals (copper, nickel, iron, chromium, zinc, etc.) that arise from thermal corrosion processes. The most pronounced effects of concentrate direct discharge on receiving waters are eutrophication, pH value variations, and accumulation of heavy metals, as well as the sterilizing properties of disinfectants (Meerganz von Medeazza, 2005). Due to these negative effects, direct disposal to sea of RO concentrates will stop with time. Lin *et al.* (2013) monitored the presence of heavy metals in concentrate discharges, the receiving sediments, and bivalves to investigate the impacts of the discharges on a marine environment; relatively higher concentrations of certain heavy metals in the sediments and bivalves indicated a possible anthropogenic effect for these elements. Their findings suggest that heavy metals in concentrate discharges at trace levels may still be transported and accumulated, leading to elevated concentrations in various matrices of the receiving marine environment. They demonstrate the difficulties associated with current regulations that typically predict the influences or assess the impacts with short-term environmental monitoring.

Currently there is no regulation that limits the physical parameters or chemical concentrations that are distinctive of concentrate effluents from desalination processes. The Water Quality EU Directives set critical limits on the discharges of effluents and receiving water bodies in order to guarantee water protection. However, they do not include critical limits for the chemical and physical properties of RO concentrates (Palomar and Losada, 2010).

This lack of legislation and the vulnerability and ecological importance of marine ecosystems justifies the diverse set of studies that have been carried out in recent years regarding the impact of hypersaline discharges into the marine environment (Lin *et al.*, 2013; Loya-Fernández *et al.*, 2012; Palomar and Losada, 2011; Van der Merwe *et al.*, 2014). The following negative effects related to concentrate discharges in coastal waters have been detected: anoxia at the bottom of the water column, turbidity and reduction of the percentage of light filtered through the water column to the seabed and reduction of echinoderm populations. In relation to the Mediterranean seagrass *Posidonia oceanica*, a decrease in growth has also been detected as well as necrosis in the tissues, leaf loss and an increase in mortality rate. To create critical salinity limits that would guarantee the conservation of *Posidonia oceanica* meadows, exhaustive research was carried out in Spain by several universities and specialized research centers; based on their results, critical salinity limits were established as quality criteria for *Posidonia oceanica* meadows (Table 9.7) (Palomar and Losada, 2010, 2011).

Critical limits are fundamental for the design of environmentally safe discharge systems and require comprehensive engineering analysis, including hydrodynamic modeling of discharges, whole effluent toxicity testing, salinity tolerance analysis of the marine species endogenous to the area of discharge, and reliable intake water quality characterization (Voutchkov, 2011). The discharge system design determines the degree of concentrate dilution in the near field region, where density differences (between concentrate and seawater) and momentum (depending on the discharge system) control the geometry and mixing processes of the concentrate effluent. The concentrate dilution influences the salinity of the gravity current in the far field region and, consequently, the risk of impact on benthic communities located far away from the discharge point (Palomar and Losada, 2010). Numerical modeling is a prediction tool useful for the design of discharge configurations and for environmental impact assessments. The models CORMIX, VISUAL PLUMES and VISJET can be used for simulating concentrate discharges. However,

Table 9.7. Suggested salinity limits for different ecosystems and species present in the Mediterranean Sea. Salinity in “psu”, practical salinity units (Palomar and Losada 2010).

Ecosystem/species	Critical salinity limits
<i>Posidonia oceanica</i> (seagrass)	Should not exceed 38.5 psu in more than 25% of measurements: S25, limit = 38.5 Should not exceed 40 psu in more than 5% of measurements: S05, limit = 40
<i>Cymodocea nodosa</i> (seagrass)	Should not exceed 39.5 psu in more than 25% of measurements: S25, limit = 39.5 Should not exceed 41psu in more than 5% of measurements: S25, limit = 41
<i>Caulerpa prolifera</i> (algae)	Threshold established around 50–60 psu
<i>Zostera noltii</i> (seagrass)	Threshold established around 41 psu
Mussels	Threshold established around 50–70 psu

these commercial models present several limitations and drawbacks. A detailed analysis of the major assumptions, capabilities, limitations and reliability of these models has been carried out by Palomar *et al.* (2012a, 2012b). Conclusions and recommendations about the use of the commercial tools and their degree of reliability aim to help promoters, designers and environmental authorities in discharge design and environmental impact assessments of desalination projects to minimize the adverse environmental impacts of concentrate direct discharges.

Another mechanism that has been applied to reduce the adverse environmental effects of concentrates relies on their dilution with power plant cooling waters (Einav and Lokiec, 2003; Sadhawani *et al.*, 2005). Concentrates can also be diluted with natural seawater or municipal wastewaters to reduce salinity prior to discharge (Meneses *et al.*, 2010; Roberts *et al.*, 2010), although the disposal of diluted concentrates can still affect sensitive species, so any solutions should be appropriately adapted to local conditions (Meneses *et al.*, 2010). To minimize areas of ecological impacts and limit the intrusion of concentrates into seawater intake areas, optimum infrastructure design and construction has been studied (Altarayan and Madany, 1992). Dispersion models are used to choose discharge points with the least environmental impact (Del Bene *et al.*, 1994), but these structures appear to have limited success and environmental damage is often still incurred.

Traditionally, options for disposal of RO concentrates from inland desalination plants have included deep well injection and surface water discharges (Ahmed *et al.*, 2001; Arnal *et al.*, 2005; Chelme-Ayala *et al.*, 2009; Gabelich *et al.*, 2010; Greenlee *et al.*, 2009; Malaeb and Ayoub, 2011; Muniz and Skehan, 1990). Similar options for their management have been used for potable water production from brackish groundwater (Malaxos and Morin, 1990; Squire, 2000; Van der Bruggen *et al.*, 2003). Surface water discharges have worse environmental effects than those discharged to sea, because the receiving rivers, lakes and aquifers have lower salinities than seawater. Moreover, surface discharges require huge land extensions and have adverse environmental impacts on subsurface soil properties. Regarding deep well injection, although some studies indicate that this practice is technically feasible without any risks of clogging of the injection well or the target aquifer due to precipitation of minerals (Wolthek *et al.*, 2013), the lifetime of wells is limited by their capacity. Besides this, the weaknesses of deep well injection as a method include the deterioration of the quality of potential groundwater resources and the loss of energy and mineral resources that may be of strategic interest in the future (Zarzo and Campos, 2011). The costs of concentrate disposal are another important issue that must be taken into account. With regard to inland desalination plants, the costs associated with concentrate disposal can be considerably higher than for coastal plants. Inland plants have to solve the problem of concentrate disposal without the possibility of discharging to sea, so the development of viable and sustainable management options is an urgent issue.

## 9.6 TREATMENT TECHNOLOGIES OF RO CONCENTRATES: REVIEW

Research on sustainable treatments applicable to RO concentrates has continually grown in recent years. Several review articles about traditional and emerging technologies for RO concentrates have been published recently (Buonomenna, 2013; Leong *et al.*, 2013; Morillo *et al.*, 2014; Qiu and Davies, 2012; Rodríguez-Delanuez *et al.*, 2012; Subramani and Jacangelo, 2014; Xu *et al.*, 2013). In most cases, the classification of treatment technologies is done based on the characteristics of the technology or the pursued objective. However, in this section, the classification of treatment technologies for RO concentrates is based on the source and chemical characterization of such concentrates. It is considered that the source of the concentrates determines its composition and is therefore a key factor in selecting the most appropriate treatment technology.

Referring to treatments applied to the management of RO concentrates from desalination plants, it should be noted that, due to the many drawbacks of traditional disposal options (see Section 9.5), several alternative technologies have been considered, of which intensified evaporation, membrane distillation, membrane distillation-crystallization, electrodialysis, electrodialysis aided with bipolar membranes, and forward osmosis, are the most important. The main characteristics of these alternative technologies are summarized in Table 9.7. Evaporation techniques using enhanced adsorbent surfaces have potential application in warm climates as natural evaporation techniques; note that these techniques provide better performance than natural evaporation (Aravamudan *et al.*, 2014; Farahbod *et al.*, 2012; Philip *et al.*, 2013). Membrane distillation combined with RO offers promising results; several configurations in the application of this technology have been studied, including direct contact membrane distillation (Al-Obaidani *et al.*, 2008; Hickenbottom and Cath, 2014; Ji *et al.*, 2010), vacuum membrane distillation (Mericq *et al.*, 2010), and direct contact vacuum membrane distillation (Martinetti *et al.*, 2009). The main advantages of membrane distillation over conventional distillation are reduced temperature (60–80°C) and reduced equipment size, where membranes provide a large contact area per unit volume of equipment. Membrane distillation integration with a crystallizer (MDC) is able to surpass the saturation limit of the desired solutes and when the solution reaches the saturation state, the saturated solute is crystallized out from the solution (Edwie and Chung, 2013). The application of electrodialysis to RO concentrates from desalination plants allows the recovery of a higher percentage of desalinated water and the concentrate concentration, which may facilitate in final management. A combination of mono-polar and bipolar membranes permits the production of acids and bases from the salts contained in high concentrations in RO concentrates. However, electrodialysis has several drawbacks, such as reaching adequate working conditions when working with high concentrations of salts to avoid a decreased efficiency of the electric current and precipitation of salts in the membranes (Ghyselbrecht *et al.*, 2013; Jiang *et al.*, 2014; Korngold *et al.*, 2009; McGovern *et al.*, 2014; Shane Walker *et al.*, 2014a, 2014b, 2014c). Forward osmosis is presented as an innovative technique that reduces the volume of concentrate; the lower energy consumption compared to RO is presented as the major advantage. However, it requires the use of an extraction solution (draw solution) to generate the difference in osmotic pressure across the membrane. This draw solution should be easily regenerated, for the economic balance of the process to be favorable (Martinetti *et al.*, 2009; Tang and Ng., 2008; Zhao, S. *et al.*, 2012). These technologies have been analyzed in several studies (Table 9.8), achieving promising results aimed at recovering water from the RO concentrate to reduce volume and facilitate its management.

Following this approach, with the aim of reducing the volume of concentrate, several studies have focused on achieving maximum water recovery through various processing steps to minimize the generation of a residual liquid effluent. These studies can be grouped into processes aimed at achieving zero liquid discharge (ZLD). A summary of these studies is shown in Table 9.9, which classifies the studies according to the sequential treatment process as the basic ZLD scheme, and ZLD schemes type A, type B and type C. The basic ZLD scheme involves the application of two consecutive RO stages. These systems achieve an overall recovery of water higher than a single RO stage, but the results indicate that a stage of intermediate treatment is needed to prevent the precipitation of salts on the surface of the membrane (Ning and Troyer, 2009;

Table 9.8. Emerging treatment methods applied to RO concentrates from desalination plants.

	Characteristics	References
Wind aided intensified evaporation	Intensified evaporation using hydrophilic material surfaces located perpendicular to the wind. Efficiency ten times greater than with natural evaporation.	Aravamudan <i>et al.</i> (2014) Farahbod <i>et al.</i> (2012) Philip <i>et al.</i> (2013)
Membrane distillation	Thermal membrane separation process. Vapor transport through hydrophobic microporous membranes. In combination with RO this achieves over 90% recovery of water.	Al-Obaidani <i>et al.</i> (2008) Hickenbottom and Cath (2014) Ji <i>et al.</i> (2010) Martinetti <i>et al.</i> (2009)
Membrane distillation-crystallization	Able to surpass the saturation limit of the desired solutes and when the solution reaches the saturation state, the saturated solute is crystallized out from the solution.	Edwie and Chung (2013) Ji <i>et al.</i> (2010)
Electrodialysis	Membrane separation process under the influence of an electrical potential. Uses cation and anion mono-polar membranes. Recovery of desalinated water and the concentrate concentration facilitates management and/or recovery of compounds.	Pantoja <i>et al.</i> (2015) Ghyselbrecht <i>et al.</i> (2012) Jiang <i>et al.</i> (2014) Korngold <i>et al.</i> (2009) McGovern <i>et al.</i> (2014) Shane Walker <i>et al.</i> (2014a, 2014b, 2014c)
Bipolar membrane electro dialysis	Membrane separation process under the influence of an electrical potential. Uses cation and anion bipolar membranes. Production of acids and bases from salts contained in concentrates.	Badruzzaman <i>et al.</i> (2009) Ibáñez <i>et al.</i> (2013) Yang <i>et al.</i> (2014) Wang <i>et al.</i> (2014)
Forward osmosis	Membrane separation process using the osmotic pressure gradient as the driving force. Concentrate concentration in combination with RO achieves over 90% recovery of water.	Martinetti <i>et al.</i> (2009) Shaffer <i>et al.</i> (2015) Tang and Ng (2008) S. Zhao <i>et al.</i> (2012)

Table 9.9. Treatment processes aimed to achieve ZLD.

	Treatment stages				Global recovery	References
Basic ZLD scheme	Primary RO	Secondary RO			88–99%	Ning and Troyer (2009) Ning <i>et al.</i> (2010) Singh (2009)
ZLD scheme type A	Primary RO	Intermediate treatment	Secondary RO		87–97%	Gabelich <i>et al.</i> (2011) Halevy <i>et al.</i> (2013) McCool <i>et al.</i> (2013) Rahardianto <i>et al.</i> (2010) Sanciolo <i>et al.</i> (2012)
ZLD scheme type B	Primary RO	Secondary RO	Post-treatment of concentrates		75–98%	Macedonio <i>et al.</i> (2011) Ning and Tarquin (2010) Oren <i>et al.</i> (2010) Turek <i>et al.</i> (2009)
ZLD scheme type C	Primary RO	Intermediate treatment	Secondary RO	Post-treatment of concentrates	80–100%	Bond and Veerapanemi (2008) Mohammadesmaeili <i>et al.</i> (2010a, 2010b)

Table 9.10. Advanced oxidation processes applied to RO concentrates from wastewater treatment plants.

Advanced oxidation process		Objective	References
Ozonation	$O_3 \rightarrow HO^\bullet$ ( $H_2O_2$ , UV)	Beta blockers molecules removal Improving biodegradability DOC removal	Benner <i>et al.</i> (2008) Lee <i>et al.</i> (2009a) Westerhoff <i>et al.</i> (2009)
Fenton	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^\bullet$	DOC removal	Westerhoff <i>et al.</i> (2009)
Electro-Fenton	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^\bullet$	COD removal	Du <i>et al.</i> (2014)
Photocatalysis	$TiO_2 + h\nu \rightarrow e^- + h^+$ $h^+ + H_2O \rightarrow HO^\bullet + H^+$	DOC removal	Dialynas <i>et al.</i> (2008) Westerhoff <i>et al.</i> (2009) T. Zhou <i>et al.</i> (2011)
Photo-oxidation	$H_2O_2 + h\nu \rightarrow 2HO^\bullet$	DOC removal Improving biodegradability	Bagastyo <i>et al.</i> (2011) Liu <i>et al.</i> (2011) Westerhoff <i>et al.</i> (2009)
Sonolysis	$H_2O + \text{ultrasound} \rightarrow H^\bullet + HO^\bullet$ $2HO^\bullet \rightarrow H_2O_2$	DOC removal	Dialynas <i>et al.</i> (2008) T. Zhou <i>et al.</i> (2011)
Electro-oxidation	$H_2O + \text{Anode} \rightarrow \text{Anode}[HO^\bullet]_{ads} + H^+ + e^-$	COD, ammonium and emerging micropollutants removal	Bagastyo <i>et al.</i> (2011) Chaplin <i>et al.</i> (2010) Lütke Eversloh <i>et al.</i> (2014) Pérez <i>et al.</i> (2010a, 2010b) Radjenovic <i>et al.</i> (2011) Urtiaga <i>et al.</i> (2013) T. Zhou <i>et al.</i> (2011)

Ning *et al.*, 2010; Singh, 2009). ZLD scheme type A includes an intermediate treatment step, which usually consists of a precipitation step or treatment with ion-exchange resins, to remove fouling compounds (Acevedo *et al.*, 2010; Gabelich *et al.*, 2011; Halevy *et al.*, 2013; McCool *et al.*, 2013; Rahardianto *et al.*, 2010; Sanciole *et al.*, 2012).

To achieve the goal of ZLD, it is necessary to seek for the recovery of compounds, including mainly salts and water. To this end, ZLD schemes type B (Macedonio *et al.*, 2011; Ning and Tarquin, 2010; Oren *et al.*, 2010; Turek *et al.*, 2009) and type C (Bond and Veerapanemi, 2008; Mohammedsmaeili *et al.*, 2010a, 2010b) have been developed, which include post-treatment of the concentrate and super-concentration of the concentrates that coming from the second stage RO. The post-treatment usually consists of an evaporation step or crystallization, for recovering the salts and other compounds in solid form and can achieve the objective, thus ZLD. These treatment schemes are presented as a promising treatment option. Initial cost estimates indicate the feasibility of treatments. However, studies are needed to assess the applicability of these systems at the industrial scale.

The typical chemical composition of RO concentrates from wastewater treatment plants is shown in Tables 9.4 and 9.5. The presence of organic charge and persistent micro-pollutants requires the application of specific treatments, more specifically advanced oxidation processes. These processes seek to reduce the organic load present in the concentrates by the oxidation of hydroxyl radicals. A summary of the application of these treatments is given in Table 9.10. To reduce the organic load of concentrates, the application of biological processes (Choi and Lee, 2014), coagulation (Dialynas *et al.*, 2008; Ordoñez *et al.*, 2012; Zhou, T. *et al.*, 2011), and

activated carbon adsorption (Dialynas *et al.*, 2008; Joo, 2014; Tao *et al.*, 2011; Wang *et al.*, 2013; Wei *et al.*, 2014), have also been studied. A combination of coagulation processes or adsorption on activated carbon as photo-oxidation has also been studied to evaluate the synergistic effect of the combination of both technologies (Lu *et al.*, 2013; Umar *et al.*, 2014).

When the goal of treatment is the removal of recalcitrant micro pollutants, including pharmaceuticals and personal care products, the application of advanced oxidation treatment becomes necessary (Liu *et al.*, 2014; Miralles-Cuevas *et al.*, 2013, 2014; Urtiaga *et al.*, 2013, 2014). Pharmaceutical compounds in RO concentrates from wastewater treatment plants come from two sources: the common use of pharmaceuticals in humans and animals, and wastewater from the pharmaceutical industry. A more detailed description of the processes used in the pharmaceutical industry and technologies applicable to the wastewater generated in these processes is presented by Gadipelly *et al.* (2014).

The literature review presented in this chapter shows that the chemical characterization of RO concentrates is directly related to the raw water source. The chemical composition of the concentrates determines the adverse environmental impacts of direct discharges of the effluents. Most importantly, it is essential to define the chemical composition of the RO concentrates to identify the most appropriate treatment, which depends on the final objective to be achieved: to reduce the volume of concentrate, reduce its pollution load or recover valuable compounds from the RO concentrate.

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## CHAPTER 10

### Geothermal water treatment in Poland

Barbara Tomaszewska

#### 10.1 INTRODUCTION

The efficient and sustainable management of natural resources, primarily energy resources, and increasing the proportion of renewable energy resources used in the energy sector are primary goals of European Union Member States, in respect of the fight against global warming. These objectives, especially economic ones, should undoubtedly be harmonized with environmental protection (Tomaszewska *et al.*, 2017).

In Europe, low-temperature energy resources associated with deposits at temperatures below 150°C are present; the handling of chilled geothermal waters depends largely on their mineral content and the presence of specific, sometimes toxic, ingredients in their composition. The best solution – and also the safest, from the point of view of the environment – is to inject the spent water back into the formation. Such geothermal energy systems are referred to as “closed” systems. These systems require a number of injection wells, which generate significant capital and operating costs, where geothermal reservoirs are found at considerable depths (1500–2500 m below ground level (b.g.l.)).

Elevated salinity levels and the presence of microelements, such as boron, barium, strontium, fluorides, bromides and heavy metals, often lead to difficulties related to discharging spent waters into surface watercourses. Owing to the legal environment and the objectives related to improving the quality of surface waters set out in the Water Framework Directive, Member States of the European Union are gradually limiting the utilization of so-called “open-loop” or “pump and dump” geothermal systems.

The capital expenditure required and the operating costs of a geothermal system are determined to a large extent by the method of utilization or disposal of the spent chilled geothermal waters. However, measures are generally undertaken to utilize these valuable resources in the most efficient way. To achieve this efficiency, desalination and treatment may be a promising direction and an alternative to injecting water into the formation or discharging it into surface watercourses.

The desalination of geothermal waters used for energy purposes is increasingly seen as a good method of securing high-quality water for various areas of the economy. In countries with warm climates, it is mainly used for the irrigation of agricultural crops (Kabay *et al.*, 2004a, 2004b, 2009; Koseoglu *et al.*, 2010; Öner *et al.*, 2011; Şimşek *et al.*, 2005). Given the increasing deficit of freshwater worldwide, possibilities of desalinating and treating geothermal waters for drinking and household purposes should be considered.

This chapter presents the results of pilot studies conducted to evaluate the possibility of using selected membrane techniques for treating geothermal waters. An important aim of the study was to determine the possibility of using both the permeate (desalinated water) and the post-process concentrate (the water containing separated minerals) (Bujakowski *et al.*, 2012; Tomaszewska, 2011a, 2011b, 2012; Tomaszewska and Bodzek, 2013a, 2013b, 2013c, 2014; Tomaszewska and Pająk, 2012; Tomaszewska and Szczepański, 2014; Tomaszewska *et al.*, 2014). The studies were conducted using water from two different geothermal intakes in Poland: the Podhale geothermal system (Bańska Niżna IG-1, GT-1) and the Polish Lowland system (Uniejów PIG/AGH-2, GT-2). The mineral contents of the waters were 2.5 and 6.5 g L<sup>-1</sup>, respectively, with elevated and high

contents of iron, strontium, boron, silica and other macro- and microelements (Tomaszewska, 2011a, 2012; Tomaszewska and Bodzek, 2013a, 2013c).

## 10.2 CHARACTERISTICS OF GEOTHERMAL WATERS

### 10.2.1 Waters of the Podhale geothermal system

The geothermal reservoir of the Podhale Basin is located in the southern part of Poland (Fig. 10.1). It consists of several aquifers situated in the Triassic limestone and dolomite, Jurassic carbonate and Eocene carbonate layers. The reservoir is a fissure and fissure-porous aquifer (Bujakowski *et al.*, 2012; Chowaniec, 2009; Kępińska, 2006; Tomaszewska and Bodzek, 2013a), with a secondary porosity of 10%–20% and high permeability (from a few hundred to 1000 mD). The geothermal waters in the reservoir are artesian ones with high static (up to 2.6 MPa) and dynamic (up to 2.0 MPa) pressures (Kępińska *et al.*, 2011). Water-bearing layers are present directly below the insulating Podhale Flysch cover (upper Eocene–Oligocene). The thickness of reservoir rocks ranges from 100 to 700 m. The intensity of artesian flow from wells ranges from 90 to 550 m<sup>3</sup> h<sup>-1</sup> and water temperature at the outlet ranges from 20 to 86°C. The mineralization of geothermal waters ranges from less than 200 mg L<sup>-1</sup> in the southern section of the aquifer, in the vicinity of the Tatras (the region of Zakopane, Fig. 10.1), to ca. 3000 mg L<sup>-1</sup> in the northern section. The Tatra area provides infiltration recharge for underground aquifers, so the resources found there are of a renewable nature. The geothermal waters sourced in the area are used mainly for heating and recreational purposes at several bathing resorts (Bujakowski *et al.*, 2012; Chowaniec, 2009; Kępińska, 2006; Tomaszewska, 2011a).

Research work was carried out using water from the Bańska IG-1 (GT-1) intake at Bańska Nizna, a geothermal well constructed between 1979 and 1981. The final depth of the well reached 5261 m b.g.l., but geothermal waters are sourced from a zone ranging from 2565 to 3345 m b.g.l.

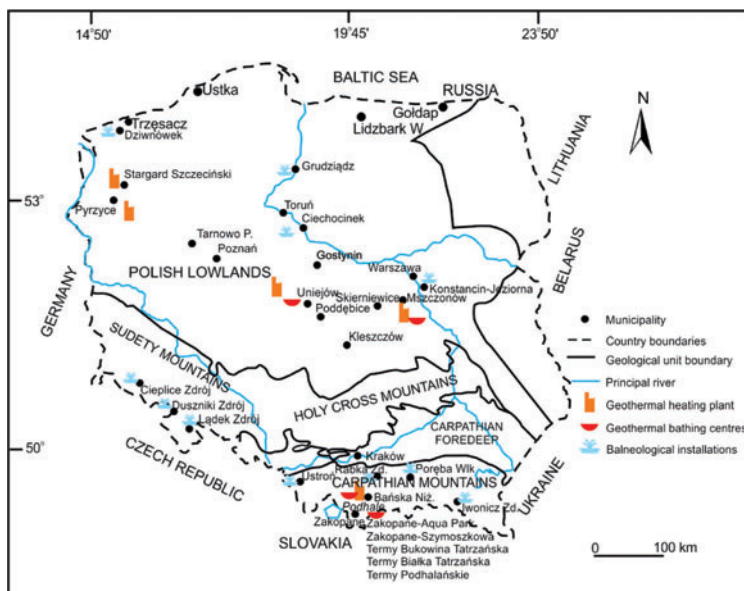


Figure 10.1. Location of geothermal water wells in Poland against the background of geological structural divisions.

The capacity of the well was  $120 \text{ m}^3 \text{ h}^{-1}$  and the temperature of the water extracted was  $82^\circ\text{C}$ . The water had a low total dissolved solids (TDS) content of  $2.5 \text{ g L}^{-1}$  and its hydrogeochemical composition was Na-Ca-SO<sub>4</sub>-Cl. The water was hard, containing more than  $600 \text{ mg L}^{-1}$  of CaCO<sub>3</sub>, with a slightly acidic pH and elevated boron (average:  $8.98 \text{ mg L}^{-1}$ ), strontium ( $6.0 \text{ mg L}^{-1}$ ), fluoride ( $2.6 \text{ mg L}^{-1}$ ), arsenic ( $0.026 \text{ mg L}^{-1}$ ), silica ( $42.73 \text{ mg L}^{-1}$ ), and iron content ( $3.89 \text{ mg L}^{-1}$ ). Moreover, small amounts of dissolved carbon dioxide, hydrogen sulfide, hydrogen, nitrogen, and helium were found (Tomaszewska, 2014). Physical and chemical properties of the water are presented in Table 10.1.

### 10.2.2 Lower Cretaceous geothermal waters in the Polish Lowlands

The Lower Cretaceous reservoir, which occupies  $115,521 \text{ km}^2$  (Górecki *et al.*, 2006), forms a complex of discontinuous, interspersed sandy, sandy-marly and sandy-mudstone layers, with thicknesses ranging from a few to 300 m. In its central area, water temperature ranges from 20 to  $40^\circ\text{C}$  (Bujakowski *et al.*, 2012; Górecki *et al.*, 2006). The reservoir exhibits high reservoir parameters, which means that the capacities of the hydrogeothermal wells tend to be high (from 25 to more than  $200 \text{ m}^3 \text{ h}^{-1}$ ) (Bujakowski *et al.*, 2012; Górecki *et al.*, 2006). The effective porosity of the sandstone reservoir rock ranges from 12% to 20% and its permeability generally ranges from a few dozen to 2000 mD, but sometimes reaches 3000 mD and in isolated cases is found at up to 3600 mD.

Water from the Uniejów PGI/AGH-2 well in Uniejów was used in the study. The well was drilled in 1991 and its total depth is 2042 m b.g.l. Its active zone is at 1892 to 2025 m b.g.l. Approved well capacity is  $120 \text{ m}^3 \text{ h}^{-1}$ , water temperature at the outlet reaches  $69.2^\circ\text{C}$  and the static pressure under artesian conditions amounts to 0.26 MPa (Kępińska *et al.*, 2011; Tomaszewska, 2014).

The mineral content of the waters studied was  $6.5 \text{ g L}^{-1}$  and their hydrogeochemical type was Na-Cl. Their pH was close to neutral. Elevated levels of boron ( $2.53 \text{ mg L}^{-1}$ ) and silica ( $35.78 \text{ mg L}^{-1}$ ) were found in the waters (Table 10.1). They also contained dissolved carbon dioxide, and small amounts of hydrogen sulfide and nitrogen.

## 10.3 RESEARCH METHODOLOGY

### 10.3.1 Apparatus

When selecting the water desalination and treatment process, the following factors were taken into account: the variability of physico-chemical composition and salinity of the waters, the forecast demand for chemical raw materials and energy, the cost of the equipment required to extract the waters, the cost of energy and labor, the building footprint, and the stable operation and reliability of the equipment.

The elevated concentration of boron ions in geothermal waters was also found to be an important factor. Many researchers (Bryjak *et al.*, 2008; Busch *et al.*, 2005; Dydo *et al.*, 2005; Faigon and Hefer, 2008; Güler *et al.*, 2011; Kabay *et al.*, 2009, 2010; Koseoglu *et al.*, 2010; Mane *et al.*, 2009; Öner *et al.*, 2011; Recepoglu and Beker, 1991; Redondo *et al.*, 2003; Tomaszewska and Bodzek, 2013a; Turek *et al.*, 2007, 2008) have shown the difficulties associated with lowering the boron content in water and wastewater. The efficiency of removing this component from the water at acidic or neutral pH is low and normally does not exceed 60%. Achieving a high rate of boron retention requires a high feed pH (Tomaszewska and Bodzek, 2013a). However, the high total hardness and carbonate hardness of geothermal waters prevents the required increase in the pH of “raw” water directly before using nanofiltration (NF) and/or reverse osmosis (RO) membranes, due to the risk of the precipitation of calcium carbonate deposits on the membrane surface (scaling). At high boron concentrations in “raw” water, a two- or multi-stage treatment process is needed (Kot, 2009). This solution was also adopted during the implementation of the project in question.



Table 10.1. Physical properties and chemical composition of the geothermal waters tested (Tomaszewska and Bodzek, 2014).

Element	GT-1**	GT-2**
TDS [ $\text{mg L}^{-1}$ ]	2561.8	6556.0
pH	6.41	7.88
Total hardness [ $\text{mg CaCO}_3 \text{ L}^{-1}$ ]	645.4	474.2
Carbonate hardness [ $\text{mg CaCO}_3 \text{ L}^{-1}$ ]	213.9	184.1
Na [ $\text{mg L}^{-1}$ ]	466.8	2297.0
K [ $\text{mg L}^{-1}$ ]	45.2	27.2
Ca [ $\text{mg L}^{-1}$ ]	196.0	146.8
Mg [ $\text{mg L}^{-1}$ ]	42.7	26.2
Cl [ $\text{mg L}^{-1}$ ]	536.0	3574.0
SO <sub>4</sub> [ $\text{mg L}^{-1}$ ]	938.2	193.7
As [ $\text{mg L}^{-1}$ ]	0.026	<0.005
F [ $\text{mg L}^{-1}$ ]	2.60	0.696
B [ $\text{mg/L}^{-1}$ ]	8.98	2.53
Cr [ $\text{mg L}^{-1}$ ]	0.012	0.044
Cd [ $\text{mg L}^{-1}$ ]	<0.0003	<0.0005
Ni [ $\text{mg L}^{-1}$ ]	0.013	<0.005
Pb [ $\text{mg L}^{-1}$ ]	0.001	<0.0005
Hg [ $\text{mg L}^{-1}$ ]	<0.0001	<0.0001
Al [ $\text{mg L}^{-1}$ ]	0.015	0.01
Mn [ $\text{mg L}^{-1}$ ]	0.041	0.181
Fe [ $\text{mg L}^{-1}$ ]	3.89	1.93
Sr [ $\text{mg L}^{-1}$ ]	6.0	5.5
SiO <sub>2</sub> [ $\text{mg L}^{-1}$ ]	42.73	35.78
Tritium [ $\text{TU L}^{-1*}$ ]	$0.0 \pm 0.4$	$0.7 \pm 0.4$
Gross $\alpha$ [ $\text{mBq L}^{-1}$ ]	$620 \pm 150$	$300 \pm 60$
Gross $\beta$ [ $\text{mBq L}^{-1}$ ]	$1150 \pm 340$	$370 \pm 110$
Uranium, $^{238}\text{U}$ [ $\text{mBq L}^{-1}$ ]	$3.7 \pm 0.3$	$2.5 \pm 0.3$
Uranium, $^{234}\text{U}$ [ $\text{mBq L}^{-1}$ ]	$5.9 \pm 0.3$	$2.2 \pm 0.3$
Radium, $^{226}\text{Ra}$ [ $\text{mBq L}^{-1}$ ]	$514 \pm 60$	$272 \pm 10$
Radium, $^{228}\text{Ra}$ [ $\text{mBq L}^{-1}$ ]	$157 \pm 55$	$242 \pm 38$
Radon, $^{222}\text{Rn}$ [ $\text{Bq L}^{-1}$ ]	$5.4 \pm 0.4$	$5.0 \pm 0.6$

\*TU: Tritium units where 1 TU is defined as the ratio of 1 tritium atom in  $10^{18}$  hydrogen atoms.

\*\* Average value.

The geothermal water desalination plant included the following equipment and components (marked according to the technological diagram shown in Fig. 10.2):

- NW50/300 pre-filter;
- pressure iron removal filter with the VIR 55 catalyst bed and NW32/150 filter for catching catalyst bed particles;
- X-Flow Uflex 80/2-P ultrafiltration (UF) module with UFC M5 UF membranes, with a diameter of 8" (Table 10.2) and IN-OUT flow (direction from the inside to the outside of the membrane);
- tank for water after UF (ZW-01), enabling the retention of rinse water for the UF unit and feeding the RO module with water;
- 3s-32-160/2.2 type UF rinse water pump;
- Multinox 80/48T RO feed pump;
- Evo TPG 500 anti-scalant and/or hydrochloric acid dosing system;

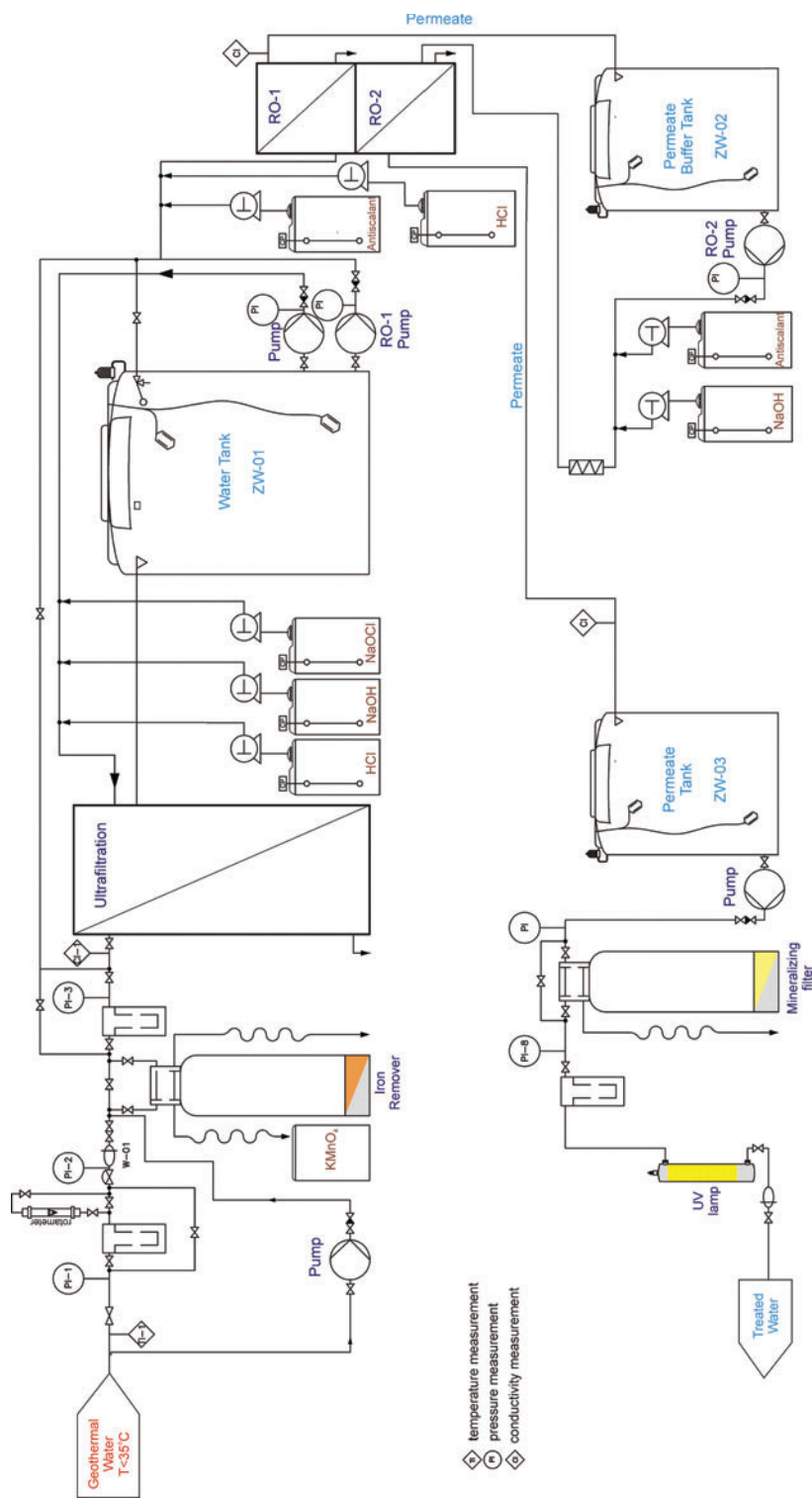


Figure 10.2. Technological scheme of the geothermal water desalination plant (Tomaszewska and Bodzek, 2013a).

Table 10.2. Technical specification of UF and RO membranes (Tomaszewska and Bodzek, 2013b).

Capfil UF Membrane UFC M5	
Membrane type	Hydrophilic capillary polyethersulfone
Maximum operating pressure [MPa]	0.3
Maximum temperature [°C]	80
pH range	2–12
Cut-off molar mass [kDa]	200
Dow Filmtec BW30HR–440I Membrane	
Membrane type	Polyamide, thin-layer composite membrane
Maximum operating pressure [MPa]	4.1
Maximum temperature [°C]	45
Maximum temperature for continuous operation for pH above 10°C	35
pH range	2–11
Maximum silt density index	5
Minimum salt removal efficiency [%]*	99.4
SiO <sub>2</sub> removal efficiency [%]*	99.9
Boron removal efficiency [%]*	83

\*Salt and solute removal under standard conditions: 2000 mg/kg NaCl, 1.55 MPa, 25°C, pH 7 and recovery rate of 15%.

- 1st reverse osmosis station – (RO-1) with connection pipes enabling the installation of a CIP (clean-in-place) system (Dow Chemical membranes with a diameter of 8" intended for the desalination of waters with elevated boron levels, Table 10.2);
- permeate buffer tank (ZW-02);
- intermediate permeate pump;
- Evo TPG 500 anti-scalant dosing station;
- Evo TPG 500 pH adjustment dosing station;
- 2nd reverse osmosis station – (RO-2) fed with permeate from the 1st RO stage, with connection pipes enabling the installation of a CIP system (Dow Chemical membranes with a diameter of 8" intended for the desalination of waters with elevated boron levels, Table 10.2);
- desalinated water tank (ZW-03);
- Multinox 80/48T desalinated water pump;
- Evo TPG 500 pH adjustment dosing station;
- VMF 33 mineralizing filter; and
- V12 ultraviolet (UV) sterilizer with an NW 32/5 protective filter.

The components, accompanying equipment and hydraulic installation were constructed inside a container that enabled the plant to be located anywhere, without fixing it permanently to the ground. The plant was equipped with a system for controlling individual processes and automation that ensured the synchronized operation of individual system elements. Additionally, given the research purpose of the plant, meters were mounted at certain points to register basic hydraulic and water quality parameters, including pressure, temperature and specific electrolytic conductivity. To allow the sampling of water for physico-chemical analyses, specially designed sampling pipes were placed after each technological component.

### 10.3.2 Water desalination and treatment procedure

The instantaneous flow rates of the geothermal waters that fed the desalination system were approximately 4–5 m<sup>3</sup> h<sup>-1</sup> (with an average flow of 2.4 m<sup>3</sup> h<sup>-1</sup>) for the desalination of water

from the GT-1 well and  $2\text{--}3\text{ m}^3\text{ h}^{-1}$  (with an average flow of  $1.5\text{ m}^3\text{ h}^{-1}$ ) for the water from the GT-2 well.

Geothermal water, cooled to below  $35^\circ\text{C}$  and pre-filtered, was directed to the iron removal filter. Water at a pressure of ca.  $0.3\text{--}0.5\text{ MPa}$  flowed through a catalyst bed layer (MTM type), of which oxidized iron hydroxides were retained on the surface, precipitating as flocs that settled easily (Tomaszewska, 2011b; Tomaszewska and Bodzek, 2013a). To remove the pollutants accumulated during operation, the filter was regularly rinsed in two stages: backwashing (counter-current rinsing) and concurrent rinsing. The rinse process was initiated and conducted fully automatically in line with the schedule programmed. After filtering major contaminants and removing iron, the water was fed to the UF module, which was an extension of water treatment prior to RO. UF membranes were used to remove micro suspensions that limited the possibility of feeding the water tested to the RO stage. It was envisaged that after the UF module, the silt density index would be below 3. The pressure of the water fed into the UF module was  $0.3\text{ MPa}$ .

Following the UF process, the water was directed to an intermediate tank with a capacity of  $2\text{ m}^3$  and some of it was used to rinse the UF membranes. Apart from water, hydrochloric acid and sodium hydroxide were also used during the washing of the UF membranes; these were supplied by independent dosing pumps. All processes related to the operation of the UF module were fully automated.

After the intermediate tank, separate pumps for the water fed into each RO stage were installed. Before the water was fed to the RO membranes, anti-scalant was added to it. Owing to the high content of boron in one of the feed sources (Bańska IG-1, GT-1), the RO module was divided into two separate units, which operated in series. The permeate from the first RO stage (RO-1) was dosed with anti-scalant and amended to raise its pH, then fed to the second RO stage (RO-2). It was assumed that only this technological solution, together with the use of a special type of membrane (Table 10.2), would reduce boron to the values permissible for drinking water. Transmembrane pressure at the RO-1 and RO-2 stages was  $1.1\text{ MPa}$ .

Desalinated water was produced at a rate of  $1\text{ m}^3\text{ h}^{-1}$  in a continuous cycle, 24 h a day. After subjecting the water to subsequent processing (mineralization by filtering it through a dolomite bed and UV sterilization), the technological cycle was complete.

### 10.3.3 Physico-chemical, microbiological and radiological analysis

The quality of “raw” water, permeate and concentrate was assessed through online measurements of the unstable physical parameters of the waters, including temperature and electrolytic conductivity. Water pH was measured using the electrometric method immediately after sampling water from the plant. Inorganic components were determined in an accredited laboratory at the Department of Hydrogeology and Engineering Geology of the AGH University of Science and Technology in Kraków (PCA-AB 1050), using inductively coupled plasma mass spectrometry (ICP-MS). The scope of analysis included the determination of sodium, potassium, lithium, beryllium, calcium, magnesium, barium, strontium, iron, manganese, silver, zinc, copper, nickel, cobalt, lead, mercury, cadmium, selenium, antimony, aluminum, chromium, molybdenum, vanadium, zirconium, titanium, arsenic, thallium, tungsten, bromides, iodides, sulfates, phosphates, silica, and boron contents. Chloride ion content and water alkalinity were determined by titration in accordance with accredited testing procedures (Tomaszewska, 2012; Tomaszewska and Bodzek, 2013a, 2013b). The contents of fluoride ions, nitrites, nitrates, and free cyanides were measured using the accredited testing methods of the Laboratory of the Regional Environmental Protection Inspectorate in Kraków (AB 176).

Retention factors,  $R$  [%], were calculated by:

$$R = \left(1 - \frac{C_p}{C_n}\right) \times 100 \quad (10.1)$$

where  $C_p$  and  $C_n$  are the concentrations [ $\text{mg L}^{-1}$ ] of the permeate and feed, respectively.

Table 10.3. Committed unit doses [ $\text{mSv Bq}^{-1}$ ] of four key isotopes by age group (based on regulations of the RRM (2005), after Tomaszewska and Bodzek, 2013c).

Radionuclide	Age group (year)					
	<1	1–2	2–7	7–12	12–17	>17
$^{238}\text{U}$	$3.4 \times 10^{-4}$	$1.2 \times 10^{-4}$	$8.0 \times 10^{-5}$	$6.8 \times 10^{-5}$	$6.7 \times 10^{-5}$	$4.5 \times 10^{-5}$
$^{234}\text{U}$	$3.7 \times 10^{-4}$	$1.0 \times 10^{-4}$	$8.8 \times 10^{-5}$	$7.4 \times 10^{-5}$	$7.4 \times 10^{-5}$	$4.9 \times 10^{-5}$
$^{226}\text{Ra}$	$4.7 \times 10^{-3}$	$9.6 \times 10^{-4}$	$6.2 \times 10^{-4}$	$8.0 \times 10^{-4}$	$1.5 \times 10^{-3}$	$2.8 \times 10^{-4}$
$^{228}\text{Ra}$	$3.0 \times 10^{-2}$	$5.7 \times 10^{-3}$	$3.4 \times 10^{-3}$	$3.9 \times 10^{-3}$	$5.3 \times 10^{-3}$	$6.9 \times 10^{-4}$

Concentrations of organic compounds were also determined at the laboratory, including dibenz(a,h)anthracene, 1,2-dichloroethane, benzo(b)fluoranthene, benzo(k)fluoranthene, trichloroethylene, indeno(1.2.3-cd)pyrene, fluoranthene, perchloroethylene, anthracene, benzo(a)pyrene, tri-chloromethane (chloroform), benzo(ghi)perylene, naphthalene, bromoform, benz(a)anthracene, pyran, benzene, chrysene, acenaphthalen, fluorene, phenanthrene, and total organic carbon.

Microbiological tests were carried out at the accredited laboratory of the State Sanitary and Epidemiological Station, in Nowy Targ (PCA-AB 595). The total number of microorganisms at  $22^\circ\text{C}$  after 68 h was determined in accordance with PN-EN ISO 6222:2004, and the numbers of coliform and *Escherichia coli* bacteria were determined in accordance with accredited test procedures (Tomaszewska, 2012).

Measurements of total activity of the radioactive  $\alpha$  and  $\beta$  nuclides, and the concentrations of radon ( $^{222}\text{Rn}$ ), uranium ( $^{238}\text{U}$ ,  $^{234}\text{U}$ ) and radium ( $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ) isotopes, were performed at the Environmental Physics Group of the Faculty of Physics and Applied Computer Science, University of Science and Technology in Kraków. An Alpha Spectrometer Model 740I with a semi-conductor detector was used as well as an alpha/beta detector with a Wallac Guardian 1414 liquid scintillation counter. The same laboratory performed tests for tritium on an electrolyte-enriched sample, using the liquid scintillation counting method and a Packard Model 2500 P TR/AB device (Tomaszewska and Bodzek, 2013c, 2014).

The following equation was used to calculate the doses (Chau and Michalec, 2009; IAEA, 1996; RRM, 2005; Tomaszewska and Bodzek, 2013c):

$$D(g) = N \sum \eta_i W_i \quad (10.2)$$

where:

$D(g)$ : annual effective dose equivalent (g-person in the age group) [ $\text{mSv year}^{-1}$ ]

$N$ : intake of water per person per year

$\eta_i$ : the age dependent dose conversion factor [ $\text{mSv Bq}^{-1}$ ] for the  $i$ -th isotope

$W_i$ : the concentration of the given radioisotope [ $\text{Bq L}^{-1}$ ].

The values of  $\eta_i$  for different elements were taken from IAEA (1996) and Polish Regulations (RRM, 2005). Table 10.3 shows the committed unit doses of four key isotopes, uranium-238, uranium-234, radium-226, and radium-228 (Tomaszewska and Bodzek, 2013c).

## 10.4 RESULTS AND DISCUSSION

### 10.4.1 Permeate test results

Iron content in the water tested was reduced from a level of up to ca.  $4 \text{ mg L}^{-1}$  to  $0.013 \text{ mg L}^{-1}$ , a retention factor of 99%, using a pressure iron removal filter (the maximum allowable concentration in drinking water is  $0.2 \text{ mg L}^{-1}$ ). After the removal of large pollutant particles and iron, the water

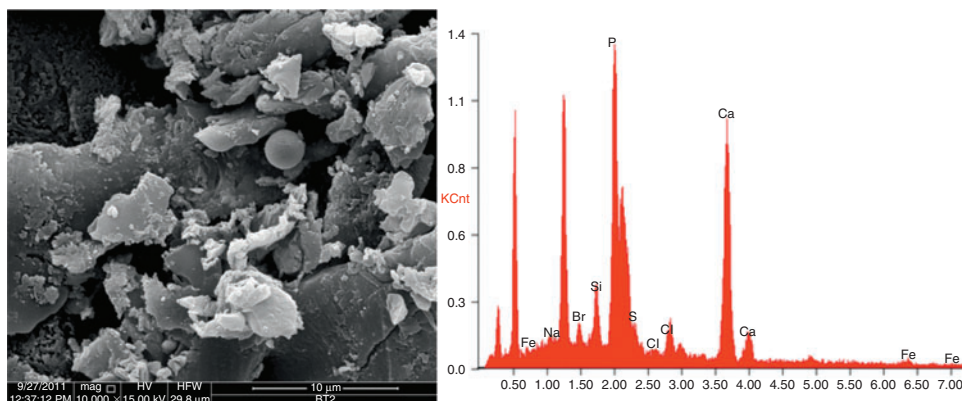


Figure 10.3. SEM-EDS images of precipitated hydroxyapatite deposits on the RO membrane.

was fed to the UF module. The electrolytic conductivity of water and its hardness were decreased by approximately 10% after passing through the UF membrane. A significant reduction in aluminum concentration (about 30–60%) was also found. During the pre-treatment of water, there was no reduction in silica concentration. In the geothermal waters studied, 99% of silica was present as orthosilicic acid ( $\text{H}_4\text{SiO}_4$ ) (Tomaszewska, 2012; Tomaszewska and Bodzek, 2013a). The silt density index for “raw” water amounted to approximately 5; after the UF process it was reduced to 2–2.8 (with an average of 2.4). This positive effect was significant from the point of view of protecting the RO membrane surfaces against fouling (Tomaszewska and Bodzek, 2013a, 2013b).

Due to the high total and carbonate hardness of the waters and to protect the membranes against fouling and scaling, testing was conducted into using anti-scalants – agents that complex divalent ions. Substances that reduce the precipitation of carbonate, sulfate and silica minerals were tested. Hydrex 4104 and 4109 preparations were selected for these tests. Anti-scalant doses were determined on a theoretical basis, based on the physical and chemical properties of the waters. Unfortunately, satisfactory results were not achieved. After a few hours of continuous plant operation, RO efficiency decreased and the RO membranes had to be regenerated. The removal of deposits using the “chemical etching” process proceeded very smoothly and quickly. Detailed physico-chemical analyses of the waters after the addition of the aforementioned substances demonstrated that phosphate concentration in the water increased and, as a result of a reaction with other geothermal water ingredients, hydroxyapatite deposits precipitated on the membranes. This factor contributed to the deterioration in membrane efficiency and thus the effect of the anti-scalant application was opposite to that intended. Figure 10.3 shows some deposits found during the microscopic examination of membranes.

The experiments conducted demonstrated the need to change the methodology for anti-scaling protection. It was decided that better results would be achieved by dosing the feed with dilute hydrochloric acid to lower the pH of the RO-1 feedwater to 5.5. The tests were carried out assuming high permeate recovery of 75–78% for the RO-1 stage and 75% for the RO-2 stage.

During the desalination of water from the GT-1 well, the chemical composition of the permeate obtained after the RO-1 stage generally met the requirements for drinking water, with the exception of boron concentration, which was lowered from 8.98 to 4.51  $\text{mg L}^{-1}$  with an acidic feed pH; the retention factor was 48%. The retention factor for TDS was 93%, and for silica ( $\text{SiO}_2$ ) it was 94%. After the RO-1 stage, the permeate pH was adjusted to be alkaline ( $\text{pH} = 10$ ) and fed to the RO-2 stage, and a 97% retention factor for boron was achieved (Table 10.4). High retention ratios were also achieved for other elements; 97% after RO-1 and 99% after RO-2 for chlorides and 99% for sulfates after RO-1 (Table 10.4).

Table 10.4. Retention factors for individual chemical components after RO-1 (including the iron removal and UF systems) and RO-2, relative to their concentration in the feed (RO-1/RO-2).

Element	GT-1 [%]	GT-2 [%]
TDS	93/96	91/96
Total hardness	99/100	88/100
Carbonate hardness	99/100	68/100
Na	92/91	93/93
K	91/98	81/94
Ca	95/99	88/99
Mg	99/99	88/99
Cl	97/99	88/99
SO <sub>4</sub>	99/99	99/99
As	95/96	–
F	2.60	0.696
B	48/97	56/94
Cr	99/99	89/99
Cd	–	–
Ni	88/93	–
Pb	99/99	–
Hg	–	–
Al	99/00	99/99
Mn	99/99	99/99
Fe	99/99	87/98
Sr	99/99	90/96
SiO <sub>2</sub>	94/99	81/99
Tritium*	–	–
Gross $\alpha^*$	91.9	83.3
Gross $\beta^*$	91.3	73.0
Uranium <sup>238</sup> U*	86.4	80.0
Uranium <sup>234</sup> U*	91.5	77.3
Radium <sup>226</sup> Ra*	96.5	99.3
Radium <sup>228</sup> Ra*	70.7	95.9
Radon <sup>222</sup> Rn*	–	–

– element concentration in the feed and permeate below the quantification limit.

\*retention factor after RO-2 as compared to concentration in the feed.

Retention ratios for key components of the water from the GT-2 well following RO-1 were in general lower than those for the water from the GT-1 well, but sufficient with respect to the requirements for drinking water. As already mentioned, the one microelement for which retention was insufficient was boron. Although its concentration in the feed was relatively low ( $2.53 \text{ mg L}^{-1}$ ), after the RO-1 stage the permeate exhibited a boron content slightly above the limit for drinking water ( $1 \text{ mg L}^{-1}$ ).

The World Health Organization (WHO) and the European Union strictly limit the permissible boron content in drinking water due to its impact on the human body. Currently, according to WHO guidelines (WHO, 2011), the recommended limit for boron in drinking water is  $2.4 \text{ mg L}^{-1}$ . However, these guidelines have not yet been incorporated in EU directives and national standards; according to these, the allowable amount of boron in drinking water as well as in the waters discharged into surface watercourses or into the soil may not exceed  $1 \text{ mg L}^{-1}$  (RMZ, 2015).

Taking into account the new 2011 WHO guidelines, a single-stage low-pressure UF–RO system for the desalination of waters with a mineral content of up to approximately  $7 \text{ g L}^{-1}$  would be sufficient to achieve favorable drinking water parameters. Table 10.6 presents the detailed analysis results obtained during the desalination of water from the GT-2 well.

Table 10.5. Comparison of permeate after RO-2 (GT-1 and GT-2 wells) with standards.

Element	GT-1	GT-2	Permissible content in water intended for consumption <sup>1</sup>	Standards for water used to irrigate crops	Permissible content in water discharged into watercourses and soil <sup>2</sup>
Conductivity, [mS cm <sup>-1</sup> ]	0.098	1.887	2.500	0.760–3000**	–
pH	10.01	10.0	6.5–9.5	4.5–5.5**	6.5–9.0
Total hardness [mg CaCO <sub>3</sub> L <sup>-1</sup> ]	0	0.6	50–500	–	–
Na [mg L <sup>-1</sup> ]	27.31	151.8	200	100*	800
K [mg L <sup>-1</sup> ]	1.81	1.76	–	100*	80
Ca [mg L <sup>-1</sup> ]	<10	0.241	–	150*	–
Mg [mg L <sup>-1</sup> ]	<0.1	<0.1	30–125	50*	–
Cl [mg L <sup>-1</sup> ]	13.4	11.2	250	100*	1000
SO <sub>4</sub> [mg L <sup>-1</sup> ]	6.4	<0.3	250	100*	500
Cr [mg L <sup>-1</sup> ]	0.0016	<0.005	0.05	<0.05–0.23**	0.1
B [mg L <sup>-1</sup> ]	0.44	0.159	1.0	<1.0**	1.0
Fe [mg L <sup>-1</sup> ]	<0.001	0.03	0.20	5.0**	10
As [mg L <sup>-1</sup> ]	<0.005	<0.005	0.01	0.1**	0.1
F [mg L <sup>-1</sup> ]	0.137	0.078	1.5	–	25.0

<sup>1</sup>RMZ (2015); <sup>2</sup>RMS (2014); \*the highest safe content based on Breś *et al.* (2010); \*\*content based on Al-Shammiri *et al.* (2005).

With the low transmembrane pressure applied (1.1 MPa), favorable results were obtained when desalinating geothermal waters with low mineral content (up to approximately 7 g L<sup>-1</sup>) and elevated boron content (up to approximately 10 mg L<sup>-1</sup>). Retention factors for key water ingredients after the first and the second RO stages were as follows:

- after RO-1: TDS 91–93%, Na 92–93%, Cl 94–97%, SO<sub>4</sub> 99%, As 95%, Cr 99%, Al 99%, Fe 87–99%, Sr 90–99%, Si 81–94%; and
- after RO-2: mineral content 93–96%, Na 91–93%, Cl 99%, SO<sub>4</sub> 99%, As 96%, Cr 99%, Al 99%, Fe 98–99%, Sr 96–99%, Si 99%.

The use of low pressure in the pilot tests for the desalination of geothermal waters was of key importance, from the point of view of process economics, since it enabled the natural artesian pressure of the geothermal waters to be used. As a result, during the research stage alone, the need to use circulating pumps for the iron removal and UF processes was eliminated, which reduced electrical power consumption by ca. 0.7–0.9 kW (Tomaszewska and Bodzek, 2013a).

Table 10.5 shows the results of physico-chemical analyses of the permeate obtained after the iron removal process, UF, RO-1 and RO-2; it is compared with the requirements for drinking and crop irrigation water, and those for the water discharged into surface watercourses. pH, total hardness and magnesium content were not verified, since these parameters were adjusted during the final treatment process.

The results of the physico-chemical analyses (Table 10.5) confirmed the high quality of the desalinated geothermal waters from the Bańska IG-1 (GT-1) and Uniejów PIG/AGH-2 (GT-2) wells. In respect of the requirements for drinking water, no standards concerning the content of organic and toxic substances (Table 10.6) or microbiological pollution (Table 10.7) were exceeded, in either of the desalinated geothermal waters. Pursuant to applicable national legal regulations, the permissible total number of microorganisms at a temperature of 22 ± 2°C after 68 ± 4 h is



Table 10.6. Toxic and organic compounds in the desalinated waters.

Element	GT-1	GT-2	Permissible value, according to RMZ (2015)
Dibenz(a,h)anthracene [ $\mu\text{g L}^{-1}$ ]	<0.005	<0.005	–
1,2-dichloroethane (EDC) [ $\mu\text{g L}^{-1}$ ]	<0.2	<0.2	3.0
Benzo(b)fluoranthene [ $\mu\text{g L}^{-1}$ ]	<0.005	<0.005	$\Sigma$ THM
Benzo(k)fluoranthene [ $\mu\text{g L}^{-1}$ ]	<0.005	0.005	0.10
Benzo(ghi)perylene [ $\mu\text{g L}^{-1}$ ]	<0.005	<0.005	
Indeno(1,2,3-cd)pyrene [ $\mu\text{g L}^{-1}$ ]	<0.010	<0.010	
Trichloroethylene (TRI) [ $\mu\text{g L}^{-1}$ ]	<0.2	<0.2	–
Fluoranthene [ $\mu\text{g L}^{-1}$ ]	<0.005	<0.005	–
Perchloroethylene (PER) [ $\mu\text{g L}^{-1}$ ]	<0.2	<0.2	–
Anthracene [ $\mu\text{g L}^{-1}$ ]	<0.005	<0.005	–
Benzo(a)pyrene [ $\mu\text{g L}^{-1}$ ]	<0.005	<0.005	0.010
Trichloromethane (chloroform) [ $\mu\text{g L}^{-1}$ ]	<0.2	<0.2	30
Naphthalene [ $\mu\text{g L}^{-1}$ ]	0.015	0.027	–
Bromoform [ $\mu\text{g L}^{-1}$ ]	<1.0	<1.0	–
Nitrites [ $\text{mg L}^{-1}$ ]	<0.003	<0.003	0.50
Fluorides [ $\text{mg L}^{-1}$ ]	0.137	0.078	1.5
Benz(a)anthracene [ $\mu\text{g L}^{-1}$ ]	<0.005	<0.005	–
Nitrates [ $\text{mg L}^{-1}$ ]	<0.4	<0.4	50.0
Pyrene [ $\mu\text{g L}^{-1}$ ]	<0.005	<0.005	–
Benzene [ $\mu\text{g L}^{-1}$ ]	<0.1	<0.1	1.0
Chrysene [ $\mu\text{g L}^{-1}$ ]	<0.005	<0.005	–
Acenaphthene [ $\mu\text{g L}^{-1}$ ]	<0.005	<0.005	–
Fluorene [ $\mu\text{g L}^{-1}$ ]	<0.005	<0.005	–
Phenanthrene [ $\mu\text{g L}^{-1}$ ]	<0.005	<0.005	–
Total organic carbon [ $\text{mg L}^{-1}$ ]	1.09	<1.0	<5.0
Free cyanide [ $\text{mg L}^{-1}$ ]	<0.003	<0.003	0.050

Table 10.7. Microbiological analyses of the desalinated waters (Tomaszewska, 2012).

Element	GT-1	GT-2	Standard in drinking water <sup>1</sup>
Coliform bacteria count [cfu/100 mL]	0	0	0
<i>Escherichia coli</i> count [cfu/100 mL]	0	0	0
Total number of microorganisms at a temperature of $22 \pm 2^\circ\text{C}$ after $68 \pm 4$ h	9	21	100

<sup>1</sup>RMZ (2015).

100 cfu mL<sup>-1</sup>; 9 cfu mL<sup>-1</sup> were found in the desalinated water from the GT-1 well and 21 cfu mL<sup>-1</sup> were present in the desalinated water from the GT-2 well.

An effective assessment of the potential of using desalinated geothermal waters as drinking water requires an analysis of the feed water quality and of the permeate produced across a wide range of items, including organic, microbiological and radiological elements, in addition to the inorganic indicators mentioned above (Tomaszewska and Bodzek, 2013c). Radioactive substances in geothermal waters are principally of natural origin, from the dissolution of gases and rock minerals, and as a result of recoil nuclides. Naturally occurring radionuclides are isotopes of

Table 10.8. Gross  $\alpha$  activity, gross  $\beta$  activity, annual effective dose equivalent, and contents of tritium, uranium and radium isotopes in the product waters (Tomaszewska and Bodzek, 2013c).

Element		GT-1	GT-2	Standard
Tritium [TU L <sup>-1</sup> ]		0.0 ± 0.3	0.0 ± 0.4	100 Bq L <sup>-1</sup> (850 TU L <sup>-1</sup> )
Gross $\alpha$ [mBq L <sup>-1</sup> ]		≤50	≤50	500 <sup>3</sup>
Gross $\beta$ [mBq L <sup>-1</sup> ]		≤100	≤100	1000 <sup>3</sup>
Uranium concentrations [mBq L <sup>-1</sup> ]	<sup>238</sup> U	≤0.50	≤0.50	10000 <sup>3</sup>
	<sup>234</sup> U	≤0.50	≤0.50	1000 <sup>3</sup>
Radium concentrations [mBq L <sup>-1</sup> ]	<sup>226</sup> Ra	18.0 ± 2	≤2.0	1000 <sup>3</sup>
	<sup>228</sup> Ra	≤47.0 ± 5	≤10.0	100 <sup>3</sup>
Annual effective dose equivalent [mSv year <sup>-1</sup> ] <sup>1</sup>		0.028	0.005	0.1 <sup>2</sup>

<sup>1</sup>) Annual effective dose equivalent for adults who daily are drinking water in average about 2 L;

<sup>2</sup>) concentration adopted from RMZ (2015), <sup>3</sup>) concentration adopted from WHO (2011).

uranium and thorium, and their daughter products; some of them are  $\alpha$  emitters and are dangerous when ingested (Görür *et al.*, 2011; Jobbágy *et al.*, 2009; Kozłowska *et al.*, 2007).

The samples of geothermal waters had near-zero tritium levels, within the error margin (Table 10.1), which means that these waters came from infiltration that occurred before 1952, when atmospheric tests of thermonuclear weapons began.

The radon concentrations measured in the waters were low (Table 10.1). One should note that the RO process does not reject dissolved gases and that the decrease in <sup>222</sup>Rn measured is due to its evaporation from the water during the treatment process. This evaporation is the cause of part of the measured decrease in radioactivity. The carcinogenic gas <sup>222</sup>Rn should be separately removed by enhanced aeration prior to RO during the treatment of contaminated geothermal waters, as carried out in this project (Tomaszewska and Bodzek, 2013c).

The efficiency of the water treatment system on natural radionuclides was assessed by testing the water from the second RO stage. In accordance with the guidelines of the EU Directive (EU, 1998) and the national drinking water standards (RMZ, 2015), radiological water quality testing involves: (i) tritium and (ii) total permissible dose (excluding tritium, potassium <sup>40</sup>K, radon and its decay products). Table 10.8 contains the results of radiological testing. The nuclide concentration did not exceed the drinking water standards and the rejection rate ranged from 70.7 to 99.3% (Table 10.4). The highest rejection rates, ranging from 96.5 to 99.3% were measured for the <sup>226</sup>Ra isotope. The other radium isotope, <sup>228</sup>Ra, ranged from 70.7% rejection rate in the water from well GT-1 to 95.8% in the water from well GT-2. In fact, the chemical properties of the two radium isotopes, <sup>226</sup>Ra and <sup>228</sup>Ra, that influence the RO membrane are identical, because these membranes do not distinguish radioactivity. This rejection level result is probably simply due to the high uncertainty encountered in the radiocounting of the much lower concentrations of this isotope. The rejection of 70.7% measured for the higher concentration isotope <sup>226</sup>Ra from GT-1 in this case represents both isotopes (Tomaszewska and Bodzek, 2013c). The two-pass RO process was more than 77.3% effective in removing natural uranium elements from water. The gross  $\alpha$  and  $\beta$  activities in the permeate were too low to quantify. Taking into account the substitution method (that radionuclide values below the lower limit of detection are equal to that limit), the rejection rates of the gross  $\alpha$  and  $\beta$  activity were 83.3% and 72.9%.

The annual effective dose equivalents of natural radioactivity that would be absorbed by adults (> 17 years) through consuming the waters tested, assuming a daily water intake of 2 L per person, would be considerably lower than the permissible level (0.1 mSv). Based on the activity of isotopes <sup>238</sup>U, <sup>234</sup>U, <sup>226</sup>Ra and <sup>228</sup>Ra, measured in the desalinated water, their annual dose in adults would be 0.028 mSv for GT-1, or 28% of the permissible level, and 0.005 mSv for GT-2, or 5% of the permissible level. Assuming an infant (<1 year) annual water intake of 250 L, the annual

Table 10.9. Comparison of the annual effective dose equivalents ( $\text{mS year}^{-1}$ ) in product waters for adults, children and infants of lactation age, with the standards (Tomaszewska and Bodzek, 2013c, 2014).

Product water	Age group (Year)						National standard (RRM, 2005)
	<1	1–2	2–7	7–12	12–17	>17	
GT-1	0.373	0.099	0.059	0.069	0.096	0.028	0.1
GT-2	0.077	0.020	0.012	0.014	0.019	0.005	

effective dose equivalent absorbed from uranium and radium in desalinated water from GT-1 would be 0.37 mSv, or 3–4 times more than the acceptable level for drinking waters (Table 10.9). As mentioned above, the effective unit equivalent doses take into account the varied effect of the ionizing radiation on the human body depending on the isotope and the consumer's age. This is one of the reasons why the committed unit dose was exceeded in this age group. The other reason is the water consumption, which is markedly lower in infants when compared with other age groups (Tomaszewska and Bodzek, 2013c).

#### 10.4.1.1 Retentate test results

Concentrate (or brine) is generated as a by-product of the separation of the minerals from source water used for desalination (Bodzek and Konieczny, 2011; Voutchkov, 2011). The characteristics of the waste stream depend on the quality of the feed water, the quality of the produced water (dependent on recovery levels), the pre-treatment method (added chemicals) and the cleaning procedures used (Bodzek and Konieczny, 2011; Pérez-González *et al.*, 2012; Voutchkov, 2011). In sea water desalination, the concentrate is usually discharged back into the sea. More difficulty is generally expected when desalination systems are operated inland. The concentration of minerals and contaminants in concentrate is usually approximately double (or higher) than in feed water (Bodzek and Konieczny, 2011; Pérez-González *et al.*, 2012; Voutchkov, 2011). Therefore, the manner in which the concentrate is disposed of will largely determine the cost of desalinating water in an inland setting (Tomaszewska *et al.*, 2014).

Geothermal waters contain large amounts of silica, potassium and microelements, such as Li, Sr, B, Br, I. The extraction, electrolysis and precipitation of sulfate salts from geothermal waters is performed in many regions of the world (Gallup, 1998, 2007). Boron is a particularly valuable microelement, but for its recovery to be possible the solution must be highly concentrated; that is, its content in the solution should amount to several hundred  $\text{mg L}^{-1}$ . The addition of hydrochloric acid to a saturated borax solution allows the precipitation of boric acid  $\text{B(OH)}_3$  from water. It crystallizes in the form of soft, pearly white triclinic crystals. Boric acid can be used as a fertilizer, wood preservative, gentle disinfectant and also food preservative (Tomaszewska and Szczepański, 2014). Industrial-scale measures related to the recovery of borax and boric acid from geothermal water have been undertaken in Italy (Barbier, 2002; Gallup, 1998; Lund and Freeston, 2001). In Lardarello (Tuscany), 50,000 metric tons of boric acid and 12,000 tons of borax are produced annually from geothermal waters (Carella and Sommaruga, 2000).

The examination of physical and chemical properties of the concentrate obtained during desalination of the waters from the GT-1 and GT-2 wells demonstrated that the concentrate may be widely used, including as an alternative balneological product. The microelements present in geothermal waters, such as arsenic, barium, boron, and heavy metals, among others, may restrict the potential for this in some cases (Tomaszewska and Szczepański, 2014).

The range of services on offer at bathing resorts and recreation facilities (pools, spas) that use geothermal water may be extended, for example by using the concentrate in graduation towers or pools; to differentiate water type salinity in individual pools, it may be mixed with low mineral content water. The main factor that would influence how the concentrate is used will

be the chemical composition of the concentrate, which is strictly determined by the chemical composition of the desalinated water.

Polish regulations specify the highest admissible concentrations of ingredients that are undesirable in excessive amounts and toxic ingredients in therapeutic waters. A comparison of the concentrate analysis results with the aforementioned guidelines demonstrates that the concentrates met the expected parameters for waters used externally. The TDS of the concentrate obtained by desalinating the water from the GT-1 intake was  $8.78 \text{ g L}^{-1}$ , with elevated concentrations of specific substances that determine the therapeutic/balneological properties of the water: metasilicic acid ( $262.99 \text{ mg L}^{-1}$ ), fluoride ions ( $5.92 \text{ mg L}^{-1}$ ) and iodide ions ( $2.47 \text{ mg L}^{-1}$ ). As a result of the solution having been concentrated, the boron ion content of the water increased to  $22.86 \text{ mg L}^{-1}$ . Concentration limits of chromium ( $0.01 \text{ mg L}^{-1}$ ) and nickel ( $0.03 \text{ mg L}^{-1}$ ) were only exceeded ( $0.081 \text{ mg L}^{-1}$  and  $0.079 \text{ mg L}^{-1}$ , respectively) for water that would be used for drinking therapy and inhalations, while boron ion content ( $22.86 \text{ mg L}^{-1}$ ) exceeded the admissible limit ( $5.0 \text{ mg L}^{-1}$ ) for drinking therapies lasting longer than 1 month.

The TDS of the concentrate obtained by desalinating the water from the GT-2 well exhibited a mineral content of  $17.506 \text{ g L}^{-1}$ , with an elevated concentration of metasilicic acid ( $106.03 \text{ mg L}^{-1}$ ), and boron content of ca.  $13.8 \text{ mg L}^{-1}$ . The thresholds for water used for drinking therapy and inhalation for arsenic ( $0.05 \text{ mg L}^{-1}$ ), chromium ( $0.01 \text{ mg L}^{-1}$ ) and boron ( $5.0 \text{ mg L}^{-1}$ ) were exceeded ( $0.07 \text{ mg L}^{-1}$ ,  $0.437 \text{ mg L}^{-1}$ , and  $13.81 \text{ mg L}^{-1}$ , respectively) (RMZ, 2006). In both cases (GT-1 and GT-2), no substances were found that would prevent the utilization of the concentrate for external use. It should be emphasized that owing to its temperature (ca.  $30^\circ\text{C}$ ), the concentrate could still be used as geothermal water.

The concentrate produced during the study had a similar physical and chemical composition to the natural brackish medicinal waters extracted and used in Rabka Zdrój, which is a Polish spa (Fig. 10.1). The Rabka Zdrój spa resort is associated with the saline springs present there and dates back to the 1230s. Currently, nine wells are used to extract the waters and their mineral content can reach  $27.8 \text{ g L}^{-1}$ . The chloride-sodium waters extracted have elevated iodine levels and are used for medicinal baths and inhalations at sanatorium and hospital facilities. They also provide basic material for the production of cosmetics and medicinal salts.

The presence of specific components in the concentrate determines its benefits when used for balneological and therapeutic purposes. An important factor to be determined during tests is the stability of the concentrations of these compounds as a function of the changes in the following parameters and factors, associated with the desalination process: (i) physical: pressure, pH, and temperature; (ii) the type and quality of the membranes used; (iii) the chemical substances used. In order to determine its health safety and pharmacodynamic effects, the concentrate should be assessed by relevant institutions that are competent to determine the therapeutic properties of waters/substances. These opinions should also indicate the desired forms of treatment, based on the concentrate obtained from desalinating the geothermal waters. These measures should be aimed at determining the optimum utilization of the concentrate's chemical and physical properties. In practice, the following types of waters are recommended for inhalation purposes:

- chloride-sodium, iodide; and
- chloride-sodium bicarbonate-calcium at concentrations of up to 1.5%.

The following types of waters are used most frequently for bathing purposes:

- brines (chloride-sodium waters), iodide, and/or sulfide-hydrogen sulfide waters; and
- specific thermal waters: radon and sulfide-hydrogen sulfide waters.

Temperature is of importance mainly when the water is used for bathing purposes.

Some geothermal waters, in their natural state or after the removal of unstable ingredients ( $\text{H}_2\text{S}$ , Rn, Fe(II)), and some concentrates obtained from these waters, may be considered "dietary foods for special medical purposes". This includes natural waters or their concentrates containing ingredients such as iodides, fluorides, calcium, magnesium and sodium in significant concentrations,

from the point of view of physiological functions of the human body. At the same time, these waters or concentrates must not contain potentially toxic ingredients in concentrations considered harmful to health.

Some alkaline waters with low calcium content (soft waters) and also concentrates with significant levels ( $>100 \text{ mg L}^{-1}$ ) of silicon compounds may be used in cosmetics, including in combination with plant extracts.

It is also important that in industrial RO facilities, various chemicals are widely used, such as (Bodzek and Konieczny, 2011) chemicals (for cleaning membranes), biocides, anti-scalants, and acids and bases used to adjust feed water pH. Currently, the use of environmentally friendly substances is promoted; these are easily biodegradable in the natural environment. Examples are (Bodzek and Konieczny, 2011) polymeric additives based on maleic anhydride that have lower eutrophication potential. It is important to note that acids and scale inhibitors added to the desalination plant source water are rejected by the RO membranes in the concentrate and also have an impact on its overall mineral content and quality (Tomaszewska *et al.*, 2014).

During the pilot studies into desalination of the geothermal water from the GT-1 intake, the Hydrex anti-scalant (an inhibitor based on a blend of phosphonates) was used in the first month. During the next seven months, water was dosed with hydrochloric acid only, to reduce its pH before the RO-1 stage; before the RO-2 stage, only sodium hydroxide was added to improve the retention of boron ions. No biocides were used. The desalination process proceeded in a stable manner (Tomaszewska and Bodzek, 2013a, 2013b, 2013c). The desalination of water from the GT-2 intake was conducted in the same fashion. To enable the utilization of the concentrate following the RO process, it is advisable to limit the amount of chemicals used. The efficiency of the process for desalinating water from the wells studied has demonstrated that this is feasible.

## 10.5 CONCLUSIONS

Before projects that aim to extract geothermal waters for heating and/or balneological purposes are planned, detailed analyses of geological, hydrogeological and geothermal conditions at the location in question, and in its vicinity, are conducted. The probability of obtaining assumed reservoir and operational parameters at the projected drilling site is evaluated, financial expenditure is estimated, and project financial feasibility is analyzed. Knowledge of geological features and underground conditions at the location in question is key towards making decisions concerning exploration drilling. At the project-planning phase, an equally important question that requires detailed analysis is the evaluation of the potential utilization of spent water.

A model procedure should take into account the renewable aspects of geothermal energy resources, the possibility of safe long-term reservoir operation, and ensure that the activities undertaken are both cost-effective and environmentally sound. Closed systems are the best and safest, from the point of view of the thermal water reservoir. However, owing to the high cost of drilling, the popularity of closed systems remains limited.

Pilot desalination studies of geothermal waters extracted from different geological structures in Poland – the Podhale Basin (GT-1) and the Polish Lowlands (GT-2) – using selected membrane techniques have demonstrated that, after treatment, spent geothermal water may provide an alternative potable water source, leading to the decentralization of the water supply for drinking and household purposes. It has been demonstrated that the use of a hybrid system based on iron removal, UF and RO with BWRO (brackish water reverse osmosis) membranes enables water (permeate) of high quality to be obtained. The division of RO units into two separate stages that operate in series, with an increase in feed pH to approximately 10 before the second RO stage, is often required where high concentrations of boron are present in geothermal waters.

Taking into account the low pressure of 1.1 MPa used at the RO stage, an efficient and stable desalination process was achieved for geothermal waters with a TDS of up to  $7 \text{ g L}^{-1}$  and boron content of up to approximately  $10 \text{ mg L}^{-1}$ , with relatively high retention factors. The analysis conducted for the treated geothermal waters with respect to the requirements for water intended

for human consumption demonstrated compliance with these requirements, in terms of physical and chemical, microbiological and radiological indicators.

Assessment of the feasibility of implementing the UF-RO system on an industrial scale is largely dependent on the manner and possibility of disposing of, or using, the concentrate. The potential balneological use of the concentrate is strictly determined by its physico-chemical properties. In this context, the extraction of geothermal energy and the efficient and rational management of spent water may result in a number of benefits, not only in terms of energy and the economy, but socially as well. A very important aspect when undertaking such measures is the sustainable management of natural resources and respecting all elements of the natural environment at every stage of business activity.

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*Section III*  
*The uses of geothermal water in agriculture*



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## CHAPTER 11

### Coupling geothermal direct heat with agriculture

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#### 11.1 INTRODUCTION

In the agriculture and agri-food chain industries there is a strong nexus between food, energy and water as it consumes about one-third of the global energy and 80–90% of the world's freshwater production; freshwater production consumes about 15% of the global energy production (FAO, 2011a, 2011b; Hoff, 2011; IEA, 2012; IRENA, 2015). Therefore, the agri-food chain should be made independent from the use of fossil fuels, which have decreasing and fluctuating reserves but increasing long-term trend in cost, by coupling it to renewable energies such as geothermal. Geothermal water can not only provide energy, but at the same time a source of freshwater (possibly requiring prior treatment, that can, in turn, be done using geothermal heat as the energy source) thereby providing secure, accessible and environmentally sustainable supplies for both of these commodities. It can therefore play a significant role in contributing to future global food security and climate protection as well as other aspects of the Sustainable Development Goals (SDGs). The benefits of using geothermal energy are often underestimated, despite it being a limitless, sustainable and constant heat source, available 24 hours a day, 365 days a year. This makes its use technically simple, which contrasts with other renewables such as solar energy. Development and commercialization of geothermal water as energy and freshwater sources could have a significant contribution in the reduction of costs in the agro-food sector. However, much work remains to be done to make better use of geothermal energy.

The aim of this chapter is to critically review potential geothermal applications and recent developments in geothermal direct applications in agriculture and the agro-food sector, such as processing, distribution, retail, preparation and cooking. Topics linking agriculture and the agro-food sector to questions such as (i) energy demands in agriculture, (ii) energy management processes, (iii) water-energy-food-climate nexus, (iv) greenhouse gas emissions, (v) carbon footprint of agriculture, and (vi) environmental impact of different foods, are not dealt with as they are treated elsewhere (e.g. Bundschuh *et al.*, 2017 and references therein).

#### 11.2 SUSTAINABILITY BY INTEGRATING GEOTHERMAL OPTIONS INTO AGRICULTURE

Integrating geothermal options – either alone, or combined with other renewable energy sources, introducing water- and energy-efficient technologies, the reuse of wastewater and waste energy (energy-recovering systems), and the use of geothermal aquifers as a source of water supply for agri-food chain sectors are all ways to overcome the present-day overdependence on, and related risks of, fossil fuels. The future supply and pricing of fossil fuels are highly uncertain – and there is limited availability to the poor due to the depleting resources of, in particular, conventional hydrocarbons and their contribution to global warming. By contrast, the price of geothermal and other renewable technologies are, due to continual improvement but, in particular, because of increasing mass production, continually decreasing. Substituting fossil fuel energy resources with

renewables, using alternative water sources such as seawater or saline groundwater, or water from geothermal aquifers that are desalinated or treated using renewable energy such as geothermal, becomes progressively important due to the permanent increase in food demand which leads to a corresponding growth of the agricultural intensity, in particular through increased mechanization, expansion of irrigated land, fertilizer production and transportation, all of which require ever more energy and water (IRENA, 2015; Van Nguyen *et al.*, 2015). Including geothermal options either alone or together with other locally available renewables into food-energy-water systems allows optimization of the whole system and could directly save farmers' money, which alone is an important factor for its implementation; indirectly, and most importantly, it can significantly contribute to (i) creation of local development through the generation of jobs, (ii) poverty reduction, (iii) improved gender equity, (iv) food security, and (v) climate protection which are all SDGs.

### 11.3 GEOTHERMAL DIRECT HEAT APPLICATIONS

In agriculture and the agri-food chain, geothermal heat can be employed for many processes which presently use heat provided from burning fossil fuels, firewood or heat produced from electric equipment such as heaters. In agriculture, they comprise: (i) heating/cooling of spaces and buildings, (ii) soil heating, (iii) greenhouses, (iv) thermal water desalination and contaminant removal from naturally (geogenic) contaminated water or industrial (including agricultural) wastewater, (v) sea/brackish water greenhouses, (vi) heating of greenhouses, (vii) aquaculture (fish and shellfish), (viii) algae cultivation for energy production, and other purposes. In the agri-food chain sector, geothermal heat can be used for (i) preheating and heating processes, (ii) evaporation and distillation processes, (iii) peeling and blanching processes, (iv) sterilization processes, (v) milk pasteurization, (vi) drying of crops, grains and fruits, and (vii) drying of food. Globally, 4.5% of geothermal energy is used for greenhouses and open ground heating, 2.0% for aquaculture pond and raceway heating, 1.8% for industrial process heating, and 0.4% for agricultural drying (Lund and Boyd, 2015). Suitable temperature ranges of the geothermal heat source required for the different applications are shown in the Lindal diagram (Fig. 11.1). In addition to these applications of geothermal heat, geothermal water can be used for irrigation purposes, which in some cases needs treatment to make it suitable for such application (where again geothermal can be used as the source of energy) (see, for example, Lund and Boyd, 2015; Van Nguyen *et al.*, 2015; IRENA, 2015).

Global installed thermal capacities, thermal energy utilization and capacity factors for different applications in agriculture and the agri-food chain using geothermal resources and their change from 1995 to 2015 are shown in Table 11.1. In Section 11.3, different applications of geothermal heat are presented individually, whereas integrated configurations are presented in the following sections, including multiple use applications (cascading) of geothermal heat (Section 11.4), geothermal water desalination including geothermal-solar hybrid systems (Section 11.5) and geothermal heat for integrated geothermal applications for greenhouse development including heating/cooling, ventilation, humidification and water desalination (Section 11.6).

#### 11.3.1 *Heating/cooling of spaces, buildings, and water*

Geothermal heat can be used for temperature control, i.e. heating and cooling, the last by using heat in mechanical or evaporative cooling cycles. It is an important option since heating and cooling are important energy consumers in many agricultural applications; in particular, in pig and poultry production, which is mostly conducted in closed buildings and which requires constant temperature and air quality conditions for the animals' well-being and their optimal growth. Geothermal heat driven air/space heaters/coolers/dehumidifiers can also be used for replacing contaminated indoor air (moisture, gases, odor, dust, etc.) through ventilation and heating which constitute another large energy consumer in agriculture.

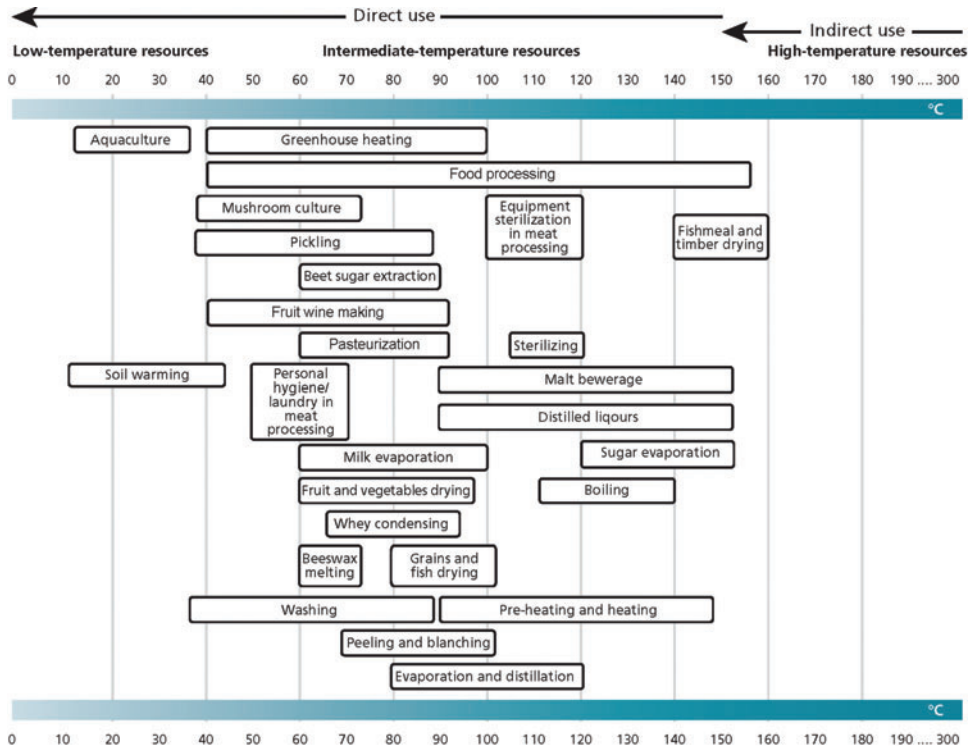


Figure 11.1. Lindal diagram indicating suitable temperature ranges for different applications of geothermal heat in the agriculture and the agri-food chain (Van Nguyen *et al.*, 2013).

Table 11.1. Global use of geothermal heat in agriculture by application category (after Lund and Boyd, 2015).

Category		1995	2000	2005	2010	2015
Greenhouse heating	Capacity [MWt]	1085	1246	1404	1544	1830
	Utilization [TJ year <sup>-1</sup> ]	15742	17864	20661	23264	26662
	Capacity factor	0.46	0.45	0.47	0.48	0.462
Aquaculture pond heating	Capacity [MWt]	1097	605	616	653	695
	Utilization [TJ year <sup>-1</sup> ]	13493	11733	10976	11521	11958
	Capacity factor	0.39	0.61	0.57	0.56	0.546
Agriculture drying	Capacity [MWt]	67	74	157	125	161
	Utilization [TJ year <sup>-1</sup> ]	1124	1038	2013	1635	2030
	Capacity factor	0.53	0.44	0.41	0.41	0.400

Heating and cooling of water (as well as milk and agricultural products) is energy-intensive and an economic burden, especially in developing countries and areas remote from electric power plants as many agricultural areas are, which leads further to distribution losses in the electricity grid. Here, geothermal heat could provide an economical energy source to replace electricity produced from fossil fuels, or to replace diesel and other fuels which are burned for heating and cooling of water. An example of high energy demands are commercial dairy farms where geothermal heat can be used to heat water for cleaning equipment, warming and stimulating the

cows' udders but also for cooling milk; these processes account for up to 40% of the farms' total energy demand (IRENA, 2015).

#### 11.3.2 *Drying of crops, fruits, grains and animal products*

Thermal drying of agricultural products and food is a globally widespread procedure. The energy consumption for this purpose is high as numbers from industrialized countries show that drying processes use 7–15% of the total industrial energy consumption (Chou and Chua, 2001). This offers many options for using heat from geothermal sources for drying crops and grain, ranging from very simple and cheap, to sophisticated and expensive (Ogola, 2013).

Where geothermal sources are naturally available and accessible (at shallow depth springs, etc.) geothermal drying, e.g. using heat exchanges to heat the air used for the drying process, is an excellent option. In contrast to the solar option, geothermal drying is also suitable in areas with little solar radiation, such as in colder climates. The use of geothermal energy for drying various grains, milk, vegetables and fruit crops has been reported from 15 countries. Examples include: drying of seaweed (Iceland; Ragnarsson, 2015), onions (USA; Boyd *et al.*, 2015), wheat and other cereals (Serbia; Oudech and Djokic, 2015), fruits (El Salvador, Guatemala and Mexico; Montalvo and Gutierrez, 2015; Lund and Boyd, 2015; Gutiérrez-Negrin *et al.*, 2015), lucerne or alfalfa (New Zealand; Carey *et al.*, 2015), coconut and meat (Philippines; Fronda *et al.*, 2015), and timber (Mexico, New Zealand and Romania; Gutiérrez-Negrin *et al.*, 2015; Carey *et al.*, 2015; Bendea *et al.*, 2015). The largest uses of geothermal drying are found in China, USA and Hungary (Lund and Boyd, 2015). A total of 161 MWt and 2030 TJ year<sup>-1</sup> were utilized by the end of 2014, which is an increase of 28.8 and 24.2% respectively, compared to 2010. Geothermal drying has a long history as the examples of Iceland and Nigeria show. In Iceland, geothermal energy has been utilized for about 35 years for drying fish and nowadays about 15,000 metric tons of cod heads are annually dried before their export to Nigeria (IRENA, 2015). In Kenya, pyrethrum drying is still being carried out at a plant, constructed in the 1920s near Eburru, estimated at 1.0 MWt and 10 TJ year<sup>-1</sup>. In Vietnam, the drying of bananas, coconuts and medicinal herbs occurs using 11.83 TJ year<sup>-1</sup> (capacity: at 0.5 MWt) (Lund and Boyd, 2015).

#### 11.3.3 *Milk pasteurization*

A significant amount of energy is required in the production of liquid milk. Heating and cooling are common processes in the dairy industry and specifically in pasteurization. For example, pasteurization requires both thermal and electrical energy, which is about 600 MJ and 200 MJ per metric ton of the final product, respectively. The requirement of cooling and heating in pasteurization makes geothermal energy one of the best options as a renewable energy resource for dairy processes. A water-ammonia absorption cycle can provide the required refrigeration temperature necessary for pasteurization, and this would be an economical option if it could be powered by geothermal energy resources between 100 and 200°C (Yildirim and Genc, 2015).

Geothermal hot water and steam can be used for milk pasteurization and milk evaporation, respectively. A geothermal plate heat exchanger is used for pasteurization, where it is heated to at least 78°C for 15 seconds. The temperature of the inlet geothermal hot water is about 87°C and the outlet is 77°C (Van Nguyen *et al.*, 2015).

#### 11.3.4 *Heating of greenhouses*

Geothermal heat can be an ideal, cost-effective energy source for heating greenhouses and it is commonly used in many European countries where geothermally heated greenhouses are used for year-round commercial production of vegetables, fruits and flowers (Van Nguyen *et al.*, 2015). The heat can be employed to heat air and soil, thus replacing or adapting heaters which are powered by fossil fuels or electricity produced from non-renewable conventional energy resources.

The related cost-reduction of geothermally heated greenhouses is in particular high in remote areas without electricity access.

In the year 2015, a total of 31 countries reported geothermal greenhouse heating (compared to 34 in 2010); the leading countries being: Turkey, Russia, Hungary, China and The Netherlands (Lund and Boyd, 2015). The main crops are vegetables and flowers, however, tree seedlings (USA) and fruit such as bananas (Iceland) are also grown. The worldwide use of geothermal energy for greenhouses and covered ground heating increased by 19% from 2010 to 2015 in installed capacity, and 16% in annual thermal energy use. Here, the installed capacity was 1830 MWt and energy use was 26,662 TJ year<sup>-1</sup>, respectively (Lund and Boyd, 2015). In Turkey, geothermal greenhouses covered an area of 3 million m<sup>2</sup> (612 MWt) in 2015 where tomatoes are a favorite product in these greenhouses, with their major markets in Russia (60%), Europe 20%, and around 10% elsewhere internationally, while 10% are sold domestically (Mertoglu *et al.*, 2015, Lund and Boyd, 2015).

Integrated operation and case studies of greenhouses using geothermal greenhouse heating/cooling, humidification, ventilation and water desalination for irrigation will be treated separately in Section 11.6.

### 11.3.5 Heating of uncovered ground

Maintaining optimal temperature, geothermal heating of uncovered ground can quicken the growing of produce and expand the growing season; it is mostly used for growing carrots and cabbages (Kumoro and Kristanto, 2003). In this case, the soil is heated using a grid of pipes of 1–2 m spacing generally located at a depth of 65–85 cm below the earth's surface (Johannesdottir *et al.*, 1986). A constant soil temperature (20–30°C) is controlled by the inlet flow rate of the system.

### 11.3.6 Aquaculture (fish, shellfish, frogs, algae, etc.)

Geothermal water can either be mixed (if chemical composition allows) or used via heat exchangers for heating other water to optimize growing of fish, shellfish or algae in ponds or raceways. This also allows production of these goods in colder regions, where production otherwise would not be possible or economic (Boyd and Lund, 2003); it also allows year-round breeding. Use of geothermal heat for fish farming is a fast-expanding industry in France, Greece, Hungary, Iceland, New Zealand and the USA. However, in many other countries where the necessary low temperature waters are available, this promising economic option is little, or even not used. The most common species are fish such as carp, catfish, tilapia, mullet, eel, salmon, and sturgeon, shellfish including shrimps, lobster, crayfish, crabs, oysters, clams, scallops, mussels and abalone, but also other animals such as frogs, alligators and algae (Boyd and Lund, 2003). Geothermally heated water can also be used for cultivating algae for different purposes, including those for energy production. Other algae such as *Spirulina* are sold as health foods and medical cures; since this alga has its optimal growth at a temperature of 35–37°C, geothermal heating of the cultivation water is an ideal option (FAO, 2008; Andritsos *et al.*, 2009).

### 11.3.7 Application of geothermal heat-energy in food-processing

Thermal energy in the temperature range below 150°C is used in the basic processes of: preheating, washing, peeling and blanching, evaporation and distilling, sterilizing, drying and refrigeration.

#### 11.3.7.1 Preheating and heating

Geothermal energy can be effectively used in many industries to preheat water that goes to boilers.

Water introduced to boilers at a temperature of typically around 10–16°C will be raised to 93–149°C. The geothermal resource can be used to preheat the water to reduce the energy required for operating the boiler (Popovska, 2001).

In the food-processing industry, both steam and hot water at temperatures in the range of 90–150°C from geothermal sources are commonly used. Two types of heating tanks are typically



used for heating the food; a twin-shell heating tank and a heating tank with internal spiral. In both cases, the heat is transferred through the tubes/shells to the surrounding food and the outlet water is discharged through a float valve (Van Nguyen *et al.*, 2015).

#### 11.3.7.2 *Evaporation and distillation processes*

Evaporation and distillation processes are aimed at the concentration of food products. They are applied in many food-processing industries such as sugar processing, mint distillation and liquor processes. Evaporation can be performed either as a batch process or in a continuous system. The common operating temperatures required for evaporation and distillation are in the range of 80–120°C. Geothermal fluid/steam is supplied to a heat exchanger, which transfers heat to the diluted liquid. In the case of multi-stage evaporators, geothermal steam is supplied to the first evaporator, then vapor from the first evaporator becomes steam for the second, and so on (Van Nguyen *et al.*, 2015).

#### 11.3.7.3 *Peeling/blanching processes*

In the food industry processes such as peeling and blanching (of fruits and vegetables) are important pre-processing steps. Common temperatures for peeling and blanching processes typically range from 77–104°C. Geothermal hot water or steam is either applied directly to produce stream, or indirectly by heating the hot-water bath for the peeling process. Some processing operations, such as canning, freezing or dehydration, often involve blanching to inhibit enzyme activity and condition the properties of the food. In blanching, food is heated rapidly to a fixed temperature and then, in many cases, cooled rapidly. Geothermal fluids can be used to provide the required energy through heat exchangers (Van Nguyen *et al.*, 2015).

#### 11.3.7.4 *Sterilization*

Geothermal hot water or steam at a temperature of 105–120°C is normally used for food sterilization processes and sterilizing equipment. Sterilization is an important step in industries such as meat and fish canning. The aim is to stop the growth of bacteria, particularly *Clostridium botulinum* (Van Nguyen *et al.*, 2015).

### 11.4 AGRICULTURE WITHIN THE CASCADE SYSTEM OF GEOTHERMAL DIRECT HEAT UTILIZATION

In many cases the cascade system of geothermal energy use is the best solution for effective geothermal energy utilization. Space heating requires temperatures in the range of 50–100°C, with 40°C useful in some marginal cases and ground-source heat pumps extending the range down to 5°C. Cooling and industrial processing normally require temperatures over 100°C (Lund, 2010; Gude, 2016). Agricultural and aquacultural uses require the lowest temperatures, with values from 25 to 90°C. Agricultural and agro-industrial uses form a very important part of geothermal energy applications (Van Nguyen *et al.*, 2015). Popovski (2009) distinguished four types of direct application of geothermal energy in agriculture identified as: (i) greenhouse heating, (ii) aquaculture (fish farming and algae production), (iii) agro-industrial processes, and (iv) soil heating (of open-field plant root systems). Geothermal waters were first used in greenhouse heating in Iceland in the 1920s (Barbier, 2002). In Greece, the use of geothermal waters for greenhouse heating started in the early 1980s (Andritsos *et al.*, 2011) and in the cultivation of *Spirulina* in the late 1990s. In the region of Klamath Falls (Oregon, USA) the system with temperatures of 27–93°C makes use of cascading for agriculture and aquaculture. The main well is used for greenhouse heating at 93°C. Subsequently, the greenhouses' water effluent at a lower temperature is used to heat 37 shallow ponds of tropical fish (Lund, 1994). The use of geothermal energy for heating and agriculture in a cascade was also implemented in 1993 in the Mineral and Energy Economy Research Institute of the Polish Academy of Sciences (PAS MEERI) in Bańska Niżna (Bujakowski, 2000, 2007). In southern Poland, the first geothermal plant

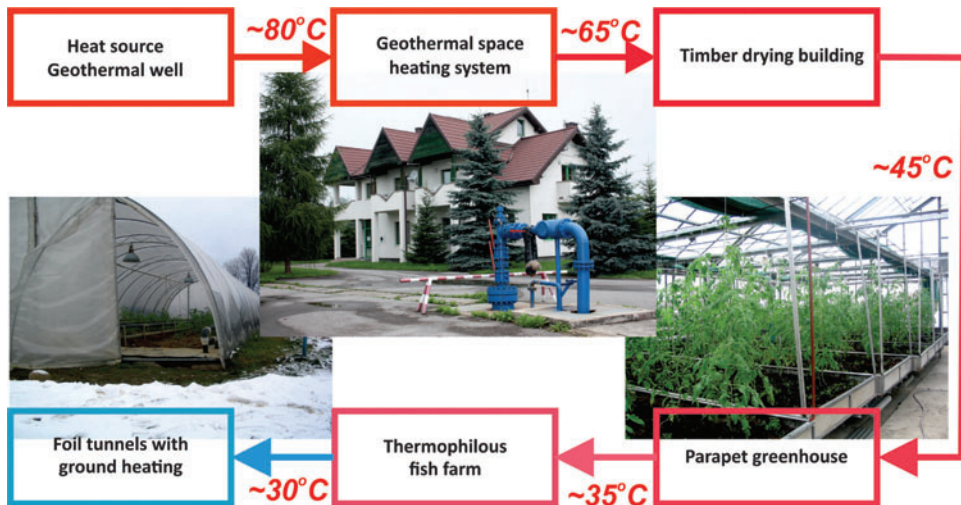


Figure 11.2. The cascade system of geothermal energy utilization at PAS MEERI (Poland).

in Poland, Podhale Basin, was built and put into operation (Bujakowski, 2007; Bujakowski and Tomaszewska, 2012). In the 1995–98 period, the installation process has been developed. The cascaded heat supply includes five stages of heat distribution based on a secondary circulation loop. The first step provides hot water for district heating for apartments and buildings, and hot water for domestic use (85–65°C). After the first thermal utilization the water has a temperature between 60 and 65°C, which is sufficient for drying timber buildings. Next steps include parapet greenhouse (45°C), thermophilous fish farm (35°C) and the last – foil tunnels with ground heating (30°C) (Fig. 11.2). This setup enables studies on the multi-directional development of geothermal energy. New ideas comprise studies on the use of geothermal water in the culture of microalgae. Geothermal energy could be used to heat up the greenhouse and maintain the optimum temperature for growth of *Spirulina* by heat exchangers which are located below and next to the tanks. The application of geothermal water in the cultivation of *Spirulina* can reduce the cost associated with the use of medium components (e.g.,  $K_2SO_4$ ,  $NaCl$  or  $MgSO_4 \times 7H_2O$ ) (Godlewska *et al.*, 2015). Grown and harvested biomass can be dehydrated by means of geothermal drying. The algae homogenate produced may be utilized as microelement fertilizer, biostimulant or bioregulator for crop production on selected ground areas heated by geothermal energy (Godlewska *et al.*, 2015). This solution also allows plant production during the winter.

In Africa, a new project of geothermal energy use in Eburru (Kenya) is being considered (Mburu, 2012). The cascaded use of the geothermal energy will involve different applications: drying of agricultural products, greenhouse heating, honey purification, poultry hatching, recreational facility in a steam sauna, and the provision of much needed potable water (Mburu, 2012). Nowadays, cascade use of geothermal energy is more and more popular. Consequently, hundreds of hectares of greenhouses are operating throughout the world (Table 11.2).

In high-enthalpy geothermal energy sources, electricity production with heat recovery for space heating is well known, as can be shown by examples from Iceland, USA, Italy and other countries. The most popular spa in Iceland (Fig. 11.3) used the same geothermal water which is exploited for the Svartsengi Power Station (Fig. 11.4). The electricity power station, next to Reykjavik, was built in 1976 and it was the world's first geothermal power plant for electric power generation and hot water production for district heating (Lund and Chiasson, 2007). Apart from direct method electricity production, a binary system based on the organic Rankine cycle (ORC) is exploited for clean energy utilization. The total generation capacity of the plant is 46.4 MW<sub>e</sub>.

Table 11.2. Cascade utilization of geothermal energy proposals around the world (based on Rubio-Maya *et al.*, 2015).

Geothermal cascade products											
Country	Region	Aquaculture	Balnearology	Drying	District heating	Electricity	Greenhouses	Irrigated agriculture	Pisciculture	Vegetables growth	Wood products
Albania	Tirana	X	X		X	X	X		X		
Austria	Geinberg		X		X		X				
Iceland	Husavik		X		X	X	X	X	X		
Italy	Sienna				X	X	X				
Kenya	Eburru			X		X			X		
Kenya	Samburu										
Mexico	Maguarichi	X	X	X			X				
New Zealand	Kawerau						X				X
Poland	Podhale		X		X		X		X		X
Romania	Oradea	X	X		X	X	X				
Slovenia	Lendava	X			X	X	X				
Thailand	Egat			X		X		X			
Turkey	Kutahya				X	X	X				
USA	Klamath Falls						X	X	X		
USA	New Mexico					X		X			
USA	Canby		X		X	X	X				



Figure 11.3. Blue Lagoon in the foreground of the Svartsengi Power Station (photo B. Tomaszewska).

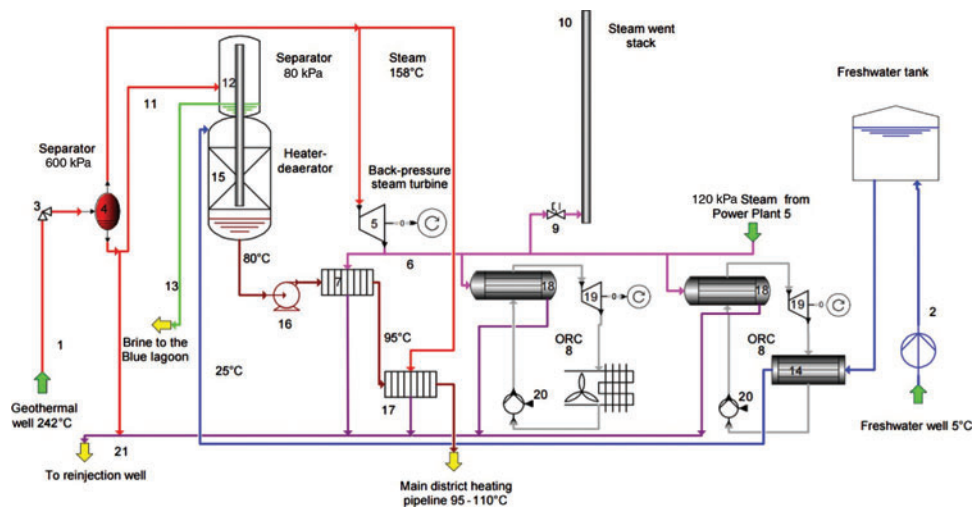


Figure 11.4. Svartsengi Power Plant flow diagram (after Thorolfsson, 2005).

and  $200\text{MW}_{\text{th}}$  ( $2700\text{TJ/year}^{-1}$ ) in the form of hot water for district heating. The geothermal system has 12 production wells and only one of reinjection (Thorolfsson, 2005). Water, rich of minerals like silica, sulfur is used in one of Iceland's popular bathing resorts, the Blue Lagoon which is the most visited attraction in the country (Fig. 11.4). People started bathing in the lagoon in 1981. In 1992, the Blue Lagoon Company was established and the bathing facility was opened to the public (Lund and Chiasson, 2007). One should note that geothermal water exploited in the Svartsengi Power Station is also used in the first renewable methanol plant Carbon Recycling

International (CRI, 2017). The company's emission-to-liquid process uses carbon dioxide, water and renewable electricity to create methanol fuel. A multi-purpose scheme of medium-enthalpy resource utilization is also present in Husavik, where heat supplies industrial processes, farms and greenhouses, a fish farm, the melting of ice, and recreational use in the thermal lagoon (Eliasson and Björnsson, 2003). Among the improvements in progress is wood drying, production of glucosamine and a tilapia hatchery (Rubio-Maya *et al.*, 2015).

For low-enthalpy geothermal resources, the warm water can be first run through a space heating installation and then cascaded to swimming pools, greenhouses and/or aquaculture ponds for heating. These kinds of projects maximize the use of the resource as well as improving the economics, geothermal resources management and sustainability. There are a lot of examples and technologies used for this type of system, which depend on the temperature of the geothermal resources. Furthermore, some methods of analysis are presented in literature and the main advantages and disadvantages have been analyzed. A comprehensive review from different regions around the world has been presented by Lund and Boyd (2015), Rubio-Maya *et al.* (2015), and Gude (2016). Rubio-Maya *et al.* (2015) emphasize that in general, it is possible to identify two main groups: (i) cascade systems with electricity production and thermal uses, and (ii) cascade systems comprising only of thermal uses. In low-enthalpy resources the main use is the second solution.

## 11.5 GEOTHERMAL ENERGY FOR THERMAL WATER DESALINATION

Natural availability of freshwater is unevenly distributed around the world and at different seasons, and its resources are limited. Desalination technologies of salty water, which are energy-intensive, play an increasing role in the provision of water and food security for future generations. At present desalination is producing 70 million m<sup>3</sup> of freshwater per day from 16,000 desalination plants around the world (IRENA, 2015). Desalination consumes annually at least 75.2 TWh of electricity, which is equivalent to about 0.4% of global electricity consumption (UN Water, 2014).

Because conventional desalination technologies are high in demand for energy from fossil resources, they are limited in use (IRENA, 2012). The energy costs are as high as half the cost of operating the desalination plants (Herndon, 2013). The increase in fossil energy demand due to the increase in desalination capacity makes the processes economically and environmentally unsustainable. Using alternative energy such as renewable energy to power desalination technologies is becoming more and more important to meet the growing demand for increasing freshwater production.

Renewable energy such as geothermal can be used to drive different desalination technologies (Ghaffour *et al.*, 2015; Goosen *et al.*, 2014). Geothermal can be used directly in some thermal technologies (multi-stage flash (MSF), multi-effect distillation (MED)), and indirectly in mature membrane technologies (reverse osmosis (RO), Electro Dialysis (ED) and electrodialysis reversal (EDR)), as well as other technologies which are not mature and still require further research (Ghaffour *et al.*, 2014) and others (Figs. 11.5 and 11.6).

Over the past two decades, great efforts have been made to convert/alter conventional desalination techniques to be powered by Renewable Energy Sources (RES). The transition to RES has been hindered, especially when upscaling to larger sized plants, by factors such as technological, economic and political/regulatory (e.g. subsidies for fossil fuels). Nowadays, there are commercial units available on the market. Many medium-sized desalination plants are driven by RES. Most of these plants operate on electricity from solar photovoltaic and wind energy rather than using the heat from solar or geothermal directly, which would provide more sustainable desalination processes.

Desalination units powered by electricity obtained from RES are usually implemented on a small scale (community level). Nowadays, installations of larger scale desalination plants connected to the grid are increasing. Combination of solar thermal with desalination techniques such as MSF, MED, vapor pressure (VC) and MD, is clearly best suited for regions with high solar

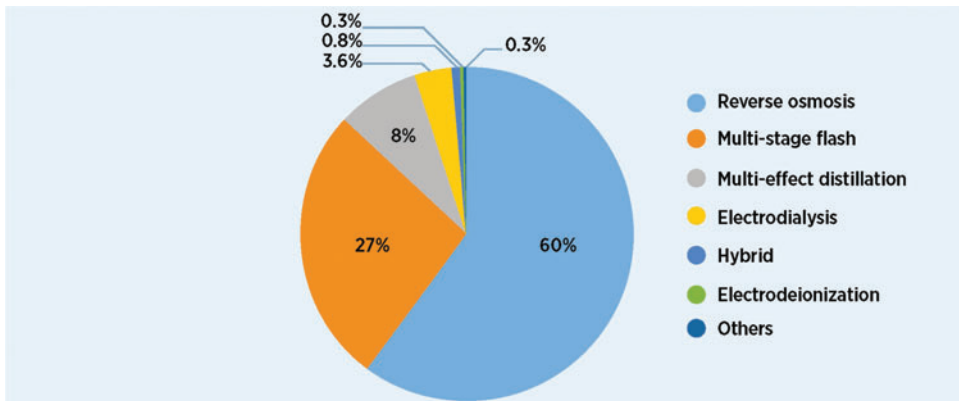


Figure 11.5. Capacities for different technologies for desalination (Koschikowski, 2011).

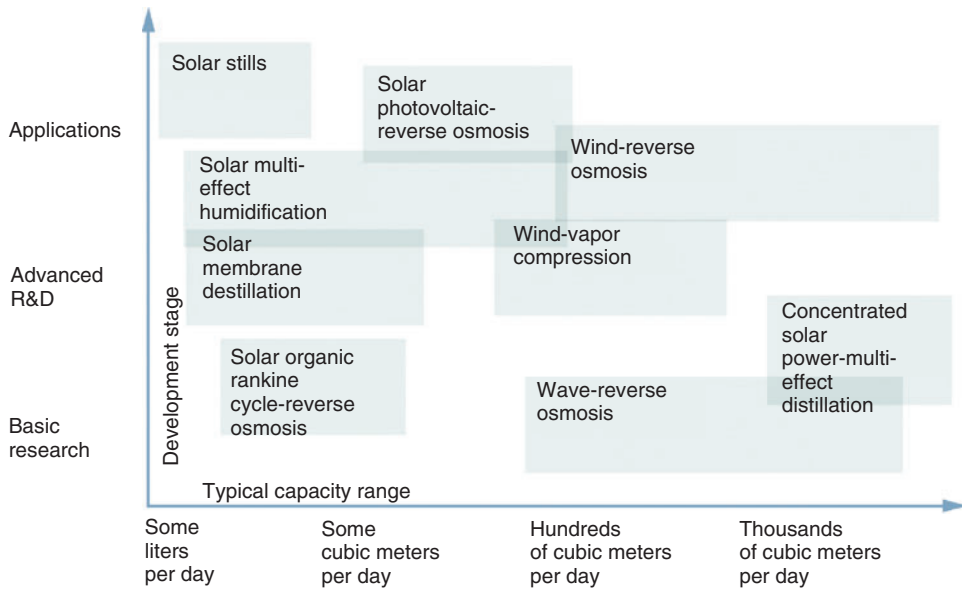


Figure 11.6. Principal renewable energy powered desalination technologies and their development state (Papapetrou *et al.*, 2010).

radiation such as North Africa, and parts of Australia (Zaragoza *et al.*, 2014; Ghaffour *et al.*, 2014).

Desalination varies from one process to another and the energy requirements correspondingly differ (Ghaffour *et al.*, 2013). Both thermal and electrical energy is required in thermal desalination for purposes such as evaporation, process hydraulic flow and transport of the feed and product water. Only electrical energy is required in the pressure-driven membrane desalination process; this is to supply the mechanical energy for membrane separation and pretreatment, and pumping into and distribution out of the plant (Gude, 2016). Gude (2016) presented the specific kinds of energy consumption for thermal and membrane desalination processes in terms of kJ of the specific energy required for producing one unit of freshwater in kilograms (Fig. 11.7; Table 11.3).

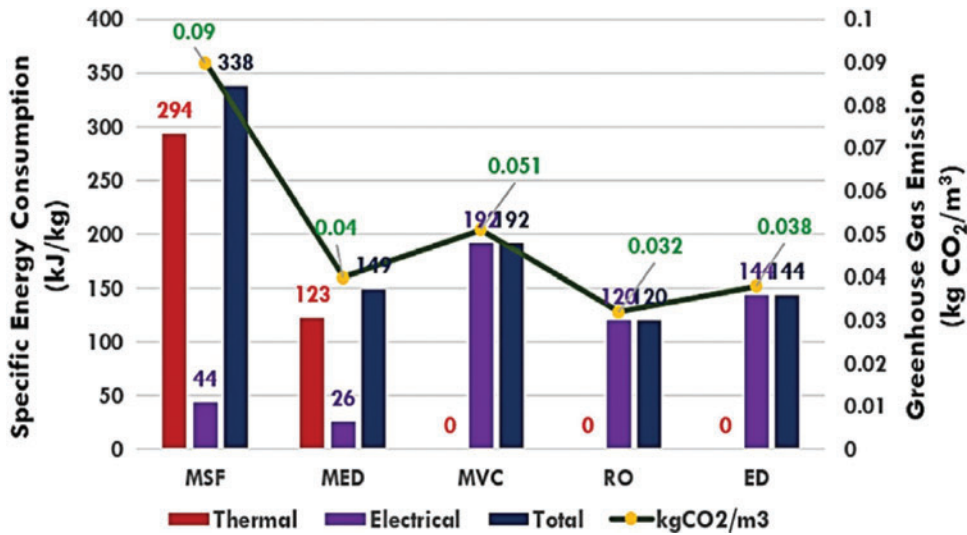


Figure 11.7. Specific energy consumption for thermal and membrane desalination processes and greenhouse gas emissions for unit freshwater production (after Gude, 2016).

Table 11.3. Typical capacity, energy demand and cost for some combinations of solar and desalination technologies (Ghaffour *et al.*, 2015).

	Typical capacity [m <sup>3</sup> day <sup>-1</sup> ]	Energy demand [kWh m <sup>-3</sup> ]	Water cost [US\$ m <sup>-3</sup> ]
Solar still	<0.1	Solar passive	1.3–6.5
Solar (MEH)	1–100	Ther: 100 Elec: 1.5	2.6–6.5
Solar MSF	1	Ther: 81–144 <sup>1)</sup>	1–5 <sup>1)</sup>
Solar tower MSF	1	T: 53.7 <sup>2)</sup>	–
Solar/CSP MED	>5000	Ther: 60–70; Elec: 1.5–2 <sup>3)</sup> T: 50–94 <sup>1)</sup>	2.3–2.8 <sup>3)</sup> (prospective cost) 2–9 <sup>1)</sup>
Solar tower MED	1	T: 42.4 <sup>2)</sup>	–
Solar tower VC	1	Elec: 55.5	–
PV-RO	<100	Elec: BW: 0.5–1.5; SW: 4–5 <sup>3)</sup> ; BW-SW: 1.2–19 <sup>1)</sup>	BW: 6.5–9.1; SW: 11.7–15.6 <sup>3)</sup> ; 3–27 <sup>1)</sup>
Solar tower RO	1	Elec: 41–45 <sup>2)</sup>	–
PV-EDR	<100	Elec: BW: 3–4 <sup>3)</sup> BW: 0.6–1 <sup>1)</sup>	10.4–11.7 <sup>3)</sup> 3–16 <sup>1)</sup>
Solar MD	0.15–10	Ther: 150–200 <sup>3)</sup> ; 100–600 <sup>1)</sup> ; 436 <sup>4)</sup> ; 180–2200 <sup>5)</sup>	10.4–19.5 <sup>3)</sup> 13–18 <sup>1)</sup>
Solar AD	8	Elec: 1.38 T: 39.8 <sup>6)</sup>	0.7 (electrical cost only) <sup>6)</sup>

BW: Brackish water; Elec: Electrical; SW: Seawater; T: Total; Ther: Thermal.

AD: Adsorption desalination; CSP: Concentrated solar power; ED: electrodialysis; EDR: electrodialysis reversal; MD: Membrane distillation; MED: Multi-effect distillation; MEH: Multi-effect humidification; MSF: Multi-stage flash; PV: Photovoltaic; RO: Reverse osmosis; VC: Vapor compression. <sup>1)</sup>Ali *et al.* (2011); <sup>2)</sup>Ahmad and Schmid (2002); <sup>3)</sup>Paparetrou *et al.* (2010); <sup>4)</sup>Kim *et al.* (2013); <sup>5)</sup>Saffarini *et al.* (2012); <sup>6)</sup>Ng *et al.* (2013).



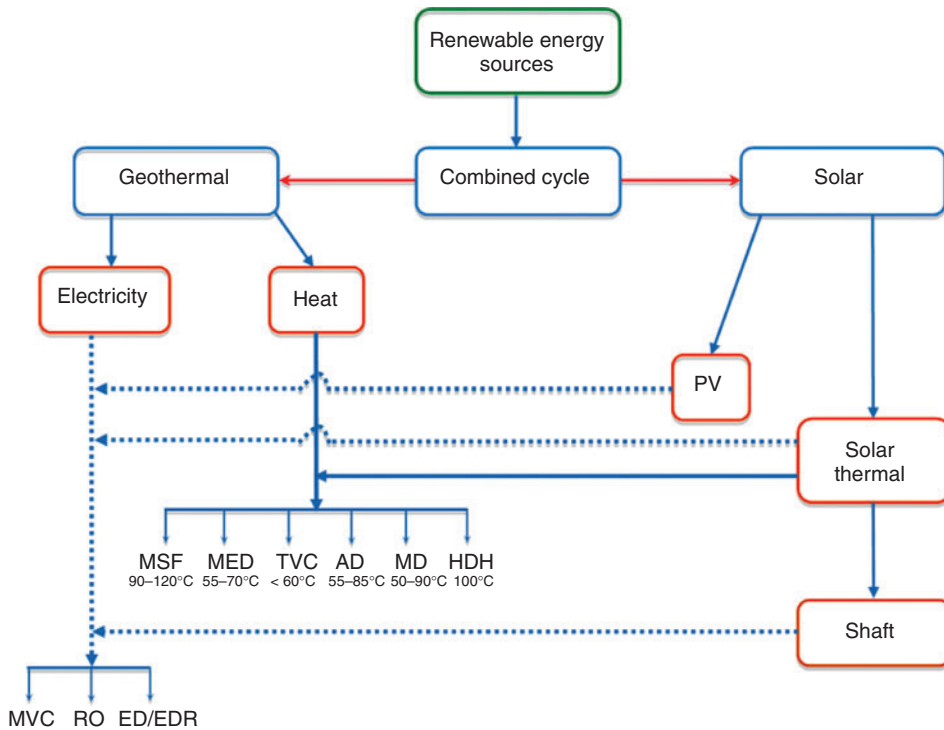


Figure 11.8. Possible combinations of integrated systems: RES with conventional and innovative desalination processes (AD: Adsorption desalination; ED: electro dialysis; EDR: electro dialysis reversal; HDH: Humidification-dehumidification; MD: Membrane distillation; MED: Multi-effect distillation; MSF: Multi-stage flash; MVC: Mechanical vapor compression; PV: Photovoltaic; RO: Reverse osmosis; TVC: Thermal vapor compression) (Ghaffour *et al.*, 2015).

Regarding specific energy consumption, the seawater reverse osmosis (SWRO) process has the lowest and the MSF process the highest consumption. Because of the energy required for these processes, membrane methods have been targeted to replace thermal technologies and primarily RO, especially when there is no cheap waste heat available.

With regard to renewable energy-driven desalination technologies, this level of detailed analysis is still missing. Each technology has particular characteristics which would need to be matched to a market analysis to enable investment decisions to be made (Papapetrou *et al.*, 2010). Renewable energy-driven desalination costs vary based on location and situation; on average it is still expensive when compared to conventional desalination. Table 11.3 provides an overview of water production costs and energy demand for some possible combinations of solar and desalination technologies. A detailed assessment of the benefits of these technologies and their limitations is discussed in Tzen (2012) using wind energy, Bundschuh *et al.* (2015) and Gude (2016) using geothermal heat, and by Ghaffour *et al.* (2015) for solar and geothermal.

Figure 11.8 shows several possible combinations of solar and geothermal powered desalination, the individual suitability of which depends on the specific site conditions (plant scale, feed water salinity, remoteness, electricity access or not, technical infrastructure, RES and its availability, potential and exploitation cost).

A critical review of the state of renewable energy-driven desalination technologies has been presented by Ghaffour *et al.* (2015). They highlighted the potential applications of integrated systems and the current technological and economic constraints and challenges. Tzen (2012) and



Ghaffour *et al.* (2015) showed that desalination processes are best suited to continuous operation. However, renewable energy (wind, solar) are distinctly non-continuous sources; only geothermal is a continuous and constant energy source. Desalination driven by renewable energy requires special design and operation which increases complexity, in particular for autonomous systems. Renewable and desalination as individual technologies are mature and are produced en masse; at present, merging these two technologies in large-scale applications is hindered by technological and economic constraints.

In cases where low-cost, low-enthalpy geothermal sources are available, geothermal energy can be an attractive option. These sources comprise geothermal resources at shallow depth, water co-produced from onshore and offshore hydrocarbon wells, or from already existing deep wells, and residual heat from geothermal power plants (Bundschuh *et al.*, 2015). The advantage of geothermal energy is that it is accessible 24 hours a day, every day of the year and can thus serve as an add-on to energy sources which are only available intermittently (Goosen *et al.*, 2010). The application of geothermal energy in desalination is still a relatively unexplored technical concept (Davies and Orfi, 2014). The production of electricity and freshwater from geothermal brines using MSF units has been studied by Awerbuch *et al.* (1976). Karytsas (1996) conducted a case study of a low-enthalpy geothermal energy-driven MED unit on Milos Island in Greece. A more recent project from the USA was the vertical tube evaporation (VTE) geothermal desalination pilot, where geothermal steam provides the thermal energy for the VTE distillation process (Sephton Water Technology, 2012).

Although limited to areas where geothermal resources are available, a rapid expansion of geothermal electricity and heat production is expected in the near future (Bertani, 2015). Gude (2016) showed the benefits of using MSF and MED technologies in utilizing high-enthalpy geothermal sources for simultaneous power and freshwater productions. Because low temperature desalination processes have lower specific energy requirements and a higher thermodynamic efficiency, they can be coupled with low-enthalpy geothermal sources.

The production of freshwater from desalination, combined with renewable energy, is a technological option for small or medium-size operations and economically viable for water supply in remote areas. In contrast to geothermal energy, solar and wind are not available in a continuous mode, which hinders upgrading to large-size desalination systems using solar and/or wind energy. It is worth mentioning that the implementation of combined solar and geothermal powered desalination process does not need energy storage. Development of innovative desalination technologies which do not need continuous operation, such as AD and MD, will be more suitable for renewable energy use compared to those which must run in continuous mode.

A promising technology is desalination based on concentrated solar power (CSP). There is a potential for large-scale desalination plants to be powered by CSP with thermal energy storage which also can simultaneously produce electricity for other purposes (Ghaffour *et al.*, 2015; Goosen *et al.*, 2014; IRENA, 2015). According to Trieb *et al.* (2011), CSP-based desalination could become a major process for the production of freshwater in the MENA region, amounting to about 16% of its total water production in 2030 and 22% in 2050.

## 11.6 GEOTHERMAL GREENHOUSES DEVELOPMENT HEATING/COOLING, VENTILATION, HUMIDIFICATION, DESALINATION

Energy efficiency and good economics are crucial in the development of geothermal greenhouse systems. Results of studies on achieving energy-efficient buildings may be translated to agricultural greenhouses. Angrisani *et al.* (2016), for example, performed a dynamic simulation to evaluate the energy and economic performance of a novel heating and cooling system based on the coupling between a low or medium-enthalpy geothermal source and an air-handling unit, including a desiccant wheel. This has applications in space heating and domestic hot water, as well as agricultural uses. During the summer season, a downhole heat exchanger supplied heat to regenerate the desiccant material, while geothermal fluid was continuously extracted by the

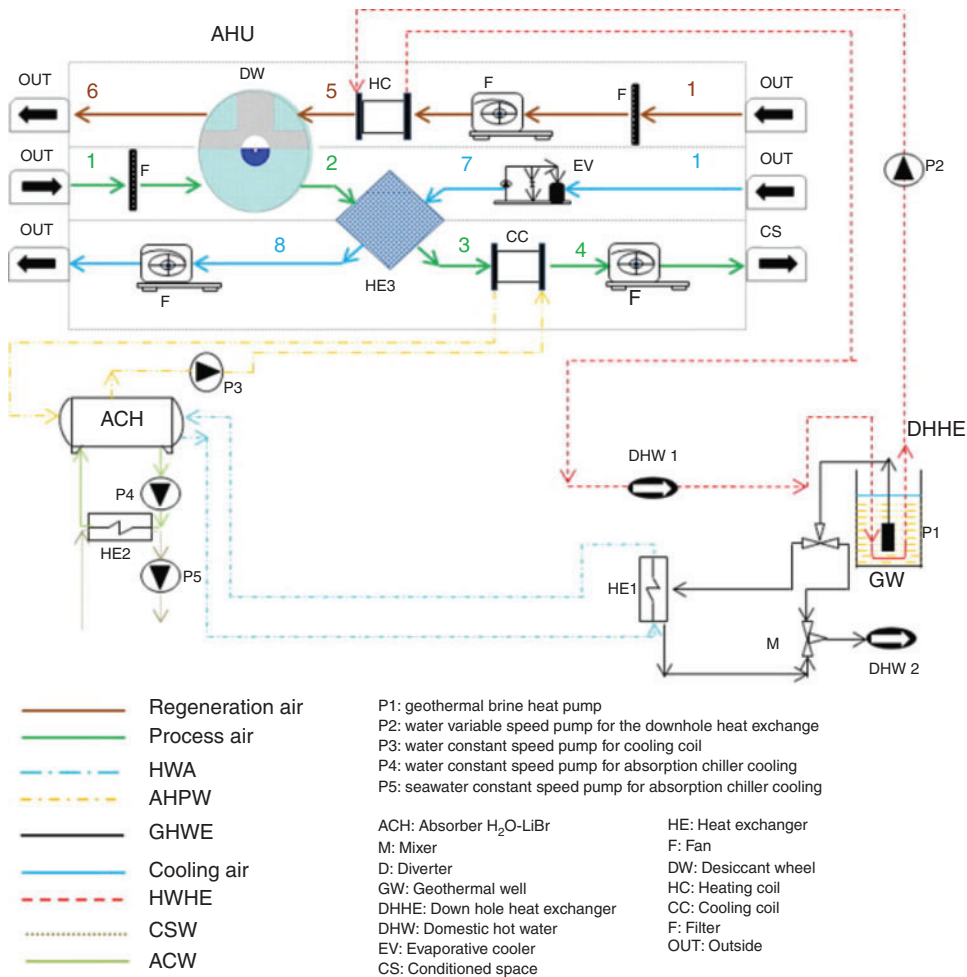


Figure 11.9. Sketch of the system layout during summer period (Angrisani *et al.*, 2016).

well in order to maintain high operating temperatures (Fig. 11.9). Simultaneously, the extracted geothermal fluid drove an absorption chiller, producing chilled water to the cooling coil of the airhandling unit. Conversely, during the winter season, geothermal energy was used to cover the space heating demand. The results of the simulations show that the novel geothermal heating and cooling system can be extremely profitable in terms of energy and economic performance. Zhou *et al.* (2016) achieved energy-efficient buildings via retrofitting existing buildings using a case study. It can be speculated that greenhouses could also be retrofitting with geothermal energy sources in order to improve energy efficiency.

Reviews on the state-of-the-art solar and geothermal technologies in agricultural greenhouse improvement have been published by Mahmoudi *et al.* (2010), Hassanien *et al.* (2016), Harjunowibowo *et al.* (2016), and Lund and Boyd (2016). The integration of thin film solar PV panels into the roof area of glass greenhouses was one of the advances reported by Hassanien *et al.* (2016). It can be argued however, that the conversion of agricultural land into PV plants could cause friction between farmers and energy producers. By combining PV panels and crops on the same area of land the increasing competition for land between food and energy production may be alleviated.

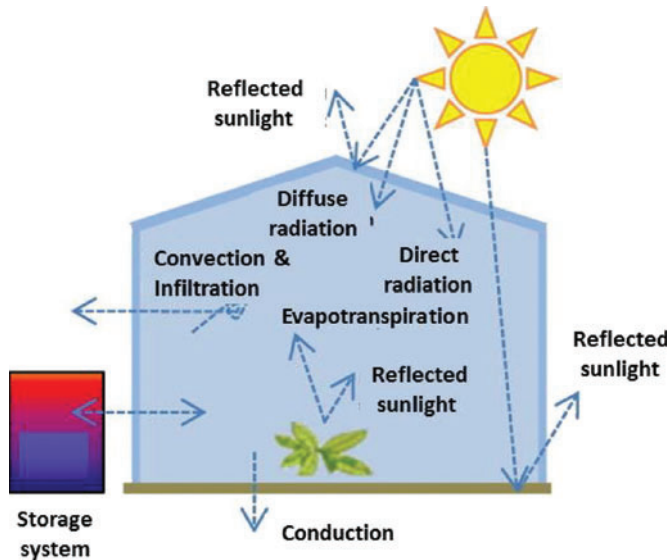


Figure 11.10. Closed greenhouse thermal flow with heat storage system (adapted from Harjunowibowo *et al.*, 2016 and Vadiée and Martin, 2013).

Çakır and Şahin (2015) evaluated solar greenhouses in cold climates and assessed the optimum type according to sizing, position and location. They concluded that one of the chief operational parameters for solar energy acquisition rates of greenhouses is the roof shape. Elliptic greenhouses were preferred, at least for cold climates. Harjunowibowo *et al.* (2016) presented the latest technological developments used in greenhouses to control the microclimate by focusing on passive techniques. For example, heat can be taken from the greenhouse during the day and deposited in a thermal storage system such as water, rocks, phase change material and soil water collectors. This heat is then used at night in accordance with the required heat in the greenhouse (Fig. 11.10). In a related study by Bouadila *et al.* (2014) the excess heat in the greenhouse was stored in a packed bed through the daytime period and extracted at night. Over a 20-year period from 1995 to 2015, greenhouse heating using geothermal energy has increased by about 50% (Fig. 11.11).

Chinese *et al.* (2005) established technical and economic optimization models in order to exploit a renewable energy source characterized by waste heat coming from the condenser of a waste-to-energy plant built to convert wood scraps from a chair manufacturing industrial district in northeastern Italy. The authors argued that coupling a greenhouse with a waste-to-energy plant could represent an important step towards sustainable development of such industrial structures, since it encourages both business diversification and full exploitation of internal resources. Rubio-Maya *et al.* (2015) presented a comprehensive review of different regions around the world employing geothermal resources of medium and low-enthalpy in a cascade manner. It is possible that the fluid temperature at the outlet of the generation process has sufficient thermodynamic quality and can be useful at a sequential process in a second or third level of temperature. Such processes or direct uses are, for instance, heating systems, hot water supply, intermediate drying processes of food or wood, and other direct uses of geothermal heat, such as aquaculture and greenhouses.

Finally, economic and environmental assessments of solar-geothermal greenhouse systems are critical in their effective development & commercialization (Vourdoubas, 2015; Russo *et al.*, 2014; Ozgener and Hepbasli, 2006). Profitability analysis data of various applications of renewable energies in greenhouses in Crete, Greece, by Vourdoubas (2015) are presented in Table 11.4. Direct heating with geothermal fluid was found to be the most profitable. The Net Present Value

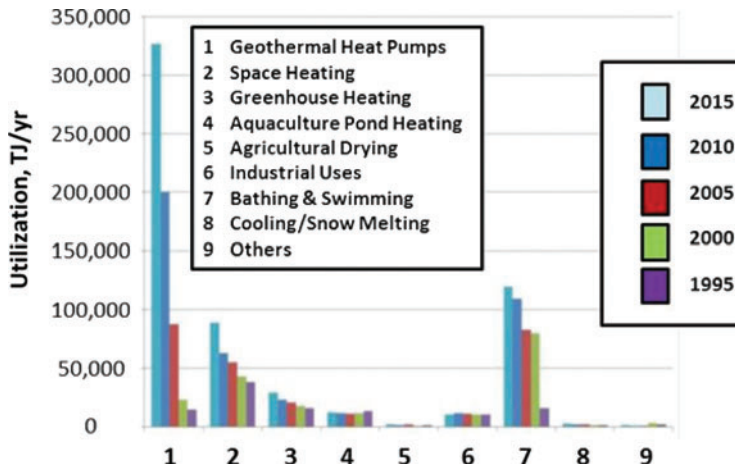


Figure 11.11. Comparison of worldwide direct-use geothermal energy in  $\text{TJ year}^{-1}$  from 1995, 2000, 2005, 2010 and 2015 (Lund and Boyd, 2016).

Table 11.4. Profitability analysis data of various applications of renewable energies in greenhouses in Crete, Greece (Vourdoubas, 2015).

Type of renewable energy	Energy generated	Operating period [years]	Initial investment [€]	Payback period [years]	NPV [€]
Solar PV	Electricity	20	13062	16.98 12.30*	1622 6030*
Solid biomass	Heat	15	14864	2.95	53880
Direct heating with geothermal fluid	Heat	20	12500	1.25	129268
Geothermal heat pumps	Heat (and cooling)	20	122130	—	−19116

Note. \*In the case of 30% higher than current electricity prices.

(NPV) was the highest at € 129,268. In finance, the NPV or Net Present Worth (NPW) is a measurement of the profitability of an undertaking, which is calculated by subtracting the present values of cash outflows (including initial cost) from the present values of cash inflows over a period of time.

Geyer *et al.* (2017) noted that low temperature residual heat and heat potentials of renewables below  $70^{\circ}\text{C}$  are often not exploited, as either the distance between source and demand is too large, or the heat does not occur at demand times. They argued that hybrid thermo-chemical networks have a high potential to improve this situation, to transport thermal energy potential over long distances and to bridge short- to medium-time differences between demand and supply. The storage and transport potential of thermo-chemical substances were identified and examined comprehensively by Geyer *et al.* (2017). Their paper reported on the use of thermo-chemical fluids (TCF) in district networks showing, for example, the theoretical potential to reduce primary energy consumption by up to 85%. Technological components were also developed for thermo-chemical systems.

Speerforck and Schmitz (2016), using a pilot installation at Hamburg University of Technology, investigated the coupling operation of an open-cycle desiccant-assisted air-conditioning system with borehole heat exchangers (Fig. 11.12). Results showed that the electricity demand of the system can be reduced to that required by the fans, wheels and pumps. An electric energy

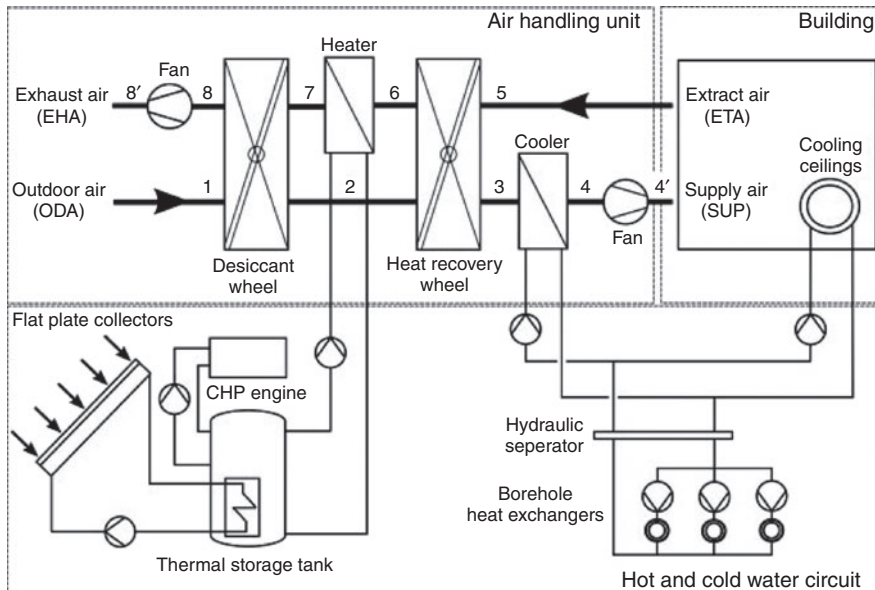


Figure 11.12. Layout of a pilot installation for investigating the coupling operation of an open-cycle desiccant-assisted air-conditioning system with borehole heat exchangers (Speerforck and Schmitz, 2016).

efficiency ratio of 6.63 was achieved, enabling electricity savings of more than 70% compared to a conventional reference system, and 54% compared to a desiccant-assisted hybrid system relying on an electric chiller. The layout of the pilot installation shown in Figure 11.12 indicates three major parts: the air-handling unit, the hot and cold water circuit, and the reference room. The air-handling unit was designed as a hybrid system. The outdoor air was dehumidified in a desiccant wheel (1–2) and precooled by the sensible heat regenerator (2–3). Lithium chloride was employed as a desiccant. The air was then cooled down by a water-to-air heat exchanger (3–4) to achieve the desired supply air temperature. The extracted air was preheated by a heat recovery wheel (5–6) before being heated further to the required regeneration temperature (6–7). The air regenerated the desiccant wheel (7–8) before it exited the installation. Speerforck and Schmitz (2016) concluded that the cooling load was reduced in comparison to a conventional air-conditioning unit, by employing a desiccant wheel to separate dehumidification and cooling.

### 11.7 GEOTHERMAL AQUIFERS AS FRESHWATER SOURCE

Geothermal systems not only provide a valuable renewable energy, but can also be considered as the source and solution for freshwater production. Key factors that determine the conditions in which geothermal waters are used, the amount of energy obtained and the manner in which cooled water is utilized, include water salinity and the presence of specific ingredients. The geothermal waters present in the geological structures are freshwaters and waters with low mineral content, as well as brines with mineral content exceeding  $100 \text{ g L}^{-1}$  (Tomaszewska and Szczepański, 2014). Consequently, the salinity of geothermal waters varies widely. Elevated salinity levels and the presence of microelements, such as boron, barium, strontium, fluorides, bromides and heavy metals, often lead to difficulties related to the utilization of spent waters. Low mineral content and fresh geothermal waters are mostly made available for heating and leisure purposes.

Waters with a mineralization below  $1000 \text{ mg L}^{-1}$  normally meet the requirements for drinking, potable and sanitary water. Borovic and Markovic (2015) report that the total geothermal

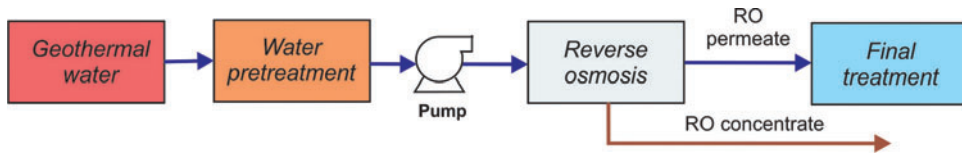


Figure 11.13. Simplified diagram of the RO water desalination.

waters in Croatia – five natural springs and one deep borehole – are exploited as sanitary water (e.g. in Stubičke toplice), one natural spring and one deep borehole for public water supply, and one borehole as table water. Geothermal water is also bottled as a table and mineral water. High-quality geothermal waters as an energy and freshwater source are exploited in Mszczonów (central Poland). Water with low mineral content (ca.  $0.5 \text{ g L}^{-1}$ ) and with an intake temperature of  $42^\circ\text{C}$  has been extracted since 2000 from the Mszczonów IG-1 Well (Lower Cretaceous horizon composed of sandstones interbedded with mudstone and claystone). These are high quality  $\text{Cl-HCO}_3\text{-Na-Ca}$  waters that are fed to the municipal water supply network as drinking water following cooling and simple treatment. The extraction of these waters in an open system with a maximum capacity of  $60 \text{ m}^3 \text{ h}^{-1}$  (without reinjecting cooled water into the formation) has significantly improved the economic performance of the project, and the utilization of cooled water as drinking water has additionally enhanced the management of ordinary water resources (Tomaszewska and Szczepański, 2014). A similar manner of utilization of geothermal waters is envisaged in Poddębice (central Poland) where geothermal water exhibits a mineralization of ca.  $0.4 \text{ g L}^{-1}$  at intake.

Water is the basis for life and culture. Nowadays, when the world's most common problem is a shortage of drinking water, research plays a very important role for the better utilization of geothermal water and its waste. Geothermal water can first be used as an energy source but after treatment processes, can also be used as a source of drinking water and/or public water supply. The crucial implementation of these solutions at industry scale would reduce the negative impact of discharged saline waste geothermal water to streams. Waste recycled in this way could be reused, which is very important, especially in areas with problems of a lack or deficit of water.

Depending on the turbidity and organic matter content, water should be subjected to multi-layer bed filtration after optional coagulation, or microfiltration/ultrafiltration and disinfection before being introduced into the water supply network. The use of medium salinity geothermal waters ( $1\text{--}10 \text{ g L}^{-1}$ ) as a freshwater source requires the use of water treatment systems. In brackish water treatment processes it has become more common for membrane processes to be used, especially RO and nanofiltration (NF). RO stops ions and most low molecular weight organic compounds. The NF process is used to stop colloids, many low and medium molecular weight organic compounds, and divalent ions. A typical RO water desalination plant consists of a raw water pretreatment system, a membrane desalination system – including a high pressure pump – and a final treatment system, whose purpose is to ensure that the legal requirements applicable to drinking and household water for the jurisdiction in question are met (Fig. 11.13).

The most important application of research is recycling waste of geothermal water and its valorization due to specific micro and macro elements content, good quality and lack of salinity components. Some technological propositions and the results of research of geothermal water treatment have been presented by Gallup (2007), Kabay *et al.* (2004a, 2004b, 2009, 2013), Koseoglu *et al.* (2010), Bujakowski *et al.* (2012), Gude (2016), Tomaszewska and Bodzek (2013a, 2013b) and Tomaszewska *et al.* (2014, 2016). One of the first propositions for geothermal water treatment for potable purposes was presented by Houcine *et al.* (1999). The geothermal brackish groundwater ( $2.8 \text{ g L}^{-1}$ ,  $30^\circ\text{C}$ ) of the Chott el Fejj (70 km from the city of Gabes, Tunisia) was used to feed the RO desalination plant in the city of Gabes at a flow of  $2000 \text{ m}^3 \text{ h}^{-1}$ . The authors explain the advantage of productivity of RO membranes with increasing the temperature

of the feed geothermal water, unless the temperature tolerance of the membrane is respected. The viscosity of water decreases with an increase in water temperature and consequently membrane productivity increases by about 2–3% per one °C. This is an important fact because really small water resources are available in African countries, where more than 70% of the population do not have access to potable water (Kana *et al.*, 2015). The results of the study aim to investigate geothermal potential and groundwater aquifers in the Mayo Kani area (Cameroon) to contribute to the improvement of the living conditions of the population, using the electrical resistivity model that was presented by Kana *et al.* (2015). The presence of two low-enthalpy geothermal potential reservoirs, which can also be used as a potable water source has been discovered at Djangal and Moundjou. In Eburru (Kenya), the cascade utilization of geothermal water proposed includes the production of the much needed potable water. Mburu (2012) suggests that this will be used as a demonstration center for the utilization of geothermal energy as well as a source of income to the local community. Countries which have good geothermal conditions are ideal candidates for producing freshwater from brackish water (Mahmoudi *et al.*, 2010).

## 11.8 CONCLUSIONS

Geothermal sources have become progressively important due to the permanent increasing food demand which leads to a corresponding growth of the agricultural intensity in particular, through increased mechanization, expansion of irrigated land, fertilizer production and transportation, all of which require ever more energy and water.

In agriculture and the agri-food chain, geothermal heat can either eliminate or significantly reduce the energy produced by fossil fuels. Geothermal steam and hot water can provide the energy required for heating/cooling of spaces (buildings, greenhouses, and aquaculture), soil heating, thermal water desalination for irrigation purposes, drying, sterilization, and many other purposes. Globally, 4.5% geothermal energy is used for greenhouses and open ground heating, 2.0% for aquaculture pond and raceway heating, 1.8% for industrial process heating, and 0.4% for agricultural drying at present (2015). Depending on the characteristics of the geothermal source, the applications can vary. Geothermal can not only provide energy but at the same time can provide a source of freshwater which would contribute to future global food security and climate protection, as well as other sectors of the SDGs. Geothermal energy is a constant heat source, available 24 hours a day, 365 days a year.

To overcome the present-day over-dependence on and related risks of fossil fuels, geothermal sources can be integrated, either alone, or combined with other RES, to provide water- and energy-efficient technologies with the required energy.

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*Section IV*  
*The uses of geothermal water in balneotherapy*



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## CHAPTER 12

### Short history of thermal healing bathing

Barbara Kielczawa

#### 12.1 INTRODUCTION

For thousands of years, people have been using thermal baths to stay healthy and feel good. This is why balneology, that is, using natural spring water for medicinal purposes, has a very long history. Archaeological findings from continental Asia prove that making use of hot spring waters was known there as early as in the Bronze Age, about 3000 years before Christ. In Japan, this date could be pushed back even to 11,000 years ago (Fridleifsson, 2001). As thermal waters were regarded as gods' gifts in Egypt and the Mediterranean region, they were considered sacred and were used for religious ceremonies there. Ancient Greeks, Turks and Romans were known for developing bathing facilities practically everywhere where they went in their conquests. Baths were taken from Persia to present-day England (Lund, 1996). To emphasize their belief in the beneficial effect of hot baths on staying fit and preserving physical and spiritual health, ancient Romans quoted the Latin motto *salus per aquis* ('health through water'), which they often supplemented with the borrowed Greek saying *mens sana in corpore sano* – 'healthy spirit in a healthy body' (Fyticas *et al.*, 1999). It is difficult to say precisely where and when the medicinal properties of thermal waters were first recognized and first put to use. Discovering geothermal springs was a natural process resulting from the growing needs of developing societies and it is most likely that men were led to hot waters by animals.

#### 12.2 THE AMERICAS

North American Indians considered the areas of hot water occurrence to be sacred and they believed in their miraculous powers. Such areas were neutral territories, where everyone could go, regardless of the tribe which they represented. People could bring their injured and ill there; they could drink spring water or bathe in muddy pools accompanying the springs. The American Indians have lived here for about 10,000 years. After the arrival of the Europeans (1500), the usage of geothermal resources changed considerably, especially by being commercialized.

Almost every spring in the USA and Canada has some records about being used by Indians. Native Americans often protected information about these springs from being discovered by European settlers. The "Fountain of Youth", which Spanish settlers searched for, was probably only a tale which had originated from legends about healing properties of hot spring waters.

The first European settlers (in the 18th–19th centuries) used hot springs medicinally like Indians did. In time, they became aware of their commercial potential and, following the European tradition, established numerous health resorts (Saratoga Springs in New York State; White Sulfur Springs in West Virginia; Hot Springs in Virginia; Warm Springs in Georgia; Hot Springs in Arkansas; Calistoga in California or Harrison Hot Springs in British Columbia). The lack of government interest (until 1940) in supporting health resorts resulted in the demise of many of them. Nowadays, a growing interest in hot springs, baths and a fashion for fitness have all restored an interest in spa resorts (Lund, 1999).

The Greenbrier in White Sulphur Springs, lying in a mountain valley on the border of West Virginia, is the location of a large health and spa resort with 200 years of history. Originally, this area was inhabited by Indians hunting in the nearby salt marshes. In the 18th century, the springs were visited by a woman suffering from chronic arthritis. Local Indians provided her with an improvised bathtub (made from a hollowed-out tree) filled with water heated in rocks. For a few weeks, the woman was regularly immersed in the bath. After that period, the pain ceased. The news spread very quickly among other settlers and a spa was subsequently built near the spring (sulfurous Bowyer's Spring) (Benedetto and Millikan, 1996).

The three main springs in West Virginia: Hot, Warm and Healing springs, flow out in Warm Spring Valley. They were discovered by Native Americans in the early 17th century and in the 1830s one of the leading Virginian health resorts developed here. The Homestead is the major center of Virginia Hot Springs (Lund, 1996).

Among Georgia's seven thermal springs, the Warm Springs are the most popular. They were originally known as Meriwether Warm Springs. Indians called this place "the land where the waters are warm". Between 1890 and 1920, baths were opened here. After 1925, when the Warm Springs Foundation was organized, the resort developed as a center for the treatment of polio. The US president Franklin Roosevelt, who was also treated here, played an active role in the development of the complex (Lund, 1999).

Saratoga Springs lie 40 km north of Albany, New York. There are 18 outflows of water used for drinking, bathing treatment and bottling. The area has been a state reservation and park for the sole purpose of preserving water resources since 1909. In 1916, there were three bathhouses, which were later replaced by new facilities: Washington Bath House, Lincoln Bath House and a drinking hall. In the next years, the resort developed quickly using heated waters.

Arkansas Hot Springs is the place with one of the best-known commercial spas in this area. In 1832, it was turned into a Federal Reservation and in 1921, a National Park of the United States was created here. The place is unique in that it is the only park created to protect hot springs (there are 47 of them) reserved for balneological purposes. It is likely that Native Americans used these waters for treatment at least 10,000 years ago. They believed that the Valley of the Vapors, where the springs flow out, was the home of the Great Spirit, who warmed water with his breath. The first scientific analysis of these waters was performed in 1804, and in 1832 the first bathhouses were opened. In the late 19th century, bathhouses stylized as contemporary European spas were built, equipped with bathtubs and showers for hot baths. The resort flourished, especially in the early 20th century. In the 1990s, there were two treatment complexes within the park and five treatment centers, each with bathtubs and pools, outside the park area (Benedetto and Millikan, 1996; Lund, 1999).

Another known group of springs, Thermopolis, lies in the north-central part of Wyoming, about 160 km south of Yellowstone National Park. Hot waters flowing from eight thermal springs produce travertine terraces on the ground surface. Archaeological findings indicate that this area was populated by the Shoshone Indians, starting about 2000 years ago. They knew the water from the springs as 'healing' or 'smoking' water. The chief of the Shoshones had his own bath at one of the Thermopolis springs. At the end of the 19th century, the area was brought under protection as 'Hot Springs State Park' (Lund, 1999).

When Europeans started to settle the western part of North America, especially California, its area of geysers was inhabited by several (six) native American tribes, varying in language and culture, and living in strictly defined areas. The geysers were available equally to all the tribes. The main spring area was the Castle Rock Springs in the eastern part of the geyser field known as 'The Geysers', which had been used medicinally for centuries. In the so-called 'Big Sulfur Creek', lying in the zone of hot springs and fumaroles forming 'The Big Geyser', Indians bathed in hot waters and steaming muds. Not far from the springs, there was the 'Geyser Resort Hotel', and the surrounding area was sacred according to Indian beliefs. The waters flowing out of the mountains varied in temperature (ice-cold, medium-warm and hot). They were used for curing various illnesses. In spring areas, water was supplied to special bowls by small canals. The desired temperature of water was obtained by closing and opening the appropriate canals. In the mid-19th

century, the surrounding area started to be covered with buildings which provided accommodation to patients (Hodgson, 1999b). About 120 km north of San Francisco, there are areas which were settled by Indians at least 4000 years ago. They have natural thermal springs, gas exhalations and hot muds for soothing different ailments. In the mid-19th century, a resort (Calistoga) started to develop here in the form known from European spas and Saratoga Hot Springs. In the 1990s, it underwent intensive development. New spas were built, offering mud baths, massages, steam baths, wraps, mineral water pools and pools with water of varying temperatures. Moreover, waters are bottled and distributed (Lund, 1999, 2005).

In New Mexico, the first health resort was opened in 1880 near Ojo Caliente Spring, but water from the spring is known to have been used much earlier by local tribes (Erfurt-Cooper and Cooper, 2009).

In Alaska, a well-known spring used for bathing was Kruzgamepa Spring (80 km north of Pilgrim). Visitors to another 'spa', Chief Shakes Hot Springs, used wooden buildings left over by Native Americans. Other known Alaskan thermal springs are Kilo, Hooniah and Tanakee, situated in the south-eastern part of the state. The last one was the most popular resort in this area in the early 20th century (Lund, 1999).

Settlement in the volcanic regions of Central America has been developing for 4000 years. It is thought that about 3000–3500 years ago, people started using the earth's heat for farming, medicine and convalescence after fighting or hunting. Hot waters were used for irrigation, bathing and cooking. Some hot springs were used for therapeutic purposes by early Aztecs. Chiefs (including Montezuma I and Montezuma II), together with their warriors, rested by Agua Hedionda spring after their duties and fights. The Aztecs believed in the curative properties of thermal springs and used them to keep or improve their health (Erfurt-Cooper and Cooper, 2009).

Spanish colonists also used thermal waters for therapeutic purposes. Missionaries and chroniclers wrote down Indian legends related to various geothermal phenomena (Hernández-Galán *et al.*, 1999; Suárez-Arriaga *et al.*, 1999). In the 19th century, the ancient resort Peñón, situated on the edge of today's Mexico City airport, was well known. Its 19th-century description mentions natural boiling-water fountains, bathhouses and a pool, probably used for curing arthritis. The bathhouses were stone buildings containing 5–6 empty rooms equipped with square bathtubs (Hernández-Galán *et al.*, 1999).

Near the southern edge of the Los Azufres Geothermal Field in Mexico lies the Lagoon of Sulfurs. It is an area of hot springs, for centuries known to P'urhépecha Indians and used for medicinal purposes. It is a national park nowadays (Hodgson, 1999a).

The indigenous population of the Andes settled in areas with natural geothermal manifestations. Thanks to this, they used the natural heat of thermal waters and hydrothermal products (for making tools). The Incas highly valued the curative properties of thermal waters, which also influenced the development of their religious practices. Inca palaces had baths using water supplied from the mountains, probably by means of canals. As Erfurt-Cooper and Cooper (2009) say, the most famous baths were those in Cajamarca, where Spanish conquerors found the Inca ruler Atahualpa with his suite. Nowadays, this place is known as Baños del Inca or Inca Baths. Indians used hot waters for curing battle wounds, general convalescence and for ritual baths (Calderón, 1999).

### 12.3 ASIA AND THE MIDDLE EAST

The Asian civilizations have used hot springs for many centuries. The ancient Indian civilization is one of the oldest in the world. The history of this country and its people is linked to numerous myths and religious beliefs. As in other regions of the ancient world, thermal springs, being manifestations of divinity, were regarded as gods' holy gifts. Numerous archaeological excavations near springs have revealed remnants of ancient temples of Shiva and Buddha, for example in the village of Devnimori situated north of the thermal spring Tuwa. It was believed that bathing in hot springs would guarantee longevity. Faith in the healing powers of thermal waters is not a new phenomenon in India. For centuries, Indian people have been using these waters for curing



diseases (leprosy, gout, paralysis, arthritis and skin diseases). During their rule in India, Mongols paid less attention to medicinal properties of waters, but they built tanks for bathing water and arranged beautiful gardens near springs.

In the mid-20th century, the idea of bottling and selling thermal waters first appeared. Waters were classified as medicinal and those intended for consumption. The latter were free from religious beliefs or cult. Consumption waters were aimed at for trade.

The belief in the divine origin of thermal springs is still alive in India, despite scientific advances and the possibility of scientific explanation of the genesis of these waters. The presence of Shiva temples in almost every settlement having thermal waters proves the Indians' deep belief in the sacred character of these waters. The creation of worship and pilgrimage centers in these places proves how strong the old beliefs and myths still are (Chandrasekharam, 1999).

In China, thermal baths have been known for 3000 years. The hottest waters were used for curing diseases and relaxation. Some of them were considered "miraculous" while others were reserved only for chosen groups of the society. For instance, the Jiuquan spring (the Golden Spring) in Gansu province could only be used by soldiers. The best-known spring used for luxury recreation was Huaqing Hot Spring. At the time of the Qin Dynasty (221–206 BC), they started bathing and development of treatment facilities. In the 7th century it was encircled with a palace, which was the most luxurious residence at that time. Daily baths were taken there and water, believed to be capable of preserving youth, was drunk. The royal families of the Ming (1368–1644) and the Qing (1644–1911) dynasties lived in a palace not far from Beijing. The oldest written records about hot springs (Tangshan Hot Spring, Xiaotangshan) in that area go back to 800 years ago (Erfurt-Cooper and Cooper, 2009). The remains of palace pools have been preserved to date. As time went by, Chinese medicine started paying attention to the influence of the temperature of waters used for treatment on the human organism. The first observations of this influence resulted in recommendations for curing so-called 'cold illnesses' (e.g. rheumatism, arthritis or digestive diseases) with hot waters, but not using them for feverish diseases (typhoid and jaundice). Skin diseases were cured with sulfur water and mud treatment (Czellecz and Petrea, 2013; Wang, 1999).

Japan abounds in geothermal manifestations in the form of hot springs. In many parts of this country, evidence of prehistoric use of thermal springs for bathing has been discovered. The oldest traces of bathing, dated back to 11,000 years ago, have been found near the hot spring Yuda in Iwate Prefecture. Later evidence (11,000 BC–300 AD) comes from the hot springs Oyu in Akita Prefecture, Kawazu in Nagasaki Prefecture, Kaminodan in Nagano Prefecture and Kamanokuchi in Ehime Prefecture (Fridleifsson, 2001). Thus, the history of using geothermal waters, from prehistoric times to the industrial age, can be associated with development of natural hot baths. Near Lake Suwa in Nagano Prefecture, 6000-year-old ruins, probably of public thermal baths, have been discovered. It is likely that local people took hot baths in it to get warm. In historical records, particular attention was paid to imperial family visits to spas and health resorts. The first of such visits took place in 631. Later (in the 8th–12th centuries), courtiers and nobility also started using medicinal baths. In the 13th century, samurais cured their battle wounds in health resorts. In the latter part of the 13th century (1287), water was brought to the royal palace in Kyoto from a spring situated 100 km away from the capital and after the mid-17th century, royal palaces in Edo, Kyoto and Osaka had water supplied regularly from Kaga. In the 18th century, in the Edo period (1603–1868), medical descriptions of diseases which had been successfully treated with thermal baths were printed. In the mid-Edo period, one doctor investigated the effect of hot waters from Kinokuni and Hyogo resorts on various diseases (e.g. oedemas, lumbago and paralysis). Another physician worked out home treatment formulae for those patients who were unable to come to resorts. At the end of the Edo period (1828–1843), analysis of the chemical composition of water samples from 36 health resorts were performed. Based on these analyses, the medical benefits of using them were described (Czellecz and Petrea, 2013; Sekioka, 1995, 1999).

In the so-called 'old geothermal zone' in South Korea, thermal waters have been used for centuries. Legends mention injured animals and birds which recovered after bathing in these

springs. Water from the 'the Heavenly Blessing' spring was used for curing skin diseases. Historical records prove that hot waters have been used in many places for a long time. As early as 286, royal families and ruling elites bathed in hot springs. Onyang (in Chunchong province), one of the oldest natural thermal springs in Korea, has been used for over 600 years. King Sejong the Great used to go there with his family to seek treatment (Erfurt-Cooper and Cooper, 2009). In the 14th century, the remaining population obtained permission to bathe, although until the Japanese occupation (1910) the springs were used chiefly by royal families and noblemen (Yum, 1999).

The areas between the Black Sea and the Caspian Sea are among the oldest civilization centers. Regular healing usage of thermal waters has been documented there for about 2500 years.

During archaeological excavations conducted in Armenia, remains of an open pool carved in travertine have been found. It contained a lot of Roman coins varying in age (between 100 BC and 200 AD). Although the construction of the pool dates it back to the beginning of the Christian era, Buachidze *et al.* (1999) claim that curative baths in this region had been practiced long before the Roman occupation of these areas (probably since the 5th century BC). In Azerbaijan, therapeutic baths were used for curing skin diseases and rheumatism. In a place called Barjomi in Georgia, baths in special bathhouses were taken as early as in the 1st century AD. The capital of Georgia, Tbilisi, developed in the 4th century. The city had a large spa, which was modernized in the 5th century, when the fortress became the capital. The baths used to be visited by people from the surrounding regions. The Turkish rule brought another extension of the facilities, which could be used by anybody, regardless of their religion (Christian or Muslim) or social status. Men and women bathed separately on designated days of the week. In the early 18th century, waters were analyzed and classified according to their temperature (Buachidze *et al.*, 1999).

Anatolia (part of Turkey) is abundant in manifestations of geothermal heat in the form of hot springs, fumaroles, mud pools and hydrothermal minerals. People inhabiting these areas have been making use of geothermal resources since the prehistoric times. This has been proved by numerous archaeological findings. Hot springs were already used at the time of the Hittite Empire (1450–1200 BC).

Intensive growth of hot spring usage came at the time of the Roman Empire. Turks took the idea of bathhouses over from the Romans and, in compliance with their own traditions, they introduced the order of treatments. Bathing centers had their specific architecture and they were very large. They used natural thermal waters or heated waters. Archaeological findings prove the existence of shrines in the vicinity of hot springs. Pausanias, a Greek geographer, living in the 2nd century AD, reported that the first temple dedicated to Asclepius, the god of medicine, was built near Pergamum as early as the mid-4th century BC. In time, it developed into a curative center known as Asclepion. The buildings were used for religious ceremonies and medical treatments. The treatment methods used there were described by Aristotle. The most important were bathing in thermal waters and muds, using herbs, drinking cold spring water and running barefoot through cold water. In the center, there were three pools for bathing and drinking water. The patients sat on steps inside the marble bathtubs and washed themselves with water from the holy spring.

In Izmir, western Anatolia, we can find another center of balneotherapy, established near Balçova thermal spring. The ancient name of the spring, Agamemnon, recalls the leader of the Greek army fighting in the Trojan War. On their way back home, his soldiers rested here and healed their wounds in the waters of the spring (Özgüler and Kasap, 1999).

In the area between the Dead Sea in the south and the Sea of Galilee in the north, four springs were used for hygienic and therapeutic bathing in ancient times (during the Hellenistic period, and the time of the Roman Empire and the Byzantine Empire). Two of them, Tiberias (Hammei Tiberis) and Hammat Gader, are still known and used. On the eastern side of the Gulf of Suez, not far from Gebel Hamman, hot springs had already been known at the time of the pharaohs. Soldiers and miners of the pharaohs of the Third Dynasty took hot baths in these springs as early as 1000 years before the arrival of the Jewish tribes in these areas. Similar springs can be found in Ayun Musa, to the north-east of Gebel Hamman (Rosenthal, 2001).

Certainly, as in the surrounding regions, the popularity of thermal waters peaked at the time of Roman rule. Thermal springs in this region were mentioned by Strabo, Plinius the Elder,

Flavius, Ptolemy, Eusebius and Placentia. They all described the curative properties of thermo-mineral waters. After Jews had settled in these areas, they developed their religious institutions. Descriptions of particular springs were included in the Talmud, together with the list of diseases that could be cured with them (urinary tract diseases, rheumatism, arthritis and neurological disorders). Generally, however, the religion objected to bathing, particularly on the Sabbath. Rabbis were opposed to common baths, when men and women could share one thermal pool.

In Hammei Tiberis, warm mud was used for treatment. The city was founded as the capital of Galilee by Herod Antipas in 20 AD. Nowadays, a thermal spring flows out in the southern corner of the city, where a modern luxury spa has been built.

Hammat Gader, not far from Naples, had one of the largest bathhouses in those times. The sick came from various faraway regions. The center had a complex of interconnected baths, the main five and a smaller one. Each of them had a large pool. In the 1990s, a modern functional balneological complex was built there.

Zara, known as Kallirhoe (“beautiful spring”) in Greek, has never been a well-developed spa. It was more of a luxurious royal holiday residence with private baths during the rule of Herod the Great and his son Herod Antipas. In a deep gorge, 3.5 km south-east of Zara, two Zarga Ma’in springs flow out. In ancient times, they were mistaken for Kallirhoe spring. However, there are no reliable data concerning the usage of waters from this spring for balneology in ancient times, but the curative properties of these springs were surely known to the first settlers. Like in Hammat Gader, the waters from these springs were used for bathing therapy (Jaffé *et al.*, 1999; Suárez-Arriaga, 2005).

## 12.4 EUROPEAN COUNTRIES

In the Mediterranean region, particularly in Greece, thermal energy has been known and recognized for thousands of years. Volcanic eruptions, hot springs, gas exhalation, geothermal field areas – all these phenomena have been the source of legends, myths, beliefs and cults. Thermal waters enabled ancient people to create treatment centers, where visitors left gifts to thank gods and deities for healing them. They believed that gods had entrusted springs into the care of nymphs and thus the properties of those springs reflected the temperaments of their careers. They built altars, shrines, and temples to Asclepius, the god of medicine, around the springs. This custom was observed until the beginning of Christianity.

Natural manifestations of geothermal energy have been described by chroniclers, poets and historians. Ancient scholars attempted to explain their genesis. This is true of Homer, Herodotus, Hippocrates, Aristotle, Pliny the Elder, Plutarch and Pausanias. Hippocrates (460–377? BC), who is regarded as the father of medicine, formulated a hypothesis stating that all diseases are caused by the absence of balance between body fluids in the organism (Routh *et al.*, 1996; Tubergen and Linden, 2002). He emphasized the necessity of taking into account the properties of every kind of water, as waters vary in temperature, density or taste, which give each kind of water its unique medicinal properties. Aristotle (384–322 BC) tried to explain the genesis of thermal waters flowing out in the northern part of the region of Euboea. Pliny the Elder (23–79) recommended using various kinds of waters according to the type of disease (Tubergen and Linden, 2002). Pausanias (110?–180?) described the vast majority of springs in Greece. He paid particular attention to the springs Methana and Methone, presenting the genesis of their waters.

Based on archaeological findings, legends and customs, one could conclude that therapeutic thermal baths were used in many parts of prehistoric Greece long before the rise of Rome. Depending on the properties of waters and the accompanying thermo-mineral muds, various illnesses were cured: psoriasis, eye infections, rheumatism, gout, urinary tract infections and respiratory tract infections. Hippocrates was the first to use regular balneological therapy to treat his patients. In the 5th century BC, he treated people from practically all the Mediterranean region in Asclepius’ center. Sending people home after treatment, he recommended continuing the therapy in waters from springs near the patients’ homes.

Among the many places visited by people from various parts of the Mediterranean region, Aedipsos, Loutraki, Epidaurus and Thermopylae were best known.

Aedipsos baths in the north-western part of Euboea was the most renowned resort in those times. They were as popular as Hierapolis in western Anatolia or Baia in southern Italy (near Naples). These baths had been in use since the prehistoric times and they underwent intensive development in the Roman period. The first fully organized hydrotherapeutic facilities in Aedipsos appeared around 84 BC. Their visitors included Roman emperors Hadrian (in 126) and Mark Aurelius (in 176).

In the north-western part of the Peloponnesus, not far from Corinth, Thermae Loutraki were located. Likewise, Aedipsos, Loutraki had already been visited by prehistoric people. The complex was renewed and extended in the 8th century BC when an athletic contest was organized in Corinth. Another bathing center, Epidaurus, was located in the middle-eastern part of the Peloponnesus. At the time of the Roman Empire (around 163 AD), new baths were erected near the old Asclepius thermal center. It was one of the most important balneological centers in those times.

In a narrow gorge, not far from the coast of Thessaly, in front of Euboea Straits, there is a group of springs called Thermopylae flow out. Around 150 AD, a large thermal complex with pools was erected there. The springs had already been known in the Antiquity, long before the famous battle fought between the Greeks and the Persians, which is confirmed by the ruins of an altar in honor of Hercules.

A lot of people would come to the above places for treatment, which was always performed under the direction of Asclepius' priests (Fyticas *et al.*, 1999).

Bulgaria, like many other countries on the Balkan peninsula, was occupied by the Romans. Both Thracians (4000 years ago) and the Romans left behind facilities which operated both as temples (of Asclepius, Hygeia, Telesphorus, and Apollo) and baths. The bathing centers which enjoyed particular popularity in the Roman times were Aqua Calida (today's Aitos), Serdika, Germanea (today's Sapareva Banja) and Scaptopora (now Blagoevgrad). Pautalia and Augusta (now Hisar), with their numerous pools and temples, were the main centers visited by Roman emperors and their families. The interest in medicinal waters and their protection in Bulgaria developed and persisted throughout the centuries. In 1891, protection of mineral waters was first regulated by laws, whose provisions included making springs the property of the state and ensuring free usage for everyone. In 1929, the Bulgarian Balneological Society, grouping scientists representing various fields, was formed (Bojadgieva *et al.*, 2002; Vassileva, 1996).

Macedonia, which is the central-Balkan country, has always had a strategic importance. Its trading and military routes connected Europe with the Middle East and it formed a border between the Greek and the Roman cultures. From both, it adopted the methods of utilizing warm waters in baths. However, little is known about the management or usage of geothermal resources. There is no evidence of thermal water usage during the times before the Greek conquest of Macedonia. While the Greeks brought their bathing habits to the Balkans, the Romans (200 BC–395 AD) expanded public baths and used them especially in the cold months. Similarly, the Turkish rule (1340–1918) was the time of common access to hot baths and operation of numerous bathhouses.

In the first half of the 20th century, due to its division between Serbs, Croats and Slovenes, Macedonia witnessed numerous cultural and political changes. This did not hamper the revitalization and extension of some of the baths. In the following years, spas were modernized with a focus on the balneological and tourism function.

Macedonia has about 200 mineral or mineral-thermal springs. Many of them have been used medicinally for centuries (Popovski and Dimitrov, 1999).

The tradition of using mineral and thermal waters in Bosnia and Herzegovina, like in other countries of the Mediterranean region, is centuries old. The usage of thermal waters in Roman times has been proved by the finding of Roman coins near Teslić. Inscriptions on the ruins of Roman bathhouses from 220 AD have been preserved in Guber and excavations in Ilidža near Sarajevo have shown that the first bathhouses in this region were erected by the Romans. The first written information about medicinal application of waters in a place called Kiseljak go back to the 14th century. Organized medicinal usage of water can be dated to the late 19th century, when

the areas of Bosnia and Herzegovina were ruled by Austria-Hungary. In 1888, the first analyses of thermal waters from Fojnica were conducted and the results confirmed the medicinal properties of these waters. In 1895, the construction of therapeutic facilities was started (Operta and Hyseni, 2013).

It is difficult to determine clearly why prehistoric and ancient people visited hot springs – whether they came there to cure their diseases or to perform some rituals. There is no archaeological evidence confirming beyond doubt therapeutic applications of thermal waters in prehistoric times. In Stufe di San Calogero in Sicily, vases dated to 3000 BC have been found in natural tunnels with sulfuric fumes. They were probably the remains of offerings left for gods thought to be responsible for earthquakes, gas exhalations and hot springs.

In the area of today's Italy, the usage of thermal waters for curing different ailments probably started in the Neolithic (or even earlier). An example of using hot waters for therapeutic purposes comes from San Calogero on the island of Lipari, north of Sicily. There are remains of a building erected by Mycenaean colonists during the Bronze Age. It was built of blocks enclosing a room filled with hot steam (a *sudatorium*). A stone-laid canal supplied water from the nearby thermal spring to a pool used for hot baths. From there, the water flowed through the main outlet to the next room (*tholos*) dated to 1430 BC. Another example could be the Phlegraean Fields not far from Naples. On Sardinia, the 'ill man's spring' and the 'pain spring' – sacred places with healing waters recommended for rheumatic diseases – were probably known in the 2nd century BC. In Santa Lucia di Bonorva, we can find a wide enclosure with numerous outflows of sparkling water. Ancient writers and chroniclers also mentioned places of cult near springs with hot acidulous waters. Wells near temples were best known. Pozzo della Panighina in Romagna, a well equipped with wooden pipes, is dated to the end of the Copper Age. It was used to extract medicinal saline. The dishes found nearby prove that it had already been used in the Bronze Age and it was a place of worship (Grifoni-Cremonesi, 1999).

From the early 12th century BC onwards, the inhabitants of today's Tuscany, the Etruscans, started to group together to form larger villages. Very soon, they achieved a high level of development in many areas (extraction of hydrothermal products, agriculture, trade, etc.). They used natural resources extensively and highly valued thermal waters as a medicinal product. These were the Etruscans who familiarized the Romans with the tradition of therapeutic and recreational bathing in thermal waters. Based on the Etruscan and Greek ideas and experience, the Romans organized baths with several rooms offering baths with different temperatures of water. A steam bath was the first, followed by hot water, warm water and room temperature water baths. At the end, there was a physiotherapy room. This system, devised by Caius Sergius Orata, was used for the following three to four centuries in baths using both natural thermal waters and heated water (Cataldi and Chiellini, 1999).

Balneotherapy became popular with the Romans between the late 3rd and early 2nd centuries BC, but it was only used in places with natural occurrences of thermal waters. In the latter part of the 2nd century BC, public thermal baths started to appear. After adopting the system of artificial heating from the Greeks, the practice of taking hot baths developed very fast to peak in the 3rd century AD. At that time, the particularly large and luxurious complexes of Trajan (80–110), Titus or Caracalla (217) baths were in use. The latter were still in operation in the 6th century AD.

*Thermae*, being chiefly recreational complexes, consisted of places for exercising, a library with a reading room, rooms for massage and beauty treatment, as well as rooms for recreation (ball games or entertainment). *Thermae* became a place of social, business, cultural and political meetings. An example resort using a system of baths was Baia, then the most important health resort, which reached its peak in the 1st century BC. *Thermae* were built near hot water springs so that full usage of natural heat and the curative properties of waters, salts and hydrothermal muds would be possible. In the 4th and 5th centuries, the interest in *thermae* declined all over Europe (Cataldi and Burgassi, 1999; Routh *et al.*, 1996).

In the following millennia, thermal baths either lost popularity or were reintroduced into everyday life to a varying degree. Only in late 16th-century Italy were works written recommending baths as a form of treatment. At the turn of the 16th century, numerous curative centers

were established. The already known resorts included Montecatini and Lucca in Italy, Varna in Bulgaria, Budapest and Hajdúszoboszló in Hungary, and Cieplice, Łądek and Iwonicz in Poland. In France, Vichy, Forges and Bourbon-Lucy were established. In England, alongside the restoration and extension of Bath, Epsom and Tunbridge were built. Other new European resorts created included Carlsbad, Ems and Marienbad in Germany, and Spa in Belgium (Czellec and Petrea, 2013; Kępińska and Łowczowska, 2002; Sokołowski *et al.*, 1999).

The first written records about springs in Łądek (Poland) come from the early 17th century. They refer to events from the first half of the 13th century. During the Mongol invasion in 1241, a house standing near the spring was reputedly destroyed. The spring was probably rebuilt and continued to be used, as 14th-century chronicles reported the existence of warm springs there. In the late 15th century, the first analyses of spring waters were performed. In 1577, the town authorities issued the first set of resort regulations, which was modified in 1601. In the late 16th century, the first medical text about the curative properties of local waters appeared. In the following years, new springs were discovered and bathing facilities were built soon afterwards. In 1765, King Frederick II of Prussia came for treatment here. About a dozen years later (in 1790), Łądek was visited by Johann Wolfgang Goethe. In the late 18th century (1797), a new set of regulations for resort facilities was issued. It also specified the scope of competence of the resort commission, already in operation by then. At the turn of the 18th century, Queen Louisa, the wife of King William III of Prussia, stayed in the resort. The King himself came for treatment in 1813.

At the same time, the resort was visited by Tsar Alexander I, Duke Radziwiłł and guests from England, who came to celebrate William III's birthday. In the following year (1814), a ban on mixed-sex baths was imposed. Alongside bathing in pools, baths, and "drop baths" (being poured over with water), drinking treatment and mud baths (since 1849) were practiced. For hygienic reasons, patients often took individual baths. New natural therapy centers, sanatoria, a walking hall, a thermal pool, and a mud treatment center were built (Brzeziński, 2000; Cieżkowski, 1998; Dębicki, 2000; Kincel, 1994).

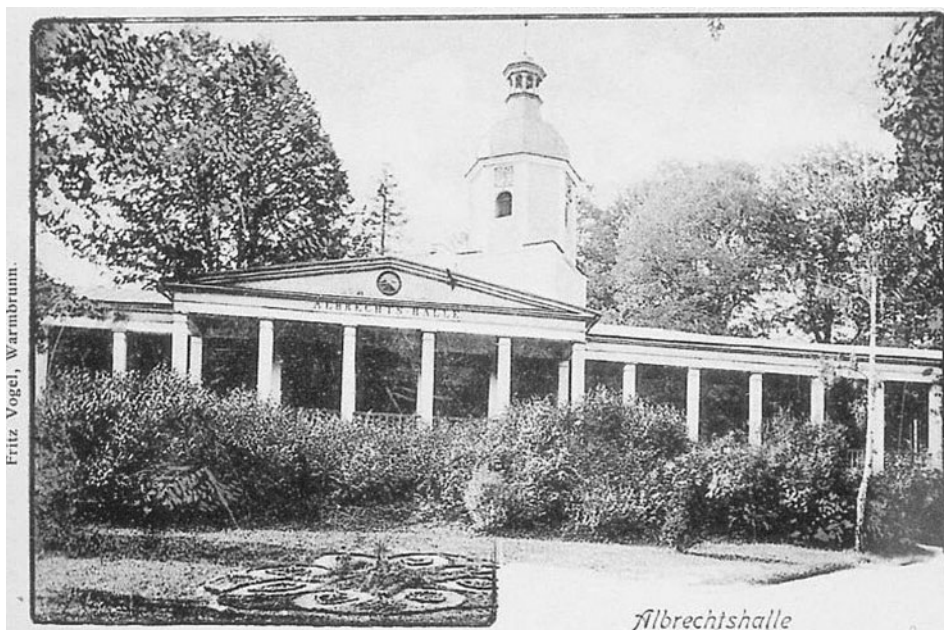


Figure 12.1. "Albrechtshalle" – The Walking Hall in Łądek, 1902 (Wziątek, 1999).



Figure 12.2. The interior of Natural Treatment Center “Wojciech” (photo: courtesy Z. Pilip).

The earliest written record about warm springs in Cieplice comes from the latter part of the 13th century. At that time, the monks who owned warm springs in Ciepłowodzie (the Polish name of the settlement used then) built a monastery and a hospital in this area. In the early 15th century, the main spring was surrounded with a wooden palisade and the others with stone. In 1537, the first spa house was built (so-called Long House) and in 1566, the first physician was employed. At that time, the village already had a German name, Bad Warmbrunn. In 1569, the first chemical analyses of local waters were conducted. At that time, there were two springs: Count's Spring (available to the public, including the poor) and Monastery Spring, where only the richest visitors received treatment. In the early 17th century (1607), a treatise on the curative properties of waters and their physical and chemical features appeared. Successive works presented the offered treatments as well as indications and contraindications to them. The illnesses cured in Cieplice at that time included scabies, diarrhea, gout and fever. In 1618, the first resort statute was issued. In 1627, the springs were surrounded by stone rotundas with cubicles. In 1689, a new spa house was built. At that time the resort was visited by many of the Polish nobility, including Queen Marysieńka Sobieska, Michał Radziwiłł and Crown Prince Jakub Sobieski. At the turn of the 18th century, thinker and political reformer Hugo Kołłątaj received treatment here. Likewise, Łądek, Cieplice was visited by Johann Wolfgang von Goethe (in 1790), King Frederick William III of Prussia with his consort (1800), US diplomat (later president) John Quincy Adams (also in 1800) and poet Józef Wybicki (in 1802).

The resort grew intensively in the latter half of the 19th century. A drinking hall and a bathhouse were built then and pools were laid with marble. Thermal and mud baths, massages, hydrotherapy, electrotherapy as well as nose and throat rinsing were perfected. Along with the development of the resort, demand for waters grew. This is why Nowe intake, the first borehole in Cieplice, was drilled in 1849–1853, followed by today's Antoni-Wacław intake in 1879. In 1882, work on the third borehole, now known as Marysieńka, was completed, and in 1924 new natural therapy facilities were opened (Ciężkowski, 1994).

Besides being used for treatments, spring water was bottled. In 1931, a modern spa house and new 'male' and 'female' pools were built, and after 1938 mud baths using modern equipment were organized (Jasiak, 2011; Kincel, 1994; Łaborewicz, 1994; Potocki, 1975a).

While the first historically confirmed information about Iwonicz goes back to 1427, the first record about the medicinal properties of its waters comes from the latter part of the 16th century. In 1578, the royal physician to King Stefan Batory of Poland, Wojciech Oczko, wrote about the village and its waters. Following advances in medicine and chemistry, scientific analyses of these waters were performed and successive dissertations were written. The waters were described by Braun and Conradi, the royal physicians to King Jan Kazimierz and Queen Marysieńka Sobieska (in the 17th century), respectively. As Conradi sent his findings to be assessed by French physicians, the waters of Iwonicz became known also outside Poland. Two mineral springs are known to have existed then: one of fresh and one of saline water. Bathing and drinking therapies were taken at that time. By one of the springs (nowadays known as Bełkotka), one could observe a



Figure 12.3. Bathing in pool in Cieplice in the early 17th century (photo: courtesy W. Ciężkowski).

specific phenomenon – the burning of gases released from water (now the water is known to contain large amounts of dissolved gas). The 18th century was a period of stagnation or even oblivion. Restoration came in the first half of the 19th century. Waters were analyzed again, and new treatment centers, bathhouses and a summerhouse over the existing springs were built. The buildings were modeled on fashionable Swiss resort architecture. In the 1860s, balsamic baths were introduced and mud baths were available after 1879. Visitors from Russia, Bohemia, Hungary and Austria came for treatment. By the outbreak of World War II, the resort had grown so much that the owners had to employ ten doctors to take care of patients (Kruczek and Weseli, 1987; Potocki, 1975b). In the early 1980s, one of the most advanced Polish natural therapy centers was opened. After World War II, the communist authorities nationalized Polish health resorts, which operated as state-owned enterprises till the end of 1998. In 1999, privatization of these enterprises started, which often had a positive influence on the development of treatment in these centers.

The development of science at the turn of the 18th century provided possibilities for detailed studies of waters. Thanks to this, the properties of waters were analyzed to improve their application for balneotherapy. In 1830 in Jeseník (then Gräfenberg), Vincenz Priessnitz opened a treatment center where he used cold baths, showers, wrapping in wet blankets and drinking therapy to cure chronic diseases (Kincel, 1994). Priessnitz and Sebastian Kneipp developed the principles of balneotherapy (medical application of thermal waters) and hydrotherapy (immersion of the body in thermal water for therapeutic purposes). They suggested using individual treatment series (warm, cold and herbal baths, mud wraps, massages and exercising) depending on the temperature and properties of water. In those times, resorts were used mainly by the upper classes. At the same time, the curative effects of those visits lost their importance. Going to resorts became more of a fashion and luxury than a need. In England, visiting health resorts was less popular. Balneotherapy was less organized there and resorts focused more on recreation than treatment (Czellec and Petrea, 2013). In Poland, thanks to the efforts of J. Dietl, a Balneological Commission was founded by the Cracovian Scientific Society in 1857, and in 1905, the Polish Balneological Society was established (Kochański and Kochański, 2000).

In south-western Germany lies one of the oldest and the most prestigious health resorts in this country, Baden-Baden. Thermal springs were known here as early as the Roman times (Roman soldiers were cured here). The city underwent the fastest development at the time of the Empire.





Figure 12.4. “Trinkhalle” – open colonnade in Baden-Baden (photo: courtesy EHTTA, 2015).

In the 2nd century, imposing buildings and thermal baths were constructed, attracting people from all over the empire. Even Emperor Caracalla received treatment in the local *thermae*. After the fall of the Roman Empire, bathing treatment was resumed in the 15th century. In 1473, Emperor Frederick III came to take baths in Baden-Baden. In the early 16th century, a bathing fee was introduced. In 1601, peloid bath treatment was launched and in the 19th century, steam baths (in 1819 and in 1846–1848), as well as a thermal water drinking hall (in 1824) were built. In 1804, Queen Louise of Prussia tried to improve her health in the resort and Otto von Bismarck stayed here briefly in 1858. Other famous guests included F. Dostoyevsky, J. Brahms, V. Hugo, R. Wagner, F. Nietzsche, and Queen Victoria of England. To enhance spring discharge and keep a higher temperature of waters, systems of tunnels supplying water from the springs straight to the resort facilities were built in 1868–1871 and 1894–1897. In 1845–1970, Baden-Baden was the most prominent European resort. To satisfy the growing demand for water in the 20th century, research was launched and wells were drilled (Sanner, 2000; Wohnlich, 2001).

Although the baths in Spa (a town in southern Belgium, not far from Liège and the German border) have been using artificially heated waters for many years now, the place itself is worth mentioning due to the popularity of the word “spa”, which is in common use nowadays. As early as the 14th century, a spring with medicinal properties was known in the area of today’s Spa. Once it was visited by a smelter worker hoping to find relief from his rheumatic pains. When his condition improved, he built some facilities near the spring, which later developed into a popular and beautiful health resort known as Espa, meaning ‘a spring’ or ‘a fountain’ in the Old Walloon language. In time, the place became so popular that the name Spa (slightly altered in English) started to be used to denote all places of this kind. Near Spa, there are about 300 springs, whose waters are heated to a temperature of 30–34°C before being used for treatment (Lund, 2000b).

In France, in Aix-Les-Bains on Lake Bourget, ancient Celts discovered medicinal thermal springs, whose waters were later used for bathing by the Romans. At the time of the Roman Empire, the place was known as Aquae Grantianae. The bathing traditions continued for the next

few centuries. In the 17th century, a treatise on therapeutic baths in Aix-en-Savoie was published. In the same century, the new baths called Établissement Royal des Bains were built, enlarged in the following century with more pools, steam baths and massage showers. The French national health care system reimbursed treatments offered in this health resort (Lund, 2000a).

One of the hottest European springs, Chaudes-Aigues (82°C) flows out in the Central French massif. In the seepage area, around 30 springs flow out, the main one being Le Par. The first written records about this spring go back to the 14th century. The water was used for heating houses. In time, a resort developed, attracting visitors from faraway countries. Other known resorts were Vichy, La Bourboule, and Forges, as well as Chaudes-Aigues, where lepers and paralytics were treated. In the 16th century, there was probably an open-air pool at Chaudes-Aigues. Certainly, baths were taken in small pools inside the spa buildings. Between the 18th and the 19th centuries, the resort declined. Revitalization started in the early 20th century, when new hydropathic and therapeutic clinics were opened. In the 1970s, a well to extract thermal waters was drilled, and the resort regained popularity in Europe. In 1993, the Museum of Geothermal Energy and Hydrotherapy was opened in Chaudes-Aigues (Gibert and Jaudin, 1999).

Bath is one of the oldest European health resorts. The town is located in England, south-east of Bristol. The first traces of settlement in this area of England go back to 8000 BC. The local Celts probably bathed in springs, which has been proved by coins tossed into the water as gifts for the goddess Sulis, which have been found in the royal baths during archaeological excavations. At the time of the Roman Empire, from 43 AD onwards, the Romans developed Bath into a luxury relaxation and leisure center with thermal water reservoirs and a temple of Minerva. With the fall of the empire, Bath, like many similar centers in the Mediterranean Basin, started to fall into ruins. Records of the 11th century mention the construction of royal baths over the spring. The 12th-century rediscovery of the spring is attributed to the legendary King Bladud, who allegedly cured himself of leprosy in spring waters and later built large baths around the spring to enable everyone to use the waters as he had. In the 12th century, people came to Bath to seek treatment and in the 16th century, King's, Hot and Cross Baths were known. The resort started to develop again. In time, the Queen's Baths and the Royal Mineral Water Hospital were built, and the old baths were rebuilt. In the 19th century, private baths started to appear and in the early 20th century water bottling was started (White, 2000).

It is difficult to assign when people started to make use of hot springs in Iceland. The Icelandic sagas (written in 12th–13th century AD) made frequent references to bathing in hot springs and before that not much recorded information is available.

The first settlers in Iceland were the Vikings, who appeared on the island in the 9th century BC. They were followed by the Irish and Norwegians, who established their dwellings close to thermal springs and hot vapor exhalations. Since the beginning of their settlement, they probably used thermal waters for cooking, washing clothes and hygienic baths.

During archaeological excavations in Reykholt in the western part of the island, a circular pool measuring about 4 m in diameter and 0.9 m in depth was discovered. It had been made of stone blocks closely fitting to each other, likewise its floor and the inner bench (with about 30 seats). The pool had been filled with hot water supplied from Skrifla spring (about 120 m away) through an underground stone canal (a ditch laid with stone slabs). Excavations proved the existence of three canals, two of which had probably been used to supply bathing water to Snorralang. The third one had supplied water from wetlands to The Homestead (Fridleifsson, 1999). The island has a long history of health resort treatment. In 1937, the Icelandic Society for Natural Methods Treatment was established. In Hveragerði, east of Reykjavik, a treatment complex offering treatments based on local thermal waters and vapors was built (Kępińska and Łowczowska, 2002).

In individual regions people used thermal springs in different ways and for various purposes depending on their needs and opportunities. Not all of these localities have reliable records of water use. Hot springs have been used for their therapeutic benefits in treating many diseases. Thus, many of these have not lost their reputation and are still in operation. As a result, new sources of thermal healing water have been recognized and new facilities in the vicinity of antique ruins have been erected.

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## CHAPTER 13

### Balneological use of geothermal springs in selected regions of the world

Barbara Kielczawa

#### 13.1 INTRODUCTION

Water has always symbolized the source of life and longevity as well as physical and emotional strength. The occurrence of natural thermal springs, alongside other manifestations of geothermal energy, has been regarded as supernatural and treated as gods' gifts. They aroused admiration and respect. However, it did not stop people from using such waters when there was an easy access to springs. Among ancient civilizations, using hot springs is attributed to the Hittites, Cretans, Minoans, Japanese, Chinese and Mesoamericans. They knew how to protect such waters from contamination and stored them in nephrite (the Chinese) or obsidian (the Aztecs) containers to keep them fresh. Often, divine healing powers made thermal springs famous and events related to healings were described in sagas or legends. For centuries, people have traveled to springs to remove, or at least alleviate the symptoms of their diseases. With this aim, they set off on long journeys, often taking a lot of time.

Advances in medicine and pharmacy brought about a serious crisis for spa treatment in the latter part of the 20th century. Fast-acting pharmaceuticals and modern therapies replaced balneological treatment, which usually took more time to bring effect. Nowadays, however, one can observe a renewed interest in spa treatment, likewise in herbalism and other natural remedies and treatments, not causing (when applied properly) side effects (Brzeziński, 2000).

The 21st century has brought a new approach to "traveling for health" and to treatment itself. Economic development and the related rise in the standard of living have changed people's attitude to their appearance, fitness and state of mind. Nowadays, classic health resorts using balneological therapy have to satisfy the expectations of more and more demanding customers. It should be noted here that the term health resort is classically used for places where medical mineral water, medical peloides and natural gases are used for bathing, drinking, inhalations, water jets, jacuzzis, body masks, and so on. Balneotherapy, hydrotherapy and climatotherapy are main (and basic) elements of healing in these resorts (Gutenbrunner *et al.*, 2010). More and more often, people expect to recover physically and mentally as quickly as possible. Moreover, it often happens that they visit health resorts preventively, without a need to use thermal waters as a remedy. Therefore, health resorts cannot limit themselves to serving the patients only. In compliance with a global trend focusing on "healthy lifestyle", it is becoming essential to be able to combine the curative function with relaxation and general regeneration and, consequently, with tourism. Introducing modern balneological methods, alternative medicine and treatments aimed at maintaining physical fitness, good state of mind and appearance, combined with active tourism, changes the notion of health resort therapy to health resort tourism. Therefore, many historic resorts have been forced to supplement balneological treatments with massages, relaxation, slimming, rejuvenating and cleansing treatments, aromatherapy, relaxation techniques, yoga, special nutrition, health-promoting education, psychotherapy, and so on (Agishi, 2001). These treatments, as well as sports, are offered in health resort medicine (Gutenbrunner *et al.*, 2010).

More and more often, younger and younger social groups undertake preventive healthcare activities and try to keep fit by exercising, joining fitness clubs or visiting wellness centers or spas. At this point, one must realize the differences between the above terms.

In its general meaning, the term wellness includes domains such as physical, spiritual and mental health, social harmony, emotional well-being and intellectual development. Wellness addresses human health and assumes that each person will actively participate in protecting their health and in preventing diseases. The concept of health and wellness are increasingly being used interchangeably, but it should be emphasized that wellness is more preventive than curative. Depending on motivation and interests, people will select the form of wellness they require (Smith and Puczkó, 2009, 2014).

Erfurt-Cooper and Cooper (2009) define about 50 kinds of spas and spa centers, which include, for example:

- health spas – all-inclusive centers or hotels offering health-improvement programs or spa treatments. They focus entirely on fitness, but also include health-promoting elements, wellness and recreation. These could also be medical spas,
- health resorts, which combine medical and health care with the best rejuvenating treatments. Some health resorts pay particular attention to healing the body while providing calm and keeping stress away.

They separately define hot spring spas as being known for their curative properties and therapeutic benefits, and thermal spas, where warm and hot springs are used in therapeutic treatments (thermalism), including balneological treatments and baths.

The authors emphasize that many of their definitions overlap, are interrelated or similar, as despite the common origin, they are used in different parts of the world, with different religions or cultures.

The International Spa Association (ISPA) defines both medical spas and mineral spring spas. In the former, a licensed medical doctor provides professional medical and wellness care. In the latter, natural minerals, thermal water or seawater are used in hydrotherapy treatments (EUROSPA, 2016).

The therapeutic value of thermal waters is determined by their temperature, variety of dissolved ions, gases and trace elements. In many countries, there are specific regulations and law rules used for the classification of groundwaters. Water can be used for medicinal purposes if it is naturally cold or hot and if it contains a minimum number of at least one of the components (Altman, 2000; Gutenbrunner and Hildebrandt, 1998). In Japan (Altman, 2000), Poland (PGG, 2016), Germany, Iceland (Kristmannsdóttir and Björnsson, 2003), Italy (Andreassi and Flori, 1996) and Spain (Ledo, 1996) waters are classified by chemical character, temperature and balneological properties. In Poland if groundwater is not contaminated but with natural variations in physical and chemical parameters, contains at least one specific component (pharmaco-dynamic factors), and/or has a temperature above 20°C, it is then considered as therapeutic water (PGG, 2016). Moreover, whole mineral water (mineralization more than 1 g L<sup>-1</sup>) can be medicinal water, regardless of whether it contains specific components (Table 13.1).

It should be noted that a specialist in balneology and balneotherapy discusses such a classification (Gutenbrunner *et al.*, 2010; Varga, 2010, 2011). Particular spa water used for therapy and/or prevention can contain a wide range of organic, colloidal and suspended components which are ignored in water analyses. These ingredients can have a primary role in healing or toxicity. As a consequence, the classification of medicinal waters should be determined with many more parameters, for example, microbiological, toxicological, hydrobiological (Varga, 2010, 2011).

In balneotherapy one of the major therapeutic factors is the temperature of water. Based on temperature, balneologists classify therapeutic waters as: cold (<20°C), hypothermal (20–30°C), thermal (30–40°C) and hyperthermal (>40°C). Balneotherapy as a part of balneological treatment is defined as bathing in thermal and mineral waters (Matz *et al.*, 2003). In many countries, this

Table 13.1. Example of balneological classification of waters in Poland (PGG, 2016).

Total dissolved solids (TDS)	Temperature [°C]	Pharmaco-dynamic factors – specific components	Chemical type of water
$\geq 1 \text{ g L}^{-1}$ – mineral	$>20$ – thermal water	2 mg F 1 mg I	Fluoride Iodated
$< 1 \text{ g L}^{-1}$ – slightly mineralized	$<20$ – cold water	1 mg S(II) 70 mg $\text{H}_2\text{SiO}_3$ 10 mg Fe(II) 74 Bq 250 mg free $\text{CO}_2$ 100 mg free $\text{CO}_2$	Sulfuric Silica Ironic Radon or radioactive Carbonate $\text{CO}_2$ -rich, carbonized

term is used as an equivalent to balneology (Gutenbrunner *et al.*, 2010). This form of treatment is indicated not only for chronic diseases. It is suitable to prevent health problems (life habit-related ailments) that cannot be cured pharmacologically (Agishi, 2001). Bathing in thermal waters causes an increase of blood circulation, cell oxygenation and body metabolism (stimulating intestinal tract, liver and digestion). It improves the function of the endocrine glands and nervous system. It stimulates the immune system, physical and mental relaxation, and production of endorphins (Altman, 2000).

The main indications for balneotherapy are chronic ailments (e.g. skin diseases, diabetes, obesity, peripheral circulatory and respiratory disorders, gynecological diseases, rheumatism, arthritis, trauma), rehabilitation (e.g. spinal paralysis, chronic rheumatic ailments, after-knee surgery) and prevention (building up physical strength) (Agishi, 2001; Gutenbrunner and Hildebrandt, 1998). Gutenbrunner (2014) emphasizes the differences between balneotherapy and rehabilitation and their overlaps.

Beneficial effects of balneotherapy for indications given above can be found e.g. in Agishi (2001), Bojadgieva *et al.* (2005), Gutenbrunner and Hildebrandt (1998), Nasermoaddeli and Kagamimori (2005) and Matz *et al.* (2003) for dermatology.

Many natural thermo-mineral waters are not characterized by strong concentrations of ionic components. For this reason, they are classified as lightly mineralized or oligomineral waters. However, they are valuable for their sedative (helps to reduce stress) and thermal (increases body temperature) properties. These waters relieve joint and muscle pains and bring relief in rheumatoid and musculoskeletal ailments (Altman, 2000).

Waters contain the combination of main cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ), anions ( $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ) and specific compounds (which can determine the medicinal value of water) in varying amounts. These dissolved components bring out varied therapeutic benefits of thermal bathing. Table 13.2 presents the recommendations for the treatment of different diseases depending on the type of thermal water (bicarbonate, chloride-sulfate).

Hot and mineral springs used for health range from primitive natural springs, through developed facilities to commercialized centers. In many countries, it depends on tradition of hot spring use, culture, religion, economic conditions and political situation.

A traditional use of thermal springs is bathing. Using different kinds of peloids matured with natural hot water can produce a natural product – biofango/fango. It is used, for example, in Italy, Germany, Spain and Japan for mud therapy (Gutenbrunner and Hildebrandt, 1998; Rossi *et al.*, 2014a, 2014b; Sugimori and Owada, 2014; Vela *et al.*, 2012). Sugimori and Owada (2014) defined it as the best method in body treatment (for keeping thermal effects on body and blood pressure). It is also a good remedy for knee osteoarthritis (Giannitti *et al.*, 2012; Vela *et al.*, 2012) and musculoskeletal system changes (Armijo *et al.*, 2012).



Table 13.2. Therapeutic effects and recommendations for thermal treatment depending on the type of water (based on Altman, 2000).

Main type of thermal water	Recommendations and therapeutic benefits
Bicarbonate water	<ul style="list-style-type: none"> <li>– Especially in cardiovascular diseases, nervous exhaustion, autonomic nervous system imbalance, severe heart and circulatory illnesses, gout, hepatic insufficiency;</li> <li>– Opens the peripheral blood vessels, improving circulation</li> </ul>
Sulfate and sulfur water	Chronic skin diseases, metabolic poisoning, gynecological disorders, rheumatism, liver and gastrointestinal complaints, osteoporosis, nervous system disorders
Chloride water (brine)	Arthritis, rheumatism, nervous system diseases (central and peripheral), orthopedic, postoperative dysfunctions, gynecological and skin diseases, joint disorders, asthma and respiratory problems

### 13.2 AFRICA

In Africa, there are many areas with thermal waters, used by indigenous tribes wherever they can be accessed. In northern Africa, thermal springs are found in Morocco, Egypt and Tunisia. However, well-developed thermal spa tourism exists only in the last of the mentioned countries. About 80 thermal springs and boreholes are known there and they have probably been used for balneological purposes by local communities for centuries. Hot and mineral water occurrence in Tunisia, referred to as *Hammam* (*hammi* meaning hot in Arabic), is observed in northwest and southern parts of this country, in the Gabes and Tozeur regions. The most famous are Djebel Oust, Korbous, Djerba and Hammam Bourguiba spas. Such thermal sites/areas are exploited both for therapeutic treatments and relaxation in its broad sense (Ben Mohamed, 2010, 2015; Boekstein, 2012; Erfurt-Cooper and Cooper, 2009). Springs at Korbous flow directly into the sea and the temperature of water ranges from 40 to 60°C. The amount of total dissolved solids (TDS) is about 12.4 g L<sup>-1</sup> with a predominance of sodium chloride and sulfuric acid (Khemiri *et al.*, 2010).

Some travel blogs and tourist guides provide information about Korbous, a small resort, known for a hot sulfurous spring, which is said to cure, for example, skin diseases (Kolumber, 2016).

In the countries of Sub-Saharan Africa, local people used to know many thermal springs, which they visited for curative purposes. However, written records about hot springs are very scarce there. The countries most abundant in thermal waters lie along the Great Rift Valley and they include Ethiopia, Kenya, Tanzania and Cameroon. However, there are very few well-developed thermal health resorts there.

Southern Africa is known for 87 thermal springs, 11 of which are found in the Western Cape Province. They form the basis for nine thermal resorts, four of which are private investments. Currently, none of them provides typical medical treatments. The majority of thermal springs used to be exploited for medicinal purposes, both by indigenous tribes and later by European settlers. The best and the longest known is Caledon Spring, whose water is very effective in treating skin diseases and arthritis. In 1902, the Caledon Baths and Sanatorium were founded near this spring. The range of provided treatments was very wide for those times and it included massages, hydrotherapeutic, diathermy or ionization treatments, carbonic acid Nauheim baths, water massages/showers and Plombières treatments. Unfortunately, the whole resort was destroyed in 1946 and only one pool, Victorian Spa Bath, remains in operation nowadays.

The hottest waters of southern Africa were found to be that at Siloam in the Limpopo Province (71°C) followed by Brandvlei springs (64°C), not far from Rawsonville. Brandvlei is privately owned (Boekstein, 2012). Other known thermal water resorts in the Western Cape are Montagu, Warmwaterberg, Worcester (Goudini Spa) (Tshibalo *et al.*, 2015).

Table 13.3. Physicochemical characteristics of thermal springs in Africa (concentrations in mg L<sup>-1</sup> unless otherwise specified).

Location and/or hot spring	Na	K	Ca	Mg	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	TDS	Temp. [°C]
North Limpopo <sup>1,4</sup>									
Mphephu	44.4	1.1	13.7	11.3	39.4	9.3	151.3	199.4	43
Sagole	65.2	1.1	1.3	0.1	47.9	18.2	102.5	203.8	45
Tshipise	156.3	4.3	5.6	0.2	169	53.2	126.9	460.6	58
Die Eiland	621.9	21.8	53.6	9.4	982.6	143.6	149.5	1937	42
Evangelina	360.9	6.2	79.4	27.6	535.2	226.0	244.0	1385	29–45
Minwamadi	10.6	1.0	9.36	13.3	19.5	3.0	80.52	104.7	31.6
Môreson	99.2	3.2	4.8	0.3	117.3	48.2	54.9	340.6	43
Siloam	66.2	2.8	1.4	1.3	44.4	10.7	107.4	197.3	67.5
South Limpopo <sup>2,4</sup>									
Warmbad (Bela Bela)	132.5	2.9	13	1.8	85.2	12.1	102	340	52
Loubad	7.9	2.9	30.9	6.4	2.2	2.2	161.7	134.2	30
Vischgat	56	6.1	36.1	3.3	31.7	92.8	140.3	303	40
Libertas	22	3.6	23	3.5	7.2	5.9	134.3	138	52
Die Oog	34.2	3.6	24.8	3.1	28.3	13	125.1	175.5	40
Rhemardo	32.7	3.6	25.6	3.3	28.6	13.7	134.2	180	44
Western Cape <sup>3,4</sup>									
Brandvlei	9	2.3	2.4	2.6	14.5	1.6	0.0	47	57–64
Caledon	22.9	5.6	7.5	3	33.5	4.5	49	115	49–53

<sup>1</sup>Tekere *et al.* (2012), Olivier *et al.* (2011); <sup>2</sup>Olivier *et al.* (2008); <sup>3</sup>Boekstein (2012); <sup>4</sup>Durowoju *et al.* (2015).

Generally, the Western Cape springs have been recognized to be particularly effective in healing wounds and curing skin diseases, chronic arthritis, hepatitis and indigestion. The largest, best known and only resorts with well-developed therapeutic and wellness infrastructure are Warmbaths in Limpopo and Badplaas in Mpumalanga. Both springs have been known to local people for a long time. The former is also known as Bela (meaning ‘water that boils’). The other one used to be called *Emanzana* by the Swazi population, translated as “the place where water heals”. Currently, besides the prevailing wellness and relaxation treatments, both resorts offer treatments curing rheumatic diseases including arthritis, for example, ‘rheumatic’ baths, mineral baths, wraps and inhalation (Boekstein, 2012, 2014b; Erfurt-Cooper and Cooper, 2009). In the Limpopo Province, there are more thermal springs and thermal resorts than in any other province in South Africa (Olivier *et al.*, 2008). Located there are 24 (of the 83) thermal springs and boreholes. They occur mainly in the Waterberg (S Limpopo) and Soutpansberg (N Limpopo) regions. According to Olivier and Jonker (2013), only the Western Cape thermal springs and Loubad are fit for swimming and bathing. Generally, the waters are not fit for consumption and the use for recreational purposes should be monitored (Olivier *et al.*, 2011). Chemical compositions of selected springs are given in Table 13.3.

In central Namibia, there are two resorts where one can find relief from rheumatic pains, Gross Barmen Hot Springs Resort and Reho Spa. In the Fish River Canyon in the southern part of this country lies the resort Ai-Ais (66.5°C), known for outflows of warm sulfurous waters (Christelis and Struckmeier, 2011; Erfurt-Cooper and Cooper, 2009).

Details regarding the South African thermal springs resorts, chemical composition of waters and their utilization can be obtained from Olivier and Jonker (2013).

### 13.3 THE AMERICAS

The United States of America has a large number of known thermal springs. According to data from 1886, there were 8843 known springs, about 640 of which were used in spas (Stearns *et al.*, 1937). However, lack of governmental support and a decline in the interest in balneological treatment caused the demise of many of them. According to Erfurt-Cooper and Cooper (2009), 1702 thermal springs were known in the 23 states of the USA in the late 20th century, and 1661 were officially described by the US Geological Survey (USGS) in 2007. Modern US health resorts and spas are not directly dependent on the presence of natural thermal waters in their area. If such waters flow out in the resort, they are treated as an attraction or a bonus and the customers can decide if they want to use natural or artificially heated and mineralized waters. The emphasis placed on relaxation and fitness has resulted in the fact that medicinal properties of waters, and consequently the possibility of improving one's health, are neglected. Hot springs are broadly described in currently published guidebooks to particular areas of spring occurrence or national parks. The following paragraphs give some examples of thermal centers and spas in selected countries in the Americas.

In Hot Springs National Park in Arkansas, there are 47 thermal springs (61°C). The curative and relaxing properties of these waters have been known and appreciated for many years (Lund, 2006). It is the only national park whose sole purpose is to protect springs whose water is intended for medicinal and day-spa usage (Lund, 2005). Currently, only two springs are available to the public, and despite a drop in the general interest, visitors can still take a bath in one of the pools or bathtubs, have a shower, use a jacuzzi or a sauna and take hot or cold wraps and massages (Lund, 2000a). Waters are used for curing rheumatism and skin diseases, and for rehabilitation treatments (Benedetto and Millikan, 1996; Josayma, 2014).

Warm Springs is an area of thermal spring occurrence in Georgia. The best known of its health resorts is Meriwether Inn, where polio patients were treated from 1920–1960. After the invention of the polio vaccine, the interest in balneological treatment dropped, but disabled people can still use a wide range of rehabilitation treatments (Lund, 2000a).

At the estuary of the Wind River Canyon in Wyoming, about 150 km south of Yellowstone National Park, there are a few geothermal springs known as Thermopolis. At least eight of these springs form impressive travertine terraces along the river. The springs are known worldwide for their big discharge (especially the Big Horn Spring) and the outflow temperature of 22–57°C. The springs, formerly used by the Shoshone and the Arapaho Indians, are now protected in Hot Springs State Park. In the area of the park, one can visit the Fountain of Youth spa (using waters from Sacajawea Well), the State Bathhouse and the Gottsche Rehabilitation Center specializing in curing strokes, spinal cord injuries, bedsores, arthritis and rheumatism.

In northern California, we can find an area with the occurrence of thermal springs, fumaroles and hot muds. For centuries, American Indians used to go there to heal their wounds and relieve pains. In the mid-19th century, the resort Calistoga was founded and the next 30 bathing centers followed in time. Nowadays, only four of them are operating, curing pains and arthritis. All of them have shallow intakes of thermal waters (77–93°C), which supply the nearby pools (the water for pools is cooled to the temperature of 27–40°C). Some spas also offer mud baths with an admixture of volcanic ashes and peat moss (Josayma, 2014; Lund, 1996, 2000a, 2005).

In the Warm Springs Valley in Virginia, there are three known springs: the Hot Spring, the Warm Spring and the Healing Spring, referred to collectively as Virginia Hot Springs. Near the Hot Spring, the large, now historical resort Homestead developed, using thermal waters (39–41°C) from several smaller springs. A few kilometers to the northwest lies the Warm Spring (36°C) with two separate pools: one for men (the oldest spa in North America) and one for women. The Healing Springs (30°C) flow out eight kilometers southwest of Hot Springs. Currently, the resort provides

Table 13.4. Composition of thermal waters from several locations in US (concentrations in mg L<sup>-1</sup>).

Location and/or hot spring	Na	K	Ca	Mg	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	TDS
Arkansas/ Hot Springs <sup>1</sup>	4.0	1.5	45.0	4.8	1.8	8.0	165.0	
Wyoming/ Thermopolis <sup>2</sup>	4.0	1.5	38–48	4.2–5	1.9	6.8–8.6	144–200	174–194
	326.2	89.6	624.0	121.6	217.6			2400
California/ Calistoga <sup>3</sup>	150–270	10–11	9.3–18		180–190	2.9–12	110–150	540–580
New York/ Saratoga Springs <sup>4</sup>	10–4530	27–390	450–950	4–430	22–74700	0.1–12		
Virginia/ Hot Spring <sup>5</sup>	7	13	132	40	2.6	130	454	
New Mexico/ Ojo Caliente <sup>6</sup>	110–1000	6–36	7.3–152	2.9–60	108–270 100–155	66.5–286	609–2220	1400–3724

<sup>1</sup>Lund (2000a, 2005), Bell and Hays (2007); <sup>2</sup>Lund (2000a); <sup>3</sup>Poux *et al.* (2012); <sup>4</sup>Kitto *et al.* (2005); <sup>5</sup>White (2010); <sup>6</sup>Vuataz *et al.* (1983), Witcher (2002), Sophy and Kelley (2014).

Table 13.5. Main ion content of thermal waters of Alaska (concentrations in mg L<sup>-1</sup>).

Location and/or hot spring	Na	K	Ca	Mg	Cl	SO <sub>4</sub>	HCO <sub>3</sub>
Chena					29	110	115
Elim/Kwiniuk	500	9	130	0.1	912		10
Elim/Clear Creek	53.1	1.4	2.2	<1	4.3	25.9	28.5
Elim/Molly's Hot Spring	120	1.9	4.7	0	130	50	29

Source: Holdmann (2015), Lund (2006).

a wide range of hydrotherapeutic treatments (baths, saunas, and mineral baths), aromatherapy, massages and fitness centers (Benedetto and Millikan, 1996; Lund, 1996). Chemical analyses show the main constituents of selected thermal springs in the US (Table 13.4).

In Faywood in New Mexico, there is a commercial thermal health resort offering a wide variety of treatments. The first thermal spa in this area was Ojo Caliente, which is regarded as the oldest healing center in America (Erfurt-Cooper and Cooper, 2009). The thermal water (26.7–42.8°C) is used to cure arthritis, digestive and skin problems (OJO, 2016).

In Alaska, a thermal spring was discovered in 1905 and the complex of Chena Hot Springs Resort was built there after 1911. Nowadays, it uses waters from 20 boreholes. They are similar to the well-known springs in Karlovy Vary (German Carlsbad) in the Czech Republic. The resort uses waters for many purposes in indoor and outdoor pools, jacuzzis and a health spa (Lund, 2006). The partial analyses of selected springs in Alaska are given in Table 13.5.

Argentina has geothermal resources located in various parts of the country, which facilitates their many-sided usage. Low-temperature resources are the most widely used in all possible variants of balneology. The possibilities of using thermal waters for curing different ailments have been known in this area for centuries, but it was not until the 1920s and 1930s that research focusing on medical and therapeutic issues and comparing local waters to European waters was conducted. The native inhabitants of these areas had been perfectly familiar with places of thermal water occurrence like Rosario de la Frontera, Puente del Inca or Cacheuta (in Mendoza province) and they had used them until organized European-style and European-standard thermal centers started to appear in the late 19th century. The first medical thermal resort in Argentina (and in South America), was Rosario de la Frontera in Salta Province. In the 1930s, the interest in

Table 13.6. The approximate types of several thermal springs in Chile.

Location	Hydrochemical type of thermal water
Mamiña Hot Springs	SO <sub>4</sub> -Cl-Na
Puritama Hot Springs	SO <sub>4</sub>
Thermas del Flaco	Cl-SO <sub>4</sub> -Na-Ca
Thermas de Colina	Cl-SO <sub>4</sub> -Na-Ca
Panimávida	SO <sub>4</sub> -Ca
Del Huife Hot Springs	SO <sub>4</sub> -Cl-Ca
Aguas Calientes Hot Springs	Cl-Na
Termas de Chillán	SO <sub>4</sub> -Mg-K

Source: compiled on base GoChile (2014) (Disclaimer: the author cannot guarantee the accuracy of this data).

using spa facilities fluctuated, depending on social and economic factors. At the turn of the 20th century, actions to extend the thermal centers offering traditional treatments (balneological or rehabilitation) and more specific services (aesthetic and appearance-improving) were taken (Boekstein, 2014a; Miranda, 2005).

Owing to its location on the Pacific Ring of Fire, Chile has a lot of places with manifestations of geothermal energy such as geysers, hot fumes and over 270 thermal springs, not all of which have been well explored yet. Generally, three regions of thermal water occurrence have been distinguished there: Altiplano (northern, from San Pedro de Atacama to Putre), Falla de Pucuro and Falla de Liquiñe-Ofqui (southern Chile, between Llaima and Hudson).

The northern area contains 20% of thermal water occurrences with high temperatures (up to 90°C). The most popular and particularly valued for their medicinal properties are the waters in Mamiña (in de Tarapacá region). Other known complexes in this part of Chile are Puritama Baths (in de Antofagasta region), Termas de Socos (in de Coquimbo region) and Termas de Juncalito (in de Atacama region).

The second of the mentioned areas has 35 springs with several older spa centers like Jahuel Thermal Springs (north of Santiago), where Charles Darwin stayed in 1834, Termas del Corazon (in de Valparaíso region), Baños Morales and Termas de Colina (in Metropolitana region). More to the south, in de O'Higgins region, there are Termas del Flaco and the traditional thermal center Cauquenes operating since the 19th century. Equally famous resorts are Quinamávida and Panimávida (in del Maule region). Based on the concentrations of major ions, in Table 13.6 the approximate types of listed springs are given.

The southern area has 70 thermal water occurrences (20–80°C). The development of spring facilities in this area is very uneven, ranging from simple wells to luxurious baths in high-standard hotels. The best known centers are Termas de Chillán in del BíoBío region, Termas del Huife, Menetué, and San Luis and Palguin springs in de la Araucanía region. In de Los Lagos region, there is Puyehue (known for its mud baths) and Coñaripe, Liquiñe, Aguas Calientes, and El Amarillo springs.

The medicinal properties of these waters are useful for curing skin diseases (acne, psoriasis), stomach and liver disorders, rheumatic diseases, arthritis, sinusitis, muscle pains, neuralgia, disorders of the nervous system and respiratory diseases. Thermal waters are used in baths, combined with volcanic muds, and in steam baths for dermatological treatments (GoChile, 2014).

### 13.4 ASIA AND MIDDLE EAST

Many Asian countries use their thermal and mineral springs in a variety of ways. However, not all the regions with such waters have centers offering thermal therapeutic treatments. The vast



Figure 13.1. Beppu steam vents (photo: courtesy B. Kępińska, 2000).

majority of springs are used by local people or have developed into tourist attractions (Erfurt-Cooper and Cooper, 2009).

In Japan, hot springs have been used for centuries and bathing culture is associated with specific traditions. Family relaxation baths, taken together with friends and neighbors, have not changed to date. The country has more than 27,000 thermal springs, over 3000 thermal health resorts and about 6400 public bathhouses (Boekstein, 2014a). Hot springs facilities typically lack qualified medical staff and health insurance in Japan does not cover balneotherapy, so hot springs are sporadically visited for medical treatment (Hayasaka *et al.*, 2014).

Dōgo Spring is one of the oldest and most popular thermal springs in Japan. Flowing out in Ehime Prefecture, it used to be the place where imperial families took therapeutic baths. Similarly, Arima Spring (on Honshu island) was visited by emperors and their families.

Using natural thermal waters is recommended for maintaining or regaining health and well-being in Japan. The popularity of baths and balneotherapeutic treatments has contributed to the considerable development of Beppu, a resort lying in Oita Prefecture, on the east coast of Kyushu island. Over 2600 natural hot springs flow out in the city and its surroundings and the volume of the discharged water places Beppu right behind Yellowstone National Park in the USA. Takegawara *onsen*, traditional Japanese hot baths (with temperatures of 41–48°C), offer regular *onsen* baths and sand baths. Diluting or cooling natural hot waters is essential, since their temperatures are between 50 and 100°C. Away from the city center, hidden on the forested hills on which Beppu is located, there are Hebinyu *onsen*. They are totally natural, not commercialized,

Table 13.7. Chemical composition of geothermal springs from several locations in Asia (concentrations in mg L<sup>-1</sup>).

Prefecture and/or hot spring	Na	K	Ca	Mg	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	TDS
Japan (source: Homma and Tsukahara, 2008; Taguchi <i>et al.</i> , 1996; Yoshiike, 2003)								
Nagano (Northwestern)	1–3704	1.5–190	1.2–166	0–405	0.9–5450	0–589	0–3880	200–15000
Beppu	26.8–882	5–103	20.4–57	1–33.2	3–1104	45–1649	49–188	
Tamagawa Spa	56	41	148	44	2800	930		
Korea (source: Hann, 1996; Matz <i>et al.</i> , 2003)								
Icheon	45.3	2.4	21.6	1.4	33.6	13.1	125.7	306
Onyang	59.5	1.9	1.4	0.1	39.5	9.2	61.5	194.5
Bugok	95	3.4	2	0.2	12.8	123.5	29.3	348
Mongolia (source: Tseesuren, 2001)								
Bayankhongor	77–95	2.4–2.5	3.2–6	0.5–3.5	5.7–24.8	50.6–72.5	61.1–76.3	415–448
Arkhangai	84.3	2.9–108.8	2.0–3.2	0.9	17.7–24.1	45.3–54.3	24.4–68.3	438–505.7

but very popular and eagerly visited. On the beach near Beppu, one can take a sand bath, for years used medicinally by local people. In addition to simple baths, *onsen* water is used for treating rheumatism, skin diseases, neuralgia, diabetes, gynecological diseases, gastrointestinal disorders and fatigue (Erfurt-Cooper and Cooper, 2009; Taguchi *et al.*, 1996). The partial analyses of selected thermal springs are given in Table 13.7.

Particularly attractive resorts include Nikko (in Tochigi Prefecture, NE of Tokyo), Kusatsu (in Gunma Prefecture W of Tokyo), Hakone (in Kanagawa Prefecture, south of Tokyo), Katsuura and Shirahama (in Wakayama Prefecture), Arima (in Hyogo Prefecture), Dōgo (in Ehime Prefecture), Unzen (in Nagasaki Prefecture) and others (Itallie and Hadley, 2000). In Kusatsu, for example, the most prominent public bath is the Sainokawara Rotenburo (with large outdoor pools), the Otakinoyu (with unique Awaseyu baths) and Gozanoyu (wooden building with two traditional baths) (Japan, 2016).

In Mongolia, 42 hot springs are known and some of them are used in health resorts and sanatoriums. Mainly they are distributed in the central (Bulgan: 55°C, Uvurkhangai: 30–72°C, Bayankhongor: 23–92°C, Arkhangai: 38–86°C, Zavkhan: 36–56°C and Khuvsgul: 21–62°C) and western provinces (Khovd: 29°C and Bayan-Ulgii: 25–32°C). Water is used for curing high blood pressure, skin disease, rheumatism, nervous disorders and mainly for recuperation. An example is the Tsenkher Hot Spring, whose waters are used for traditional (ancient) medicinal treatments (Bignall *et al.*, 2005; Erfurt-Cooper and Cooper, 2009; Tseesuren, 2001).

Chinese traditions of using hot and mineral waters were written down a long time ago. People from many provinces have benefited from thermal therapy using natural springs, and have also taken pleasure in hot baths, especially during cold seasons. In Lintong Province, east of Xian, the Huaqing Hot Spring has been known since prehistoric times. It used to be visited by imperial families who came there for relaxation and medicinal baths. Recently the historical buildings have been restored and extended (one of them houses the museum of the Tang dynasty) and waters can be used to treat rheumatism, arthritis and skin diseases.

In Anhui Province, in a national geopark in the Yellow Mountains, there are hot springs (Huangshan area) which have been used for baths and drinking treatments for 1000 years. Yunnan Province abounds in hot springs, most of which are used by local people directly for heating

their homes or for medicinal purposes. In Guangxi Province, there is Longsheng Hot Spring National Park, which is often described as a perfect place for improving health. In mainland China, Guantang Thermal Springs (on Hainan island) and Zhuhai are known. The former lies in a geothermal zone and its waters reach temperatures of 52–74°C. In this area, the largest Chinese thermal recreation center, the Guantang Thermal Spring Recreation Center has been built. The other spring, Zhuhai, lies ca. 60 km from the urbanized part of the city with the same name, in the southern part of Guangdong Province. In the village of Doumen, hot springs have been used to develop the first Japanese-style thermal complex ‘Imperial Hot Spring’, with classic *onsen*, a large sauna and massage facilities. Lampu Garden is known for its Chinese Medicine Valley. It is a thermal complex divided into several areas varying in function. One can take traditional Chinese therapeutic baths or hydrotherapeutic treatments there (Erfurt-Cooper and Cooper, 2009).

China generally has large geothermal resources. Over 2500 places with thermal springs or boreholes are known (groups of springs in one place have been counted as one). The largest number of springs are concentrated on the Tibetan plateau, especially on both sides of the river Yarlung Zangbo. This area is rich in manifestations of hydrothermal activity (geysers, ‘boiling’ springs and hot springs). Fewer natural occurrences of thermal waters are observed in the northern and the northwestern parts of the country. In the past, thermal health resorts were founded only in selected places and they were intended for the use of only a few people. After the proclamation of the People’s Republic of China (mid-20th century) the health resort sector was expanded and over 80 centers were opened to the public. Since that time, people of all nationalities living in China have been able to use the well-equipped resorts Lushan, Ling Tung and Cunhua in the Huangshan Mountains, Xinjiang in the Tianshan Mountains and others in the Aer Mountains (Keshi, 1980).

In Korea, the majority of hot springs are situated in the NW and SE parts of the peninsula. Therefore, according to Korean law, hot springs are those whose waters are warmer than 25°C (Yum, 2000). The temperatures of their waters vary between 23 and 78°C, but the SE of the peninsula abounds in waters with temperatures above 60°C. Most of thermal waters in Korea are HCO<sub>3</sub>-Na type with TDS 200–400 mg L<sup>-1</sup> (Yum, 2000). Until 1996, Korea had 24 thermal health resorts including the oldest one, Onyang Spa, which has been known since the 15th century. Their water is used for curing skin diseases (psoriasis, atopic dermatitis), allergy, gout, hypertension and indigestion. The Korean medical community do not demonstrate interest in using natural thermal waters for therapeutic treatments as their colleagues in other countries (e.g. Japan). Nevertheless, Korean waters have a big potential for the development of balneology combined with oriental medicine (Hann, 1996).

In Thailand, 27 areas of hot spring occurrence have been recognized. There is a total of about 114 thermal springs, 50 of them in the northern part of the country, in Lampang and Mae Hong Son regions. The water temperature ranges from 32 to 99°C in the northern part of country, whereas in the central region it varies between 34 and 80°C. Most of TDS is below 750 mg L<sup>-1</sup> with average HCO<sub>3</sub><sup>-</sup> content 248 mg L<sup>-1</sup>. Chloride concentrations in thermal waters are from 1 to 9579 mg L<sup>-1</sup>, sulfate from 2 to 1328 mg L<sup>-1</sup> and Na between 4 and 5479 mg L<sup>-1</sup>. Water composition of thermal springs indicate that calcium content varies from 1.2 to 1005 mg L<sup>-1</sup>, potassium from 1 to 208 mg L<sup>-1</sup> and average content of magnesium is 25 mg L<sup>-1</sup> (Subtavewung *et al.*, 2005). All-inclusive therapeutic treatments are offered in San Kamphaeng and Rung Arun w Chiang Mai centers. Table 13.8 shows the content of main cations in waters of San Kamphaeng and other thermal springs in Thailand. This is also where the thermal spring Pa Pae is located. The spring has preserved its natural beauty thanks to the fact that it has never been commercialized. In Ratchaburi Province, there are thermal waters used by local people to treat muscle pains (Erfurt-Cooper and Cooper, 2009).

India is a country with over 300 thermal and mineral springs, and the available literature mentioning the history of using these waters in balneology is very scarce. It is difficult to say how long Indian hot springs have been used for therapeutic purposes, as their medicinal functions are often entwined with religious rituals practiced in temples located near them. Well-known hot springs in India are Vajreshwari, Taptapani (Tattapani), Bakreswar, Atri, Thingbu and Tsachu, Rajapur, Ganeshpuri, Anthoni and Rajgir. Those springs which are free from religious



Table 13.8. Major cations content in thermal waters from locations in northern Thailand (concentrations in mg L<sup>-1</sup> unless otherwise specified).

District and/or hot spring	Na	K	Ca	Mg	TDS	Temp. [°C]
Mae Chan	120	8.1	1.7	<0.1	620	93
Wiang Pa Pao/Sop Pong	100	7.8	2.1	<0.1	460	79.3
San Kamphaeng	150	15	1.5	<0.1	710	42
Doi Saket/Ban Pong Kum	110	15	4	<0.1	550	96.3
Fang	115	8.4	1.1	<0.1	545	98.1
Mae Taeng/Pong Duet	85.5	6.3	1.7	<0.1	375	95
Pai/Tha Pai	77	2.9	2.2	<0.1	350	78.9
Pai/Mueng Paeng	100	4.6	2.6	<0.1	490	96

importance are selected for medicinal use (Bisht *et al.*, 2011; Chandrasekharam, 1999). Hot springs in West Coast Maharashtra Province (e.g. Rajapur, Ganeshpuri, Rajwadi) contain chloride (from 78–4800 mg L<sup>-1</sup>), sulfate (85–225 mg L<sup>-1</sup>), sodium (76–410 mg L<sup>-1</sup>) and calcium (152–186 mg L<sup>-1</sup>). Potassium content ranges from 14 to 26 mg L<sup>-1</sup> and TDS varies from 1723 to 2331 mg L<sup>-1</sup> (Sarolkar, 2005). Some of these are listed in Table 13.9.

Taptapani is a popular Indian health resort with thermal sulfurous waters (Table 13.9), known for years for their curative effect on various illnesses, and a destination of religious pilgrimages at the same time (Erfurt-Cooper and Cooper, 2009).

Among the 23 identified and studied thermal springs in Iran, waters from ten of them are used for balneological purposes. They are used chiefly to cure rheumatism, arthritis, skin diseases, cardiovascular diseases and neurological disorders (Erfurt-Cooper and Cooper, 2009).

A large number of hot and warm springs in Israel flow out along the shores of Tiberias Lake (the Sea of Galilee) and at the bottom of the lake. On the western side of the lake, there is a group of three springs, known since pre-Biblical times. They are known as Hamei Tveria or Hammath (Tiberias Hot Spring). Their temperatures reach 59–62°C. Nowadays, the water is used for curing rheumatism, osteoarthritis and skin diseases. Additionally, water therapy is supplemented with inorganic mud treatments. Currently it is the center of balneotherapy in Israel. Hammat Gader (in Hammat Gader province) is a resort known since Biblical times. Five springs, the main one being Ein Balzam (temperature: 42°C), supply bathing pools, but no research has been conducted to define the possibilities of therapeutic application of these waters (Rosenthal, 2001). In the southern part of Israel, not far from Tel Aviv, there is a thermal water intake called Hamei Yoav (39°C). Physicians using these waters for skin and musculoskeletal diseases have recommended them as a remedy, although until 1996 the curative effects were not confirmed by research (Wolf, 1996). On the eastern rims of the Suez Graben, there are two thermal springs, Ayun Mussa (27°C) and Hammal el Far'un (72°C). On the western coast of the Dead Sea (in its SW part), there emerges En Noit Spring (temperature: 39°C), which was used in baths by the soldiers from the nearby Boqeq garrison in Roman times. The water from this spring was supplied to the town by an aqueduct. According to Rosenthal (2001), waters from this spring can be used in bathing and drinking treatments for chronic constipation and skin diseases. The content of main ions in selected thermal springs is given in Table 13.9.

The Mediterranean countries have one of the longest traditions of using thermal waters both for recreation and medicinal purposes.

Even today, almost every town or city in Turkey has public baths based on natural or heated waters (Erfurt-Cooper and Cooper, 2009). Skin or cardiovascular diseases, osteoporosis or allergies are only a few examples of illnesses cured in Turkish health resorts by using thermal waters combined with thalassotherapy, physiotherapy or kinesiotherapy (Dal, 2007).

The regions of Anatolia, southern Marmara and South Aegean are abundant in thermal waters with temperatures ranging from 36 to 45°C and the occurrence of very hot waters, that is, with temperatures of 93°C (Kozaklı-Nevşehir area). The majority of waters belong to the latter group.

Table 13.9. Chemical compositions of geothermal springs from several locations in India, Israel and Iran (concentrations in mg L<sup>-1</sup>).

Location and/or hot spring	Na	K	Ca	Mg	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	TDS
India (source: Dash <i>et al.</i> , 2013; Mongra, 2014)								
Odisha/Atri Taptapani (Tattapani)	270	240	8.8–12.8 164	2.4–3.7 4.8	246.5–273 35.00	28.2–35.5 115		11800
Israel (source: Rosenthal, 2001; Wolf, 1996; Woith <i>et al.</i> , 2011)								
Tiberias Hot Spring (Hamei Tveria)	5600–6860	291–372	2752–3525	595–685	15051–18468	695–808	144–152	29712–31000
Hammat Gader	45–225	1–13	80–155	30–45	72–500	49–167	305–395	283–1432
Hamei Yoav	800	15	123	66	1566	22	286	
En Noit	1212	59	606	130	2018	1687	190	1574
Iran (source: <sup>1</sup> Ghadimi <i>et al.</i> , 2012; <sup>2</sup> Moeini <i>et al.</i> , 2014) – average ions content								
Mahallat <sup>1</sup>	128.6	4.5	257.4	48.9	49.9	877	207	1139
Abgarm <sup>2</sup>	79.3	2.1	388.7	44.6	59.8	1055	210.5	2191

They are HCO<sub>3</sub>-Ca, HCO<sub>3</sub>-Na, Cl-Na and SO<sub>4</sub>-Na-Ca type waters. Generally, there are about 190 thermal springs concentrated in 46 places (Azakli, 2012). Places with spas and health resorts include, for example, Balçova (90–125°C), Gediz (78°C), Sivas Sıcak Çermik Spa (46°C), Afyon Gazlıgöl Spa (68°C), Çankırı-Çavundur (56°C), Bolu-Karacasu (44°C) (Mertoglu *et al.*, 2003; Mutlu and Güleç, 1998). Characteristics of chemical compositions of selected thermal springs are shown in Table 13.10.

Balçova Thermal Resort, one of the biggest centers of thermal medicine in Turkey, lies 25 km from İzmir (western Anatolia). Its water is used for curing rheumatic pains, digestive and metabolic disorders as well as in post-traumatic and postoperative treatments. Çeşme in İzmir Province is a resort with two main treatment centers: Şifne Ilıca and Alaçatı. Heated (to 55°C) seawater is used for treating rheumatic, dermatological and gynecological diseases. Pamukkale, one of the oldest and best known treatment centers, spas and wellness centers in Turkey lies 20 km from Denizli (SW Turkey). Its thermal waters (42–56°C) are applied in drinking and bathing treatments to cure rheumatism, skin diseases, neurological disorders, gynecological diseases, digestive disorders and general fatigue. The place is known for its snow-white terraces formed around the springs from precipitated minerals. Natural pools formed in this way are used for bathing treatments.

Not far from the water channel connecting Köyceğiz Lake with the Mediterranean Sea lie Rıza Çavuş Thermal Baths, known for a natural mud pool used for therapeutic baths. North of Rıza Çavuş, there is a thermal spring used in baths and drinking treatments for rheumatic, neurological, skin and gynecological disorders. Kangal Hot Springs is a center located ca. 100 km from Sivas (eastern Anatolia) and it is known for thermal springs (35°C) and the fish living in the pools. The fish increase the effectiveness of dermatological treatments (for psoriasis). Additionally, rheumatic and neurological disorders are cured here (Dal, 2007; Özçelik and Akyol, 2011).



Figure 13.2. Limestone travertine terraces at Pamukkale (photo: courtesy M. Sikora, 2012).

Table 13.10. Major element analyses of thermal waters in Turkey (concentrations in  $\text{mg L}^{-1}$ ; source: Mutlu and Güleç, 1998; Özçelik and Akyol, 2011).

Location and/or hot spring	Na	K	Ca	Mg	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	TDS
Sivas/ Kangal Hot Spring	3.2	1.1	54.2	45	23.9	46	302.4	
Nevşehir/ Kozaklı	440	21	208	28	632	486	427	2323
Sivas/Çermik	200	38	360	97	193	50	1903	2668
Yalova/Termal	248	4.6	163	1	93.4	831	45	1431
Bursa/Çekirge	23.5	3.7	86	24.4	7.6	95.5	307	571
İzmir/Çeşme	10075	388	1551	609	20431	2981	153	36240
İzmir/Balçova	16.6	16.8	81.4	72	39.7	102	507	837
Denizli/Pamukkale	230	22	530	110	35	830	1415	3118
Muğla/ Köyceğiz	8840	290	962	888	16400	2748	317	30479

### 13.5 EUROPEAN COUNTRIES

In European states, the term health is associated with medical treatment and thermalism is a part of traditional medicine. For healing, hot waters in combination with mud, peloids and brine are used. The healing properties of waters depend on the presence of trace elements and gases, temperature and radioactivity. However, in many cultures balneotherapy is not known or understood and visitors might be surprised by such treatments and sanatoriums (Smith and Puczkó, 2009, 2014).

Among the Mediterranean countries, Greece holds one of the top places as regards the history of development and management of geothermal waters. Gradual progress in the organization of health resorts and spas in Greece came at the turn of the 19th century. Most of the baths, which are still used nowadays, were modernized in the 1930s. Over 70 health resorts or spas operated in this country in the latter half of the 20th century. Their number rose steadily with the reconstruction of the formerly deserted establishments. These structures can be found both on the mainland and on the Greek islands. It should be noted here that Greek resorts are classified according to the temperature of the used water. Cool hot springs with temperatures of waters up to 20°C; hypothermal hot springs – 20–40°C, like those in Loutraki Aridaia, Pozar, Loutraki of Corinth, Platistomo, Ypatis of Fthiotida and Krinides of Kavala. Mesothermal hot springs have waters which have a temperature of 35–50°C. Such springs, for example, are in Smokovo, Langada, Nea Apollonias Thessaloniki, Eleftheres Kavala, Edipsos and others. Hyperthermal spring waters reach temperatures above 50°C, like those in Edipsos, Polychnitos and Ikaria, Kimolos, Kythnos and several others (Thermal springs in Europe, 2012).

The best known (since the ancient times) Greek spa is Edipsos. Its waters are thought to be the warmest (78.2°C) in Europe. The Greek health resorts offer treatment of respiratory and circulatory system disorders as well as gynecological and skin diseases (psoriasis, eczema, atopic dermatitis). The last of the mentioned illnesses is cured in Thermopyles, Kaiafa, Ipati, Kammena Vourla and Methana (Katsambas and Antoniou, 1996).

In Bulgaria, there are 520 springs of mineral waters and 57 balneological resorts. Not far from the city Stara Zagora, there is one of the oldest health resorts of this country, Jagoda Spa, known for the offered thermal water (ca. 43°C) treatment of skin diseases (mainly psoriasis). Skin diseases are also cured in Kjustendil (ca. 72–75°C) and Marikostinovo. In the latter resort, baths in sulfurous thermal waters are combined with peloid treatment. The health resort in Kjustendil first opened in 1966. Its waters have a beneficial effect on the treatment of neurological disorders, joint disorders, osteoporosis and gynecological diseases. The therapeutic complex comprises sanatoriums, a polyclinic and public baths (Bojadgieva *et al.*, 2002). Another popular resort is Momin Prohod (73 km from Sofia) with its nine thermal springs (64.2°C) used for curing eczema by means of bathing, drinking and inhalation treatments. The health resort Haskovo has been known since prehistoric times. Nowadays, thermal waters (58°C) from 11 boreholes, are used in the therapy of sclerosis multiplex (Tsankov and Kamarashev, 1996). In the central part of Bulgaria, there is a spa center of national importance, Pavel Banya. Among its nine natural springs, the Kademliata Spring stands out for its temperature of 50°C. In the 1970s, 15 wells were drilled in this area, which allowed the exploitation of the water with temperature of ca. 60°C. Local water is used for treating musculoskeletal disorders, injuries and disorders of the central and peripheral nervous system (Hristov *et al.*, 2010). One of the largest Bulgarian spas is Sapareva Banya (SW Bulgaria). Thermal water in this region reach the temperature of 100°C, and some springs in the resort have temperatures of 60–98°C. The resort was founded at the turn of the 1950s. The balneological complex comprises a sanatorium with a polyclinic and a medical surgery center as well as outdoor pools. The therapeutic treatments performed here address patients with musculoskeletal and neurological disorders, chronic heavy metal poisoning and gynecological diseases. Another large spa, known for centuries, is Hisarja (S Bulgaria, at the foot of the Sredna Gora Mountain). There are 22 thermal springs (27–52°C) used chiefly for curing kidney, liver and digestive disorders. Besides, they have a beneficial effect on the prevention of osteoporosis. The health resort Sandanski (at the foot of the Alpine Pirin Mountain, near the Macedonian and Greek border) was known as early as the 2nd century BC. Based on over 20 thermal springs (35–83°C), it provides treatments of respiratory, neurological, gastrointestinal, kidney and skin diseases, as well as joint inflammations and musculoskeletal disorders. Near the town Velinograd (on the western part of the Rhodopes), there are over 70 thermal springs (20–95°C), which are used for the treatment of respiratory, neurological and musculoskeletal diseases. The spa specializes in the therapy of gynecological diseases and the treatment facilities are housed in a state-of-the-art balneological center and sanatorium. Additionally, since 1999, local waters have been bottled and sold, not only on the national market. In Devin, on the east side of the Rhodopes, a health resort has

Table 13.11. Major chemical types of thermal waters in selected Bulgarian health resorts.

Location	TDS [mg L <sup>-1</sup> ]	Hydrochemical type of thermal waters
Kjustendil	276–920	HCO <sub>3</sub> -SO <sub>4</sub> -Na; HCO <sub>3</sub> -Na
Sapareva Banja	690	HCO <sub>3</sub> -SO <sub>4</sub> -Na; HCO <sub>3</sub> -Na
Sandanski		HCO <sub>3</sub> -SO <sub>4</sub> -Na-Ca
Velingrad	210–750	HCO <sub>3</sub> -SO <sub>4</sub> -Na-F-Si
Hisarja	256	HCO <sub>3</sub> -SO <sub>4</sub> -Na-Si
Devin	290–370	HCO <sub>3</sub> -Na

Source: Bojadgieva *et al.* (2002).

developed in the place where thermal waters (37–44°C) from deep boreholes are used in physical and mental exhaustion prevention, postoperative rehabilitation and treatment of neurological disorders. These waters are also bottled and distributed on foreign markets (in Germany and Arab countries). Along the Black Sea coast in the NE part of Bulgaria, there are several resorts with thermal waters reaching temperatures from 30°C in Albena, through 48°C in 'St. Constantine and Elena' to 52°C in Varna. The main diseases recommended for treatment by this water are cardiovascular and nervous disorders, musculoskeletal malfunctions, gynecological disorders, allergies, and respiratory system disorders. The health resorts are equipped with thermal baths as well as outdoor and indoor pools (Bojadgieva *et al.*, 2002; Vassileva, 1996). Hydrochemical types of thermal waters from particular resorts are shown in Table 13.11.

Many countries on the Balkan peninsula have a long tradition of using thermal baths. Bosnia and Herzegovina has a lot of balneological centers and tourist centers at different stages of development, operating as medical centers and using thermal waters with a wide range of temperatures (hypothermal, homeothermal and hyperthermal), mainly bicarbonate-sulfate-calcium and hydrocarbon-calcium water types (Table 13.12).

In northern Bosnia, northwest of Bihać, there is the well-known Gata Spring, whose water was already used in ancient Roman times. In the resort, one can cure rheumatism, neurological and neuromuscular diseases, skin diseases, gastrointestinal diseases and limb injuries. A few kilometers from Kozarska Dubica, in Mlječanica, there is a health resort complex treating rheumatism, stomach and gynecological diseases, osteoporosis and neurological disorders. Also, in the northern part of Bosnia, near the towns Sanski and Sanski Most, there are thermal springs Tomina Ilidža (south-east of Sanski) and Thomas Ilidža (southwest of Sanski Most). For practical reasons, there are plans to build one recreation center combining both health resorts into one complex called Sanska Ilidža. The waters of this region are used for treating neurological disorders, limb injuries as well as rheumatism and gastrointestinal disorders. Other well-known health resorts located in northern Bosnia include Laktaši, Slatina or Ilidža Gradačac. Based on thermal waters, they offer treatments for curing rheumatic, neurological and cardiovascular diseases, injuries and other health problems (e.g. diabetes in Ilidža Gradačac or eye and respiratory tract diseases in Laktaši). Baths, underwater massages and inhalations were prepared with the use of thermal brine in Salt Spa in Tuzla (northern Bosnia). Treatments were offered for injuries, rheumatic, gynecological and respiratory diseases and arteriosclerosis. Currently Salt Spa is not used. The new spa complex comprising clinics, a health farm, a saline pool and an Olympic-size swimming pool is being built there. In Terme-Gračanica resort (northern Bosnia, not far from the road Doboje-Sarajevo), therapeutic and rehabilitation programs have been supplemented with sports and recreation. The thermal waters are used for treatment of skin, cardiovascular, gastrointestinal, gynecological and rheumatic diseases, a disease of the stomach, liver and gall bladder. To the northwest of Bijeljina, there is Spa Dvorovi, where thermal waters (56°C) are exploited from a deep borehole (1176 m) and used for the treatment of chronic rheumatic diseases, limb injuries, gastrointestinal diseases and other disorders.

In the central part of Bosnia, near the source of the Bosna river, lies Terme Ilidža Spa. The complex, which is regarded as one of the oldest spas in southeastern Europe, was reopened after

Table 13.12. Types of thermal waters of Bosnia and Herzegovina.

Location	Hydrochemical type of thermal waters
Bihać/Gata	SO <sub>4</sub> -Cl-Ca-Na
Sanski Most/Tomina Ilidža	HCO <sub>3</sub> -Cl
Banja Luka/Laktaši	HCO <sub>3</sub> -Ca-Mg
Banja Luka/Slatina	HCO <sub>3</sub> -SO <sub>4</sub> -Ca-Mg
Ilidža Gradačac	HCO <sub>3</sub> -SO <sub>4</sub> -Na-Mg
Tuzla/Slana Banja	Cl-Na
Gračanica	HCO <sub>3</sub> -SO <sub>4</sub> -Na-Ca
Dvorovi/Bijeljina	HCO <sub>3</sub> -Cl-Na
Sarajevo/Ilidža	HCO <sub>3</sub> -SO <sub>4</sub> -Ca-Na
Fojnica	HCO <sub>3</sub> -Ca-Mg
Olovo	HCO <sub>3</sub> -Ca-Mg
Višegrad	HCO <sub>3</sub> -Ca-Na

Source: Operta and Hyseni (2013).

a complete renovation in 2004. Currently, it has a physical medicine, rehabilitation and wellness center. Treatments are offered to patients with rheumatism, neurological and circulatory system disorders as well as endocrine, gynecological and skin diseases. Other health resorts in central Bosnia have been located in Fojnica (50 km from Sarajevo), near Olovo and north of Višegrad. The first of the mentioned towns has the Reumal Fojnica Spa with a physical medicine and rehabilitation center equipped with the latest devices. The center has a cardiac rehabilitation unit and a center for sports medicine.

Near Olovo, a health and rehabilitation center Aquaterm has been opened to provide medical and physical health care. Treatment is provided for rheumatism and arthritis, diseases of the nervous system as well as inflammatory diseases of joints and the spine.

The mineral and thermal waters of the Federation of Bosnia and Herzegovina have a wide range of uses in balneology, tourism, recreation and sport as drinking or bottled waters. For a variety of reasons, chiefly related to geopolitics, the worldwide wellness and fitness trends have not changed the main therapeutic and rehabilitation character of the Federation's spas (Operta and Hyseni, 2013).

In Macedonia, the country in the central part of the Balkan peninsula, nowadays there are only eight thermal resorts. The existing spas were built in the latter half of the 20th century. The oldest (since the ancient Greek times) and the best known are Katlanovo Spa (40.5°C) and Bansko Spa (75°C, SE Macedonia). From the Roman times, this has been known as Banja Spa (not far from Kocani) with thermal (55°C) sulfur water. To the southwest of Banja lies Kezovica Spa (54°C). Kumanovo Spa (31°C) is a resort situated to the northeast of Katlanovo. In the southern part of Macedonia lies Negorci Spa (38°C) and near the Albanian border (western Macedonia) and the town Debar are located Kosovrasti Spa and Debar Spa (38.6°C). Generally, springs have been recognized to be effective in healing rheumatism, paralysis, diabetes, anemia, female and some skin illnesses (Gorgieva and Popovski, 2003).

In Italy, there are about 2300 mineral springs, one third of them having thermal waters (20–100°C). Some of them are used by the public (180) or are privately owned resorts. The popularity of health resorts or spas puts Italy in the second place among European countries, just behind Germany. The largest Italian spa centers are Terme Euganee (NE Italy) and the area of Naples (Ischia island), where thermal springs flow out in several villages. The best-known hot spring centers are Chianciano and Montecatini in Tuscany and Sirmione (65°C) in Lombardy.

Terme Euganee is actually an extensive complex composed of several spa towns: Abano, Montegrotto, Battaglia Terme and Galzignano. The waters in this region reach temperatures ranging from 65 to 87°C and they are used for therapy together with mud treatments.



Figure 13.3. Thermal bath Tettuccio in Montecatini, Italy (photo: courtesy EHTTA, 2010).

On Ischia island, there are over 100 known thermal springs. Besides, hot waters (58–100°C) are exploited from numerous shallow wells. In Chianciano (32–36°C) and Montecatini (23–32°C), waters are used for drinking and in balneological treatments.

In the northern Apennines lies the thermal health resort Bagno di Romagna (26–43°C). Other well-known and frequently visited resorts are Porretta Terme (23–35°C), Sciacca on Sicily (26–57°C), Acqui Terme in Piedmont (35–70°C) (Carella, 2003; Carella and Sommaruga, 2000), Bagni di Lucca and Salsomaggiore (EHTTA, 2010).

According to Andreassi and Flori (1996), Italy has 85 health resorts specializing in treating skin diseases, several of which, using thermal waters, are widely recommended. These are Comano Terme (27°C) and Abano Terme (87°C) in northern Italy, Bagni di Lucca (38–54°C) and Porretta Terme (35°C) in central Italy, Acireale (22°C), Agni di San Filippo (52°C) and Casamicciola (30–70°C).

In Poland (central Europe), the longest operating thermal health resorts are Łądek-Zdrój, Cieplice Śląskie Zdrój (SW Poland) and Iwonicz-Zdrój (SE Poland). In 2012, the health resort status was granted to Uniejów (in central Poland). Besides, thermal waters occur in the health resorts Ciechocinek (central Poland), Duszniki-Zdrój (to the northwest of Łądek) and Ustroń (S Poland). The content of main ions in selected thermal springs is given in Table 13.13.

Cieplice has the warmest medicinal waters in Poland. Six natural thermal springs emerge in an inter-mountain basin in the Sudetes. Five of them (Marysieńka, Sobieski, Nowe, Basenowe Damskie and Basenowe Męskie) have temperatures ranging 22–42°C. In the 1970s, two boreholes (C-1 and C-2) were drilled. The temperatures of waters are 41°C and 63°C, respectively. In the late 1990s, borehole C-1 was deepened (to 2002.5 m), which enabled exploitation of the water with the temperature of 87.8°C (Dowgiałło and Fistek, 2003). The waters are used for therapeutic baths, underwater massages and inhalations. Also, peloid treatments (compresses, plasters, wraps)





Figure 13.4. La Bollente spring in Aquis Terme (photo: courtesy EHTTA, 2010).

are performed. Musculoskeletal disorders and injuries, rheumatic diseases, osteoporosis, kidney diseases and neurological diseases are treated in Cieplice (Kielczawa, 2016; MZ, 2016).

The operation of the health resort in Iwonicz is based on waters from six boreholes (originally drilled in search of oil), two of which (Lubatówka 12 and Lubatówka 14) have thermal waters. Mineral waters are used for drinking, in mineral baths and to obtain iodine-bromine salt, while peloid is used in compresses, baths and to produce peat cubes. The resort offers its patients prevention, therapy and rehabilitation in rheumatic diseases, osteoporosis, skin diseases, digestive disorders, upper respiratory tract diseases, neurological disorders and gynecological diseases (Kicińska, 2008; MZ, 2016). The unique raw materials are used to produce unique medicines and cosmetics (MZ, 2016).

Thermal waters of Łądek (20–44.7°C) are exploited from five natural springs (Wojciech, Dabrowka, Chrobry, Jerzy, Skłodowka-Curie) and one borehole (L-2). The health resort specializes in curing musculoskeletal disorders and injuries, rheumatic diseases, osteoporosis, neurological diseases, skin diseases and gynecological diseases (MZ, 2016). The main therapeutic treatments are bathing (in pools and baths), peloid treatment (baths and wraps), drinking treatment, inhalations, hydrotherapy and physiotherapy (Kochański and Kochański, 2000). One of the oldest and the best known spa facility is Natural Treatment Center “Wojciech” (17th century). In 1936, the Peloid Treatment Center was built. In the late 20th century, the spa facility with its bathing pools, drinking hall and bathrooms equipped with marble baths was renovated. Treatments are also provided in the Natural Treatment centers Nowy Jerzy and Adam (Ciężkowski, 1998; Łądek, 2016).





Figure 13.5. “Dom Zdrojowy” in Iwonicz (source: Kicińska, 2008).



Figure 13.6. “Wojciech” Natural Treatment Center (source: Wojciech, 2016).



Figure 13.7. The indoor pool in the “Wojciech” Center (source: Wojciech, 2016).

In the latter half of the 20th century exploration works started in Uniejów. In the three boreholes, which were drilled then, thermal waters (60–70°C) were found (Dowgiało, 2007). Near one of the boreholes, a health resort was built. It provides treatment of skin, peripheral vascular and cardiac diseases, hypertension, respiratory and neurological diseases, musculoskeletal disorders and injuries as well as rheumatic diseases (MZ, 2016). Thermal waters are used in baths and inhalations. The complex has outdoor and indoor pools, a steam bath, a set of saunas and a graduation tower (Uniejów, 2016).

The first boreholes in Ciechocinek were drilled in the early 19th century with the aim of supplying the existing salt works with water. In the interwar period, therapeutic and recreation pools were built based on the thermal brine (Terma XIV). In the baths, peloid treatments and inhalations were provided. The next two intakes (Terma XVI and Terma XVIII) were drilled in the 1950s and the 1960s. (Dowgiało, 2007). Currently, the resort offers treatments using thermal waters drawn from two boreholes, Terma XIV (28°C) and Terma XVI (35°C). The offered treatments focus on musculoskeletal disorders and injuries, rheumatic, cardiac, neurological and peripheral vascular diseases, upper respiratory tract diseases, diabetes, obesity, osteoporosis and gynecological diseases. Patients can use a rehabilitation center, a therapeutic center, resort hospitals and sanatoriums (Krawiec, 1999, 2009; MZ, 2016).

Duszniki-Zdrój is a health resort situated in SW Poland, to the northwest of Łądek. The first records about the springs in Duszniki go back to the 15th century, when the spring called Zimny Zdrój was discovered. The spring was officially designated as the Prussian monarchy health resort in the latter part of the 18th century. In 1909–1911, during exploration works planned by the Prussian Geological Institute, new boreholes were drilled in the resort area (now called Agata and Jan Kazimierz) and the existing intakes were deepened. The construction of the new Spa





Figure 13.8. Modern thermal facilities in Baden-Baden (photo: courtesy W. Ciężkowski, 1999).

House, today's Chopin's Manor, started in the early 19th century. In the middle of that century, apart from Zimny Zdrój, springs now known as Łąkowe Male, Łąkowe Wielkie, Ulryki, Darniowe and a few more were known. In the following years, the resort was gradually extended. Natural treatment centers, walking halls, drinking halls and a concert hall were built. In 1928, a small plant producing liquefied carbon dioxide (still operating nowadays) was built in the southern part of the Spa Park (Ciężkowski *et al.*, 2002). In 2000–2002, a borehole accessing carbonated thermal waters (36°C) was drilled in the resort area (Dowgiałło and Fistek, 2003). This intake is still kept in reserve for balneological and recreation purposes. The indications for balneological treatments provided in Duszniki-Zdrój include musculoskeletal disorders and injuries, rheumatic diseases, osteoporosis, cardiac diseases and hypertension, peripheral vascular diseases, lower respiratory tract diseases and digestive diseases (MZ, 2016).

Germany has 142 thermal spa complexes and 38 centers offering therapeutic treatments using thermal waters, brines and mud. In almost every region of Germany there are mineral springs, health resorts or spas. One of the oldest and the best known resorts in this country, known as Aquae Aureliae at the time of the Roman Empire, is Baden-Baden. Nowadays, it is still a leading thermal center, offering treatments in two complexes: the Friedrichsbad (operating for over a century) and the Caracallabad (opened in 1985), treating mainly arthritis, rheumatism, circulatory disorders, obesity (Erfurt-Cooper and Cooper, 2009) as well as respiratory and metabolic disorders. The resort has eight clinics with qualified medical staff (Health Travel, 2012). Currently water is exploited from seven natural springs (52.6–67°C), two wells (52 and 60°C) and three tunnels (55–67°C) collecting waters from several smaller old springs (Sanner, 2000).

Bad Füssing is a small village with sulfurous hot springs, lying in the center of Bavaria. Apart from 12 pools and therapeutic centers, there is also the recreation center Europa Therme Baths. Johannesbad is one of the largest European spa complexes using thermal waters from their own springs flowing out directly in the resort area. The water from the local spring has the temperature

of 56°C and it is used in the spa and wellness facilities, for aromatherapy, in saunas, for jet baths and in preventive treatment.

Another German health resort, Bad Nauheim, which cooperates with prestigious medical institutions, has the reputation for being a competence center for curing cardiovascular and respiratory disorders. Specialist world-renowned clinics collaborate with Max Planck Institute for Heart and Lung Research. Bad Nauheim is also known for a sports clinic offering individually tailored care. The therapy is based on baths and drinking treatment. Apart from traditional baths, Therme am Park offers inhalation treatments, which have a favorable effect on the respiratory system. Baths in carbonated hot waters have a beneficial effect on the cardiovascular system, enhance the effectiveness of treatments for rheumatism and musculoskeletal diseases and reduce hypertension. Moreover, Bad Nauheim holds the title of a “Kneipp Health Resort”.

Between Hamburg, Bremen and Hannover lies Bad Bevensen offering treatment focused on musculoskeletal diseases, spine and joint osteoarthritis, chronic inflammatory states and circulatory system disorders. In the Jod-Sole-Therme complex, water is used for baths and inhalations, and the health resort clinic specializes in curing coronary artery disease, musculoskeletal disorders and in psychotherapy.

Bad Driburg (32°C) has been a private health resort for seven generations (225 years). Its seven clinics, a therapeutic center and thermal baths offer treatments for rheumatic and circulatory system diseases, spine, joint and muscle problems and rehabilitation after surgery. Treatments are based on three main springs and sulfurous mud extracted from the nearby swamps.

One of the youngest German spas is Bad Griesbach (60°C), which obtained a health resort status in 2000. Its greatest asset is mineral and thermal water flowing out of three springs supplying pools in thermal baths in Wohlfühl. Bad Harzburg is one of the best three health resorts in Lower Saxony. Since the late 17th century, it has been offering treatments based on thermal brine. Between the Black Forest and the Vosges lies the resort Bad Krozingen known for carbonated ( $2.2 \text{ g L}^{-1} \text{ CO}_2$ ) thermal waters used for treating cardiovascular diseases. In Bad Neuenahr-Ahrweiler, patients have access to 16 clinics and over 100 doctors. The establishment offers baths in thermal water pools, massages and hydrotherapeutic treatments. Therapy using muds containing medicinal herb extracts is a patented treatment here. The resort offers preventive treatment and cures cardiovascular diseases, metabolic disorders and diabetes. Bad Salzungen in central Germany is one of the oldest health resorts in the country, with the tradition of using highly mineralized thermal brine going back to 1230. The town obtained the status of a health resort in 1923. The resort has baths, brine pools, an inhalatorium, a sauna and a therapeutic center offering treatments and gymnastics, as well as phototherapy with saline water. The treatments focus on respiratory, musculoskeletal and skin diseases. In the center of the resort there are old salt works with buildings from the turn of the 18th century. A very similar complex is Bad Sassendorf in central Westphalia with its clinics offering baths, inhalations, massages, rehabilitation, electro- and hydrotherapy as well as mud wraps and mud baths. A part of the resort is the Spa Sole Therme with pools, a sauna, a wellness center and a salt cave (Kielczawa, 2016).

In the 19th century, Wiesbaden became a world-famous health resort thanks to 26 hot springs, which are still the basis of remedial and balneological treatments. It is a traditional health resort – a center for curing rheumatic and musculoskeletal diseases, with specialist rehabilitation clinics. The resort also offers wellness treatments, such as saunas, thermal baths, steam baths, sand baths, as well as beauty treatments (*Health travel*, 2012).

Among the health resorts operating currently in England, Bath is the only one offering treatments based on natural thermal waters. According to Erfurt-Cooper and Cooper (2009), it has a unique deposit of hot water, which is exploited with three springs (deepened with boreholes now): the King's Spring (43°C), the Cross Bath Spring (44°C) and the Healing Spring (45°C). All these springs were used as early as under the Roman rule. Owing to spring contamination, new boreholes were drilled in the 1980s and a program of revitalization and extension of the complex was launched (White, 2000). As a result, in 2006, after almost 30 years of inactivity, the complex was reopened with a therapeutic treatment center (offering massages, hydrotherapy, physiotherapy and acupuncture) and a wellness center (Erfurt-Cooper and Cooper, 2009). About



Figure 13.9. The thermal facilities of Bad Salzungen (photo: courtesy M. Battek, 2014).



Figure 13.10. The Roman Bath at Bath (photo: courtesy EHTTA, 2010).

16 km northwest of Bath, in the Avon valley near Bristol, a group of thermal springs flow out. The best known and the largest of them are the Hotwells ( $24^{\circ}\text{C}$ ), flowing out near the southern mouth of the Avon Gorge. They are unused now, but are known to have been used chiefly for drinking. Jacob's Well is another spring in this group and it flows out at the bottom of a deep valley, and further to the northwest, there is St Vincent's Spring (Kellaway, 2001).





Figure 13.11. The Old Bath House in Spa (photo: courtesy EHTTA, 2010).

Spa (in Belgium) owes its worldwide fame to numerous (ca. 300) outflows of medicinal waters in the town area. Since the 1930s, the main springs have been protected from contamination by a special protection area. Water from one of the best known outflows, Marie-Henriette Spring, supplies the Spa Thermal Baths. The building was erected in the center of the resort in the latter part of the 19th century (1862–1868) and is still one of the most beautiful sights in the town. Waters are used to treat cardiovascular and respiratory diseases, rheumatism, arthritis and anemia. The offered treatments consist of baths, inhalations, massages, peloid treatment (wraps and baths) and showers. The water used for treatment is heated to the temperature of 30–34°C (Lund, 2000c). The approximate partial analyses of thermal springs from several locations in Europe are given in Table 13.13.

France is one of those western European countries where tourists willingly use mineral and thermal waters in health and wellness centers. Treatments are partly reimbursed by the national healthcare system. The French themselves think that ‘copying’ their spas is impossible due to the uniqueness of their waters. The unpolluted natural environment of the *Thermes de la Bourboule* has a beneficial effect on curing respiratory disorders, diabetes and skin diseases. In *Aix Les Thermes*, therapies make use of hot (77°C) vapors from a sulfurous spring, which is thought to be the hottest in the Pyrenees. The city *Aix-en-Provence* is famous for its 100 fountains recharged by geothermal springs. *Aix-les-Bains* is known for *Pellegrini Thermal Baths*, arranged in 19th-century buildings revitalized in the late 20th century. The resort lies near the Italian-Swiss border, south of Geneva and east of Lyon, and comprises several thermal centers. Thermal waters (46°C) are used for curing rheumatic diseases, laryngological disorders and allergies. Special showers with water massages are the principal treatments for stimulating blood circulation and in neuralgia. Another well-known thermal spring is *Vichy*, where liver and intestinal disorders, gout and malaria

Table 13.13. Composition of thermal waters from several locations in Europe (concentrations in mg L<sup>-1</sup> unless otherwise specified).

Location and/or hot spring	Na	K	Ca	Mg	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	TDS
England (source: White, 2000)								
Bath	183–195		358–390	53–57	286–340	1010–1050	189–199	
Germany (source: Knoblich, 2002; Sanner, 2000)								
Baden-Baden	851	75	129	2	1438	155	1	3013
Wiesbaden	2673		351	48	4605	65	619	
Nauheim	10416		1412	127	18124	44	2059	
Switzerland (source: Sonney and Vuataz, 2008)								
Baden	804	69	557	114	1175	1450	505	4740
Schinznach	170	12	237	57	194	600	300	1610
Bulgaria (source: Tsankov and Kamarashev, 1996)								
Jagoda		133*				120	172	556
Kjustendil						144		
Marikostinovo	231					220	414	992
Momin Prohod	233					460		934
Haskovo	292		167			867		1579
Greece (source: Dotsika <i>et al.</i> , 2010; Kelepertsis <i>et al.</i> , 2009; Katsambas and Antoniou, 1996; Verros <i>et al.</i> , 2007)								
Edipsos	12888	387	2285	452	20339	2150	347	3910–5780
Thermopyles**	2505	125	584	250	5260	736	952	14800
Ipati	1461	66	872	216	3190	22	1924	
Kammena	2805	173	531	191	5282	511	546	
Kaiafa	4799	248	702	321	8100	2302	3	
Loutraki	403–408	15–17	119–121	103	750–770	170–180	305	
Methana	2280–2690	85–205	170–400	58–320	3370–4700	420–770	1110–1280	
Italy (source: White, 2010)								
Bagni di Lucca	133–325	12.6–24.7	162.3–488	25.4–68	68–244	532–1765	107–195	
Poland (source: Cieplce Health Resort; Łądek Health Resort; Iwonicz Health Resort; Duszniki local authority; Kicińska, 2008; Krawiec, 2009; Rajchel <i>et al.</i> , 2007; Wiktorowicz, 2014)								
Ciechocinek (data in g L <sup>-1</sup> )	14.7–18.27	0.16–0.17	1.32–1.50	0.49	26.23–31.91	0.1–0.43	0.36–0.34	43.52–53.36
Cieplce	63–174	38–49	5–113	1–16	32–179	63–207	118–412	404–1035
Śląskie Zdrój								
Duszniki-Zdrój	292	90	401	139	75	52	2715	3924
Iwonicz (data in g L <sup>-1</sup> )	4.47–6.80	0.02–0.05	0.02–0.1	0.03–0.1	2.79–8.56	0–0.05	3.43–8.56	15.81–20.81
Łądek Zdrój	38–54	1	3–6	1	4–11	13–25	24–60	173–237
Uniejów	2267	22	139	24	3939	78	314	6825
Ustroń (data in g L <sup>-1</sup> )	30.5–32.1	0.55–0.78	10.07–11.03	2.78–3.06	74.24–78.02	0.42–0.47	0.08–0.1	12.0–12.61

\*The sum of concentrations (Na and K); \*\*Concentrations in mg kg<sup>-1</sup>.

are treated (Erfurt-Cooper and Cooper, 2009). Another French region known for thermal waters is the Côte-D'Azur with its thermal center formed by Barthemont-les-Bains, Digne-les-Bains, Greoux-les-Bains and Camoins-les-Bains. The best known thermal center in the Poitou-Charente region is La Roche-Posay (Dal, 2007).

Spain is a country where places with medicinal thermal waters have been used since pre-historic times as places of oracles, religious and pilgrim centers. The Romans and Arabs who occupied these areas centuries ago introduced and developed techniques of thermal water usage. Until 1996, Spain had 300 health resorts using balneotherapeutic treatments (thermalism), showers and natural peloids in therapy. The combination of sulfurous thermal water therapy with thalassotherapy is still used nowadays for curing skin diseases (psoriasis, atopic dermatitis, acne, etc.).

Sulfurous hot springs are used in 24 health resorts, the oldest being Panticosa (20–50°C), Archena (52°C) and Cuntis (22–58°C). These resorts were founded by the Romans and Panticosa, and is known to have been visited by emperors August and Tiberius. The first information about Cuntis comes from the late 17th century. La Toja is the most famous and regarded as the best health resort with thermal (37–60°C) brine in the country. Generally, there are about 22 spas using thermal saline waters and 29 using oligometalic thermal waters (Ledo, 1996).

Although they are the coldest in terms of climate, polar regions do not lack places with manifestations of geothermal energy. Particularly Alaska (mentioned among North American countries), Kamchatka (in NE Russia), Greenland and Iceland abound in hot springs. Among these regions, Iceland, lying in the mid-Atlantic rift area, has the amplest resources of geothermal energy and uses them in a variety of ways.

The most renowned tourist medicinal center in Iceland is the Blue Lagoon. The resort uses thermal waters cooled in the nearby power plant. Originally, the lagoon was used for bathing by local people, but in time a spa developed and it quickly gained popularity. Nowadays you can use a sauna, steam baths, hot waterfall massages and siliceous mud treatments there. The mean temperature of the water in the lagoon is 37°C (Ólafsson, 1996). A separate part of the infrastructure is the Health Clinic, offering special treatments based on thermal waters, silica and algae used in curing skin diseases, particularly psoriasis. It is part of a comprehensive therapy of skin diseases, unique in the world. In 2004, a similar center, Mývatn Nature Baths was opened in the northeastern part of the island. In 1996, a restored steam bathhouse was opened here, but it is likely that such bathhouses have existed in this area since the 13th century. In 2004, new facilities were made available. Like the Blue Lagoon, the resort uses power plant wastewater and offers hot and warm baths, steam baths and hotpots, which have a beneficial effect on skin. Icelandic patients have the treatment costs covered by their social insurance (Erfurt-Cooper and Cooper, 2009; Kristmannsdóttir, 2010).

According to Kristmannsdóttir and Björnsson (2003) and Kristmannsdóttir (2010), Icelandic balneology could use geothermal muds, clays and silica, not only from the Blue Lagoon. The authors find the areas in the southwest (towns Reykjanes, Svartsengi, Krisuvík and Hveragerði) and the northeast (Námafjall, Húsavík, Theistareykir, Krafla) of the island very promising for balneology. In 1955, a health clinic was opened in Hveragerði, where geothermal mud baths can bring relief from arthritis.

Near the small town of Stykkishólmur lying on the Snaefellsnes peninsula, highly mineralized thermal brines have been found and approved as medicinal (for treating psoriasis) to be used in drinking and bathing treatments (Kristmannsdóttir and Björnsson, 2003; Kristmannsdóttir *et al.*, 2005). Selected chemical parameters of Icelandic thermal waters are given in Table 13.14.

### 13.6 SPA, WELLNESS AND HEALTH RESORT ORGANIZATIONS

Regardless of the location of springs, their number, accessibility or tourist attractiveness, the development and functioning of a health resort or a spa center depends on the volume of thermal



Table 13.14. Physicochemical characteristics of thermal springs of Iceland (concentrations in mg L<sup>-1</sup> unless otherwise specified).

Location	Na	K	Ca	Mg	Cl	SO <sub>4</sub>	TDS	Temp. [°C]
Krafla	175–244	16–51	2–3.6	0	40–219	17–228	778–1580	205–280
Námafjall	113	18	0.6	0	45	25	1060	270
Theistareykir	118	24	0.5	0	106	9.3	1185	280
Húsavík	827	26.2	237	0	1760	83	3020	70
Öxarfjörður	949	46	178	0.3	1671	99	3136	116
Stykkishólmur	740	14.5	1170	0.5	2960	315	5430	86.7
Blue Lagoon*	9280	1560	1450	1.4	18500	38.6	31900	
max/min	7643	1117	1274	0.6	15740	31.8	25000	

\*In mg kg<sup>-1</sup>.

Source: Haraldsson and Cordero (2014), Kristmannsdóttir (2010), Kristmannsdóttir *et al.* (2005), Ólafsson (1996).

water resources. Therefore, in many countries, the exploitation and management of thermal waters is regulated by their own laws and regulations. The requirements to obtain appropriate licenses and often to establish protected zones around springs aim at preventing overexploitation, protecting the physicochemical properties and the bacteriological quality of waters. Furthermore, it ensures rational land management around springs. Below there are examples of organized global initiatives focused on wellness and fitness, in line with popular world trends. Initiatives focused on classic health resorts usually have a national/local range, for example, the Association of Polish Spa Communities (founded in 1991) or the Polish Spa Union (since 1998). In Germany, for example, there is a national association grouping wellness centers, the German Wellness Association (DWV), in France French Association for Balneotherapy Research (AFRETH, 2016), and in China – China Hot Spring Tourism Association (FEMTEC, 2016).

The growth of resorts and luxurious spa centers has contributed to the development of health tourism – a profitable branch of tourism industry. In 2000, a group of investors founded the Global Spa & Wellness Summit modeled on the World Economic Forum. It is an international organization grouping spa and wellness industry investors.

One of the initiatives of the Global Spa & Wellness Summit is the Global Hot Springs Initiative, aimed at studying the impact of different properties of geothermal waters on health, recreation and tourism. Members of the initiative have taken action to launch and develop cooperative global activities of investors in the health, tourism and recreation markets. The main objectives of the initiative include providing a forum for sharing practices from around the world, promotion of geothermal waters for ecotourism, building a global database of hot springs in order to enable industry contacts, developing a framework for global sustainable management of hot springs while preserving environmental values and educating potential consumers and communities about the additional values of hot springs.

The Global Spa & Wellness Summit (GSWS) website features the logo of hot springs, used in Japan for over 100 years. This symbol has spread to other countries, for example the USA, New Zealand, Australia and China. It can be downloaded from the GSWS website free of charge and used to mark hot springs in any country. Moreover, there are interactive ‘dials’, so far created for eight countries: Australia, France, India, Iran, Japan, Canada, New Zealand and the USA. Each dial shows a particular country with its hot spring locations. The arrows on a particular dial, going from the country in different directions, show the distance between hot springs in this country and hot springs all over the world. The names of springs have hyperlinks to their websites. Every country interested in the dissemination of information about their hot springs can provide data for generating such a dial. On the summit’s website, there is a list of spa associations and global hot springs organizations around the world, which includes a link to each association’s website (Global Wellness, 2014).



Figure 13.12. Hot springs universal logo (source: Global Wellness, 2014).

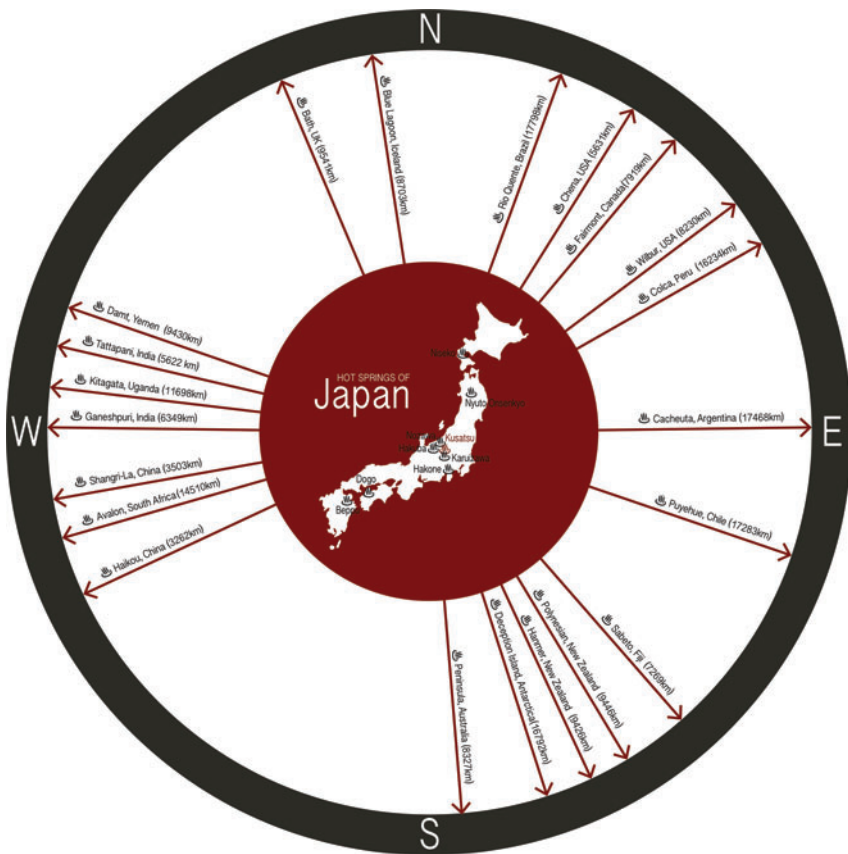


Figure 13.13. Interactive dial with the hot springs locations in Japan (source: Global Wellness, 2014).

In the early 1990s, the International Spa Association was formed. It has over 70 member countries now. The association focused on the promotion of spa centers and medicinal properties of mineral springs, as well as providing a forum to exchange experience among physicians, therapists, physiotherapists, dieticians and professionals in various areas of health tourism business. Part of the Association's activities is organizing international conferences and media meetings, enabling contacts and promotion of spas and health resorts. Annually, specialists from around the world present their experience and familiarize themselves with the recent spa products (EUROSPA, 2016).

In Europe, the European Spa Association (ESPA), grouping members from 19 countries, has been formed. The organization was established to promote European health resorts and balneotherapy and enable close cooperation between the members and better understanding of their common problems. The chief goals of the association are to analyze and monitor the condition of health resorts, sanatoriums and medical centers, exchange the experience and practices used in different centers, and to unify programs and training courses. The organization wants to enable the greatest possible number of people to make use of medicinal, thermal and mineral waters (EUROSPA, 2016).

With the aim of protecting the cultural heritage of old spas, particularly their architectural monuments, the European Historic Thermal Towns Association (EHTTA) was founded in 2009. The organization deals with issues like promoting historical European spas, obtaining financial support for their development and revitalization as well as conducting research and preparing analyses concerning the artistic and cultural heritage of spas (EHTTA, 2010).

The Balneology Association of Northern America (BANA) was established to support the research, education and information of natural mineral waters for health and wellness. The main objectives of the organization include recognizing natural and geothermal mineral waters as beneficial to health, promoting treatment of disorders and rehabilitation as well as preventive care and supporting the management of natural waters (BANA, 2016).

Similar professional organizations are, for example, World Federation of Hydrotherapy and Climatotherapy (FEMTEC) (FEMTEC, 2016), International Association of Medical Hydrology and Climatology (IAMHC, 2016), International Medical Geology Association (IMGA, 2016) and Center for Research in Medical Bioclimatology, Biotechnologies and Natural Medicine of Milan (NATURMED, 2016).

### 13.7 SUMMARY

The recent decades have brought large changes in resort treatment. The significance of baths for curing rheumatic and dermatologic diseases has grown. Baths are usually used alongside physical exercises, hydrotherapy or mud wraps. Steam baths, jacuzzis and saunas are becoming standard facilities in spa buildings, using heated and natural thermal waters. At the same time, the development of pharmacy and the form of a spa offering a wide range of health-promoting treatments have been replacing traditional balneotherapy.

Unlike in other parts of the world, the usage of thermal waters for medicinal purposes in European countries is enhanced by health resorts employing qualified medical staff cooperating with hospitals, university hospitals and research institutes. This certainly raises the prestige of health resorts. At the same time, limiting the financial resources allocated for health resort treatment (provided by the national health care of particular countries) reduces the interest in such treatment. The growing focus on relaxation, wellness and spiritual renewal, combined with medicinal traditions of health resorts are transforming them into multifunctional centers of broadly defined health renewal. Such a profile may discourage prospective visitors, particularly from older generations. The following examples of using thermal waters for curing various ailments and chronic diseases (Table 13.15) prove the essential need for further development of balneology and thermalism.

Table 13.15. Examples of using thermal waters for health treatments.

Country	Location and/or hot spring	Water temperature [°C]	Therapeutic use	Source
Argentina	Federaçion Thermal Spa	41	Digestive and respiratory systems, chronic rheumatism, vertebral arthritis, locomotive apparatus, skin	Erfurt-Cooper and Cooper (2009)
Belgium	Spa	30–34 (heated)	Rheumatism, arthritis, respiratory system, anemia	Erfurt-Cooper and Cooper (2009); Lund (2000c)
Bosnia and Herzegovina	Bihać/Gata	36	Rheumatism, neurological and neuromuscular diseases, skin illnesses, digestive system and gynecological problems, diseases and injuries of extremities	Operta and Hyseni (2013)
	Sanski Most/Tomina Ilidža	29	Rheumatism, stomach disorders, neurological disorders, diseases and injuries of extremities – sciatica	
	Banja Luka/Laktaši	30	Gastritis, kidney disease and urinary tract, eye illnesses, psychiatric and cardiovascular diseases	
	Banja Luka/Slatina	40.7	Rheumatic, urinary, neurological and cardiovascular illnesses	
	Ilidža Gradačac	28.3	Rheumatic, neurological diseases, injuries, diabetes, and gynecological ailments	
	Tuzla/Slana Banja	27	Rheumatism, injuries, respiratory illnesses, gynecological and neurological diseases, arteriosclerosis	
	Gračanica	37	Rheumatic disorders, mild forms of hypertension, disease of the stomach, liver and gall bladder, gynecological and skin diseases	
	Dvorovi/Bijeljina	56	Chronic rheumatism, diabetes, chronic gastritis, extremity injuries	
	Sarajevo/Ilidža	57	Rheumatism, diseases of the peripheral nervous system, the circulatory damage, gynecological and endocrine disorders, skin diseases	
	Fojnica	28.3	Rehabilitation, cardiac rehabilitation	

(continued)

Table 13.15. Continued.

Country	Location and/or hot spring	Water temperature [°C]	Therapeutic use	Source
Bulgaria	Olovo	34.5	Rheumatism, arthritis, spine problems, diseases of the central nervous system	Bojadgieva <i>et al.</i> (2002); Vassileva (1996)
	Višegrad Kjustendil	34.2 72–75	Rehabilitation Bone joints, peripheral nervous system, chronic lead poisoning, gynecological multifunction, osteoporosis, skin diseases, respiratory illnesses	
	Sapareva Banja	60–98 (103)	Musculoskeletal locomotor system diseases, gynecological disorders, musculoskeletal system, peripheral and central nervous system, bones, joints, skin, upper respiratory system, acute and chronic poisoning with salts of heavy metals	
	Sandanski	35–83	Musculoskeletal locomotor system diseases, peripheral nervous system, neuralgia, neuritis, digestive disorders, skin and allergic problems, kidney diseases, rheumatism, diseases of the respiratory system	Bojadgieva <i>et al.</i> (2002); InvestBulgaria (2014)
	Velingrad	20–95	Chronic respiratory system illnesses, musculoskeletal system, neurological diseases, peripheral and central nervous system, cardiovascular diseases, skin diseases (dermatitis, eczema, mycosis), orthopedic and post-injury conditions	
	Hisarja	27–52	Liver, kidney, digestive and gall bladder problems, prophylactic of osteoporosis, orthopedic problems	InvestBulgaria (2014)
	Bankja	33–36	Cardiovascular system diseases, nervous system, musculoskeletal system and metabolism ailments	

(continued)

Table 13.15. Continued.

Country	Location and/or hot spring	Water temperature [°C]	Therapeutic use	Source
Chile	Varshets	33–36	Ailments of musculoskeletal system, central nervous system, endocrine and metabolic diseases, cardiovascular diseases, kidney disease, rheumatic diseases	Bojadgieva <i>et al.</i> (2002)
	Narechen	23–31.2	Digestive system, nervous system, metabolic diseases, cardiovascular diseases, rehabilitation and post-stroke conditions, liver and biliary diseases	
	Hissar	37–49	Digestive system, metabolic diseases, neurological and musculoskeletal system	
	Devin	37–44	Nervous system, musculoskeletal system, post operational rehabilitation, aging prevention, osteoporosis, radioactive overdose exposure healing, overweight problems	
	Pavel Banya	50–54	Musculoskeletal system, orthopedic, trauma, central and peripheral nervous system, neurological diseases, gynecological	Hristov <i>et al.</i> (2010); InvestBulgaria (2014); Vassileva (1996)
	Haskovo	58	Sclerosis multiplex	
	Momin Prohod	64.2		Tsankov and Kamarashev (1996) GoChile (2014)
	Mamiña Hot Springs	45–57	Respiratory illnesses, neurological illnesses, nervous system, skin conditions, rheumatism, fatigue, sciatica	
	Puritama Hot Springs	33	Rheumatism, rheumatic illnesses	
	Socos Hot Springs	28	Combat tension, stress, metabolism problems	
Chile	Thermas del Flaco	73–96	Arthritis, rheumatism, respiratory ailments, rhinitis, sciatica, gout, gynecological ailments	
	Thermas de Colina	25–30	Arthritis, rheumatism, neuralgia, stress, respiratory illnesses, dermatitis, sinusitis	

(continued)

Table 13.15. Continued.

Country	Location and/or hot spring	Water temperature [°C]	Therapeutic use	Source
	Panimávida	32	Arthritis, rheumatism, gout, cardiovascular and respiratory ailments	
	Del Huife Hot Springs	38–58	Rheumatism, arthritis, skin diseases, hypertension, renal illnesses, exhaustion, stress	
	Aguas Calientes Hot Springs	57–75	Rheumatism, respiratory illnesses, arthritis, sciatica, neuralgia, gynecological ailments, skin conditions, nervous system illnesses	
	Termas de Chillán	70	Arthritis, skin diseases, respiratory illnesses	
	Del Amarillo	52	Rheumatism and rheumatic problems	
China	Huaqing	43	Skin illnesses, rheumatism, muscular pains, arthritis, relaxation	Erfurt-Cooper and Cooper (2009)
England	Bath	43–45		White (2000)
France	Royat Chamalières	22–37		EHTTA (2010)
	Le Mont-Dore	36–44	Peripheral blood circulation	Erfurt-Cooper and Cooper (2009); Lund (2000b)
	Aix-les-Bains	43–45	Rheumatism, neuralgia, allergy	
	Thermes de la Bourboule	45–56	Respiratory system, anti-stress treatments	
	Aix Les Thermes	77	Rheumatism, injuries, respiratory system, trauma, stress	Erfurt-Cooper and Cooper (2009)
Germany	Baden-Baden	52–68	Cardiovascular, rheumatic and joint complaints, metabolic disorders and respiratory conditions	Health Travel (2012); Sanner (2000); Knoblich (2002); Gutenbrunner and Hildebrandt (1998)
	Bad Füssing	28–56	Advanced preventive healthcare	Health Travel (2012); Gutenbrunner and Hildebrandt (1998)
	Bad Nauheim	33	Cardiovascular and pulmonary diseases, heart and circulatory diseases, hypertension and cardiovascular problems, rheumatism and disorders of the musculoskeletal system, skin diseases	Titzmann and Balda (1996); Health Travel (2012) Knoblich (2002); Gutenbrunner and Hildebrandt (1998)

(continued)

Table 13.15. Continued.

Country	Location and/or hot spring	Water temperature [°C]	Therapeutic use	Source
	Bad Driburg	32	Diseases of the joints and spine, rheumatic ailments, circulatory disorders, cardiovascular problems, diseases of the muscles and joints, after surgical procedures	Health Travel (2012)
	Bad Dürenheim	37	Joints and muscles, heart and circulation, skin regeneration	
	Bad Griesbach	30–60	Chronic inflammatory rheumatic diseases, chronic polyarthritis, ankylosing spondylitis	Bad Griesbach (2016); Health Travel (2012)
	Bad Harzburg	24–32	Stroke, traumatic brain injury, multiple sclerosis and other neurological disorders in the rehabilitation phase, orthopedic and rehabilitation	Bad Harzburg (2014) Health Travel (2012)
	Bad Krozingen	41	Cardiovascular system, diseases of the motion systems, nervous system, metabolic diseases, chronic skin diseases	Health Travel (2012); Gutenbrunner and Hildebrandt (1998)
	Bad Neuenahr-Ahrweiler	37		Gutenbrunner and Hildebrandt (1998)
	Bad Salzuflen	34	Respiratory conditions, musculoskeletal disease and skin disorders	Health Travel (2012)
	Bad Sassendorf	33	Musculoskeletal system and skin disease	
	Wiesbaden	67	Rheumatic and orthopedic diseases	Wiesbaden (2014); Health Travel (2012); Knoblich (2002); Gutenbrunner and Hildebrandt (1998)
				Katsambas and Antoniou (1996)
Greece	Ipati	33.5	Psoriasis, eczema, (various types), atopic dermatitis	
	Kammena Vourla	32.7	Psoriasis, eczema, (various types), atopic dermatitis	
	Kaiafa	34.6–35.6	Psoriasis, eczema, (various types), atopic dermatitis	
	Thermopyles	41	Psoriasis, eczema, (various types), atopic dermatitis	
	Methana	34.4	Psoriasis, eczema, (various types), atopic dermatitis	

(continued)



Table 13.15. Continued.

Country	Location and/or hot spring	Water temperature [°C]	Therapeutic use	Source
Iceland	Edipsos	33–86	Rheumatism, sciatica, gout, neuralgia, post-injury treatments, degenerative arthritis, back pain, neck pain, gynecological diseases, post-traumatic disorders, phlebitis, varicose veins	Edipsos (2014); Keleperstsis <i>et al.</i> (2009)
	Blue Lagoon	36–70	Skin diseases – psoriasis, eczema, disability or aging problems, rheumatism	Erfurt-Cooper and Cooper (2009); Kristmannsdóttir (2010); Kristmannsdóttir and Björnsson (2003); Ólafsson (1996)
	Hveragerði		Skin diseases – psoriasis, eczema, disability or aging problems, rheumatism	Kristmannsdóttir (2010); Ólafsson (1996)
India	Odisha/Taptapani	65–83	Rheumatism, skin disease	Bisht <i>et al.</i> (2011); Chandrasekharam (1999)
	Odisha/Atri	55–58	Alternative cures	Bisht <i>et al.</i> (2011)
	Bihar/Rajgir	45	Rheumatism, paralysis, dyspepsia, leucoderma, metabolic disorders	Chandrasekharam (1999); Bisht <i>et al.</i> (2011)
Iran	Madhya Pradesh/Anthoni	30–50 42	Skin diseases Rheumatism	Sarolkar (2005)
	Maharashtra/Rajapur	43–49	Leprosy, gout, goiter, paralysis	Bisht <i>et al.</i> (2011)
	Maharashtra/Vajreshwari	52–85	Goiter, paralysis	Patil and Unnikrishnan (2015)
	Maharashtra/Ganeshpuri			
	Qazvin	50.5	Rheumatism, neuralgia and circulation problems	Erfurt-Cooper and Cooper (2009)
	Bostan Abad	31.1	Rheumatism, arthritis and neuralgia	
	Sarein	36–44	Circulation disease	
	Semnan	24.8–38.5	Rheumatism, skin disease, neuralgia	
	Ahwaz	38.5	Skin disease	
	Dasht Kwir	44.3	Arthritis	
	Gorgon	30.7	Skin disease	
	Bam	46.3	Skin disease, arthritis	
	Yadz	26.5	Arthritis, neuralgia, circulation system	
	Iranshahr	43.7	Arthritis, neuralgia	
	Bandar	39.6–41	Arthritis, neuralgia, rheumatism, circulation system	

(continued)

Table 13.15. Continued.

Country	Location and/or hot spring	Water temperature [°C]	Therapeutic use	Source
Israel	Mahallat	29.8–45.6	Skin diseases, rheumatism, gout, kidney stone, foot pain, atherosclerosis, sinusitis, back pain, discopathy and digestive disorders	Moeini <i>et al.</i> (2014)
	Hammad Gader	20–42	Rheumatism, diseases of the joints and spine, muscular problems	Erfurt-Cooper and Cooper (2009); Wolf (1996)
	Tiberias Hot Spring	59–62	Rheumatic diseases, rheumatoid arthritis, osteoarthritis, skin disease	Wolf (1996)
	Hamei Yoav	39	No scientific studies on the effect of these waters	
Italy	En Noit	39	Skin disease, chronic constipation	Rosenthal (2001)
	Abano Terme	65–87	Acne, seborrheic dermatitis, eczema, respiratory, disorders	Carella and Sommaruga (2000); Erfurt-Cooper and Cooper (2009)
	Acireale	22	Acne, eczema	Carella and Sommaruga (2000)
	Bagni di Lucca	38–54	Seborrheic dermatitis, eczema	
	Bagni di San Filippo	52	Acne, psoriasis, atopic dermatitis	
	Casamicciola	30–72	Acne, seborrheic dermatitis	
	Comano	27	Psoriasis, urticaria	
	Poretta Terma	35	Seborrheic dermatitis, atopic dermatitis	
	Acqui Terme	50–75	Motor rehabilitation, arthrosis, peripheral vascular diseases	EHTTA (2010)
Japan	Beppu	50–100	Arthritis, bronchitis, and circulatory problems	Itallie and Hadley (2000); Taguchi <i>et al.</i> (1996)
	Jigoku Beppu	60	Gastrointestinal ailments, neuralgia, and rheumatism	Itallie and Hadley (2000)
	Prefecture Tochigi/Yumoto	59.8	Chronic dermatitis, eczema, neuralgia, diabetes, muscle and joint pain	Erfurt-Cooper and Cooper (2009)
Korea	Onyang Spa	56.4	Chronic skin illnesses, allergies, arthritis, hypertension and indigestion	Hann (1996)
	Bugok	76	Psoriasis, atopic dermatitis	
	Icheon Hot Springs	28–31	Relaxation, blood circulation, eye problems, arthritis, rejuvenation	Erfurt-Cooper and Cooper (2009)

(continued)

Table 13.15. Continued.

Country	Location and/or hot spring	Water temperature [°C]	Therapeutic use	Source
Macedonia	Kumanovo	31	Stomach, liver, kidney and urinary illnesses	Gorgieva and Popovski (2003)
	Katlanovo	40.5	Rheumatism, paralysis, neuralgia, diabetes, female and stomach illnesses	
	Banja	55	Rheumatism, skin and female illnesses, gall and urinal problems, muscle and joint pain	
	Kezovica	54–66	Ischias, rheumatism, female illnesses, skin problems	
	Bansko	73–75	Rheumatism, ischias	
	Negorci	38	Rheumatism, ischias, paralysis, neuralgia, female and skin illnesses	
	Debar	38.6	Rheumatism, ischias, eczema, diabetes, anemia, kidney and urinary illnesses	
Poland	Kosovrasti		Ischias, rheumatism, female problems	Dowgiałło and Fisteł (2003)
	Cieplice	22–87.8	Orthopedic and traumatic diseases, rheumatism, osteoporosis, kidney diseases and disorders of the nervous system	
	Lądek	20–45	Traumatic, orthopedic and rheumatologic diseases, and osteoporosis, nervous system, skin and gynecological problems	
	Iwonicz	25–26	Prevention, treatment and rehabilitation of rheumatic diseases, osteoporosis, skin diseases, digestive system, upper respiratory system, nervous system and gynecological diseases	
	Ciechocinek	28–35	Orthopedic and traumatic diseases, rheumatism, cardiovascular, nervous system disorders, peripheral vascular disease, upper respiratory system, diabetes, overweight, osteoporosis and gynecological illnesses	MZ (2016); Krawiec (2009)

(continued)

Table 13.15. Continued.

Country	Location and/or hot spring	Water temperature [°C]	Therapeutic use	Source
	Uniejów	60–70	Skin diseases, peripheral vascular disease, cardiovascular disease and hypertension, upper and lower respiratory system, nervous system diseases, orthopedic trauma, skin and rheumatism	MZ (2016); Dowgiałło (2007)
	Ustroń	20	Rheumatism and orthopedic diseases, osteoporosis disorders of the nervous system, cardiovascular disease and hypertension, peripheral vascular problems, upper and lower respiratory tract disease, diabetes, obesity	MZ (2016)
Switzerland	Baden	35–47	Relaxation	Erfurt-Cooper and Cooper (2009); Subtawewung <i>et al.</i> (2005)
	Schinznach	35–37	Physical therapy, rheumatism	Häring (2000)
Thailand	Ranong/Ban Phon Rang	32–99	Neurological system, skin and excretory conditions	
Turkey	Balçova Thermal Resort	62–80	Rheumatic diseases, digestive maladies, post-injury and postoperative problems, metabolic disorders	Dal (2007)
	İzmir/Çeşme	56	Rheumatic, dermatological, and gynecological diseases	Mutlu and Güleç (1998)
	Denizli/Pamukkale	42–59	Rheumatic, dermatological and neurological ailments, physical exhaustion, nutritional disorders, gynecological diseases, digestive maladies	Dal (2007); Erfurt-Cooper and Cooper (2009); Mutlu and Güleç (1998)
	Muğla/Rıza Çavuş Thermal Baths	35	Rheumatism, dermatological and gynecological diseases, neurological diseases, neurological and physical exhaustion	

(continued)

Table 13.15. Continued.

Country	Location and/or hot spring	Water temperature [°C]	Therapeutic use	Source
United States	Sivas/Kangal Hot Springs	35	Skin diseases, rheumatism, and neurological disorders	Özçelik and Akyol (2011)
	Kozaklı	42–93		Azakli (2012); Mutlu and Güleç (1998)
	Bursa/Çekirge Hot Springs	39–58	Rheumatism, metabolic disorders, postoperative problems, gynecological diseases, bladder and hepatic metabolic disorders	Erfurt-Cooper and Cooper (2009)
	Yalova Hot Springs	57–66	Rheumatism, metabolic disorders, neurological disorders, digestive problems	Erfurt-Cooper and Cooper (2009); Mutlu and Güleç (1998)
	Arkansas/Hot Spring National Park	61	Rheumatism, skin diseases, rehabilitation, arthritis, general injuries	Benedetto and Millikan (1996); Josayma (2014); Lund (1996)
	Georgia/Warm Springs	31	Polio, rehabilitation, arthritis, rheumatism, neuralgia, skin disorders (acne, psoriasis, eczema, shingles)	Lund (1996); Lund (2000a)
	Wyoming/Thermopolis	22–56	Arthritis, rheumatism, stroke, head and spinal injury, bedsores, chronic pain management	Erfurt-Cooper and Cooper (2009); Josayma (2014); Lund (1996, 2000a, 2005)
	California/Calistoga	77–100	Pain and arthritis	Lund (1996, 2005); Poux <i>et al.</i> (2012)
	Virginia/Hot Springs	30–41		Benedetto and Millikan (1996); Lund (1996)
	New York State/Saratoga	37 (heated)	Skin disorders, digestive problems	
Western Cape	New Mexico/Ojo Caliente	25–54	Arthritis, digestive problems, skin problems, blood and immune system disorders	OJO (2016); Sophy and Kelley (2014); Vuataz <i>et al.</i> (1983)
	Alaska/Chena Hot Spring	43–94	Psoriasis, muscular pains, arthritis, circulatory disorders, bronchial disorders	Lund (2006); Erkan <i>et al.</i> (2007)
	Limpopo/Warmbaths	52–60	Chronic rheumatism, arthritis, skin diseases	Boekstein (2014a); Olivier <i>et al.</i> (2008)
	Mpumalanga/Badplaas	50	Chronic rheumatism, arthritis, skin diseases	Yibas <i>et al.</i> (2011)

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## CHAPTER 14

### The importance of an integrated analytic approach to the study of physicochemical characteristics of natural thermal waters used for pelotherapy aims: perspectives for reusing cooled thermal waters for treatments related to thermalism applications

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#### 14.1 INTRODUCTION

The integrated study of complex materials intended as non-homogeneous matrices (Demortier, 1999) containing elements having a different nature and concentrations, give a broad view of liquid and solid complex systems. Complex systems can be defined as systems with numerous components and interconnections, interactions or interdependencies that often are difficult to describe, understand, predict, manage, design, and/or change (Magee and De Weck, 2004). For this reason, the nature of the phenomena that govern the ‘life’ of any complex system must be investigated from the viewpoint of volume element-structure-surface correlations. The analyses of volume elements of a complex system are destructive and give information about its qualitative-quantitative profile through the separation, identification, and quantification of the chemical components of natural and artificial materials. (Holler *et al.*, 1996). It’s also necessary to consider that in the ‘use chain’ of water some ‘hidden’ factors – typical of the water – may intervene: alteration of the ionic balance, abundance of oxygen with related oxidative processes, development of conditions suitable to bacteria colonies growth, a different spatial positioning of the elementary particles looking for new energy balances. The analyses of the structure establish the relationship between the geometrical effects inducted from the application of applied forces (rheologic properties) and the molecular structure of a complex system in relation to the intermolecular interactions (Malkin and Isayev, 2006). The study of the surface energy profile of a complex system is a non-invasive analytical approach and represents an important criterion for the evaluation of adhesion properties of solid polymers (Żenkiewicz, 2007). Surface energy represents the external reflex of the forces acting inside the system and change on the base of the modifications that occur in the time. The Surface Free Energy (SFE) ( $\text{mN m}^{-1}$ ) and its polar (PC) and dispersed components (DC) can be determined through the measurement of contact angles (CA),  $\varphi$ , expressed as degrees of arc (deg), of a liquid onto a complex system’s surface (Fig. 14.1) and their mathematical conversion in SFE ( $\text{mN m}^{-1}$ ), DC ( $\text{mN m}^{-1}$ ) and PC ( $\text{mN m}^{-1}$ ) operated by specific mathematical models such as that of Owens-Wendt-Rable-Kaelble (OWRK) (Owens and Wendt, 1969).

The analyses of CA can be performed by a tensiometer, an instrument constituted by a light source, camera, support for the samples or solid tests, and a syringe containing liquid samples or tests positioned on an arm (Fig. 14.2). The liquid’s drop is produced pushing the syringe and leaving the drop on the sample. The image of the drop is captured by the camera and lit by the source. After the photo snap, the software calculates CA measured at solid/liquid interface. Contact analyses measurements were performed at temperature range of 20–25°C.

Since 2005 the Permanent Thermal Observatory – (PTO) (*Osservatorio Termale Permanente – OTP*) at the Department of Pharmaceutical Sciences of University of Padova (today Department of Pharmaceutical and Pharmacological Sciences) had developed new tensiometric models for the tensiometric characterization of different natural complex matrices, such as wood (Rossi *et al.*,

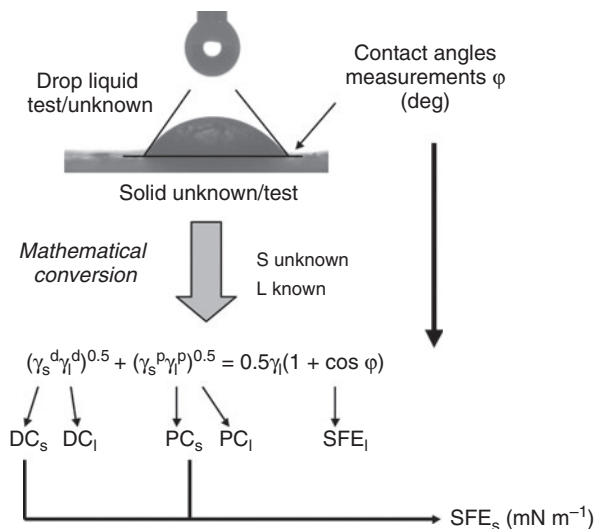


Figure 14.1. Camera image of a drop onto surface of complex matrix, contact angles at the liquid (l)/solid(s) interface and OWRK mathematical (deg into  $\text{mN m}^{-1}$ ) conversion model.

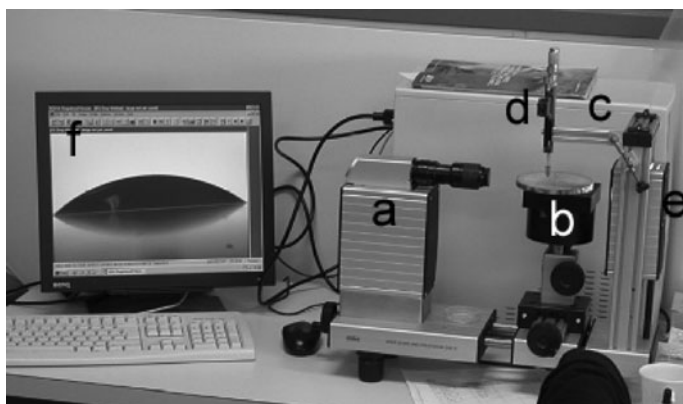


Figure 14.2. Tensiometer model DSA 10 (Krüss, Hamburg, Germany) in the Université du Québec à Chicoutimi, Canada constituted by: (a) camera body; (b) samples' support device; (c) arm; (d) syringe filled with liquid test; (e) light source; (f) drop freeze image.

2012a), coffee (Rossi *et al.*, 2012b) and, in particular, Euganean Thermal Muds (ETM) (Rossi *et al.*, 2013).

## 14.2 APPLICATION OF THE INTEGRATED ANALYTICAL APPROACH AND TENSIOMETRY ON THERMALISM

### 14.2.1 Two contrasting thermal water systems

To illustrate the capabilities and needs of an integrated research approach for raw and reused thermal water study and management, thermal waters from two systems were chosen, Euganei Hills (Veneto Region, Italy) and Jelenia Góra Valley (Sudetes Mountains, Poland) (Fig. 14.3).



Figure 14.3. Location of studied geothermal systems of Euganei Hills (Italy) and Jelenia Góra Valley (Poland).

Thermal waters of these areas differ in terms of chemical composition and scale of their use. In the Jelenia Góra Valley (Poland) are recently recognized new thermal waters, which enable efficient use by the introduction of the innovative approach proposed in this work.

#### 14.2.1.1 *Euganean geothermal system (Veneto region, Italy)*

Thermal water is considered to be a natural complex system composed of bioinorganic constituents. Generally, the chemical pattern of thermal groundwater varies significantly depending on the geological and hydrogeological settings. The Euganean Thermal Basin (ETB) (also named Euganean Thermal Area – ETA) is the most important thermal field in northern Italy. It is located in the Veneto alluvial plain, south-west of Padua, close to the north-eastern edge of the Euganean Hills (Farina, 2013). Abano Terme is the largest town of the ETB (which includes a few other smaller towns) and is one of the most important thermalism and mud-therapeutic resorts in the world. Its very well-structured hotel system offers hospitality to more than 250,000 tourists every year. Almost every hotel and thermal spa owns a well to extract thermal water at a temperature

in the range 60–87°C from the fractured carbonatic bedrock found primarily at a depth of about 150–200 m and now reaching 800 m. The ETB can be classified as a hydrothermal convection system, where the water represents the dominant phase (Antonelli *et al.*, 1995). At present about 250 drilling wells are active and the total average extraction flow rate of thermal fluids is about 17 million m<sup>3</sup> year<sup>-1</sup>. These fluids are exclusively used for sanitary purposes, as imposed by the current legislation.

Physical and chemical parameters of the Euganean thermal waters have been extensively analyzed mainly with statistical methods: temperature ranges from 60–87°C (80–87°C where the heat flux is more pronounced), and this temperature remains practically constant up to the bottom holes, confirming the presence of a system ‘with a high up flow rate’. The total dissolved solids are 6 g L<sup>-1</sup> with a primary presence of Cl and Na (70%) and secondary presence of SO<sub>4</sub>, Ca, Mg, HCO<sub>3</sub>, SiO<sub>2</sub>. Tritium (<sup>3</sup>H) and radiocarbon (<sup>14</sup>C) measurements suggest a residence time greater than 60 years, probably a few thousand years. The analyses of the oxygen isotopes show that the thermal waters are of meteoric origin and recharge the groundwater system at altitudes of about 1500 m above sea level (a.s.l.) in the South Fore-Alps (Pola, 2011). The rainwater infiltrates the South Fore-Alps and reaches depths of 3000–4000 m, is warmed up by the normal geothermal gradient and circulates towards the SE, flowing through the hills complex formed by the Lessini, Berici and Euganean Hills (Piccoli *et al.*, 1976). The lower limit of the water circulation system is represented by the Permian crystalline-schist bed and is conditioned by the regional structural shape (Gestione Unica del Bacino Idrominerario Omogeneo dei Colli Euganei – BIOCE).

In 2010, the Euganean geothermal circuit was reviewed starting from the lower part of it. A collection of seismic sections near Padova highlights a new architecture of the regional Schio-Vicenza fault and a system of normal faults (Schio-Vicenza faults system – SVFS) and buried beneath the alluvial cover. In the Abano Terme area, there is existence of a step-over structure (extensional relay zone) left between segments of the SVFS. Given the Neogene to Quaternary sinistral strike-slip kinematics superimposed on the fault system, this structure has accommodated along-strike local extension and may be responsible for rock fracturing and permeability development, enhancing migration to the surface of thermal waters. The presence of a hill of travertine, 5 m in height, in Abano Terme called Montirone, strongly supports the existence of: (i) a releasing structure in the subsurface which controls the development of the Euganean Geothermal Field (EGF), and (ii) ongoing activity of the Schio-Vicenza fault that keeps the opening of the fracture steady and enhances the outflow of thermal waters. The thermal circuit is located east to the Schio-Vicenza fault instead of west as in the previous model. The medium part of the main segment of the Schio-Vicenza fault acts as a conduit for the hot waters thanks to higher permeability of the damage zone. Moving to the north from the EGF, one finds large outcrop of upper Triassic dolomite formations which form the main thermal aquifer in the Abano area. This area is the Sette Comuni plateau area and it is also the recharge zone of the proposed conceptual model of the EGF. The altitudes of the recharge zone (from 1000 to 2036 m a.s.l.) are delimited on the basis of the oxygen-isotopic composition of the thermal waters. The waters infiltrate thanks to the high secondary permeability of the outcropping rocks and flow to the south in the carbonate reservoir (composed mainly of the Dolomia Principale formation), reach a depth of about 3000 m and warm up by a normal geothermal gradient. The cross section of the thermal circuit is constructed using the stratigraphy of deep wells (Villaverla 1 and Vicenza 1 in the northern part, Due Torri in Abano) and using a composition of seismic sections and geophysical data.

#### *The Montirone hill*

Until the sixties, the main natural occurrences of the outflow in Abano Terme were located on the top of a 5 m high hill of travertine, called Montirone (Pola, 2011). At present, the travertine hill is used as a public park. The hill is affected by a network of fractures mainly composed of two fracture sets NW–SE and NNE–SSW, which allows us to refer to the travertine deposit as a fissure ridge. These structures have been studied in the tectonically active regions of Turkey (Anatolia), Greece (Euboea Island), the USA (California) and Italy (Tuscany), showing typical features and providing significant information about stress orientation during travertine deposition. The trend

of the fissures (NW–SE) parallels the trend of the main structural elements of the region and is comparable with the direction depicted in the variogram analysis of transmissivity in the EGF area. It suggests that the fissure ridge is localized above an extensional fissure or in the hanging wall of a transtensional fault cutting the bedrock lying about 150 m beneath the alluvial cover. The sets of fissure could be interpreted as a fault/fracture mesh located in the overlap zone of two sinistral strike-slip faults. The main direction (N 115) represents the main fracture in the fault/fracture mesh model and is affected by an extensional regime that opens the fracture. Two other sets of fractures (N 15 and N 135) represent the secondary fractures of the model and are affected by a transtensional regime. Preliminary geophysical analyses using electromagnetic techniques showed areas with higher resistivity near the main fissure and where the travertine crops out, showing a possible NW–SE direction of the higher resistivity anomalies.

#### 14.2.1.2 Jelenia Góra geothermal system (the Sudetes Mountains, Poland)

In the Sudetes Mountains (SW Poland) thermal waters are reported only in a few sites located in two areas, in Kłodzko Land (E Sudetes) and Jelenia Góra Valley (W Sudetes). In the latter area thermal waters are known and have been used for therapy in Cieplice since the beginning of the 13th century. At present, Cieplice health resort is a part of Jelenia Góra town. Thermal waters in Jelenia Góra region (Ciężkowski, 1990; Ciężkowski *et al.*, 1992; Dowgiałło and Fistek, 1995) were recognized until recently only in the Cieplice Spa and its nearby surroundings. The very recent hydrogeological investigations (in 2013/14) documented thermal waters in two new sites, Karpniki and Staniszków, both located several kilometers east of Cieplice (Wektor Inwestycje Ltd., 2014; Termy Staniszków Ltd., 2014).

Thermal waters of the Jelenia Góra Geothermal Area (JGA) occur in carboniferous granitoids of the Karkonosze massif. Granitoids build the crystalline basement of the Jelenia Góra Valley and the Karkonosze Mountains range which limits the Jelenia Góra Valley from the south (Fig. 14.3). The Jelenia Góra Valley is cordoned by mountain ranges also from the west, the north, and the east, by the Izera Mountains, Kaczawa Mountains and Rudawy Janowickie Mountains, respectively. These three mountain ranges are mostly built of metamorphic, and partly sedimentary and magmatic, rocks.

Thermal waters occur in the deeper part of fissured granitoid aquifer, and their circulation is determined by the geometry of faults and tectonic zones in granitoid and its envelope rocks. Fresh, cold groundwater occurs in the shallower part of the hydrogeological system, in the thin cover of Quaternary (mainly alluvial and diluvial) porous deposits, regolith and in strongly fractured – the uppermost part of – granitoids. Thermal waters of deep circulation, which naturally ascend along tectonic zones, mix with fresh cold groundwater and are finally discharged by the main local receiver (the Bóbr River) and its tributaries.

Studies of stable oxygen and hydrogen isotopes have confirmed that JGA thermal waters are of meteoric origin. The precise ‘age’ of JGA thermal waters at particular water intakes varies and is still a subject of debate. Thermal waters of deeper boreholes (750–2002 m) are either radiocarbon-free, or contain only about 1.0–5.5 pmC of  $^{14}\text{C}$ , which suggests pre-Holocene radiocarbon age, even exceeding 35 ka. Shallower boreholes and cased springs provide old thermal water mixed partly with fresh modern tritium-containing groundwater. The exception in JGA is the thermal water of Sobieski intake, which is likely 100% modern water (Ciężkowski *et al.*, 1996).

The O and H stable isotopes composition ( $\delta^{18}\text{O}$  from  $-10.2$  to  $-10.5\text{‰}$ ;  $\delta^2\text{H}$  from  $-71$  to  $-74\text{‰}$ ) of JGA thermal waters is lighter than modern infiltration-originated groundwater in the Sudetes, which results from both altitude and climatic effects. However, because of the apparent pre-Holocene age of most JGA thermal waters ( $^{14}\text{C}$  activity varies between 0 and 5.5 pmC), the climatic effect is assumed to play a stronger impact. The modern Sobieski water has O and H isotopic composition ( $\delta^{18}\text{O}$  from 9.7 to 9.85‰;  $\delta^2\text{H}$  from 68.0 to 69.7‰) very close to present-day meteoric water in the area. Based on environmental tracer studies and altitude curves for stable O and H isotopes, the inferred recharge zones were indicated in the mountain ranges to the south and west of the Jelenia Góra Valley. Thermal waters in the Jelenia Góra geothermal system from two deepest boreholes (C-1 and C-2 wells) are tritium-free. Thermal waters from



a few shallow intakes present a mixture of low-enthalpy modern tritium-containing water with older tritium-free thermal water components. Only 100% modern water from the Sobieski intake showed high tritium activity, which allowed for the estimation of mean transit time of water at about 5 years using lumped parameter models. Currently the prevailing view is that pre-Holocene thermal waters in the JGA system were recharged by infiltration mainly at Rudawy Janowickie Mountains, at altitudes of about 700–800 m a.s.l., whereas the modern Sobieski thermal water is related to the small subsystem probably recharged on the slopes of the Karkonosze Mountains, at about 550–750 m a.s.l. (Ciężkowski *et al.*, 1996).

For the purposes of this study only the latest available chemical data on thermal water composition have been used, i.e. for Cieplice water samples taken and analyzed by authors in 2014, and for Karpniki and Stanisław sites analyses of water samples obtained during pumping tests in 2013/2014 (Wektor Inwestycje Ltd., 2014; Termy Stanisław Ltd., 2014).

#### *Thermal water of Cieplice health resort*

In Cieplice resort thermal waters are presently exploited in seven intakes. Two of them are deep boreholes (C-1 well, 2002 m depth; C-2 well, 750 m), which provide water of the highest temperatures ( $\sim 78^\circ\text{C}$  and  $\sim 59^\circ\text{C}$ , respectively) in Cieplice. When drilling spontaneous outflow of water in C-2 well,  $68^\circ\text{C}$  was obtained maximally, and in C-1 well temperatures of  $88^\circ\text{C}$  at outflow and  $97.7^\circ\text{C}$  in the depth of the borehole were recorded (Dowgiało, 2000). Other water intakes in Cieplice are cased springs or shallow wells of the depth ranges between 5.2–52.3 m. Temperature of water from shallower intakes is lower than from deep boreholes – due to the effect of mixing with shallow fresh cold groundwater – and usually varies between  $22$ – $42^\circ\text{C}$ . Various geothermometer approaches applied on Cieplice thermal waters indicated that maximum temperature in the Jelenia Góra geothermal aquifer might exceed  $100^\circ\text{C}$  (Dowgiało, 2000; Dowgiało *et al.*, 2005; Dobrzyński and Leśniak, 2010).

The thermal waters of Cieplice show low content of total dissolved solids (TDS between  $590$ – $850\text{ mg L}^{-1}$ ). In terms of chemistry, most of Cieplice's thermal waters have a composition dominated by sulfates, bicarbonates and sodium ( $\text{SO}_4\text{-HCO}_3\text{-Na}$  hydrochemical type) with increased content of silicic acid, fluorides and boron. In Poland, silicic acid is regarded as an important component which provides therapeutic profits in medical use of balneology. Cieplice thermal medicinal waters are among the few medicinal waters in Poland which have silicic acid concentration above the pharmacodynamic threshold value ( $70\text{ mg L}^{-1}$  as  $\text{H}_2\text{SiO}_3$ ). The water of Sobieski intake differs from other Cieplice waters, manifests slightly higher TDS, and is of  $\text{HCO}_3\text{-SO}_4\text{-Cl-Na-Ca}$  type. The Sobieski water also presents a higher concentration of most trace elements than other Cieplice waters. The chemistry and temperature of waters exploited in shallow intakes of Cieplice (except Sobieski) is the result of the mixing of two components; older thermal water with modern cold water.

In the Cieplice health resort there are 640 beds in sanatoriums, and about 1800 beds in hotels and guesthouses of Jelenia Góra town. Ten thousand patients benefited from treatments in resort sanatoriums and hospitals in 2014. In the Cieplice resort about 150,000 cubic meters of thermal water is used yearly for drinking, bath cures and treatments, recreation bathing in therms, and for heating. After being used for treatment the heated thermal water is discharged into the sewerage system or directly to surface water receivers.

#### *Thermal waters of Karpniki and Stanisław sites*

Newly drilled deep boreholes in Karpniki (KT-1 well, 1997 m) and Stanisław (ST-1 well, 1501 m) revealed thermal waters of chemical composition generally similar to the Cieplice thermal waters, with a temperature of  $54^\circ\text{C}$  and  $37^\circ\text{C}$  at outflow, respectively. Water in Karpniki has TDS of  $490$ – $515\text{ mg L}^{-1}$ , pH about 8.2–8.3, and composition dominated by  $\text{HCO}_3$ ,  $\text{SO}_4$  and Na. It also contains increased concentrations of fluorides and silicic acid. Water in Stanisław presents TDS of  $470$ – $610\text{ mg L}^{-1}$ , pH of 8.30–8.46, and chemistry controlled by  $\text{HCO}_3$ ,  $\text{SO}_4$ , Cl and Na. Among secondary components the increased concentration of silicic acid ( $14.6$ – $30.0\text{ mg L}^{-1}$

of Si), and fluorides ( $10.1\text{--}16.0\text{ mg L}^{-1}$ ), as well as  $\text{H}_2\text{S}$  ( $0.1\text{--}3.85\text{ mg L}^{-1}$  of  $\text{S}^{2-}$ ) and radon ( $116\text{--}290\text{ Bq L}^{-1}$ ) might be highlighted.

Stable oxygen and hydrogen isotopes confirm the meteoric origin of both waters, and infiltration at climatic conditions cooler than at present. Waters are tritium-free and almost radiocarbon-free ( $0\text{--}5.5\text{ pmC}$  of  $^{14}\text{C}$ ) which argues their pre-Holocene age (Wektor Inwestycje Ltd., 2014; Temy Stanisław Ltd., 2014).

Both deep boreholes are part of the infrastructure in hotel and thermalism centers. At present thermal waters are abstracted for heating, but the use of water for thermalism and recreation activities is planned relatively soon. The thermal waters of Karpniki-Stanisław also have therapeutic potential resulting from the presence of components which are beneficial and/or essential for human health, like silicic acid and fluorides. Waters rich in silicic acid have therapeutic and health-promoting potential (Dobrzyński and Exley, 2010) which creates very good prospects for using the newly found thermal water in Karpniki and Stanisław.

Hydrogeological conditions in the upper part of granitoid in Karpniki and Stanisław sites have not allowed to pump used thermal water into the bedrock. After cooling, used low-mineralized HSW will be discharged to the local watercourses.

Comparing groundwater data from Cieplice and new boreholes (in Karpniki and Stanisław) demonstrates that the Jelenia Góra geothermal system should be treated as a highly mosaic one where thermal water quality and quantity are governed mainly by tectonic and lithologic heterogeneity. Tectonic recognition of the Jelenia Góra Valley still seems to be insufficient.

#### 14.2.2 Chemical and biological characteristics of studied thermal waters

##### 14.2.2.1 Photosynthetic microorganisms of Euganean thermal waters

The chemical characteristics of Euganean thermal waters and the environmental pH of  $6.8\text{--}7.0$  allow the development of different photoautotrophic microorganisms that easily adapt themselves in different environmental conditions. The first investigated cyanobacterium of the Euganean thermal waters, belongs to the genus *Phormidium* and was identified by molecular analyses as *Phormidium* sp. ETS-05 (Ceschi Berrini *et al.*, 2004). This cyanobacterium, isolated from the thermal muds of Abano Terme, is able to produce glycolipids and sulfoglycolipids with anti-inflammatory action higher or similar to that of traditional substances like indometacin or betametazone and characterized by the absence of toxic effects. This finding led to a patent issued by the European Patent Office (EPO) (Lalli *et al.*, 2005). Another coccoid cyanobacterium, isolated from the biological mats growing on the mud surface, is a new species of the genus *Cyanobacterium*, *C. aponinum* (Moro *et al.*, 2007a). Analysis carried out on cultures of this cyanobacterium, maintained at different temperatures, demonstrated that *Cyanobacterium aponinum* grew at temperatures in a range of about  $20\text{--}40^\circ\text{C}$ . Moreover, a further cyanobacterium living in the Euganean thermal springs is a filamentous cyanobacterium growing in the mud maturation tanks at temperatures ranging from  $20\text{--}59^\circ\text{C}$ . This cyanobacterium is morphologically similar to species of the genus *Leptolyngbya*, but phylogenetic analyses allowed its recognition, named with the acronym ETS-08, as a member of a new group of the family *Pseudanabaenaceae* (Moro *et al.*, 2010). Finally, another cyanobacterium found in the mats covering the thermal muds of the Euganean Thermal Area is a filamentous strain, which was characterized by a polyphasic approach. Morphological, ultrastructural and molecular results allowed a more precise taxonomic identification of this cyanobacterium, ascribing it to the genus *Oscillatoria*. On the basis of the cyanobacterium taxonomy, the name suggested for this organism was *Oscillatoria duplisecta* (Moro *et al.*, 2007b).

In addition to cyanobacterial species living in the thermal muds of the Euganean Thermal Area, another group of microorganisms representing the biological constituents of the Euganean thermal waters is represented by diatoms (Tolomio *et al.*, 2004). In particular, among the diatoms an investigated taxon living in this environment is *Navicula veneta* (Moro *et al.*, 2010).

The presence of these microorganisms – particularly interesting due to the above-mentioned – makes possible the presence of other organic life forms. Even if not pathogenic, the related

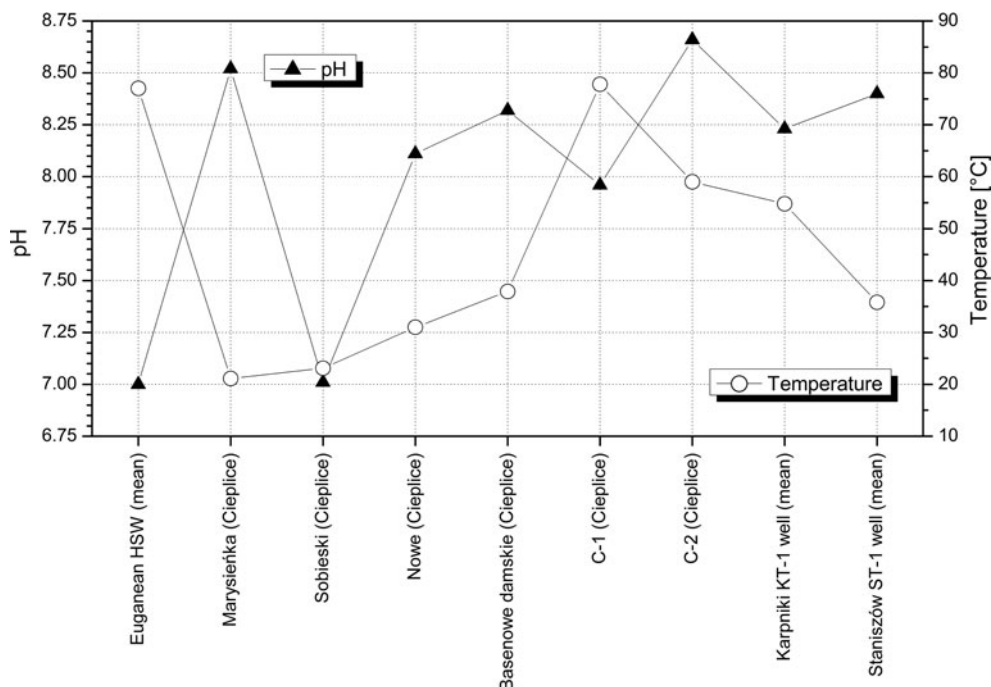


Figure 14.4. Comparison between pH and temperature of thermal waters from Jelenia Góra (Poland) and Euganean (Italy) thermal areas.

amount of colony forming units (CFU) could be a cultural medium for the birth and development of species that are potentially pathogenic. This depends on environmental factors and technology used for mud therapies. The conditions of sanitary risk can be avoided through proper periodical checks and additional attention to the technological aspects and the quality of installed materials.

#### 14.2.2.2 Temperature and pH of thermal waters

The pH levels of thermal waters are determined by the origin and amount of water available, as well as the concentration of volcanic gases such as  $\text{H}_2\text{S}$ . The pH levels also depend on the temperature. As an example, in sulfide-rich hot springs at  $70^\circ\text{C}$ , the acid is washed away, so pH stabilizes at 6. In alkaline thermal waters, the  $\text{H}_2\text{S}$  contained at the source is lower so chemical compounds such as  $\text{HCO}_3^-/\text{CO}_3^{2-}$  and  $\text{SiO}_2$  take the pH to 7–10 (Stan-Lotter and Fendrihan, 2012). Thermoacidophily and thermoalkalophily reflect the adaptability of biologic species at the base of the maturation process. The temperature range of Euganean thermal waters at source is about  $60\text{--}87^\circ\text{C}$  and the pH is generally between 6.8 and 7, although pH 8 represents the upper limit for all thermal waters of Euganean Thermal Area ( $\text{pH} < 8$ ) (Gherardi *et al.*, 2000). Figure 14.4 shows a comparison between pH and temperature of Euganean and Jelenia Góra (Cieplce and Karpniki-Staniszów) thermal waters measured at source.

Figure 14.4 shows that pH levels of Cieplce's thermal waters appear higher than Euganean ones ( $\text{pH} < 8$ ) except for Sobieski (Cieplce) and C-1 (Cieplce). The temperature range revealed in the Cieplce thermal waters is about  $20\text{--}80^\circ\text{C}$ , but only C-1 Cieplce water samples ( $77.8^\circ\text{C}$ ) is comparable with Euganean thermal waters at the source ( $77.1^\circ\text{C}$ ). Figure 14.4 shows also a comparison between pH levels and temperature at source of the Karpniki-Staniszów and Euganean thermal waters. As shown in Figure 14.4, the levels of pH of Karpniki-Staniszów thermal waters ( $\text{pH} > 8$ ) are higher than Euganean thermal waters (Gherardi *et al.*, 2000), while their temperature range is between  $35.8 (\pm 2.3)$  and  $54.8 (\pm 1.3)^\circ\text{C}$ . As the variation of temperature influence

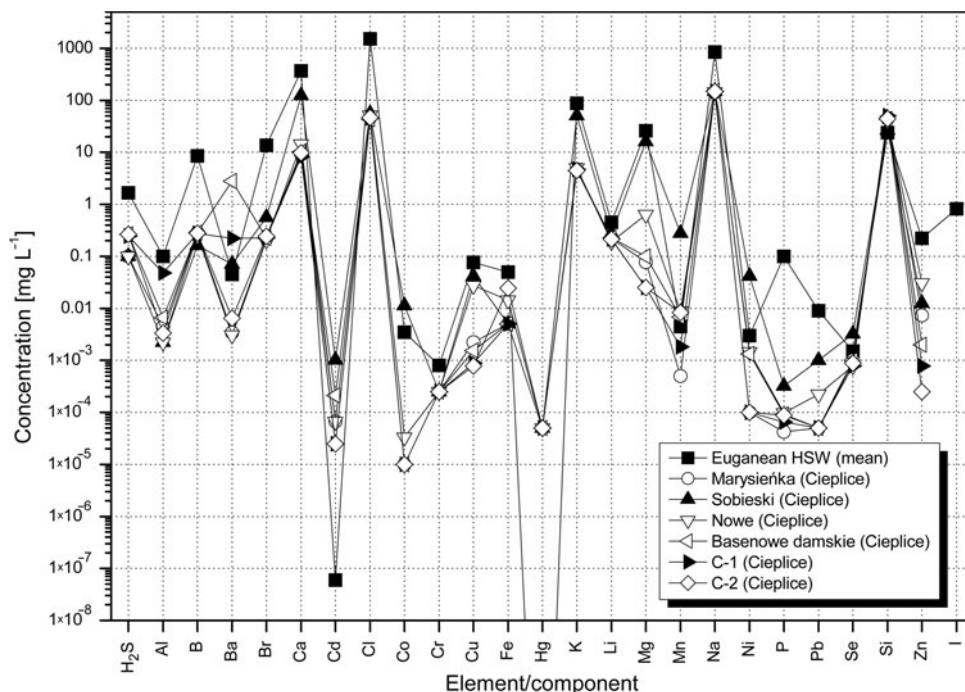


Figure 14.5. Comparison between chemistry of thermal waters from Cieplce health resort (Poland) and Euganean Thermal Area (Italy).

ions concentration shifts reflecting the behavior of pH levels, in thermal waters the equilibrium concentration of individual aqueous species as  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  can be expressed as a function of pH, highlighting its link with the temperature that in this case influences the mineral deposition of  $\text{CaCO}_3$ . Figure 14.4 shows clearly the correlation between different temperatures of thermal waters and their pH levels in function of the ions concentrations of the samples.

#### 14.2.2.3 Chemical characteristics of studied thermal waters

Chemical types and mineralization of geothermal waters reflect the geochemical processes of water-rock interaction and dissolution of minerals in the presence of  $\text{CO}_2$ , sulfurs, chlorine compounds and fluids with unsaturated gaseous element, and reflect the chemical component of rocks in which waters circulate. Hydrothermal systems are classified as two end-member types, acid-sulfate and neutral-chloride based on mineralogy and solution geochemistry (Phillips-Lander *et al.*, 2015). Neutral-chloride springs are silica-dominated and associated with near-neutral pH (6–8) waters rich in Na, Cl,  $\text{CO}_3^{2-}$ , and minor  $\text{H}_2\text{S}$ . In contrast, acid-sulfate spring mineralogy typically consists of mixed-layer smectites, nontronite, kaolinite, amorphous silica, Fe-oxides/-oxyhydroxysulfates and jarosite.

Figure 14.5 shows a comparison between some chemical parameters measured in thermal waters samples collected from the six sources in Cieplce and from the Euganean thermal areas (Gherardi *et al.*, 2000; Roghel, 2006).

Figure 14.6 shows a comparison between chemical parameters related to thermal waters of Karpniki-Stanisław thermal sites and thermal waters from the Euganean Thermal Area.

Figure 14.5 underlines the most similarity between the Sobieski (Cieplce) and Euganean thermal water behaviors of Ca, Cl, K, Mg, Na, and Si elements from other Cieplce thermal waters sources; however, the temperature is greatly different (23.1°C for Sobieski thermal waters and 77°C as the average value for Euganean one). In particular, the concentration of K, Mg, and Si

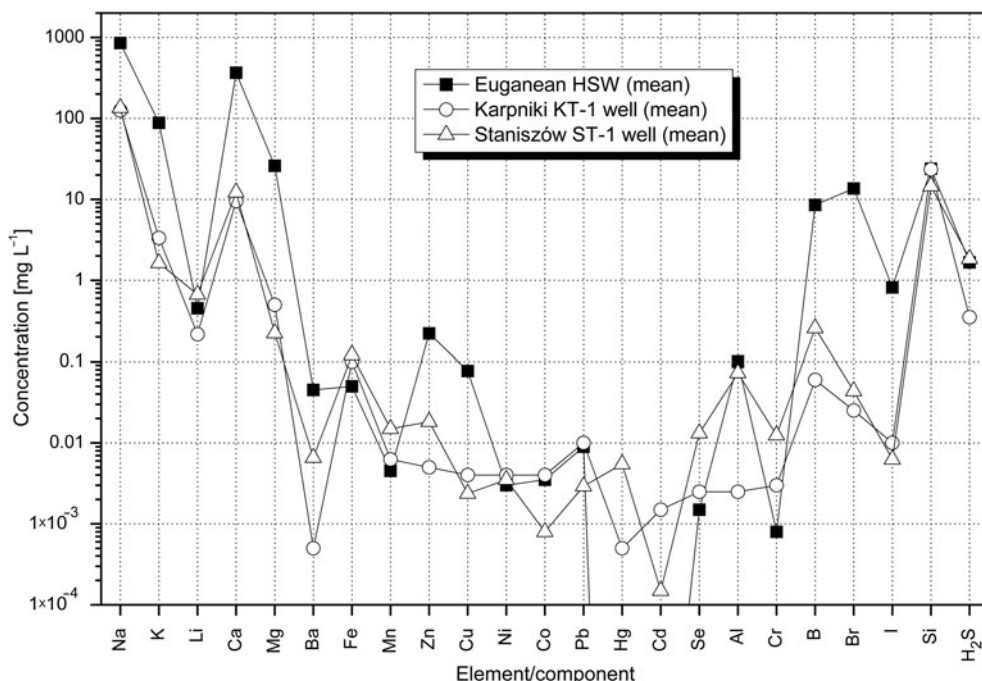


Figure 14.6. Comparison between the chemistry of thermal waters from Karpniki-Stanisław (Poland) and Euganean Thermal Area (Italy).

appears quite similar. Figure 14.6 demonstrates that Karpniki-Stanisław water and Euganean thermal waters have similar behavior of chemical patterns as Na, K, Li, Ca, Mg, Si and H<sub>2</sub>S, while the amount of SiO<sub>2</sub> appears common. Figure 14.7 shows the comparison between ion contents in thermal waters of Cieplce and Euganean thermal areas in which the concentration of Cl represents the most significant difference between Euganean and Polish thermal waters.

In Figure 14.8 the comparison between the behaviors of ion contents in Karpniki-Stanisław and Euganean thermal waters is reported.

Figure 14.7 shows the comparison between ion concentrations of HCO<sub>3</sub>, SO<sub>4</sub>, F, PO<sub>4</sub>, and NO<sub>3</sub> analyzed in Cieplce health resort and Euganean thermal waters except for the chlorine amount that is greater than others. A similar situation is shown in Figure 14.8 in which the amounts of chlorine of Euganean thermal waters is higher than the amount of the others detected in Karpniki and Stanisław. Figure 14.9 shows the correlation degrees between Euganean thermal waters elements and those revealed in the six Cieplce's thermal waters, and in Figure 14.10 the correlation degrees between Karpniki-Stanisław and Euganean thermal waters is shown.

Taking into account the state of samples, instrumental errors and water dilutions, the satisfactory correlation degree between Sobieski (Cieplce) and Euganean thermal waters elements confirms that their behaviors are very similar; however, other correlation degrees also demonstrated a good link with other elements of thermal waters from the Cieplce area. A similar situation is shown in Figure 14.10 in which are demonstrated good correlation levels are demonstrated between thermal waters from Karpniki-Stanisław and from the Euganean area.

#### 14.2.3 Evaluation of Jelenia Góra thermal waters in terms of matured peloid production

The comparison between Euganean and Jelenia Góra thermal waters represents the first step in understanding the potentialities of Polish thermal waters for use in thermal muds maturation process. The physical-chemical characteristics of thermal water are fundamental for the development

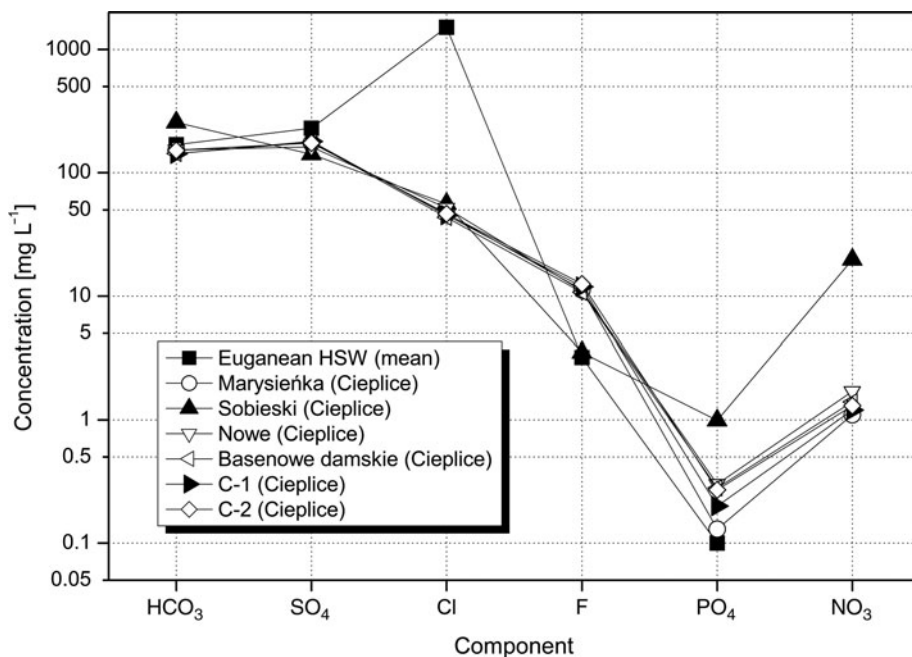


Figure 14.7. Comparison between  $\text{HCO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{NO}_3^-$  ion patterns of thermal waters from Cieplice health resort (Poland) and Euganean Thermal Area (Italy).

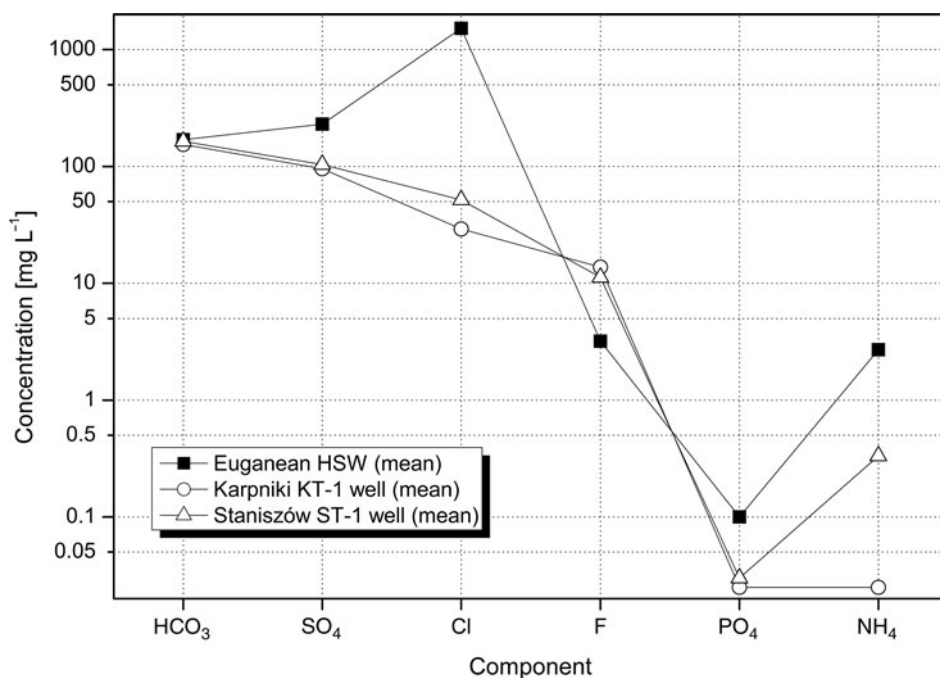


Figure 14.8. Comparison between  $\text{HCO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{NH}_4^+$  ion patterns of thermal waters from Karpniki-Stanisław (Poland) and Euganean Thermal Area (Italy).

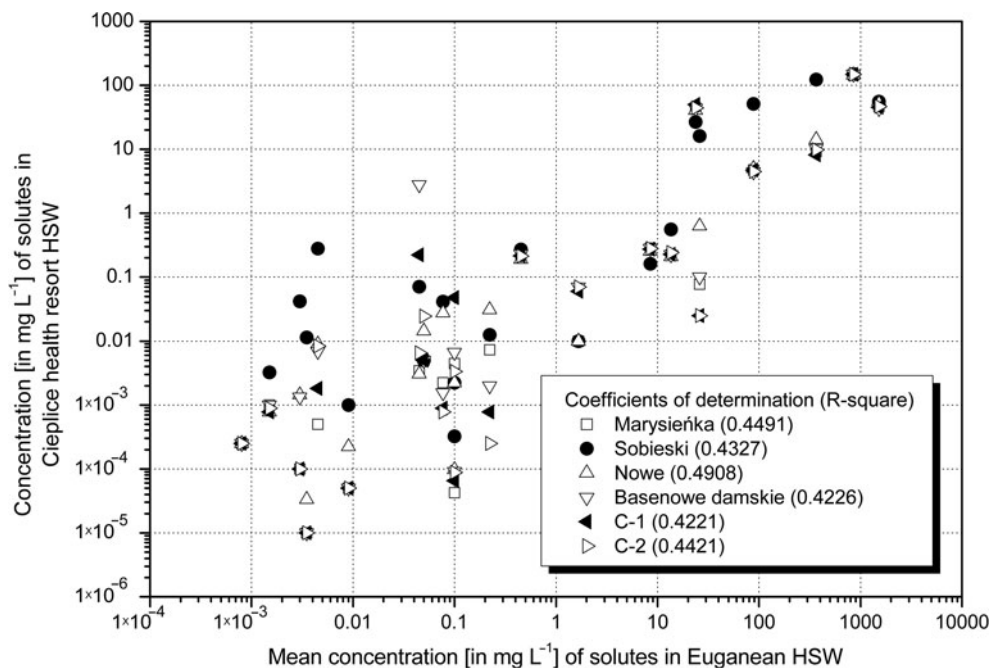


Figure 14.9. Correlation between components contained in Euganean and Cieplce's thermal waters.

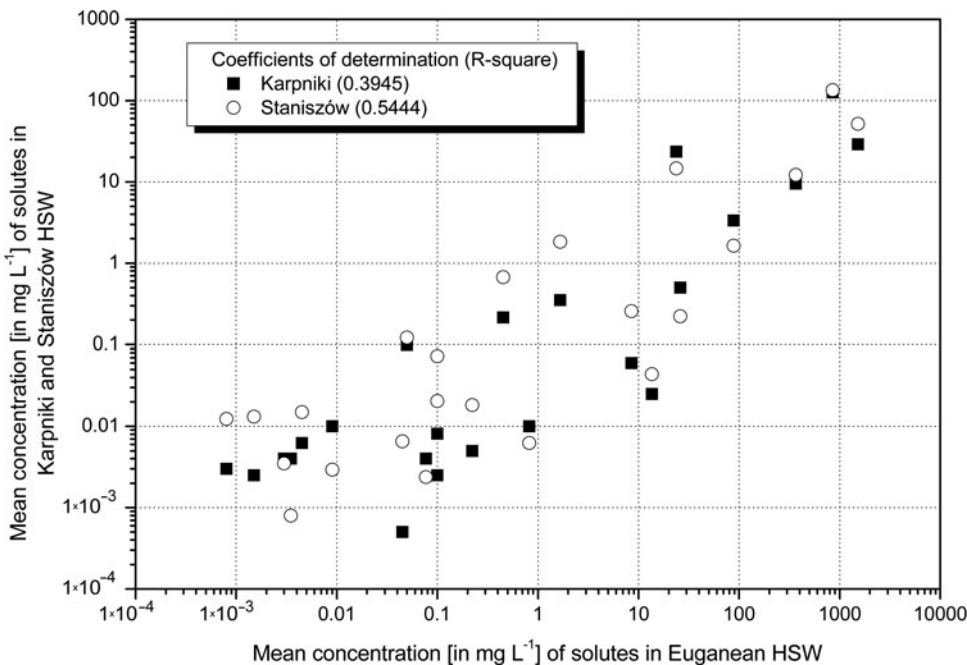


Figure 14.10. Correlation between components contained in Euganean thermal waters and Karpniki-Stanisław thermal waters.

of the biological microorganisms responsible for the maturation process. On this basis and from a biological viewpoint, comparing Karpniki-Stanisław thermal waters with Euganean thermal waters, the range of temperature appears adequate for the development of biological species as per those previously detailed (*Cyanobacterium aponinum*, 20–40°C; *Leptolyngbya* sp. ETS-04, 20–55°C). As regards the pH, thermal waters from sources of Sobieski (pH = 7.01) and C-1 Cieplce (pH = 7.96) (both Cieplce thermal waters) are more similar to Euganean thermal waters (pH 7.1) than those collected from other Cieplce and Karpniki-Stanisław waters (pH > 8). Considering the pH levels (near the range of 6.8–8.0), temperature (>60°C), and the ideal temperature range for the growth of Euganean biological species, Sobieski-Cieplce (23.1°C, pH = 7.01) and Cieplce C-1 (77.8°C, pH = 7.98) thermal waters appear suitable for peloid experimental maturation processes. This is confirmed by Figures 14.4 to 14.10, in which the physicochemical characteristics of Polish and Italian thermal waters were compared. Considering the adaptability of biological species such as *Cyanobacterium aponinum*, *Leptolyngbya* sp. ETS-04, and *Oscillatoria duplisecta* (pH 6.8–7.0), it is possible to consider Cieplce thermal waters more suitable than other Polish thermal waters for the implementation of an experimental ‘cool’ and ‘cooled’ peloids maturation process, with particular reference to Sobieski thermal waters (for ‘cool’ maturation) and C-1 thermal waters (for ‘cooled’ maturation). The realization of an experimental ‘cool’ and ‘cooled’ maturation processes could come to pass through the implementation of two simple maturation plants prototypes constituted of three pools each in which the same kind of peloid should be in contact respectively with Sobieski and C-1 thermal waters for at least 60 days. The two prototypes should be supplied with C-1 and Sobieski thermal waters *in situ*. The development of a first experimental maturation protocol based on this method should be based on an integrated analytical approach (IAA).

#### 14.2.4 *Influence of HSW on the maturation process of thermal muds in Euganean Thermal Area (ETA)*

##### 14.2.4.1 *The integrated analytical approach: volume elements analyses*

Raw thermal water is fundamental for the production of high quality muddy matrices for pelotherapy, because the maturation process depends strongly on its pH, temperature, chemical quality, stability of the chemistry over the course of time, amount of residual molecular energy measurable – function of the time and the thermometric curves – and consequently from each different thermal area. Amorphous silica and pyrite is still present in virgin mud and could decay with time. The amorphous silica appear as shells, remains of diatoms, and spicules of sponges, while pyrite crystals are generally octahedral, isolated or associated (Jobstraibizer, 1999). The presence of silica and pyrite appears more frequently in mud which has undergone the process of maturation. The maturation process is usually carried out in pools or silos plants sited in Euganean spas in which the virgin mud is submerged in thermal water for several months, during which it undergoes agitation and the surface is exposed to light with recirculating hot water maintained at a temperature of about 50°C. In the thermal waters of the Hydrothermal-Euganeo and Berico circuits, a typical thermal flora develops that also enables the development of bio-transformation elements that also have anti-inflammatory activity (Marcolongo *et al.*, 2006). The management of raw thermal water for mud’s maturation purposes is focused on the temperature’s gradient reached during the cooling process in a specific maturation plant (pools or silos). Maturation takes place in pools or special tanks built of stainless steel. Within each tank a mixer fitted with two rotating blades is installed to ensure appropriate sectioning of the mixing mud to prevent compaction (Armenante *et al.*, 2009). The maturation process starts when the thermal water is mixed with mud. Each tank has a thermal waters pipe at the top which flows continuously over the mud at a constant level. In addition, the mud is transferred from one container to another so that the constant rotation allows for a more uniform ripening of the mud because the mud is in contact with thermal water. The temperature range is between 20°C – detected in the terminal element of the plant – and about 60–85°C (depending on the area) measured in the first one closest to the well from which raw thermal water is exploited. However, most biological species – such as



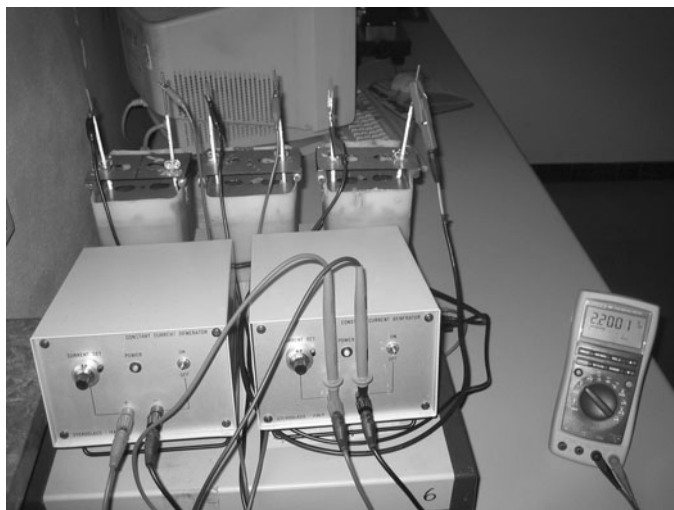


Figure 14.11. Apparatus for galvanostatic investigations of Euganean thermal waters and thermal muds (OTP lab, University of Padova, Italy).

*Cyanobacterium aponinum*, *Leptolyngbya* sp. ETS-04, and *Oscillatoria duplisecta* – grew at a temperature range of 20–59°C; the greater part of the biological maturation process takes place in those elements where raw Euganean thermal waters reach about 43–55°C. In addition to the studies of the changes of chemical, biochemical and biological patterns previously reported, many other analytical approaches have been adopted over the years for the investigation of the ETM maturation process. For example, the analyses of radioactivity of  $^{226}\text{Ra}$  content in mud during the maturation process demonstrated an enrichment with respect to the value found in the unprocessed mud, probably not linked by exchange activities but based on the ‘oxygenation’ factor, ambient temperature and the reactivity to some isotopes of the main macro and oligo elements, both of the circulating water and of the muddy matrix. Furthermore, in the same thermal waters, high concentrations of ‘unsupported’  $^{222}\text{Rn}$  have been found (Cantaluppi *et al.*, 2012). This means that a transfer process of  $^{226}\text{Ra}$  and of  $^{228}\text{Ra}$  from thermal water to mud during the maturation process normally occurs (Cantaluppi *et al.*, 2014). Electrochemical investigations on thermal water were performed in the Osservatorio Termale Permanente at the Department of Pharmaceutical Sciences of University of Padova (Italy) employing a galvanostat apparatus (Amel, France), two potentiostats (Steroglass, Italy) using titanium electrodes (DeNora, Italy), and a multimeter (Fluke) (Fig. 14.11).

Confirming the consideration about the importance of the oxygenation and the environmental temperature the galvanostatic analyses evidenced the modification of the chemical pattern of water during the maturation process of thermal muds (Fig. 14.12) through the measurement of the voltage (V) produced in the time during the treatment of thermal water with a gradient of electric current (I) (Rossi, 2005).

The similarity between the voltages behaviors of thermal water collected from the spa’s room taps and from Pool No. 10 consented to identify the common source provenience of these two raw thermal waters, while the thermal water collected from Pool No. 1 presented changes due to the maturation process performed in the pools plant. In Figure 14.13, Cyclic Voltammetry (CV) diagrams showed clear differences between the fingerprints of raw (Pool No. 10) and matured thermal water (Pool No. 1). In particular, the positive anodic area (oxidation) of the diagrams showed more different behaviors of potentials between virgin and mature matrices than the negative cathodic zone (reduction). Cyclic voltammetry supplementary investigations were performed in the Department of Chemical Sciences of University of Padova (Italy) and confirm

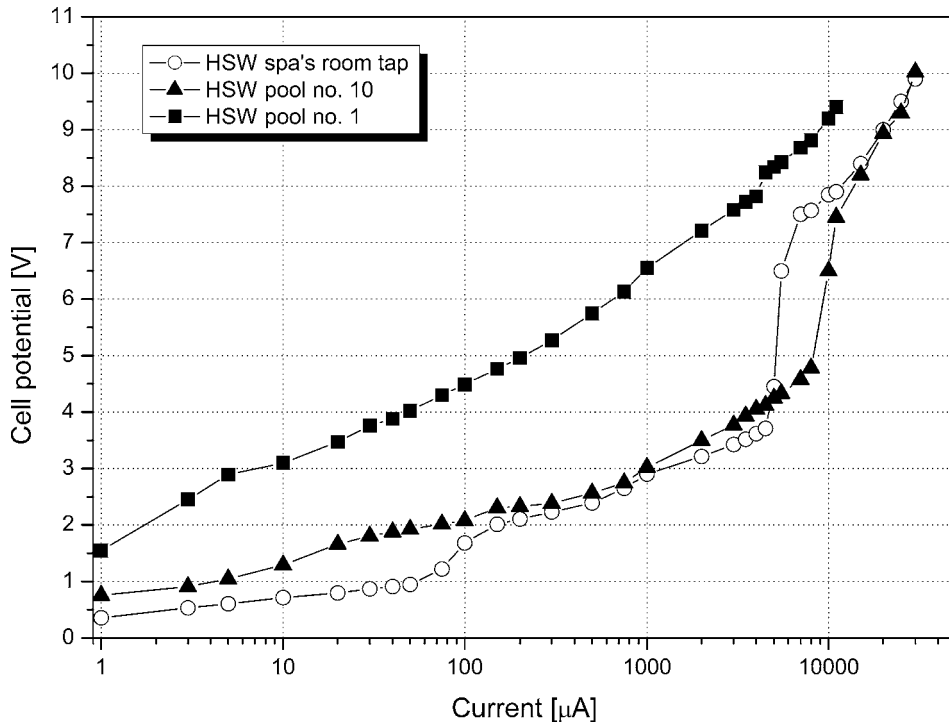


Figure 14.12. Galvanostatic analyses of thermal water collected before (Pool No. 10) and after (Pool No. 1) thermal muds' maturation process performed in a pools plant (OTP internal report, University of Padova).

the differences between the thermal water collected from Pools No. 1 and No. 10 (linked to the thermal water's wells source) (Rossi, 2005).

#### 14.2.4.2 The integrated analytical approach: rheologic analyses

The contact and combined action between thermal waters and the mineralogical components of a mud produce an evolution of viscoelastic and surface energy properties of the muddy matrix in time, called the maturation process (Bettero, 1995). The influence of thermal water on the maturation process of thermal muds depends strongly on its physical and chemical characteristics. Rheological investigations consented to assess the microstructural characteristics of thermal mud and its viscoelastic modifications as a function of maturation in thermal waters (Bettero *et al.*, 1999). The rheological profile of the ETM was determined with oscillatory motion in controlled conditions on materials previously characterized from mineralogical and chemical viewpoints. From an operational viewpoint, thermal mud was placed in oscillation and its viscous  $G'$ , elastic  $G''$ ,  $G^*$  viscoelastic and structural ( $\delta$ ) components were measured. The structural pattern and viscoelasticity constitute the rheological print of the material. The evolution in time  $t_0$ – $t_2$  of the rheological print of the ETM depending on its maturation process is defined by the rheological thermal mud (RTM) index. Matured thermal mud means a mud that has reached the limit of its RTM index (Fig. 14.14).

#### 14.2.4.3 The integrated analytical approach: tensiometric analyses

Rheological and tensiometric analyses of thermal muds are at the base of the structure-surface IAA. The changes due to a maturation process could be described at surface level also by a direct

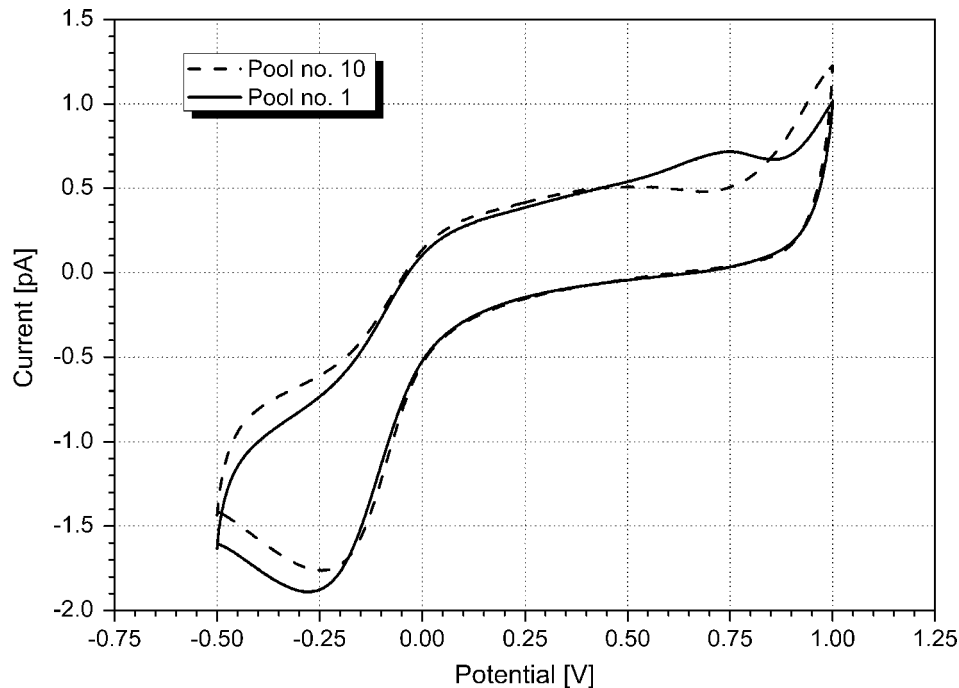


Figure 14.13. Cyclic voltammety analyses of thermal water collected before (Pool No. 10) and after (Pool No. 1) thermal muds maturation process performed in a pools plant (Department of Chemical Sciences, University of Padova, Italy).

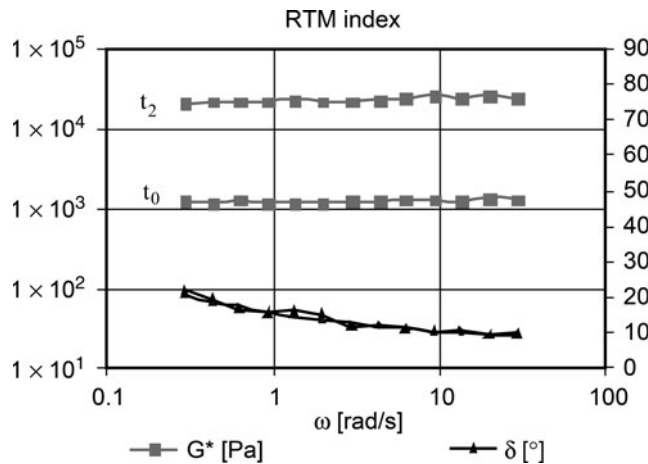


Figure 14.14. Changes in viscoelastic properties of thermal muds during maturation process ( $t_0$ – $t_2$ ).

evaluation of the variations of surface energy of thermal waters in function of the modification of its physicochemical characteristics. As an example, in Figure 14.15 the CA levels of three different kinds of cool waters measured at the interface with a film fluid of perfluoropolyether (PFPE) by the solid like method (SLM) are reported (Rossi and Pittia, 2012a; Rossi *et al.*, 2016).

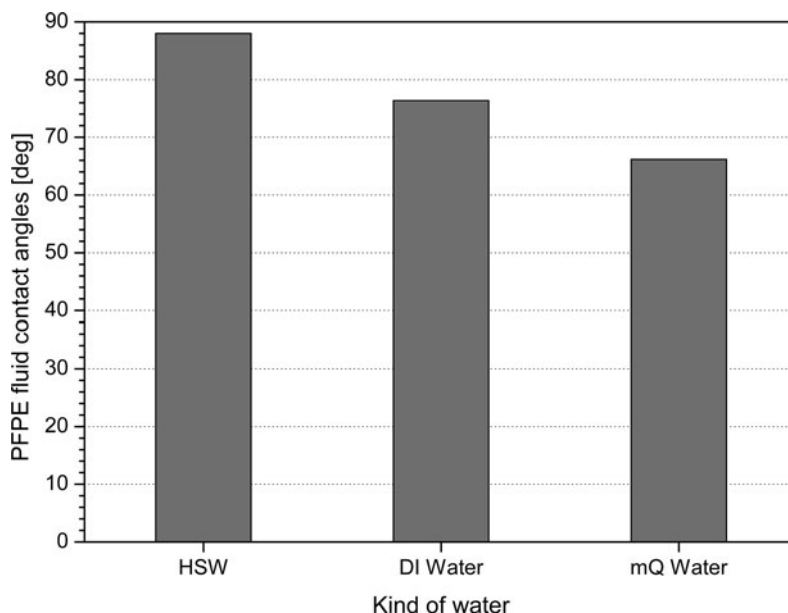


Figure 14.15. Surface energy properties of different kind of waters; a comparison between Euganean thermal water, deionized water and Millipore Milli-Q lab water (mQ).

The behavior of CA at the PFPE film fluid/waters interface is directly linked to the nature and concentration of chemical species present in the waters considered. As thermal water is responsible for the maturation process of muddy matrices, the variations of the CA measured at the interface between a drop of PFPE and clayey muds from Brenta Alluvial Plain, Italy (BrentaKer<sup>®</sup>) could be considered as an indirect measurement of the surface energy changes which occurred in Euganean thermal water at the time (Rossi *et al.*, 2014a, 2014b). In Figure 14.16, the behavior of the CA of PFPE during the maturation process of clayey muds is reported.

The decrease of PFPE's contact angles in the time represents the progress in the maturation process of the peloid and its structural evolution. The increase of the dispersed component (DC) [ $\text{mN m}^{-1}$ ] is linked to the biosynthetic activity of biological species that occurs in thermal waters during the maturation process and is proportionally inverse to the behavior of PFPE's CA measured at PFPE/peloid interface.

Basing on the investigations of the changes of CA of PFPE on clayey muds in the function of the influence of thermal waters on the maturation process, an integrated tensiometric marker linked to all components of the Euganean thermal mud called TVS mud index was developed (Rossi *et al.*, 2007; Veniale *et al.*, 2006; Rossi, 2012b). Figure 14.17 reports the TVS mud index nomogram related to 71 samples of ETM ready for pelotherapy and collected from 71 Euganean spas pertaining to the Euganean Thermal Area.

It must be remembered that – muds being equal – every aquifer is characterized by high physical-chemical variability and ionic-molecular activity depending on the time, pressure, temperature, permeability of the mud, fluid structural composition (saturated and unsaturated zones, natural radioactive components).

The acceptability range of PFPE CA values is between 53.2 and 65.6 deg. The CA values inside this range are linked to the typical chemical mineralogical pattern of an Euganean thermal mud (Rossi *et al.*, 2016; Rossi *et al.*, 2007). CA values  $>65.6$  deg and  $<53.2$  deg show a possible alteration of the composition of thermal muds. These modifications could be due to an alteration of the mineralogical composition, a modification of the maturation process, or a variation of the

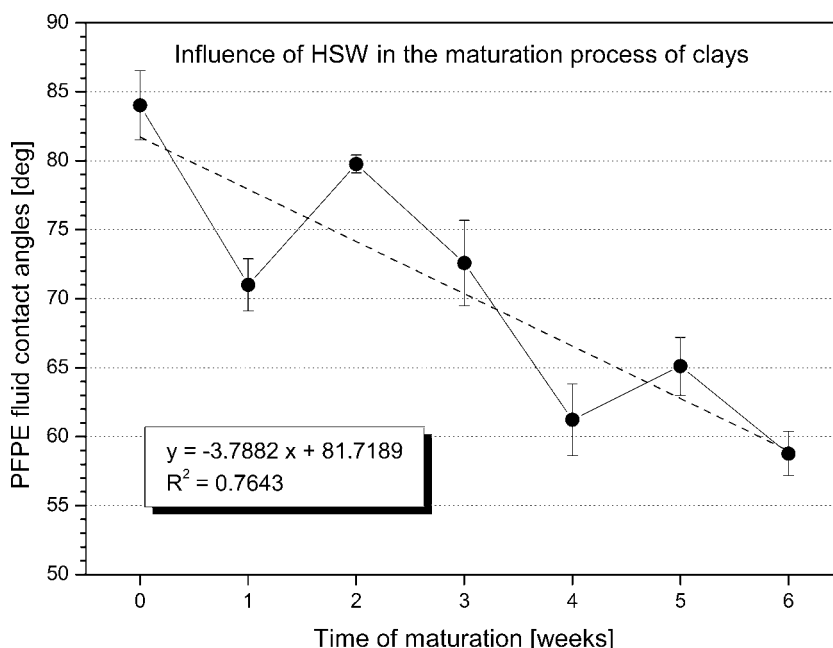


Figure 14.16. Variation in PFPE contact angles measured on clayey muddy matrices during the maturation in Euganean thermal water.

quality of thermal water used. Accordingly with structure-surface correlations, the variations of the TVS mud index during the maturation process is closely linked to the variations of its RTM index. Rheological and tensiometric analyses of ETM are at the base of the integrated analytic approach to the study of complex matrices.

#### 14.2.5 Effects of thermal peloid treatments on skin surface

Generally, mud-pack therapy (MPT) is defined as a therapeutic application of natural products containing a mix of mineral or mineral-medicinal water (including seawater or salt water from lakes) with organic or inorganic compounds resulting from geological, biological or even both processes, used in the form of a wrap or a bath. MPT has been widely used since ancient times as an effective therapy in diverse rheumatic illnesses such as neuralgias, or skin problems like acne, seborrhea or psoriasis (Espejo *et al.*, 2012). Mud-pack therapy can be considered as an alternative therapy in the improvement of pain and functionality in patients with knee osteoarthritis, reducing the consumption of drugs. From an epidermis viewpoint, experimental evidence based on measurements of contact angles of mQ water on skin after each of the Japanese biofango's therapy phases (bath-mud therapy-shower therapy) demonstrated that the major variations of skin hydration occurring during bath phase in Japanese thermal water (eight minutes) showed after MPT with Biofango for 20 minutes (Rossi *et al.*, 2014). In Figure 14.18, the trend line showing the variations of the mQ water's contact angles measured on skin surface after bath phase is reported.

Figure 14.19 shows the variations of contact angles of PFPE and mQ water measured at skin interface after MPT.

Measurements of contact angles at PFPE/skin interface and water/skin interface are reported on the Y axis for comparison. The *x* axis reports the phases of Japanese Sanraku-en spa's (Tonami, Toyama, Japan) thermal protocol comprising: (i) basal (before thermal treatment), (ii) after pelotherapy with Biofango, and (iii) after shower. The bath phase is between pelotherapy and

TVSmud index: Euganean Thermal Muds Monitoring (2010)

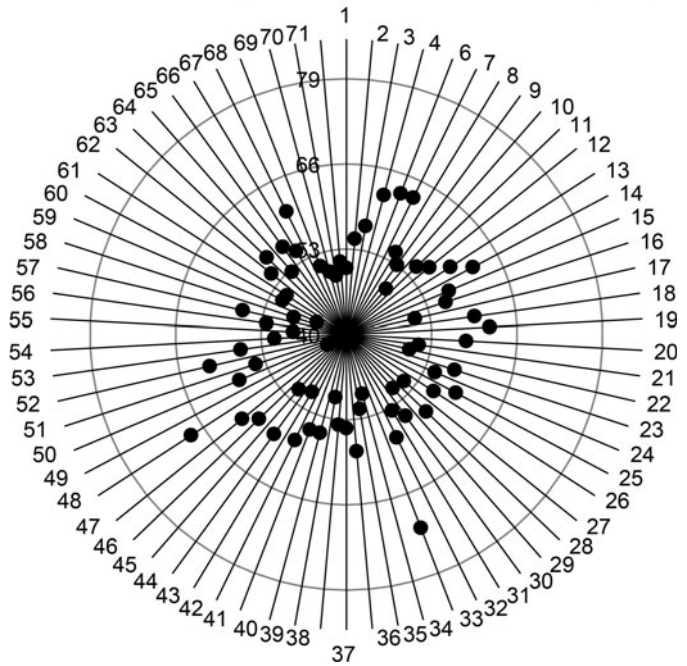


Figure 14.17. Variations of PFPE contact angles measured on ETM after the maturation process in Euganean spas.

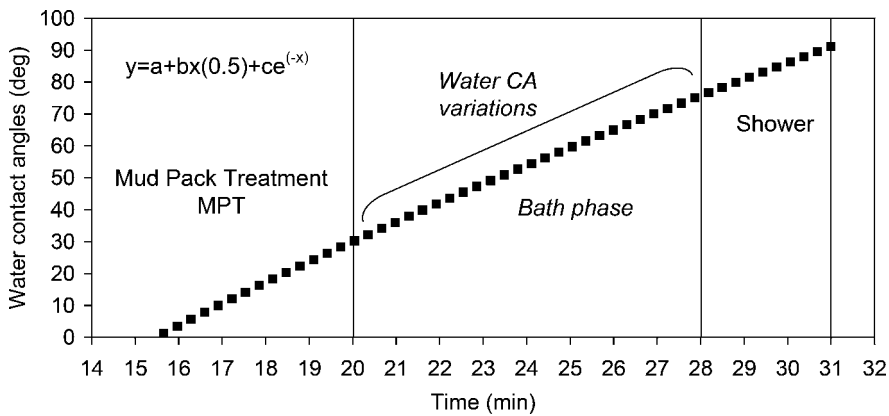


Figure 14.18. Variations of contact angles measured at mQ water/skin interface during bath phase.

shower phases. The behaviors of PFPE and water's contact angles depend on the behavior of the hydration state of skin at the time.

During MPT, the hydration of skin increases (decreasing of water's contact angle values, increasing of PFPE's contact angle values) and consequently the selective permeability of the stratum corneum (the outermost layer of the skin epidermis) changes, allowing the uptake of therapeutical substances produced in thermal waters during the maturation process of muds and absorbed on the clayey fraction of thermal muds.

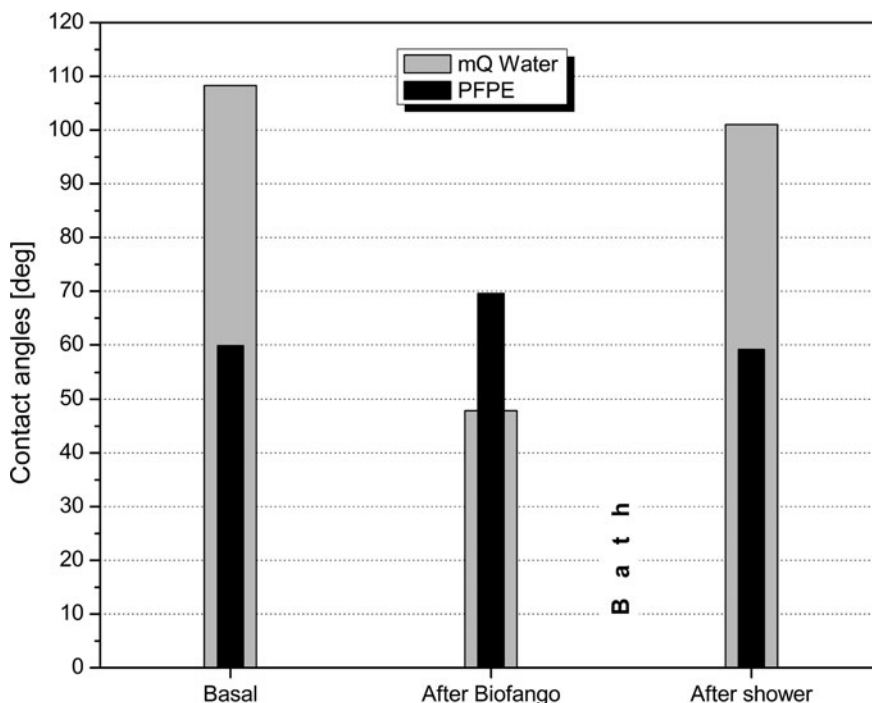


Figure 14.19. Variations of mQ water contact angles and PFPE: (a) after biofango and (b) after shower.

The effects depend on the type of dermis in contact, on its cleanliness and on the absence – or not – of contaminating elements (remains of flavors, fats, traces of oils of previous treatments).

#### 14.3 PERSPECTIVES FOR USING COOLED THERMAL WATERS FOR THERMAL WATER TREATMENTS: JELENIA GÓRA HSW AND BOROWINA MUDS

Borowina is an organic peloid, sometimes named ‘moor mud’, type of peat (turf) significantly humified by bacteria, poor in minerals and inorganic components. Borowina is widely used in Polish health resorts and spas. There are two (main) types of mires, so-called ‘low mires’ (fens), and ‘high mires’ (bogs), and consequently two kinds of borowina peloids, ‘low’ borowina (from ‘low’ mires) and ‘high’ borowina (from ‘high’ ones). Low borowina is alkaline and consists of more than 50% organic compounds, whereas high borowina is acidic, and consists of more than 95% organic compounds. The main components of borowina peloids are: (i) organic components: bitumens (waxes, resins, asphalts, fats), pectins (e.g. tannins), cellulose and hemicelluloses, humic acids, fulvic acids, lignins, other biologically active compounds; (ii) inorganic components – mineral salts, like phosphates, sulfates, nitrates, etc.; and (iii) microbiological components (oxic and anoxic bacteria, fungi). There are different indications for the medical application of both types of borowina.

All the evidence provided above suggests new perspectives for the employment of cooled HSW for thermal treatments, in particular:

- *The hot maturation process of thermal waters*: the cooled thermal water, enriched with therapeutical substances (called “matured thermal water”) should be obtained from a hot biological

maturation process (77.8°C). The maturation process should be monitored step by step by an integrated analytical approach where the chemical elements and the surface energy properties of thermal waters can be investigated simultaneously. This should be performed subjecting the sample of raw thermal water to tensiometric and chemical analyses at the same time. The maturation process should be performed in an experimental maturation plant constituted of eight pools sited near the source well in the Cieplce health resort, and thermal water samples from each pool should be investigated with the same approach used for raw thermal water. The waste cooled thermal water collected in the last cool pool should be transferred into special steel tanks ready to be used for balneotherapy.

- *The 'cool' maturation process of thermal waters:* in order to obtain a 'cool' thermal water also enriched with therapeutic substances ('matured' thermal water) it is necessary for raw thermal water (Sobieski water (23.1°C) in Cieplce) to undergo a biological experimental maturation process monitored step-by-step by a volume element-surface analytical integrated approach as purposed for the hot maturation process. The maturation process should be performed in an experimental maturation plant consisting of eight pools sited near the source Sobieski intake in the Cieplce resort and investigated in the same way as for hot maturation process. As for hot maturation process waste 'cool' matured thermal water should be collected in special tanks ready to be used for bath therapy.
- *The hot maturation process of peloids:* the maturation process of peloids for pelotherapy should be performed separately from thermal water and supplied with the same source. The maturation plant should be built under the same scheme of that employed for hot and 'cool' thermal water maturation process (eight pools). The maturation process should be monitored by an IAA considering volume elements-structure-surface correlations. The samples should be collected periodically from each pool and undergo chemical, rheological, and tensiometric investigations with the aim of evaluating chemical, viscoelastic and surface energy modifications at the time to consequently determine the quality of the product and the maturation process. The muddy matrices could be borowina peloid actually in use at Polish thermal resorts and spas in the Sudetes Mountains.

*The integrated pelotherapy-balneotherapy protocol:* on the basis of the response of the stratum corneum after pelotherapy in which its selective permeability changes during the topical application of mature thermal muds due to the increase of the hydration state, an integrated pelotherapy-balneotherapy protocol is proposed. The protocol should consist of two phases:

- (a) *Mud-Pack Therapy (MPT):* in this context MPT is functional to balneotherapy. The application of matured borowina mud allows the modification of skin hydration, thus preparing the patient for balneotherapy. With the aim of reaching this objective it is necessary for the patient to undergo a 20-minute session of MPT.
- (b) *Balneotherapy:* After MPT the patient should be treated with cooled and 'cool' 'matured' thermal water developed in controlled conditions for balneotherapeutic aims only, giving 'cool' and cooled thermal waters' treatment an added therapeutic meaning.

A possible scheme of the integrated thermal pelotherapy-balneotherapy is reported in Figure 14.20.

The scheme purposed is a general view of the integrated thermal treatment purposed for Jelenia Góra thermal waters. The temperature of balneotherapy can be chosen on the basis of the thermal gradient reached in the plant by collecting the thermal water from the pool chosen. The system consists of pools in which thermal water flows from the same well source. While 'mature' thermal water is collected from pool plant and kept in the steel tank, the patient undergoes the pelotherapy phase with borowina matured mud. After MPT the patient should be immersed in a balneotherapeutic pool supplied with the 'mature' thermal water collected from the steel tank. For this, special protocols should be prepared, both for applicative methodology and for necessary chemical experimentation.



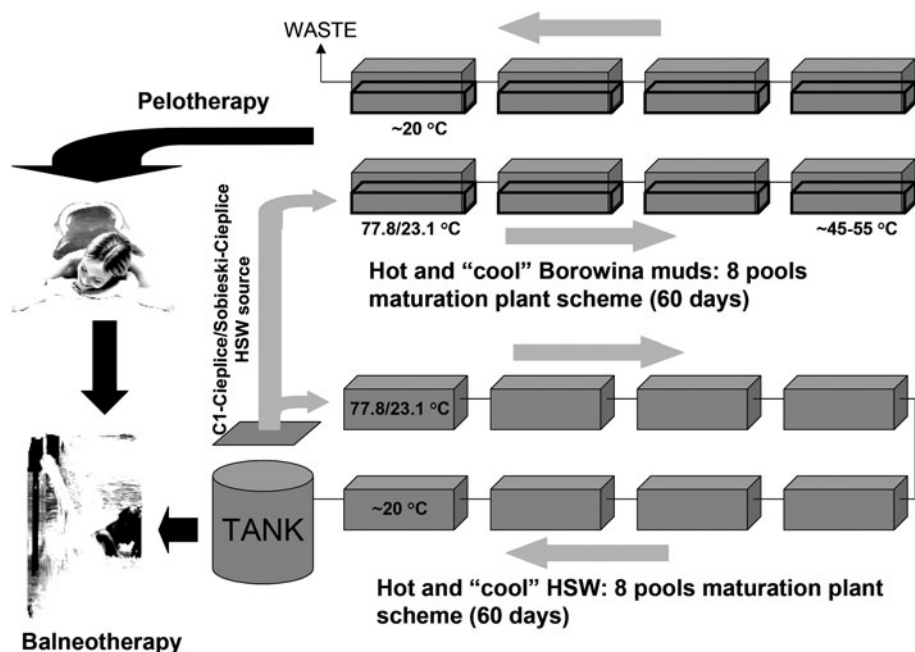


Figure 14.20. Integrated pelotherapy-balneotherapy thermal treatment scheme for thermal waters and borowina mud in resorts and spas of the Jelenia Góra thermal area (by Davide Rossi).

A clinical evaluation of the efficacy of balneotherapy should be performed with the aim of verifying the therapeutic value of the system proposed.

Our work underlines the importance of future cooperation between spas and universities for the development of new qualification protocols for local thermal products. This cooperation should be focused firstly on investigations performed by the integrated analytical approach with the aim of identifying the natural product typical of the territory. Successively, it might be possible to develop procedures for the control and monitoring of the quality of thermal products used.

Other methods of recovery might not be excluded, based on a more detailed analysis in terms of reactivity connected to the molecular behavior and to the energy produced by vibrational fields connected to physics of particles without mass (photons, bosons, etc.).

Technologically differentiated models can take into account distinct applications by simply starting from the reactions connected to thermic variations and ionic balance. The related applications will also depend on the economic and environmental sustainability.

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