Mineral and Thermal Groundwater Resources

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Introduction

Is it not generally believed that our town is a healthy place... a place highly commended on this score both for the sick and for the healthy?... And then these Baths – the so-called 'artery' of the town, or the 'nerve centre'... Do you know what they are in reality, these great and splendid and glorious Baths that have cost so much money?... A most serious danger to health! All that filth up in Mølledal, where there's such an awful stench – it's all seeping into the pipes that lead to the pump-room!

Henrik Ibsen, An Enemy of the People, 1882

Henrik Ibsen gave the 'truth about mineral water' more than 100 years ago in *An Enemy of the People.* His examples came not from the decadent bathing spas of Bohemia or Victorian Britain, but from the very edge of polite society, subarctic Norway! His masterpiece illustrates the central role that groundwaters and, in particular, mineral waters have played in the history of humanity: their economic importance for towns, their magnetism for pilgrims searching for cures, the political intrigues, the arguments over purported beneficent or maleficent health effects and, finally, their contamination by anthropogenic activity, in Ibsen's case by wastes from a tannery.

This book addresses the occurrence, properties and uses of mineral and thermal groundwaters. The use of these resources for heating, personal hygiene, curative and recreational purposes is deeply integrated in the history of civilization. Many such water sources thus had early religious, cultural, scientific and economic significance (Figure I.1).

Research related to mineral waters played an important role in the advances of science and technology. Examples include the work of Paracelsus on the chemistry of spring waters at Františkovy Lázně, that of Glauber on the extraction of the salt $Na_2SO_4 . 10H_2O$ from spring waters, and that of Ginori on the generation of electricity from the heat of thermal waters at Larderello.

Spas were places of introspection, meditation and creation, frequented by artists and writers, as well as being fashionable holiday resorts. Bottling of natural mineral waters has proved to be exceptionally profitable. Imbibers

Figure I.1 Băile Herculane: the Hercules and Hygieia springs. One third of Europe's mineral and thermal springs are located in Romania. (Reproduced with permission from the Ministry of Tourism, Romania.)

of bottled waters range from those concerned over the quality of tap water to yuppies in search of chic beverages; from Lithuanians who use ice-cold saline waters as chasers for innumerable vodkas to residents of St Petersburg for whom bottled waters may be the only safe source of supply at certain times.

In the 20th century, high temperature water resources have been used for the production of electricity, while medium and low temperature resources are used for domestic heating, from individual houses to whole communities, as well as for industrial and agricultural purposes. One of the mightiest achievements of geothermal power has been to turn Iceland into one of Europe's largest exporters of bananas!

We hope you enjoy the book, and that it stimulates your interest in the history, culture and science of unusual groundwaters.

Before we continue, however, we should point out that the terms 'mineral' and 'thermal' water are not well defined and vary from one text to another, depending partly on the use of the water. Because of the increasing use of bottled water, the term 'mineral water' is taken by some to mean any naturally occurring, bacteriologically pure water. However, in this book mineral waters are considered to be natural waters that are relatively high in either certain dissolved substances or gas content. For the sake of simplicity, thermal waters are taken as groundwaters whose temperature significantly exceeds the annual mean surface temperature.

Part One

Mineral and Thermal Groundwater Resources

Marius Albu, David Banks and Harriet Nash

1

History of mineral and thermal waters

> *Isaac's servants dug a well in the valley and found water. The shepherds of Gerar quarrelled with Isaac's shepherds and said 'This water belongs to us'.*
>
> Genesis 26, 19–20

Groundwater has always occupied a central position in the history of civilization. In the ancient Bible Lands, a well represented a continuous supply of good quality drinking and irrigation water – a base around which a settlement could grow. The control of strategic groundwater resources in the Levant has thus been a cause of strife between nations from the days of the Patriarchs to the present conflict between Israel and its neighbours.

Groundwater, wells and springs have thus become symbols of life and power in almost all religions and civilizations. The supposed burial places of saints, such as that of Olav den Hellige beneath Nidaros Cathedral in Trondheim, Norway, have sometimes come to be associated with 'holy' springs or wells. Even in pre-Christian times, wells had a religious significance. This is thought by some to be reflected in the now Christianized tradition of 'well dressing' in the English county of Derbyshire (Figure 1.1).

If normal groundwater was so powerful, imagine the significance and magic of unusual waters which emerged from the ground scalding hot or full of wonderful salts! The value of such mineral and thermal waters was known to many ancient civilizations and the waters usually had a social and religious function as well as being of economic importance. The importance that these waters have gained in today's world is amply illustrated by the thickness of the three volumes of *Proceedings of the 1968 International Geological Congress* (Malkovský and Kačura, 1969a,b,c) in Prague,

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Figure 1.1 Well dressing at Hall Well, Tissington, Derbyshire, UK. A motif is designed using dried flowers and twigs on a bed of wet clay. (After Christian, 1991. Copyright Derbyshire Countryside Ltd, Derby, UK, reproduced with permission.)

dedicated to describing and explaining the occurrence of the world's mineral and thermal waters.

1.1 THERAPEUTIC WATERS

1.1.1 The ancient world

From the earliest times humanity has associated certain springs with divine powers of healing. In the 1st millennium BC, the Greeks believed in divinities associated with thermal and mineral waters and their curative properties. The rudiments of balneology appeared as early as the 5th century BC when Herodotus called attention to the methods of prescription and application of mineral waters. The Greeks built many temples to divinities associated with curative springs. On the island of Kos (Figure 1.2), where Hippocrates was born, the healing powers of the local spring were attributed to Asclepios, the god of medicine and son of Apollo, and a magnificent sanctuary was built for him at the end of the 4th century BC. The cult of Asclepios was particularly strong in the 4th and 3rd centuries, and cures included dietetic regimes and exercise as well as bathing in spring water (Hammond and Scullard, 1970). Artemis was also considered a goddess of healing and several springs were dedicated to her, including that at Cyrene in northeast Libya (Chamoux, 1985).

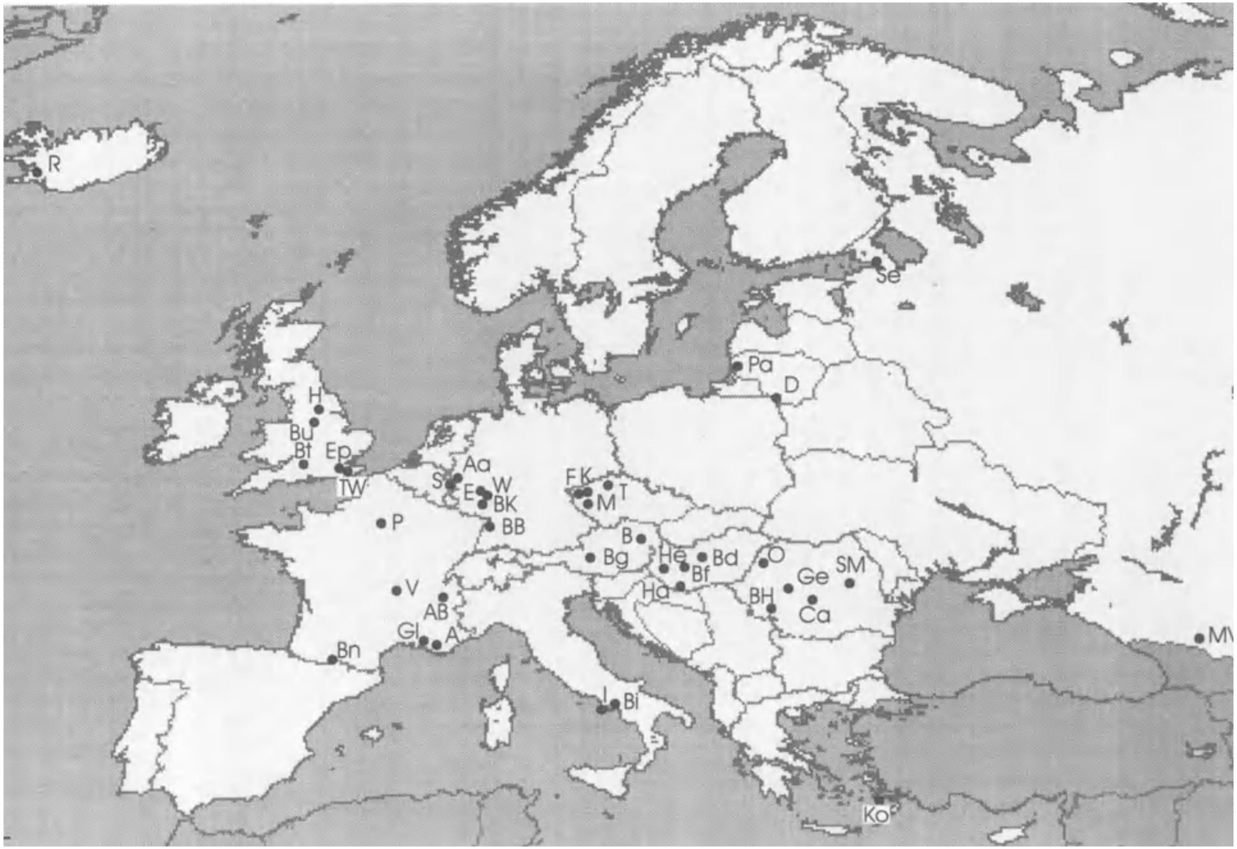
These beliefs travelled with the Greek colonists to, for example, the Provence region. The Greeks had become established at Glanon (near Saint Rémy-de-Provence) by the end of the 3rd century BC. There was already a Celto-Ligurian settlement here with a shrine dedicated to the curative waters and now a beautiful Hellenistic city was built, which reached its peak in the 2nd century BC. The city centre was dominated by a monumental temple built close to the miraculous fountain, which was dedicated to the nymphs and to Apollo the Healer (Lévêque, 1987).

The Celts of the 3rd to 1st centuries BC worshipped curative springs and the goddesses associated with them (Drimba, 1987). They used the waters of the thermal springs at Teplice (the German Teplitz) in northern Bohemia (Chyský *et al.*, 1967) and elsewhere for bathing therapy. In Britain, legend points to early appreciation of certain waters' curative properties. The founding of the town of Bath is attributed to Bladud, father of the legendary King Lear, who along with his herd of hogs was supposedly cured of leprosy in 863 BC by immersion in the steaming swamps (Hinde, 1988). These were known as the 'Waters of Sul', Sul being the Celtic goddess of wisdom.

The Romans, with other Italian tribes of the second century BC, were also attracted by the curative properties of thermal springs and often settled in their vicinity. They founded the city of Aquae Sextiae (now Aix-en-Provence), where both warm and cold springs occur between the western Alps and the Pyrenees (Mommsen, 1988). Most of the Roman *thermae*, such as Baiae (near Naples), Bagnères de Luchon (in the Pyrenees) and Paris, were established between the time of Agrippa (21 BC) and Diocletian (AD 302). Other known watering places in Roman times include Aquae Mattiacorum (Wiesbaden), whose warm springs Pliny the Elder credited with retaining their heat for three days, Aquae Aureliae (Baden-Baden) and Embasis (Bad Ems; Alderson, 1973).

The Waters of Sul (Bath) became the Roman city of Aquae Sulis following the Roman invasion of England. Construction of the *thermae* probably took place at around the time of Claudius (Kellaway, 1991b) and the elaborate baths eventually surpassed the largest establishments in Gaul. Inscriptions among the ruins record visitors from Britain and abroad, indicating the widespread attraction of the facilities. The Romans also developed several other spas in Britain, some of which are mentioned in Chapter 10.

Before the penetration of Roman influence, the Dacians practised balneal therapy and internal cures with mineral waters in present-day Romania (Drimba, 1984). In Roman Dacia (AD 106 to 271) thermal waters were used for therapy at places well known in antiquity, such as Ad Mediam (Băile Herculane) and Germisara (Georgiu). Of these, the most important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was undoubtedly Ad Mediam, where the springs were tapped and pipes, pools and buildings for balneal treatment were constructed. The curative qualities of the waters were acknowledged in dedications to the healing divinities Hercules, Aesculapius and Hygieia (Macrea, 1969), to the divine power of the waters (‘*dis et numinibus aquarum*’), to the warm springs (‘*fontibus calidis*’) and to the spirit of the place (‘*genio loci*’). Germisara, with the renowned ‘Thermae Dodonae’, was equipped for curative baths by a detachment of the XIII legion Gemina from Apulum (Szabó, 1978).

1.1.2 Middle Ages onwards

After the departure of the Romans from much of Europe, the baths they established were neglected. However, many early churches were built on sites of ancient healing throughout Europe. Springs reputed to have curative properties were often named after Christian saints. St Olav’s well, issuing from the supposed burial place of the bloodthirsty Norwegian saint-king, located under Nidaros Cathedral in Trondheim, is an excellent example of this.

Several important sites known to the Romans were rediscovered in the 13th and 14th centuries. Their use developed slowly, however, until the early 18th century, when some baths were rebuilt and many new ‘watering places’ or ‘spas’ were established. Spas then became fashionable centres of resort for the upper classes and nobility. The mineral springs of the original town of Spa, in Belgium, mentioned by Pliny the Elder, were rediscovered in 1326. However, they were not much frequented until the 16th century and the town did not reach its acme until the 18th century.

The thermal springs at Buda were known in 13th century Hungary due to the Knights of the Order of St John, who started to use them for balneal treatment. Although the springs were used in the time of Sigismund of Luxembourg, King of Hungary (1387–1437), they were not systematically exploited until the time of King Matia I Corvin (1458–1490).

Interest in the therapeutic use of thermal and mineral waters in Bohemia increased markedly in the 14th century, culminating in 1348 when the spa of Karlovy Vary (Var meaning ‘boiling’) was established by order of Charles

Figure 1.2 Map of Europe showing locations of some spas and thermal waters mentioned in section 1.1. A = Aix en Provence, Aa = Aachen, AB = Aix-les-Bains, B = Baden (Austria), BB = Baden-Baden, Bd = Buda(pest), Bf = Balatonfüred, Bg = Badgastein, Bi = Baiae, BH = Băile Herculane, BK = Bad Kreuznach, Bn = Bagnères de Luchon, Bt = Bath, Bu = Buxton, Ca = Călimăneşti, D = Druskininkai, E = Ems, Ep = Epsom, F = Františkovy Lázně, Ge = Georgiu, Gl = Glanon, H = Harrogate, Ha = Harkány, Hé = Héviz, I = Ischia, K = Karlovy Vary, Ko = Kos (Cos), M = Márianské Lázně, MV = Mineralny Vody, O = Oradea, P = Paris, Pa = Palanga, R = Reykjavík, S = Spa, Se = Sestroretsk, SM = Slănic-Moldova, T = Teplice, TW = Tunbridge Wells, W = Wiesbaden, V = Vichy.

IV of Luxembourg. The town, formerly known by its German name of Carlsbad, and its treatment facilities developed rapidly on the basis of 12 naturally carbonated thermal springs. Of these the Vřídlo spring or geyser was best known, due to its eruptive discharge to a height of 12 m.

In the UK, Bath was largely abandoned after the Saxon defeat of the Romans in AD 577, although that well-known Mercian, Osric, documented its name as 'Hat Bathu' in AD 676, implying that the Saxons were at least aware of the waters (Kellaway, 1991b). Bath recovered its importance during the mediaeval period, after the baths were purchased (in 1091) and reconstructed by John de Villula, a doctor from Tours. The thermal waters were undoubtedly employed for curative purposes by the Benedictine monastery of Bath, into whose control they passed until Henry VIII's dissolution of the monasteries in 1539.

Italy provided some intellectual and even scientific literary works on the use of spas. The monk Savonarola wrote his *Treatise on Italian Mineral Waters* in the 15th century, giving instructions on the use of mineral baths. In the 16th century the lectures of the Italian anatomist Fallopio, *Seven Books about Warm Waters*, were published. Fallopio also discussed the chemical composition of mineral waters in his lectures (*Great Soviet Encyclopedia*, 1973–1984).

In the Principalities of present-day Romania, the 13th to 19th centuries saw the gradual development of spa towns in the vicinity of thermal and mineral water sources that had long been known and used for therapeutic purposes. In mediaeval Transylvania, the warm baths southeast of Oradea were first described in 1221. The old baths stood on the shores of the thermal lakes at the springs of the Peţa stream. The Peţa's waters were later used as 'antifreeze' for the moat around the fortress of Oradea, to prevent it from icing over in winter. An accommodation building was constructed in 1744, and works to tap the thermal waters by means of a well (the 'Felix' well) in 1771. The treatments available at Oradea were described by the physician St Hatvany in his work in 1777, *Thermae Varadiensis*. The thermal baths came under the administration of the local diocese and were known for a long time as 'Băile Episcopiei' ('Baths of the Diocese'). Later, the old Băile Episcopiei were transformed and extended to become the fashionable spa 'Băile Felix-1 Mai'.

At Ad Mediam, where thermal baths were used in Roman times, the waters were not analysed until 1734. This spa was later known as 'Băile Mehadiei' (Baths of Mehadia) and, in the 19th century, its renown became widespread due both to the curative properties of its thermal waters and the patronage of such men as Goethe, Vasile Alecsandri and Aron Pumnul, the teacher of Romania's most loved poet, Mihail Eminescu. In time it became known as Băile Herculane in memory of its ancient origin.

The Slănic-Moldova spa in Moldavia was founded in 1824 when baths were built to use several different spring waters for treatment. Pointing out the purported curative qualities of the mineral waters, the doctor in chief, L. Steege, published a paper in 1856 entitled *Les eaux minérales de Slanic en Moldavie*. The properties of the waters, the attractive landscape and the subsequent development and modernization of the spa led to Slănic-Moldova being named 'Perla Moldovei' (Pearl of Moldavia).

In Wallachia the mineral waters at Călimăneşti in the Olt valley were well known at the beginning of the 19th century. Although they had been used since the reign of Prince Matei Basarab (1632–1654), they were not chemically analysed until 1829. Balneal cures utilizing these waters commenced only in 1830, under the guidance of the superior of Cozia Abbey, and until 1854 there was only a rudimentary installation for treatment. After the discovery of the Căciulata spring in 1848, and its mention in 1859 by the doctor Caillet in the journal *L'Union Medicale*, the fame of the mineral waters of Călimăneşti–Căciulata spread quickly in Europe. Emperor Napoleon III (1852–1870) underwent a cure for his kidneys with water brought from the Căciulata spring. Later, the spa was developed by building sanatoria, villas and a pavilion (Stoicescu and Munteanu, 1976; Dumitrescu, 1984; Teodoreanu *et al.*, 1984; Pricăjan, 1985).

During the Ottoman occupation of Hungary, the Turks organized several baths in Budapest, such as at Király in 1565, Rudas in 1566 and 'Barat Degrimene' at the end of the 16th century. Later, among the balneal places preferred by the inhabitants of Budapest were Császár with its old baths, Lukács where the Barat Degrimene baths had been put into service, Gellért where facilities were arranged in 1615 and Széchenyi where baths were set up in 1881. In parallel with the evolution of the baths in Budapest, other spas of European renown were developed in Hungary in the 18th and 19th centuries. including Balatonfüred, Héviz, Balf and Harkány.

New mineral and thermal water resources continued to be discovered. In Britain, the properties of the waters of, for example, Harrogate, Tunbridge and Epsom were discovered in 1571, 1606 and 1618 respectively, leading to the development of spas (Jowitt and Jowitt, 1971; Havins, 1976). The older spas were still frequented and the city of Bath was transformed in the 18th century to become a fashionable watering place, presided over by Beau Nash (1674–1764). As master of ceremonies at Bath from 1705, he introduced a polished code of manners into polite society, described in the works of the contemporary novelists Henry Fielding and Thomas Smollett. The town was still a favourite resort in the 19th century, when it featured in the novels of Jane Austen and Charles Dickens. In Victorian times, spas were as popular as ever and were sufficiently numerous to be accessible to a wide spectrum of society, not only to the rich and well connected.

The spas of Bohemia were among the most frequented in Europe and of these, perhaps the most popular was Karlovy Vary. The curative properties of the waters were studied in 1766 by the balneologist Becher. The Swedish chemist Berzelius worked out scientific methods for determining the composition of mineral waters and in 1822 made an exact chemical analysis of the springs. Development of the sources in the 19th century involved channelling the springs into a columned gallery, called 'the Gallery of the Mills', which is still the focal point of the modern spa. Baths, comfortable hotels, pensions and sanatoria were built and Karlovy Vary, together with nearby Teplice, became renowned as a place of rest and treatment, being visited by many contemporary worthies including Beethoven, Brahms, Goethe, Humboldt, Liszt, Marx, Peter the Great, Schiller, Smetana and Wagner. Goethe was prone to illness from childhood and often visited Karlovy Vary to take the waters (Boyle, 1992). In Teplice Beethoven found some relief from his depression and headaches, giving him the energy to launch into his Seventh Symphony (Matthews, 1985).

The curative springs of Františkovy Lázně in western Bohemia were analysed as early as the first half of the 16th century by the famous doctor Paracelsus. The 23 springs with carbonated mineral waters were used for many purported cures and were famous for their remarkable content of sodium sulphate ($Na_2SO_4.10H_2O$, Glauber's salt). The spa was also well known for its therapeutic muds. Another Bohemian spa, Mariánské Lázně, was founded in the early 19th century by the superiors of the Abbey of Teplá, near the 'Virgin Mary' spring. With upwards of 40 mineral springs it developed quickly and hosted such personalities as Beethoven, Chopin and Gorky for treatment.

In Russia, also, spas were founded. At Sestroretsk the residents of nearby St Petersburg enjoyed spa treatment in a bracing marine climate with an annual mean temperature of +3.5°C. Conditions were made more comfortable with the establishment of a major sanatorium building in 1898, in a park of some 37 ha. The waters were derived from Cambrian rocks at a depth of some 160 m, and have a sodium chloride composition, with total mineralization of about 1.1 g/l. The waters are used for internal and external treatment, the spa having a reputation for easing gastric and cardiovascular disorders.

The mineral water springs of North America were well known and revered by some native American peoples, as testified by Jesuit missionaries in the mid-17th century, who were shown brine springs by Amerindians in what is now New York State (Bailey *et al.*, 1902). As early as the mid-18th century, George Washington was a regular visitor to Bath (now Berkeley Springs), West Virginia, seeking medical cure (Back *et al.*, 1995). During the 19th century, the importance of mineral waters and spas became established. By 1900, 8 000–10 000 mineral water springs had been mapped in the USA (Bailey *et al.*, 1902), of which 500 purveyed mineral water at an average price of $0.12 per gallon, mainly from sources in Wisconsin, followed by Texas, Massachusetts and New York. The annual turnover was estimated as some 45 million gallons or $5.8 million. This was big business, but Bailey *et al.* also note that many springs were unimproved and 'let to run

Table 1.1 Temperature of some thermal springs of the USA, compared with famous European thermal waters (derived from Bailey *et al.*, 1902)

Thermal spring	*Temperature (°C)*
USA springs	
Hot springs, Pyramid Lake, Nevada	97–98
Hot springs, Idaho	73
San Bernadino, California	42–78
Hot springs, Bath County, Virginia	37–41
European sources, for comparison	
Carlsbad, Czech Republic	72
Kochbrunnen, Wiesbaden, Germany	69
Hauptquelle, Baden-Baden, Germany	68
Kaiserquelle, Aix-la-Chapelle (Aachen), Germany	55
Kings Well, Bath, UK	46
Sulphur springs, Aix-les-Bains, France	42

to waste in a manner scandalous in most European nations'. The spas included the hot springs of Saratoga (New York State), White Sulphur and Berkeley (Virginia), Medical Lake (Washington), Rockbridge Alum, Bedford, Cresson and the hot springs of Arkansas and California (Bailey *et al.*, 1902). The French Lick Springs of Indiana yield waters that are alleged to produce a spectacular purgative effect (*Encarta*, 1994). The main thermal springs are listed in Table 1.1.

An American perspective on mineral waters and spas is provided by Back *et al.* (1995). They argue that spas deserve a prominent place in the history of the USA for at least three reasons: (1) they provided a meeting place for the leaders of the American independence movement, (2) the presence of hot springs justified, in several cases, the westward expansion of the railway network and (3) they were an instrumental factor in the establishment of the National Park Service.

The popularity of spas as places of fashionable resort declined rapidly in the early part of the 20th century. However, their use for therapeutic treatment, often as part of the national health service, has continued (at least until recently) in many countries, especially in Central and Eastern Europe, in Russia, Germany, France, Austria, Hungary, Romania, the Czech Republic and also in China (Jianli *et al.*, 1993).

In the UK, by contrast, the use of spas for therapy ceased almost completely with the advent of the National Health Service in the late 1940s. Doctors no longer sent their patients to spas for treatment and rest, hydrotherapeutic treatment being transferred to hospitals (Gilbert and Van De Weerdt, 1991). A handful of spas did, however, offer limited hydrotherapy, particularly for rheumatic and arthritic patients, including Woodhall, Bath, Leamington and Buxton Spas. Of these, only the Devonshire Royal Hospital at Buxton is still operational (Chapter 10).

1.2 MINERAL EXTRACTION FROM GROUNDWATERS

In Europe the extraction of useful components from mineralized groundwater was practised from as early as the 7th to 6th centuries BC, when the Etruscans obtained boric acid from thermal springs at Larderello. In the second half of the 1st millennium BC, the Chinese also tackled the problem of extracting dissolved salts and associated gases from groundwater. One saline spring in Daningchang, Sichuan, is known to have been exploited since 316 BC, and another in Yunanchang, Sichuan from 199 BC (Dongsheng, 1987). By the 2nd century BC they had also begun to exploit natural gases (Drimba, 1984), probably more than 1000 years ahead of Europe.

In the Roman period, Salinae (Droitwich) in Britain was important for the production of salt by evaporation of water from brine springs (Alderson, 1973). Salt continued to be obtained in this way into mediaeval times, when Nantwich, Middlewich and Northwich were also important centres of salt production for the preservation of food and for the great fish-curing trade (Bolton, 1980; Postan and Miller, 1987). Not surprisingly, the place-name element '-wich' is the Saxon term used for special localities such as salt springs. These localities are related to saliferous evaporitic beds within the Triassic marls of the Worcester and Cheshire basins (Chapter 10).

In continental Europe, from the 9th to 14th centuries AD, common salt was obtained not only by extraction from salt mines and evaporation of sea water, but also by evaporation of water from saline springs, as in central Germany, Lorraine and Burgundy (Drimba, 1987). In Little Poland saline springs were practically the only source of salt until the 13th century, when mines were opened up to meet an increased demand. The saline springs in Lorraine and at Salins in Franche Comté became among the largest industrial units in Renaissance Europe, competing in size only with the arsenal at Venice and the alum works at Tolfa (Postan and Miller, 1987).

From the 17th century, Glauber's salt ($Na_2SO_4.10H_2O$) was obtained by crystallization from the waters of the sulphatic springs of Františkovy Lázně in Bohemia. This was utilized in agriculture and in the chemical industry for production of sodium hydroxide.

The extraction of components from groundwater was diversified in the 18th to 19th centuries to include the recovery of carbon dioxide from naturally carbonated waters, of methane from formation or oilfield waters and of various medicinal salts from saline waters. Carbon dioxide was used for several purposes including impregnation of bottled waters, mofettic treatment, as a refrigeration agent and for multiple uses in the food and other industries. Methane obtained from formation or oilfield waters was used as a fuel, while medicinal salts extracted from salt waters were used for therapeutic purposes. An example of the latter was the widespread sale of Harrogate Health Salts derived from the spa of that name in England. The salts were even blended into a special Harrogate Soap.

Table 1.2 Analysis of brine springs in the coalfield of northeast England (after Anderson, 1945). Analyses given in parts per thousand (g/kg)

	Wallsend Colliery Spring (1842)	*St Lawrence Colliery Spring*	*Redheugh Colliery Spring*	*Unidentified Spring*
Ca^{2+}	38.18	4.59	7.59	11.06
Mg^{2+}	Trace	0.70	0.79	0.79
Na^{+}	Trace	16.51	23.32	44.04
HCO_3^-	–	–	–	Trace
Cl^-	67.54	35.33	52.52	–
SO_4^{2-}	–	0.51	–	90.76
Ba	–	–	0.90	1.75
Fe	–	0.046	–	–
Li	–	–	0.051	–
Salinity	105.72	57.69	85.18	148.39

Also in the 18th and 19th centuries, hypersaline brines from natural springs and from coal mine workings (Table 1.2) in northeastern England were used for the production of alkali metals and their potential for bromine production was also recognized (Anderson, 1945). Some of these had significant yields; the Birtley spring flowed at 118 000 l/day. These saline waters often contained barium and radium in significant quantities, particularly if sulphate was absent (sulphate providing a control on the solubility of barium and radium).

In the 20th century, especially after World War II, the range of components extracted from groundwater extended rapidly in many countries of Europe, Asia and in North America. The technologies for recovery of iodine and bromine from formation or oilfield waters, and of hydrogen, helium, boron, lithium, magnesium and sodium bicarbonate from thermal waters were perfected. In fact, at some stage in the past, thermal and mineral waters have provided a significant part of world production of hydrogen sulphide, methane, ammonia, boron and sodium carbonate (Armstead, 1983; Albu, 1987; Kelk, 1992). Examples of the successful extraction of by-products from thermal waters include (Czernichowski-Lauriol and Fouillac, 1991)

- boric acid, carbon dioxide and ammonia from Larderello, Italy;
- carbon dioxide, calcium, potassium and sodium chlorides from Imperial Valley, California, USA;
- carbon dioxide from plants in Kenya and Kizildere, Turkey; carbon dioxide is also obtained in commercial quantities from low temperature waters, for example at Buziaş, Romania (Chapter 15).

At other sites, the potential recovery of dissolved metals from thermal waters has been assessed, including the following.

- Zn, Pb, Cu, Mn, Se, Ag, Au, Pt, Li and others from the geothermal brines of the Salton Sea field. Maimoni (1982) estimates that the revenue from metal extraction could exceed that from the power generated. For example, a 1000 MW_e (electric) plant could produce 14 to 31% of the USA's demand for manganese, while a 100 MW_e plant could recover up to 65 000 tonnes of lithium per year, some nine times the total world sales for 1980. One well at the Salton Sea produces 0.24 kg of gold every year (McKibben *et al.*, 1989).
- Czernichowski-Lauriol and Fouillac (1991) report that the Hatchobaru plant in Kyushu, Japan, could produce up to 53 tonnes/year of lithium, even at the relatively low fluid concentration of 10 mg/l Li.
- Pauwels *et al.* (1991) report that low temperature geothermal fluids from Alsace, France, contain 40–300 mg/l lithium.

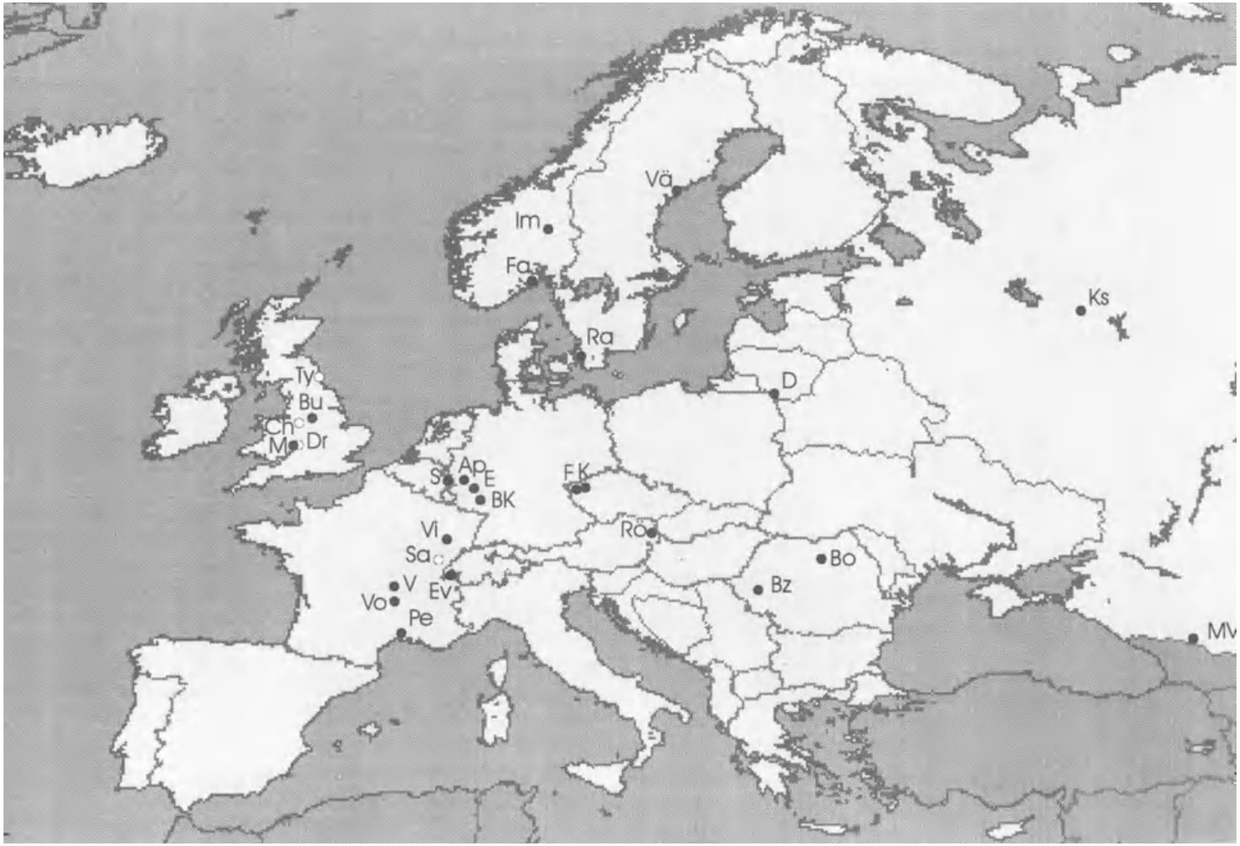
Czernichowski-Lauriol and Fouillac (1991) do stress, however, that the prognoses made for Hatchobaru and the Salton Sea are speculative. The technology to recover metals from geothermal waters still needs to be proven in full scale.

1.3 BOTTLING OF MINERAL WATERS

In the 17th to 19th centuries, simultaneously with the development of spas, there was an increased demand for mineral waters for drinking and internal 'cures'. The centres for production of bottled waters were Vichy, Vittel and Évian in France; Ems and Kreuznach in Germany; Karlovy Vary and Františkovy Lázně in Bohemia and Borsec and Buziaş in Transylvania (Figure 1.3).

Bottled water production in the 19th and 20th centuries gave an impetus to the development of techniques for analysis and abstraction of mineral waters and to the development of bottling factories, machines and transport facilities. Consumers became more exacting with regard to the quality of bottled water, especially in terms of the total mineralization, chemical composition, content of gases and the bacteriological quality (Back *et al.*, 1988). Consequently some problems of management and marketing appeared, a typical

Figure 1.3 Map of Europe showing selected centres of mineral extraction from groundwater (O) and sources of bottled mineral water (●). Ap = Apollinaris (Bad Nauenahr), BK = Bad Kreuznach, Bo = Borsec, Bu = Buxton, Bz = Buziaş, Ch = Cheshire (Nantwich, Northwich, Middlewich), D = Druskininkai, Dr = Droitwich, E = Ems, Ev = Evian, F = Františkovy Lázně, Fa = Farris, Im = Imsdalen, K = Karlovy Vary, Ks = Kostroma, M = Malvern, MV = Mineralny Vody, Pe = Perrier (Vergèze), Ra = Ramlösa, Rö = Römerquelle (Edelstal), S = Spa, Sa = Salins, Ty = Tyneside, V = Vichy, Vä = Västersel, Vi = Vittel, Vo = Volvic (Bourge-la-Reine).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example being at Borsec. According to Dr H.J. Krantz's account in his book *De Aquis Medicalis Transylvaniae* (On the medicinal waters of Transylvania) published in Vienna in 1773, the naturally carbonated mineral waters of Borsec were exported for drinking as early as the 18th century to Austria, Moldavia and Wallachia. The bottling and marketing of these waters were the responsibility of the chemists, but they soon began to add 'preservatives' to prevent the precipitation of salts, thus compromising the trade. As a result, a decree of 1783 forbade the chemists to market the waters and granted the local populace the right to transport them to consumers in Transylvania, Hungary and the Tyrol. In 1804 J.V. Günther, as the leaseholder of Borsec, joined with A. Zimmenthausen to construct a bottling factory. After 1832, when the contract with Zimmenthausen expired, the successive leases of Borsec continued to be profitable from the export of bottled water to Italy, Greece, Russia, Turkey and even America. Later, tampering with the waters was again detected, and from 1861, the bottles were sealed.

In the 20th century the production of bottled mineral waters has continued to expand. In the UK, however, bottled water was long regarded as a 'continental' habit. Overchauvinistic Britons possibly ascribed this to the supposed inferior, or even dangerous, quality of tap water on the continent. Since the early 1980s the situation has suffered a reversal: the British, partly out of anxiety over their own tap water quality and partly due to the promotion of chic non-alcoholic drinks, turned to bottled water in droves. The selection of waters available in any British supermarket today (Table 1.3) is testimony to this shift in consumption habits and to the power of marketing.

A not dissimilar situation has existed in Scandinavia, where the inhabitants have been justifiably proud of their high raw water quality. Apart from a handful of 'old faithful' brands such as the Norwegian Farris and Swedish Ramlösa (Figure 1.4), packaged water has not been a common sight. There are signs that things are changing, however, with more brands appearing. The Norwegians have recently recognized the potential for the export of their own high purity groundwater and surface water resources, and a recent state-subsidized programme (Misund *et al.*, 1994) was undertaken to identify suitable resources in the county of Nordland (Chapter 13).

In truth, many popular bottled waters, particularly in the UK and Scandinavia, cannot really be classified as mineral waters, often having a very low mineral content. This theme will be further explored in later chapters.

1.3.1 Artificial mineral waters

It was the chemist Priestley who in 1772 first proposed impregnating normal water with CO_2 (generated by the action of acid on chalk) to make an effervescent solution. This idea was taken further by the Swede, Professor Torbern Olof Bergman, who compounded artificial mineral waters

Table 1.3 Chemical characteristics of some British and Irish bottled waters; analyses (except pH) in mg/l; information taken from bottle labels; for locations, see Figure 10.1

	Aqua Pura, Eden Valley, England	*Highland Spring, Ochil Hills, near Blackford, Perth, Scotland*	*Lowland Glen, Campsie Fells, Stirlingshire, Scotland*	*Stretton Hills, Church Stretton, Shropshire*	*Abbey Well, Morpeth, Northumbria, England*	*Brecon Carreg, Carreg Cennen, near Llandeilo, Wales*	*Ashbourne Water, Derbyshire, England*	*Buxton Carbonated Natural Mineral Water, Derbyshire, England*	*Ballygowan Irish Spring Water, Newcastle West, Limerick, Eire*	*Schweppes Malvern (Primeswell Spring) Carbonated Mineral Water, England*
Ca^{2+}	52.5	39	6.8	41.3	54	47.5	100	55	117	33
Mg^{2+}	7.0	15	9.7	7.22	36	16.5	24	19	18	22
Na^+	26.5	9	5.8	10.8	45	5.7	15	24	17	15
K^+	2.5	1	7.0	1.59	7.5	0.4	3	1	3	1.5
Cl^-	80.0	15	10.0	20	80	13	40	42	28	48
SO_4^{2-}	17.5	9	10.0	33	28	9	60	23	15	33
NO_3^-	24.0	1.5	4.0	12.6	0.9	2.2	10	<0.1	9	7
HCO_3^-	–[a]	190	16.5	106	352	206	–	248	400	123
F^-	<0.1	<0.1	0.1	0.10	0.09	–	0.2	–	–	–
Fe	–	<0.01	–	–	–	–	0.01	0	–	–
Al	–	<0.01	–	–	–	–	–	0	–	–
Dry residue at 180°C[b]	–	175	98.0	195	430	198	420	280	450	–
pH	–	7.6	–	–	7.1	–		7.4	6.9	6.0

[a] Parameter not specified on the label.

[b] Dry residue at 180°C appears to be less than the sum of the components due to the decomposition of bicarbonate to carbonate on heating ($Ca^{2+}(HCO_3^-)_2 = Ca^{2+}CO_3^{2-} + H_2O + CO_2$). The bicarbonate figure can be multiplied by 60/122 to yield a carbonate value contributing to the dry residue.

Figure 1.4 Popular Scandinavian bottled waters, Farris and Imsdal from Norway, Ramlösa from Sweden and Hartwall Vichy from Finland.

Concentration (mg/l)	*Farris*	*Imsdal*	*Ramlösa*
Ca^{2+}	26	12	Not specified
Mg^{2+}	30	Not specified	Not specified
Na^{+}	400	1	240
K^{+}	15	Not specified	1.8
NH_4^{+}	1.5	Not specified	Not specified
HCO_3^{-}	300	37	Not specified
SO_4^{2-}	Not specified	4	10.0
Cl^{-}	Not specified	Not specified	29.0
F^{-}	Not specified	Not specified	2.8
I^{-}	0.4	Not specified	Not specified

impregnated with CO_2 to simulate natural mineral waters. Such artificial 'Seltzer' waters (named after the Seltzer spa in Nassau, Germany) were first produced on a large scale by Meyer in Stettin in 1787 (Bailey *et al.*, 1902). Bergman also proposed a mixture of carbonated water and lime juice as a cure for scurvy although, in retrospect, it appears likely that the vitamin C in lime juice was the important active agent. At around the same time, Thomas Henry of Manchester, UK, devised a recipe for a water simulating that at the German spa of Pyrmont involving a mixture of 1 scruple of magnesia, 30 grains of Epsom salts, 10 grains of common salt, a few pieces of iron wire or filings and 1 gallon of spring water.

The first patent for artificial water in the USA was issued in 1809, causing a significant backlash from the operators of natural spas such as Saratoga, New York State (Back *et al.*, 1995).

1.4 ENERGY FROM THERMAL WATERS

Historically, thermal waters and hot springs were used not only for bathing and extraction of mineral salts and gases, but also for the preparation of food and for heating. Such waters were known to the Hellenes, the Etruscans, the Celts, the Romans, the Dacians, the Italians, the Germans, the Czechs, the Romanians, the Turks, the Japanese, the Maoris of New Zealand, the Mexicans and the Icelanders among others.

Interest in the use of thermal waters for energy grew contemporaneously with the rapid development of the sciences of thermodynamics and energetics, in the second half of the 19th century. At this time, the art of extracting energy efficiently from hot water was refined, either by conversion into mechanical or electrical energy by means of turbines, or by direct transfer using heat exchange elements (Albu, 1987; Coudert and Jaudin, 1989).

At the beginning of the 20th century, Prince Piero Ginori Conti explored the generation of electricity from natural steam at Larderello, Italy. On the basis of this experiment, the first power plant using geothermal steam was inaugurated at Larderello in 1904. This was followed by plants at, for example, Wairakei (New Zealand) in 1958 and at The Geysers (USA) in 1960. The latter is the world's largest geothermal power plant, with an output of about 1400 MW_e, approximately half the USA's total installed geothermal capacity, but only a small fraction of the estimated potential output of the USA of 23 000 MW_e (based on waters $>150°C$). Today geothermal power plants are operational in some 18 countries. Guffanti and Wherry (1994) estimate the total worldwide production of geothermal energy to have been 5800 MW_e in 1990 and by the end of 1993 this had reached over 6000 MW_e (Huttrer, 1996).

During the 20th century the use of thermal waters gradually expanded to include refrigeration, heating of industrial and agronomic spaces and the supply of domestic hot water and air conditioning, although traditional uses continued (Figure 1.5). The use of thermal waters for heating dwellings and greenhouses began in Iceland in the 1920s when a district of Reykjavík benefited from the first geothermal heating system (Armstead, 1983). The steam from the hot springs of this area was indeed responsible for the Viking name of Reykjavík (Smoky Bay). Thermal waters have been important to the development of processes in the chemical, mining, metallurgical, food, wood and construction materials industries. They have also been used to increase productivity in agriculture, horticulture, fruit growing and

Figure 1.5 Washing clothes at Þvottalaugar hot spring, Iceland, in about 1900. (Courtesy of the Reykjavík Municipal Heating Service and the Reykjavík Museum of Photography.)

zootechnology, and have been particularly applied to the avoidance of frost damage of crops and to melting snow (Albu, 1987). In mediaeval times Oradea, in Romania, was in the enviable position of being able to maintain its defensive moat throughout the year, using thermal waters so that ice did not form. Iceland is now one of Europe's leading exporters of bananas, thanks to geothermally heated greenhouses.

2

Uses of mineral and thermal waters

> *... bottling water is as near as you can get to printing money.*
>
> BBC Radio 4, 18 August 1994

2.1 MINERAL WATERS

2.1.1 The bottled water boom

In the UK the bottled water fad began in earnest in the 1980s, partly as a response to the need for an 'adult' non-alcoholic drink, stimulated by stricter drink-driving laws, and partly as a response to public fears over the quality of British tap water. Currently, the market stands at 500 million litres annually in Britain; a market value of some £300 million (Edwards, 1994). It is not so long ago that the Englishman abroad received warnings 'not to drink the tap water on the Continent', and was encouraged to consume only Evian water on holiday.

Such a hysterical reaction to UK tap water quality as a whole cannot be justified, but several unfortunate, highly publicized drinking water contamination incidents have forced many Britons to seek 'safe' drinking water in bottles. The average Briton's conception of a mineral water is a water that is low in minerals, but enjoys a high degree of natural source protection against environmental contamination. This is reflected by the rather boring chemical composition of most British mineral waters (Table 1.3) and the fact that the most popular continental waters sold in Britain are the relatively low mineralization Volvic, Vittel, Evian and Perrier waters (Table 2.1). In Norway, such consumers may buy 'Norwater' (a very low mineralization Norwegian mountain water from a protected source in Imsdalen; Figures 1.4 and 13.14a) in cartons, while customers in England may buy standard Chalk groundwater in bottles labelled 'Chiltern Spring Water', regardless

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M. Albu, D. Banks and H. Nash.
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Table 2.1 Chemical characteristics of some popular continental bottled waters. Analyses (except pH) in mg/l. Information taken from bottle labels and from Green and Green (1985)

	Vittel, Bonne Source, Vosges, France	*Evian, French Alps, France*	*Carbonated Selters, Löhnberg Germany*	*Römerquelle, Edelstal, Austria*	*Volvic, Bourge-la-Reine, Auvergne, France*	*Perrier, Languedoc, France*
Ca^{2+}	91	78	160	152.9	10.4	147.3
Mg^{2+}	19.9	24	50	69.27	6.0	3.4
Na^{+}	7.3	5	370	13.04	8.0	9.0
K^{+}	4.9	1	20	2.00	5.4	–
Cl^{-}	–	4.5	360	5.86	7.5	21.5
SO_4^{2-}	105	10	20	324.3	6.7	33
NO_3^{-}	0.6	3.8	–	0.90	2.0	18.3
HCO_3^{-}	258	357	1100	424.1	64.0	390
F^{-}	–	–	–	0.37	–	–
SiO_2	–	13.5	–	22.7	–	–
Dry residue at 180°C[a]	403	309	–	–	–	478
TDS	–	–	2090	1023	–	–
pH	–	7.2	–	–	–	5.7
Natural CO_2	–	–	–	4500–5500	–	3500

– parameter not specified in analysis.

[a] Dry residue at 180°C appears to be less than the sum of the components due to the decomposition of bicarbonate to carbonate on heating ($Ca^{2+}(HCO_3^-)_2 = Ca^{2+}CO_3^{2-} + H_2O + CO_2$). The bicarbonate figure should be multiplied by 60/122 to yield a carbonate value contributing to the dry residue.

of the fact that the Thames Water Company may supply identical water 'on draught' from similar wells at a fraction of the cost and with the added benefit of slight chlorination to prevent bacterial contamination.

Image plays a significant role in a consumer's choice of water. This is illustrated by the Norwegians' decision to invest government funding in prospecting bottlable groundwater resources in Nordland county, in the belief that the 'ultrapure' Arctic image would provide a significant marketing advantage (Chapter 13). The same factor is also at work in the UK, perhaps explaining why, in 1992, 18 of the UK's 37 bottled 'mineral' waters were Scottish, reflecting the average Briton's perception of Scotland as natural and unpolluted, despite the fact that nitrate levels of almost 80 mg/l can be found in at least one bottled Scottish water, according to Robins and Ferry (1992).

In some cases a hysterical reaction to tap water quality may be justified, as in St Petersburg in the early 1990s, where tap water from the River Neva was reported to contain up to 0.8 mg/l of phenols and is occasionally contaminated by unpleasant parasites from the Gulf of Finland. Here, people are increasingly willing to spend their small incomes on water filters and regular supplies of the local bottled groundwater to protect their health.

Even religion has found its way into the bottled water market. One of the more popular brands of Russian bottled water is the 'Saint Springs' water from Kostroma, northeast of Moscow. The holy water is sold in onion-domed plastic bottles with the reassuring message that it has been blessed by the Patriarch of Moscow and Russia.

Some more sophisticated imbibers of Adam's Ale will buy mineral water for what it has got in it rather than what it has not. This appears particularly true of Continental Europe. For example, the Lithuanian Birutė mineral water is a fizzy sodium chloride brine with 5–6 g/l salinity (compared with seawater, which has about 32 g/l), derived from fracture zones penetrating deep-lying Palaeozoic strata. Even stronger is the Lithuanian Vytautas water, with a salinity of 8.5 g/l (Chapter 13). A yet stronger mineral water is available in Russia: Yessentuki No.17 with 11–14 g/l total mineralization. Another record maker is the Russian Poljustrovo (Figure 2.1) from the St Petersburg area. Abstracted from moraines along the Gulf of Finland, with heavily reducing conditions, this water contains 40–60 mg/l iron, compared with the EC recommended level for drinking water of 0.05 mg/l. On opening the bottle, and allowing degassing and access to oxygen, the iron precipitates as a rather unattractive red-brown ochre.

2.2 THERAPEUTIC SPAS

Mineral water is, of course, not only found in bottles. For centuries springs have been visited for their curative properties. While spas such as Bath and

Figure 2.1 'Iron Brew' – the Russian Poljustrovo mineral water. $Ca^{2+} < 25\,mg/l$, $Mg^{2+} < 25\,mg/l$, $Na^+ + K^+ < 50\,mg/l$, $Cl^- < 50\,mg/l$, $SO_4^{2-} < 100\,mg/l$, $HCO_3^- = 80\text{–}150\,mg/l$, $Fe = 40\text{–}60\,mg/l$, total mineralization = 320–360 mg/l.

Matlock in the UK are now largely tourist curiosities, spas in continental and particularly Central and Eastern Europe are still in use, and are the basis of state 'national health' sanatoria. Some form of spa treatment has, for example, been incorporated into the national health services of Germany, France, Italy, Austria, Switzerland, Belgium, Denmark, the UK and most of the former Warsaw Pact nations farther east. Typically wealthy holiday-makers are seeking out spa destinations for healthy and relaxing breaks, notably those from nations with an already strong 'health culture', such as western Germany and Italy (Gilbert and Van de Weerdt, 1991).

Until recently several spas in the UK, such as Woodhall and Leamington, offered treatment under the National Health Service although, since the formation of that service in 1948, the medical use of therapeutic spas has been in steady decline. Currently, the only significant public spa therapy centre is at the Devonshire Royal Hospital in Buxton (Chapter 9). In times past, however, a range of therapeutic treatments was available in the UK which rivalled and probably exceeded those available in continental Europe today. Those on offer at Harrogate are described in gruesome and slightly sadistic detail by the British Spas Federation (1931) and include

- various mineral water baths;
- the massage douche;
- the Aix douche (sitting position, needle shower and massage);
- the Vichy douche (lying position, similar to above);
- baths of mixed peat and sulphur water;

- mud packs;
- the patent Harrogate intestinal douche (using guaranteed antiseptic sulphur water), involving internal application of water to the colon;
- the nasal douche.

Accessory treatments included the 'Liver Pack' (a poultice of mustard bran), 'Paraffin Wax Baths', the 'Foam Bath' (or Jacuzzi), the 'Combined Heat and Light Bath' (sitting under a hot electric light bulb), 'the Electric Immersion Bath' (a mild form of electrocution), the still-popular 'Ultra Violet Treatment' and an eccentric recreational activity named golf.

2.2.1 Water quality

The quality of thermal and mineral waters for therapeutic use (for immersion, medical use or consumption under medical supervision) is governed by their physicochemical properties (Stoicescu and Munteanu, 1976; Thomson, 1978; Pricăjan and Airinei, 1981; Dumitrescu, 1984; O'Hare *et al.*, 1991). Depending on their therapeutic use, these waters are classified according to:

- temperature: 23–36°C = hypothermal; 36–42°C = mesothermal; >42°C = hyperthermal waters;
- salinity, or more specifically in a medical context, tonicity or osmolarity; <320 mOsm = hypotonic; 320–330 mOsm = isotonic; >330 mOsm = hypertonic waters (Dyson, 1978);
- basicity: pH 7–8 = weak basic waters; pH 8–11 = basic waters; pH >11 = strongly basic waters;
- acidity: pH 6–6.9 = weak acid waters; pH 3–6 = acid waters; pH <3 = strongly acid waters.

They should fulfil one or more of the following conditions (Sturza, 1930; Dinculescu *et al.*, 1975; Evans *et al.*, 1986):

- total mineralization should be more than 1 g/l in therapeutic mineral waters;
- dissolved salts: waters should contain more than 1 g/l of sodium, potassium, calcium and magnesium bicarbonates, chlorides and sulphates and other ionic components with purported health effects;
- iron, iodide etc.: waters should ideally contain more than 10 mg/l of iron (Fe^{2+}), or more than 1 mg/l of iodide and other biologically active elements to be classed as iron or iodine waters;
- gas content: ideally, a content of more than 1 g/l carbon dioxide or more than 1 mg/l of hydrogen sulphide is desired;
- content of certain trace elements with recognized or purported physiological and therapeutic effects.

2.2.2 Medicinal value

The medicinal value of mineral waters and spa therapy is a controversial topic. Few rigorous studies have been undertaken. There is even a significant disagreement among the authors over interpretation of the available evidence, and this is probably a reflection of varying cultural and national backgrounds.

Several trace elements are essential for the metabolism of humans and/or animals, including I, Fe, Cu, Co, Zn, Se, Mn, Si, Cr, Ni, Mo, F and V (Edmunds *et al.*, 1989; Edmunds and Smedley, 1996), in addition to such obvious major elements as P, N, C, Mg, K, Na, Ca, S and Cl. Additionally, there is evidence that Be, Sc, Sn, Te, Rb, La, As, Li, Ba and Sr also play a role in the life function.

It is widely recognized that many chemical substances exhibit a characteristic dose–response curve. For many substances that serve a function in the body's metabolism, there will be an optimum intake level or 'plateau' (curve type (a) in Figure 2.2). Below this level, deficiency disorders may result, while above this level toxicity may set in. The classic example is that of fluoride. An optimum concentration of fluoride in drinking water (often quoted as between 0.7 and 1.5 mg/l) ensures healthy development of bones and teeth. Too little fluoride can result in decreased resistance to tooth decay (e.g. Rock *et al.*, 1981). Too much fluoride can also be harmful, resulting in dental fluorosis (mottled teeth), osteofluorosis or intermittent lameness. Fluorosis is widely observed in several tropical African nations, where concentrations in water can reach several tens of mg/l, and also in some parts of Norway, where fluoride levels in granite/gneiss groundwater can reach about 10 mg/l (Reimann *et al.*, 1996; Bjorvata *et al.*, 1997). Similarly, water deficient in iodide is thought to be responsible for the development of goitre in some populations, e.g. historically in Derbyshire, UK (Edmunds, 1971).

Several workers, such as Bjørn Bølviken of Trondheim, have argued that nearly all elements are likely to play some role in the body's metabolism and that all elements thus exhibit a dose–response curve of type (a), albeit with the maximum benefit plateau at very low concentrations. Backing up this hypothesis, Rohlich (1978) regards heavy metals such as tin and nickel as essential at low concentrations.

Given the lack of quantified evidence for the health effects of many elements, such as some heavy metals, at low levels, a type (b) curve is often assumed, with concentrations up to a certain threshold value having no substantial negative health effects. The level of the threshold is often dependent on the body's ability to excrete the element in question (i.e. the level below which it does not accumulate in the body).

For some parameters, notably bioaccumulating radioactive species, the usual assumption is that there is no 'safe level' and that the risk of mutanogenesis is represented by a type (c) curve passing through the dose–response

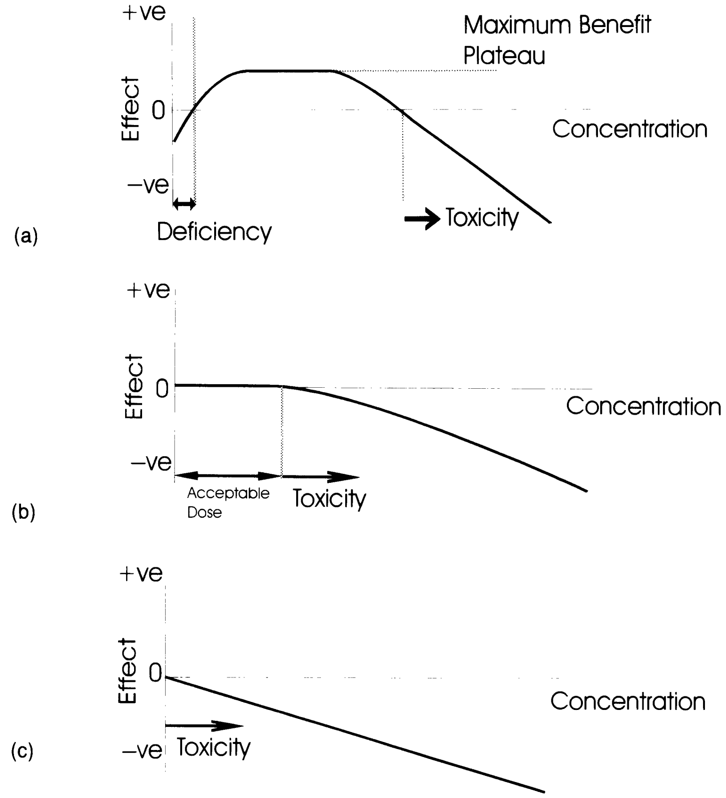


Figure 2.2 Typical dose–response curves for (a) an essential trace component, which becomes toxic in excess, e.g. fluoride, (b) a non-essential component, which becomes toxic in excess, e.g. lead, (c) a carcinogenic component for which there is assumed to be no 'zero effect' dose (although there may be an acceptable level of exposure), e.g. plutonium.

origin. Even this assumption is in doubt, however, as some recent work on low dose levels suggests that the body may have a finite capacity to repair radiation damage.

The believer's viewpoint

Spa therapy is based on drinking and the external use of waters believed to be of medicinal value. The external use of waters, for immersion (bathing), shower massage and irrigation, for example, is known as balneology.

The 'true believer' argues that spa waters affect the body by means of temperature, chemical composition and hydrostatic pressure. In addition, nerve receptors are thought to be subject to stimulation by gases (CO_2, H_2S, radon) that reach the blood through the skin, mucous membranes and respiratory passages (*Great Soviet Encyclopedia*, 1973–1984). The effects of several constituents and properties of different waters are held to be well known (through accumulated experience) and are utilized in clinical medicine. These include the bactericidal effect of sulphates on skin conditions, the purgative effect of magnesium sulphate (Epsom Salts) and highly saline waters, the tonic effect of iron-rich waters on anaemic conditions and the effect of warm and saline water on easing stiffness in joints and muscles. The effects of immersion in constant temperature baths as a diuretic and in regulating blood pressure have been documented (e.g. Epstein, 1978; Anderson *et al.*, 1986).

Other possible curative effects are less well proven and it is generally accepted that environmental and psychological factors due to altitude, climate and proximity to the sea, as well as relaxation, play a significant part in successful spa resort cures.

Some physiological effects of spa therapy have been subject to study and documentation, occasionally surprisingly rigorous, for some time. At Harrogate the British Spas Federation (1931) was able to report in a convincing manner that sulphur water had a distinct bactericidal effect on streptococcus and that ingestion had the following effects:

- increase in flux of bile;
- diuretic effect of 40% volume increase;
- increase in volume and weight of faeces;
- various other metabolic increases, including excretion of nitrogen, endogenous creatinine, endogenous uric acid, hypoxanthin, urea, calcium, manganese and potassium.

Among the most convincing studies are those carried out on bathing and immersion therapy at Bath, UK, as documented by O'Hare *et al.* (1991) and Heywood (1991). O'Hare *et al.* (1991) observed that immersion in spa water at 35°C had the following effects:

- an increase in cardiac output (from 4.6 l/min to 7.4 l/min) and stroke volume;
- haemodilution resulting, in turn, in a decreased red blood cell count and blood viscosity (the latter factor partially explains the increased cardiac output);
- a significant increase in excretion of urine and excretory flux of sodium and potassium, accompanied by a loss of weight.

It was noted, however, that a control group using tap water experienced identical effects. It thus appears that the temperature and depth and time of immersion are the controlling factors, rather than mineral water composition. O'Hare's group also note that the cardiac changes could endanger patients with certain pre-existing cardiac or circulatory conditions. The observations above help to explain why spa therapy has often been regarded as a successful, although possibly temporary, treatment for certain forms of obesity, kidney disorders and, as Heywood (1991) explains in a brilliant piece of detective work, gout and some palsies. Heywood notes that, with the establishment of the Bath Hospital in 1741, systematic accumulation of medical data on spa patients was undertaken. The records indicate little evidence of any beneficial effect for many types of disease, but gout and nervous palsy stand out as being highly treatable by immersion in the high temperature spa waters, with a cure rate of some 45%. Heywood argues that both disorders were caused by endemic lead poisoning, due to almost daily exposure to lead via cosmetics, lead piping, cooking utensils, lead glaze in cooking pots, paint and medicines. Some groups, such as occupational users of lead products, were at greater risk, as were alcoholics, drinking wine or port affected by lead-based fungicides or deliberately adulterated by lead acetate as a sweetener. In poor folk, with a low protein diet, the lead poisoning manifested itself as a combination of palsious symptoms, including partial peripheral paralysis, known as *colica pictonum* (Devonshire colic – the Devonians being partial to lead-adulterated cider). In rich patients, typically port imbibers with a high protein diet, the chronic lead poisoning was manifested as gout, due to impaired urate excretion. Later studies revealed that high temperature immersion stimulated the excretion, via urine, not only of calcium, but also of its chemical analogue, lead. Excretion of urinary urate is also stimulated, relieving gouty symptoms. It is also suspected that drinking Bath waters may have had an additional effect, due to their high calcium and iron content. It has been demonstrated in the USA that deficiency in these elements increases the absorption and retention of lead and increases the toxicity of that already absorbed.

The *Great Soviet Encyclopedia* (1973–1984) provides a list of the main disorders treated at different spas. High sulphate waters such as those at Aachen (Germany), Baden (Austria) and White Sulphur Springs (West Virginia, USA) are used for some skin conditions. The alkaline waters of Vichy (France), Ischia (Italy) and Mariánskě Lázně (Czech Republic) aid the digestion and may work as purgative agents. The springs of Karlovy Vary are valued for treating digestive disorders and liver diseases. The highly carbonated salt springs at Wiesbaden and Baden-Baden (Germany) have long been used for rheumatic and neuralgic conditions (see Figure 1.2 for locations). Saratoga Springs, New York, is one of the oldest health resorts in the USA. It consists of seven main springs with alkaline waters containing carbon dioxide, sodium and chloride. The resort is purported to treat disorders of the cardiovascular system, digestive and metabolic disorders as well as functional disorders of the nervous system.

The sceptic's viewpoint

Even the most hardened sceptic will admit that the prospect of relaxing in a warm, bubbling, spring-fed bath in a civilized spa town is likely to have a healing effect on the soul and, quite conceivably, positive psychosomatic effects on the body. The sceptic will also admit the more obvious physiological effects of certain salts, e.g. magnesium, particularly in combination with sulphates, as spectacular purgatives. The unbeliever has, however, difficulty with the more dramatic claims made for some mineral waters. For example, Narzan water (Figure 12.5), a strong (2–3 g/l) calcium bicarbonate water from the Russian Caucasus claims to be effective against 'Chronic gastritis with normal, high, and insufficient secretory gastric function, castric and duodenal ulsers [sic], chronic colitis, chronic hepatitis, chronic jaundice and urinary disease and metabolic diseases (diabetes, urate diathesis, oxalaurie and chronic pancreatitis)'. One of the more enthusiastic descriptions of Harrogate spa, UK, recommended its water for 'constipation, flatulence [although it neglects to specify whether the sulphurous waters promote or cure the ailment], disorders of the liver... resulting from free living and inactive habits,... gouty and rheumatic symptoms, chronic catarrhs of the gall bladder' and many more disorders (Blakeson, 1993).

While some waters may be beneficial, or at worst harmless, it is difficult not to feel a touch of unease at the promotion of springs such as at Františkovy Lázně (Czech Republic) as cures for infertility, while claiming to contain up to 0.5 mg/l (natural) arsenic. The Františkovy water cure is assisted by a statue of a young man standing in one of the town's squares. Superstition requires that the statue's genitalia are touched for luck, and the lucky youth's male member has become distinctly worn and shiny over the years.

Another argument in the sceptic's armoury is the past and current promotion of solutes, which are now believed to have no positive health effect and possibly a significant negative one. An example in question is the content of radionuclides in some spa or mineral waters. Until the middle of the 20th century, radioactivity was believed to have positive and life-enhancing qualities. In 1911 the inaptly named Dr Sobermann pronounced radon as enhancing the growth of healthy cells, urinary excretion and sexual activity, while curing insomnia (McNulty, 1991). Radon-containing springs in the USA were also popular for therapeutic treatments, as were the waters at Bath, UK, where, until the middle of the 20th century patients would sit in an 'inhalitorium', an inverted funnel over the spring waters, to inhale the radon-rich gases (McNulty, 1991). Currently, many springs around the world promote their services under the radioactivity banner, particularly in Central and Eastern Europe and in China. Examples include spa resources at Fangzi, China (Jianli *et al.*, 1993), the North Bohemian Rift (Czech Republic; Franko *et al.*, 1985) and Badgastein in Austria (West, 1994), which are known for their high contents of radon gas. Some examples from Europe are given in Table 2.2.

Of course, all waters contain traces of radioactivity (particularly in the form of dissolved radon, uranium and radium) and Table 3.5 details the

Table 2.2 Radon content of several mineral spring waters, converted from Mache units (1 Mache unit = 360 pCi/l = 13.3 Bq/l). The first four springs lie in the Erzgebirge on the border between the Czech Republic and Germany (after Hevesy and Paneth, 1938)

Spa/spring location	*Radon content (Bq/l)*
Oberschlema, Erzgebirge, Germany	*c.* 40 000
Joachimstal (Jachymov) Czech Republic (mine water)	27 270
Brambach, Erzgebirge, Germany (Wettin Spring)	26 600
Joachimstal, Czech Republic (Spring Head)	7 980
Ischia, Italy (Old Roman spring)	4 920
Gastein, Austria (Reissacher Stulm)	3 990
Aix-les-Bains, France (Alum Spring)	745
Karlovy Vary, Czech Republic (Mühlbrunnen)	426

results of a few recent studies of naturally occurring groundwaters. However, as yet, no documented evidence exists for the positive health effects of exposure to ionizing radiation. Indeed, guidelines for the maximum allowable levels of dissolved radionuclides in groundwater are being developed in several countries (Table 2.3), and radon exposure is regarded as a significant source of lung and even stomach cancer in the USA and Scandinavia today (Banks *et al.*, 1995b).

Several bottled mineral waters were formerly advertised as being radioactive and the shift in public attitude regarding radioactivity in the last few decades is clearly demonstrated in Figure 2.3. The old label of the Swedish mineral water 'Västersel' promotes radioactivity as one of its most valuable health-related characteristics (Åkerblom, 1994a), while Greenpeace's ingenious 'Radi-eau-active' campaign of 1995 argues that groundwaters may become contaminated by radioactivity if NIREX (a British nuclear waste disposal group) continues with its plans to dispose of radioactive waste near the Lake District. The Västersel water contained some 5000 Bq/l radon (at source, though of course this would rapidly decay in the bottle) and also dissolved uranium (Åkerblom, 1994b): it advertised itself as 'Europe's strongest radioactive spring' and was recommended especially to the elderly due to its alleged content of gold chloride.

Other constituents of many mineral waters have been alleged or demonstrated to have negative health effects after prolonged exposure to high concentrations; examples include fluoride (dental and bone discoloration and malformation; Shupe *et al.*, 1979), sodium (heart and circulatory disorders: Gardner, 1976; Robertson and Parker, 1978) and some heavy metals. Of course, a few occasional cups of mineral or spa water will not lead to a significant dose of any toxic elements. Caution would be advisable, however, for people planning to use highly mineralized waters as the basis of their entire water consumption, as well as for those spending significant periods of time in enclosed mineral or thermal water baths where significant quantities of radon may be degassed from the water.

Table 2.3 Existing drinking water standards for Rn, U, Ra and gross radioactivity (after Banks *et al.*, 1995b)

Organization	*Rn*	*U*	*Ra*	*References*
US EPA recommended limit for Rn in air	4 pCi/l = 0.15 Bq/l	–	–	Mose *et al.* (1990)
Max. permitted total radium in water (US EPA) and equivalent concentrations of U and Rn giving lifetime risk of 4×10^{-5}	2.2 Bq/l	0.74 Bq/l = <30 μg/l[b]	5 pCi/l[a] = 0.185 Bq/l	Milvy and Cothern (1990)
US EPA proposal for Rn in water (alternative levels suggested by AWWA)	11 (37–185) Bq/l	–	–	AWWA (1993)
Range of suggested MCLs	22–74 Bq/l	0.7–4 Bq/l = <30–<160 μg/l[b]	–	Milvy and Cothern (1990)
Range of suggested MCLs	8–370 Bq/l	0.37–1.85 Bq/l = <14–<75 μg/l[b]	–	Kinner *et al.* (1990); Sorg *et al.* (1990)
Radon in drinking water in Sweden (based on possibility for degassing)				Statens Strålskyddsinstitut (1996)
Action required	>1000 Bq/l	–	–	
Possible action	100–1000 Bq/l	–	–	
No action required	<100 Bq/l	–	–	
Norwegian recommended action level for radon in drinking water	500 Bq/l	–	–	Statens Strålevern (1996)
Canadian MCL for uranium in drinking water	–	20 μg/l	–	Lahermo and Juntunen (1991); Barnes (1986)
		Total α-activity		
Gross α-activity (excluding U and Rn; US EPA)		15 pCi/l = 0.555 Bq/l		Milvy and Cothern (1990)
Gross α-activity		3 pCi/l = 0.1 Bq/l[c]		WHO (1984); SIFF (1987)

[a] Fixed US EPA standard for ^{226}Ra + ^{228}Ra.
[b] Based on assumption 1 μg = ≥0.025 Bq.
[c] Based on ^{226}Ra, i.e. excluding Rn.
MCL = Maximum concentration limit.

The final argument forwarded by the sceptic would probably be that many bottled waters (as opposed to mineral waters) are a rip-off. They are expensive (costing some 800 times more than tap water in Britain; Edwards, 1994), may be susceptible to bacterial contamination, are often little different from normal tap water in their chemical composition and may even contain significant traces of the contaminants that tap-waterphobes may be trying to avoid. The Aqua Pura 'natural spring water' from the Eden Valley, UK, for example, contains 24 mg/l nitrate which, while still below the UK drinking water maximum 50 mg/l, is presumably by no means free of anthropogenic influence.

Dr Anderson's verdict

An eminently sensible viewpoint on the therapeutic value of mineral waters was given by the American Dr Anderson, as cited by Bailey *et al.* (1902):

> Mineral springs are not 'cure-alls'. As a rule, too much is claimed for them. The many marvellous cures cited and the many and improbable and ridiculous statements seen on printed circulars do more harm than good. Sensible people are not going to believe that a 'magnetic' mineral water is going to save a bad case of consumption, or that any 'mineral water' cures heart disease etc. On the other hand, it would be quite as flagrant an error to suppose that all reputed beneficial effects of mineral waters were only the result of extravagant or interested imaginings.

2.3 REGULATIONS GOVERNING MINERAL AND BOTTLED WATERS

Bottled waters must meet the quality standards prescribed by the country of production or consumption. For drinking water, most of Europe follows standards set by the Council of the European Community (EC Directive 80/778/EEC for drinking water and Directive 80/777/EEC, amended by Directive 96/70/EC for bottled mineral waters). Waters bottled for medicinal purposes are not covered by these directives but come under health regulations for each country. It is worth mentioning, in passing, that recent, tentative plans to market Harrogate (UK) spa water as medicinal water have been postponed due to the astronomical cost of satisfying the relevant pharmaceutical trials which would have been required (G. Fitzmaurice, Harrogate Borough Council, personal communication, 1997).

2.3.1 Spring water, mineral water or packaged water?

It can be a matter of taste, health-consciousness and commercial marketing which influences whether we drink tap water or buy bottled water. In the

···BORDS & HÄLSOVATTEN···

Vattnet kontrolleras i kemiskt, bakteriologiskt och hygieniskt avseende av Fil. Dr. Bertil Groth, off. aukt. handelskemist, Stockholm.

Tappat direkt från

VÄSTERSEL

starkt radioaktiva källa.

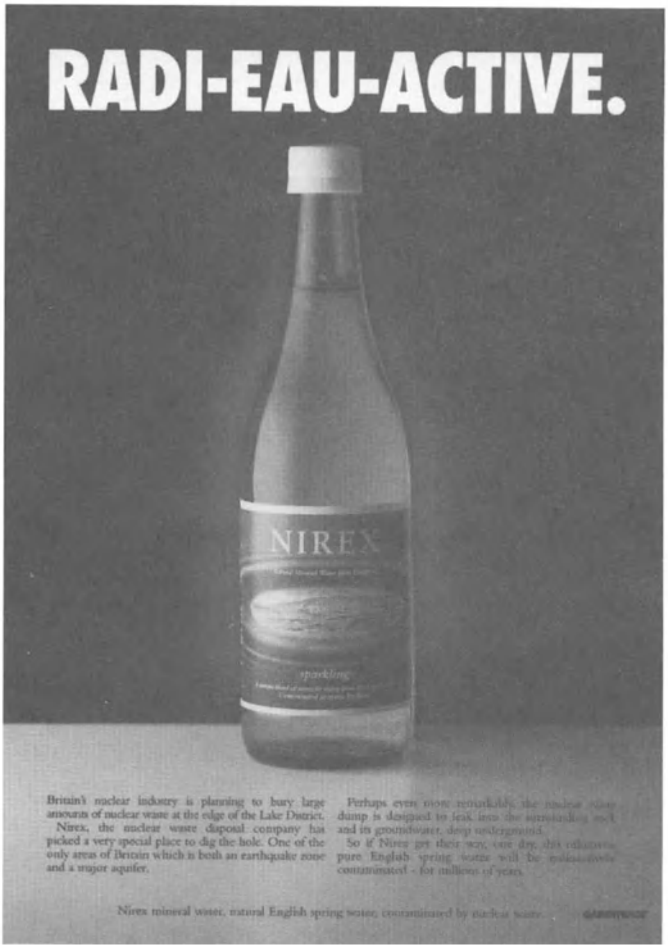
Låg alkalitet, frisk smak. Innehåller för organismen nyttiga mineraler.

ANALYS:
Huvudsakliga beståndsdelar enligt analys i milligram pr liter:

Totalhalt mineralsalter	c:a 175
Kalciumklorid ..	7,8
Magnesiumklorid	13,8
Kalciumbikarbonat	65,7
Natriumsulfat	7,1
Natriumbikarbonat	59,7
Dinatriumfosfat	19,9
Arseniksyrlighet	0,15
Natriumjodid	0,038

Radioaktivitet i källan c:a 30000 voltenheter pr liter.

(a)



Britain's nuclear industry is planning to bury large amounts of nuclear waste at the edge of the Lake District.

Nirex, the nuclear waste disposal company has picked a very special place to dig the hole. One of the only areas of Britain which is both an earthquake zone and a major aquifer.

Perhaps even more remarkably, the nuclear waste dump is designed to leak into the surrounding rock and its groundwater, deep underground.

So if Nirex get their way, one day, this [illegible] pure English spring water will be radioactively contaminated - for millions of years.

Nirex mineral water, natural English spring water, contaminated by nuclear waste.

(b)

interest of protecting the consumer the EC has produced a Mineral Water Directive (80/777/EEC), amended in Directive 96/70/EC. In this Directive natural mineral water is defined as:

> 'microbiologically wholesome water, originating in an underground water table or deposits and emerging from a spring tapped at one or more natural or bored exits'. Natural mineral water can in addition be 'clearly distinguished' from ordinary drinking water:
>
> (a) by its nature, which is characterized by its mineral content, trace elements or other constituents and, where appropriate, by certain effects;
> (b) by its 'original' state,
>
> both conditions having been preserved intact because of the underground origin of such water, which has been protected from all risk of pollution. The composition, temperature and other essential characteristics of natural mineral water must remain stable within the limits of natural fluctuation; in particular, they must not be affected by possible variations in the *rate of flow*.'

Several years of monitoring and testing a source may be necessary to prove that a mineral water satisfies these criteria. The EC Mineral Water Directive

---

Figure 2.3 The changing face of radioactivity; (a) an old label (probably from the 1930s) illustrating how desirable the radioactive content of the Swedish 'Västersel' mineral water once was (after Åkerblom, 1994a). Another version of the label (Åkerblom, 1994b) notes the water's content of uranium nitrate, and recommends 'silicic acid: good for building bones, phosphoric acid: excellent for the brain and gold chloride: increases life functions'. Ironically the label then goes on to proclaim that the water is 'free from iron'! TDS = Total dissolved solids.

	Västersels (mg/l)
Ca^{2+}	19.1
Mg^{2+}	3.52
Na^{+}	25.1
Cl^{-}	15.3
SO_4^{2-}	4.80
HCO_3^{-}	92.8
As	0.079
I^{-}	0.032
Phosphate as HPO_4^{2-}	13.45
Rn	*c.* 5000 Bq/l
TDS	*c.* 175

(b) The recent 'Radi-eau-active' campaign launched by Greenpeace in protest at the proposed disposal of radioactive waste in the vicinity of the English Lake District, raising fears of radioactive contamination of groundwater resources. (Copyright Greenpeace UK and reproduced with permission.)

emphasizes the need for a mineral water source to be 'naturally protected from any kind of pollution' and to have a 'stable mineral composition' (with an 'open' definition of the term 'stable') regardless of the fact that the concentrations of some constituents may far exceed the standards enshrined in the Drinking Water Directive (80/778/EEC). The quality of the mineral water is in fact only controlled by strict parameters regarding bacterial content and a suggestion (Annex 1) that account is taken of limits laid down for certain toxic elements. The bacterial standards are designed to ensure that bacteria are not introduced during the bottling procedure. As regards permitted 'natural' bacterial content, requirements for mineral water (fewer than 100 viable colonies per millilitre after bottling at 20–22°C after 72 h on agar) are no more stringent than those for tap water. Allowing for an increase in bacterial content between bottling and point of sale implies that bottled water at point of sale may legitimately be of inferior bacteriological quality to tap water. Nevertheless, the water, up to the point of sale, should be free from parasites and pathogenic microbes, coliforms and faecal streptococci, sporulated sulphate-reducing anaerobes and *Pseudomonas aeruginosa* (Green and Green, 1985).

Concerning treatment, the Directive's Article 4.1 specifies that natural mineral water, in its state at the source, may not be subject to any treatment or addition other than:

(a) the removal of its 'unstable elements', such as iron and sulphur compounds, by filtration and decanting, possibly preceded by oxygenation, in so far as this treatment does not alter the composition of the water as regards the essential constituents that give it its properties;
(b) the total or partial elimination of free carbon dioxide by exclusively physical methods;
(c) the introduction or the reintroduction of carbon dioxide under the condition laid down in Annex 1, Section III of the Directive.

The formal organ implementing the Mineral Water Directive in the United Kingdom is The Natural Mineral Water Regulations 1985. With respect to chemical standards, the Regulations are more detailed than the Directive in two ways, by including:

- a schedule of toxic parameters with a standard for each parameter;
- a requirement for analysis of the water as part of the recognition process.

Spring Water should meet the same criteria as mineral water regarding source protection and allowable treatment (96/70/EC). It does not, however, require a distinctive mineral composition. It would be sold under names such as 'spring water', 'natural water', 'spa water', etc., and must additionally meet the requirements of the Drinking Water Directive (80/778/EEC).

Packaged Water, *Table Water* or *General Water* are categories intended to create an opportunity to offer a safer water source for the general public in areas perceived to have a public supply of inadequate quality. The water packaged could in fact consist of high quality public water supply from a neighbouring region. In fact, the Drinking Water Directive allows the packaging of water from any source, including water known to be bacteriologically unsafe in its raw state and which has a significant proportion of waste water in its make-up, as long as it can satisfy the chemical and bacteriological standards enshrined by the Drinking Water Directive after treatment (Finlayson, 1992). In the UK, the Directive is implemented via the Water in Containers Regulations of 1994 (Edwards, 1994).

The degree of monitoring of the wholesomeness of bottled water will vary from country to country, but responsibility will typically rest with local environmental health officers and food safety officers. Edwards (1994) believes that the frequency of testing is likely to be considerably less than that employed for mains tap water. Indeed a recent survey of bottled water in South Africa revealed disturbingly high bacterial counts in a random selection of bottled waters (P. Scott, personal communication, 1995).

2.3.2 The Codex Norms for Mineral Waters

The 'Codex Norms for Natural Mineral Waters' (Commission du Codex Alimentarius, 1983) were developed by the Food and Agriculture Organization of the UN and the World Health Organization to prescribe analytical methodologies, to establish limits for certain parameters (Table 2.4), to standardize procedures internationally and to enable comparison to be made between water analyses. The Codex overlaps considerably with recommendations contained in the EC Directive, but the details are not identical. The Codex describes 'natural mineral water' as being defined by:

- its content of certain minerals;
- its derivation from an underground body of water via boreholes or springs;
- its constant composition and temperature;
- its abstraction in conditions that guarantee the original bacteriological purity of the water;
- its not being treated by anything other than a few simple authorized methods.

The Codex also contains the following regulations concerning labelling:

(a) although the term 'natural mineral water' usually describes a product containing more than 1000 mg/l of total soluble salts or more than 250 mg/l of free CO_2, a water with less than these quantities may be called a 'natural mineral water' provided adequate information is given to distinguish it from a 'true mineral water'. Alternatively, the low

Table 2.4 Maximum limits of certain parameters permitted in natural mineral waters according to Commission du Codex Alimentarius (1983)

Parameter	*Maximum permitted concentration*
Controlled parameters	
Copper (Cu)	1 mg/l
Manganese (Mn)	2 mg/l
Zinc (Zn)	5 mg/l
Borate (as H_3BO_3)	30 mg/l
Organic matter	3 mg/l as O_2 equivalents
Arsenic (As)	0.05 mg/l
Barium (Ba)	1.0 mg/l
Cadmium (Cd)	0.01 mg/l
Chromium-VI (Cr-VI)	0.05 mg/l
Lead (Pb)	0.05 mg/l
Mercury (Hg)	0.001 mg/l
Selenium (Se)	0.01 mg/l
Fluoride (F^-)	2 mg/l
Nitrate (as NO_3^-)	45 mg/l
Sulphide (as H_2S)	0.05 mg/l
Radium-226 activity	30 pCi/l = 1.1 Bq/l
Contaminants	
Total beta activity (except ^{40}K and ^{3}H)	1 pCi/l = 0.037 Bq/l
Cyanide (as CN^-)	0.01 mg/l
Nitrite (as NO_2^-)	0.005 mg/l
Phenolic compounds	–[a]
Surfactants	–
Pesticides	–
Polychlorinated biphenyls (PCB)	–
Mineral oil	–
Polynuclear aromatic hydrocarbons (PAH)	–

[a] Not detectable using specified methods.

mineralization or low CO_2 water may be termed a 'spring water' or other appropriate name.

In terms of the carbon dioxide (CO_2) content of the bottled water, the following translations apply:

Technospeak	*Translation*
• 'naturally gaseous/carbonated natural mineral water'	gas (CO_2) content same as in the source
• 'non-gaseous natural mineral water'	CO_2 absent, as in the source
• 'degassed natural mineral water'	CO_2 content less than in the source
• 'natural mineral water fortified with carbon dioxide from source'	CO_2 content may be more than in the source
• 'carbonated natural mineral water'	CO_2 has an origin other than the source

(b) the chemical content must be declared in volume and/or weight in the international system of units, in accordance with the regulations in the country where the product is sold;

(c) the place and name of the source as well as the name and address of the supplier must be declared;

(d) the country of origin must be declared in cases where its omission would be liable to mislead consumers;

(e) each container must carry clearly or in code an inscription or mark to identify the production plant and lot;

(f) when the product contains more than 600 mg/l of sulphate, excluding calcium sulphate, the phrase 'can be laxative' must be included on the label or in a visible place. Similarly, if a natural mineral water has been subjected to any form of treatment, this must be declared on the label.

(g) it is forbidden to mention:
  - any medical (preventative, therapeutic, curative) or other effects favourable to the consumers' health;
  - localities or other places other than that given as the origin of the water;
  - any indication or sign leading to confusion about the nature, origin, composition and properties of the natural mineral water;

(h) optionally, a description can be given on the label of particular properties of the mineral water, e.g.:
- 'alkaline' for $HCO_3^- > 600$ mg/l,
- 'acidic' for free $CO_2 > 250$ mg/l,
- 'saline' for $NaCl > 1000$ mg/l;
- 'fluoride' for $F^- > 1$ mg/l;
- 'ferruginous' for total $Fe > 5$ mg/l,
- 'iodide' for $I^- > 1$ mg/l;
- 'can be diuretic' for total dissolved salts > 1000 mg/l or $HCO_3^- > 600$ mg/l.

2.4 GEOTHERMAL ENERGY

The different types of thermal water system and their mode of occurrence are discussed in Chapter 4. High enthalpy systems provide steam at temperatures over 150°C which may be used for electric power generation, while low enthalpy systems, with temperatures less than 150°C provide heat for many different purposes. Figure 2.4 shows possible uses for different ranges of temperature, while the locations of some high temperature fields mentioned below are shown in Figure 4.1.

2.4.1 Power plants and heat equipment using geothermal energy

The heat energy of geothermal fluids can be utilized by its conversion into other forms of energy by means of power plants, as well as directly in heat

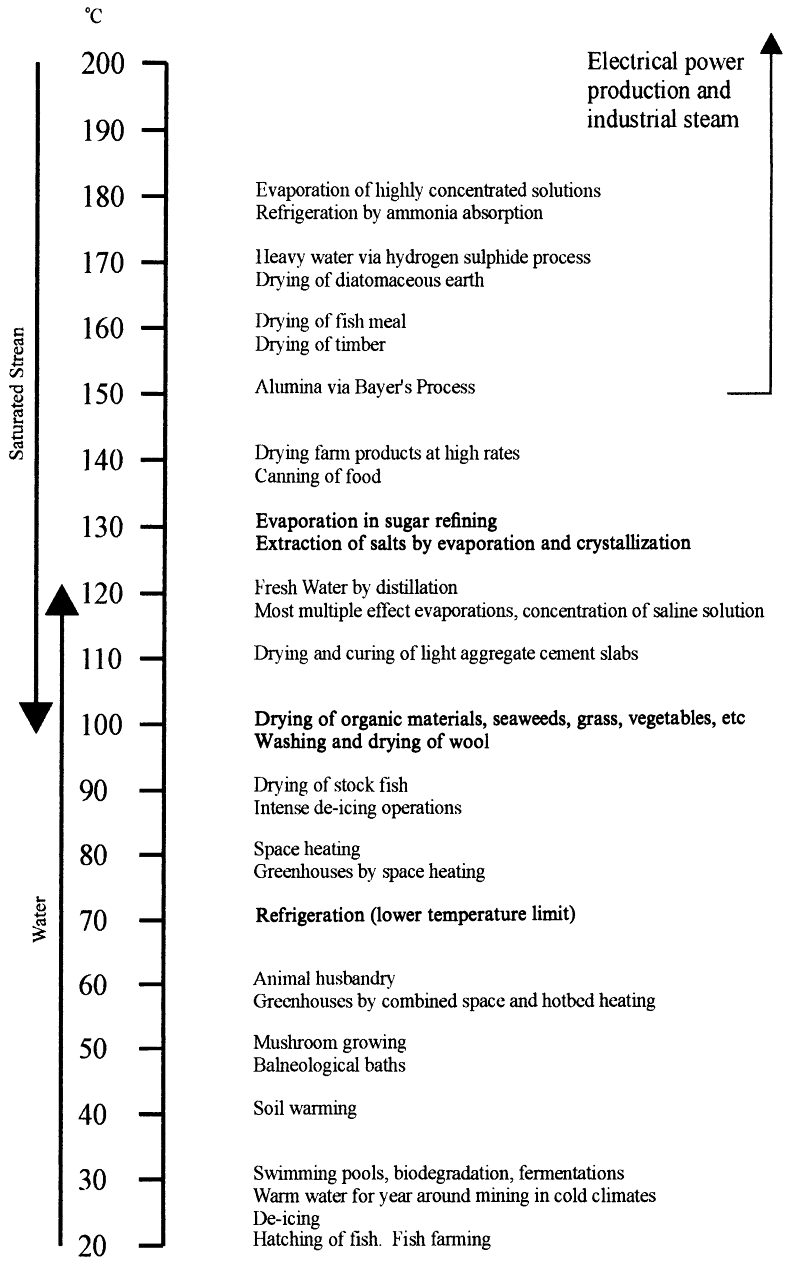


Figure 2.4 Uses of thermal water and steam at different temperatures (the Lindal diagram). (Source: Lindal, 1973.)

exchange and space-heating equipment. Among the most important of these are:

Steam power plants

The most conspicuous use of thermal water resources is in the generation of electricity (Muffler and Cataldi, 1978; Armstead, 1983; Kappelmeyer, 1979; Coudert and Jaudin, 1989). Steam power plants using the Carnot cycle and/or the Rankine cycle (Figure 2.5) use heat energy from dry or saturated steam for electric power generation and heating applications.

The Carnot cycle is essentially an idealized heat engine, where heat flows from a high temperature reservoir to a low temperature sink, performing work by means of a working medium (e.g. steam). It can also be reversed to form a heat pump, where mechanical work performed on the medium drives heat from a low temperature environment to a high temperature one. The Carnot heat engine has the following cycle:

- isothermal (constant temperature) expansion in a turbine, taking in heat and doing work;
- adiabatic (without heat change) expansion, with cooling and work being done;
- isothermal compression, losing heat to a low temperature sink;
- adiabatic compression.

The Rankine cycle follows an alternative scheme, the first and third steps using constant pressure rather than constant temperature. In its idealized form, the Rankine cycle is as follows:

- heat transfer to a boiler from the high temperature heat source T_1, evaporating water to steam, with resulting expansion at a constant pressure;
- adiabatic expansion in a prime mover from initial pressure to back pressure, with a temperature drop to T_2;
- heat transfer from the condenser to a sink at temperature T_2, at a constant pressure with wet steam being converted to saturated liquid;
- adiabatic compression of water/saturated vapour in a feed pump from low to high pressure.

The generation of electricity with acceptable efficiency can be achieved by direct use of steam with temperatures over 200°C. Dry or superheated steam produced by wells can be piped directly to the turbine, without the need for separation of water. Thus high temperature, vapour-dominated resources are used directly, as at The Geysers, Wairakei and Larderello, while liquid-dominated resources, e.g. at Cerro Prieto and also at Wairakei, are subjected to flashing: a reduction of pressure produces steam that is used for the power plant while the liquid fraction is reinjected into the aquifer or discarded (Edwards *et al.*, 1982).

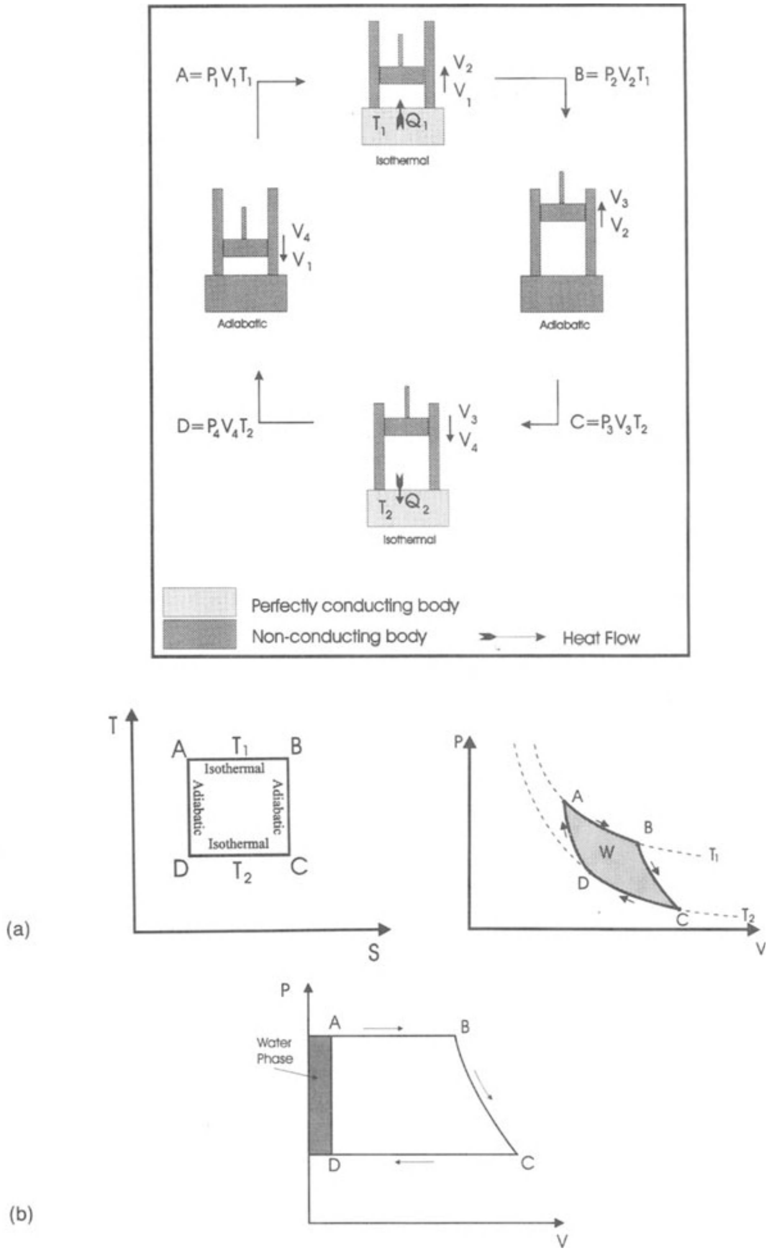


Figure 2.5 (a) The Carnot cycle showing (top) an idealized Carnot piston heat engine, (middle left) a temperature (T) versus entropy (S) diagram and (middle right) a pressure (P) versus volume (V) diagram. The area enclosed by the PV loop is equivalent to the potential work (W) performed by the engine. Heat flows are designated Q. (b) Pressure (P) versus volume (V) diagram illustrating the Rankine cycle.

In binary fluid power plants operating with the Rankine cycle, the generation of electricity is possible using water with temperatures between 150°C and 200°C, by transferring the steam's heat to a working fluid of low boiling point such as isobutane, propane or Freon (e.g. Modell and Reid, 1983; Edwards *et al.*, 1982). This method is also of value where the geothermal fluid contains non-compressible gases such as CO_2, which lower the efficiency of cycles involving the direct use of steam.

Due to the relative scarcity of accessible high temperature resources, solutions are being sought for increasing the efficiency of electricity generation from geothermal fluids with temperatures less than 150°C, by means of installations operating with the organic Rankine cycle. An example is the 40 kW generator tested on an artesian geothermal source of temperature 81°C, south of Lakeview, Oregon, USA (Peppin, 1984).

In 1990 the total installed geothermal electric generating capacity worldwide was 5827 MW_e. Of this, 2770 MW_e was in the USA, 891 in the Philippines, 700 in Mexico, 545 in Italy, 215 in Japan, 283 in New Zealand, 95 in El Salvador, 45 in Kenya and 45 in Iceland (Kelk, 1992).

Space heating and other direct uses of geothermal energy

Steam or hot water can be used in central or individual heating systems either by direct circulation or by using heat exchangers. When geothermal energy replaces fossil fuels, the polluting emissions from boilers are eliminated and the urban impact of road transport for supplying the power plants is greatly reduced.

Low and medium temperature resources may alternatively be used for the heating of greenhouses and soil, providing hot or warm water for domestic use, product processing, industrial drying, shellfish and fish farming, medicinal baths and swimming pools (Armstead, 1983; Lienau and Lunis, 1989).

Among existing direct applications of thermal water resources are the following:

- in Japan geothermal energy is used for space heating, domestic purposes, greenhouse horticulture, artificial thawing and snow melting; and for other industrial, agricultural and recreational purposes;
- in Iceland geothermal energy represents 30% of net energy consumption, primarily as domestic heating;
- in the Paris Basin of France, waters of 60–70°C are used in district heating systems, for example at Melun, Creil and Villeneuve la Garenne;
- in the Pannonian Basin of Hungary and Romania, waters of 60–120°C are used to heat buildings and greenhouses and to provide warm water for domestic, industrial, agricultural, therapeutic and recreational purposes;
- in California geothermal energy has been commercialized, not only for electrical power generation but also for direct use for industrial and agricultural purposes;

- in New Zealand thermal waters are used to heat buildings, for greenhouse horticulture and for domestic, industrial, agricultural, medicinal and recreational purposes (this is in addition to power generation from high enthalpy resources).

In 1990 the use of geothermal energy for direct heat applications corresponded to an installed thermal capacity of 11 400 $\mathrm{MW_t}$. Of this, 3321 $\mathrm{MW_t}$ was in Japan, 2143 in China, 1276 in Hungary, 1133 in the USSR and 790 in Iceland (Kelk, 1992).

Heat exchangers

Heat exchangers are devices for transferring heat from a hot stream of fluid to a cool one. There are three broad categories of exchanger:

- the recuperator or the through-the-wall non-storing exchangers, e.g. the shell and tube exchanger, the cold finger or Bayonet exchanger and several others;
- the direct contact, non-storing exchangers, e.g. fluid–fluid direct-contact non-storing exchangers (the immiscible fluids exchanger, the boiling and immiscible fluids exchanger) and gas–solid direct-contact non-storing exchangers (the moving bed contactor, the fluidized bed, the moving belt conveyor);
- the regenerator, accumulator or heat storage exchangers, e.g. the direct contact heat storing exchanger.

Heat exchangers are particularly utilized for thermal water with a high content of dissolved salts in order to minimize problems with incrustation or corrosion (Levenspiel, 1984).

Heat pumps

The heat pump (Figure 2.6) is a kind of reverse heat engine. Rather than use the heat flow down a temperature gradient to drive machinery to perform mechanical work, the heat pump transports heat from low temperature environments to high temperature ones (i.e. up the temperature gradient) by performing a certain amount of mechanical work. They are used to pump heat out from refrigerator compartments, but are also used to extract heat from low temperature air or water to heat the interior of buildings. In this latter case, heat Q_2 is extracted at a low temperature T_2 from a cool exterior environment (seawater, groundwater, air, etc.). Work (W) is performed by the heat pump system and a quantity of heat $Q_1 = (Q_2 + W)$ is transferred at temperature $T_1 (> T_2)$ to the interior receptor (e.g. a domestic hot water system). The heat pump itself typically employs a fluid with a low boiling point – ammonia is regarded as one of the most environmentally

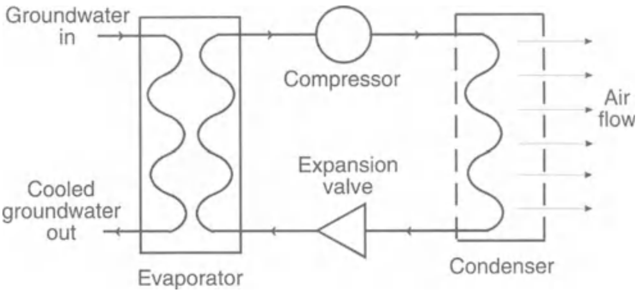


Figure 2.6 Schematic representation of a heat pump based on groundwater.

friendly options. Heat pumps are, for example, employed at Lund in Sweden, utilizing wells up to 700 m deep, extracting groundwater at relatively low temperature in the range 20–30°C for urban heating (Bergelin, 1986).

Heat pumps may also be used to extract heat from shallow groundwater systems, for converting the energy of groundwater or the heat flow through underlying rocks to a usable form. Several methods are possible:

- use of the heat content in groundwater from an ordinary well with a high water yield (thus giving a high utilizable heat flux);
- recirculating groundwater between two wells or within a single deep well; during recirculation, heat is extracted from the strata and the water temperature is increased;
- recirculation of water through a closed heating loop inserted into a single borehole or trench (again, heat is extracted from the strata to the circulating water and thence to the heat exchange mechanism of the heat pump).

It should be noted that the temperature of the extracted groundwater or circulation water need not be high (Kitching *et al.*, 1992; Skarphagen, 1995). In Sweden, for example, typical groundwater temperatures are as low as 4–5°C, yet low temperature heat pumps have proved to be a popular and effective means of space heating. In inland areas, groundwater may be the only water resource above freezing point during winter (all surface water being frozen) and it is this temperature differential between the groundwater and the ambient air that makes heat pumps so attractive. During the period 1980–1986 about 50 000 low temperature heat pump plants (of varying size) were installed in Sweden, based on geological heat flow or groundwater. This corresponds to about 500 MW (Kelk, 1992).

The ideal system for a nation with a subarctic or continental inland climate would be to use low temperature groundwater for cooling purposes in the summer, recharging the warm discharge water to the aquifer and re-extracting this heat in the winter for use in a heat pump. Such a system would, however, necessitate a thorough hydrogeological investigation of the aquifer to ensure that the injected heat would not be dissipated by advection or conduction.

Coupled systems are also utilized in some office buildings, where cold groundwater is used to cool machinery, computer installations or air conditioning units. This use results in heat being transferred to the water, which is then re-extracted by a heat pump to be employed for domestic water heating, for example.

As a final note, it has also been speculated whether contaminated water around landfills in arctic areas would provide a resource for heat pumps. For example, the groundwater temperature in the immediate vicinity of Trandum military landfill in inland Norway is up to 8°C, some 3–4° higher than the ambient groundwater temperature of 4–5°C (Sæther *et al.*, 1992), due to exothermic decomposition reactions in the waste and leachate. Pumping of warm, contaminated groundwater via a heat pump, followed by re-infiltrating it through the landfill may form the basis of an energy source and a means of leachate migration control. The system would, however, need

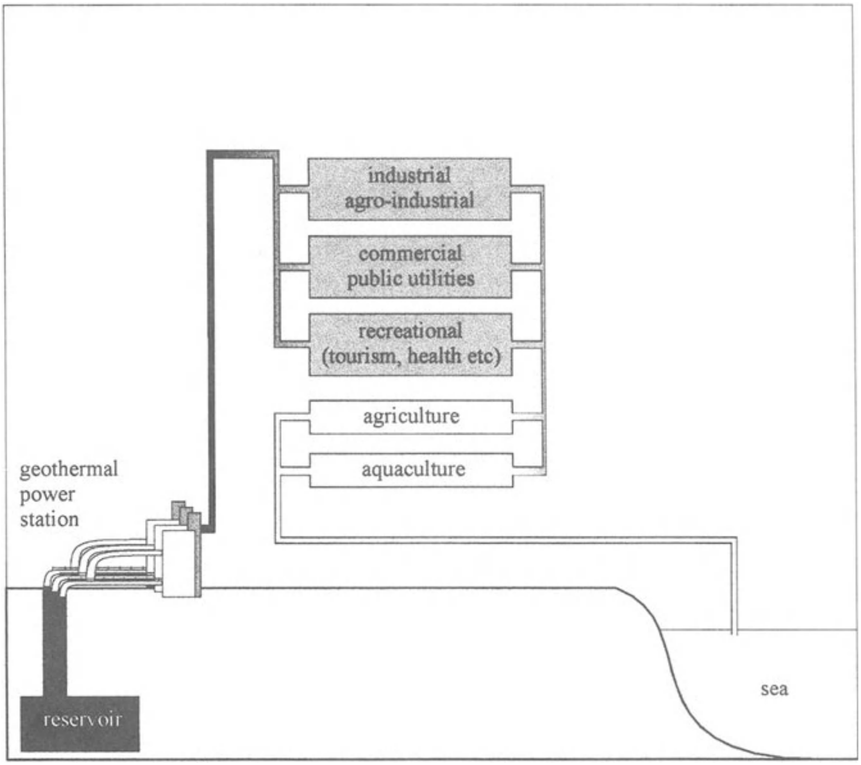


Figure 2.7 Schematic representation of cascading application. (With permission from Orkustofnun (National Energy Authority of Iceland), 1992.)

to be built to withstand the corrosive nature of the leachate-contaminated water (Misund *et al.*, 1992).

Cascading applications

The most efficient use of thermal water resources is in cascading applications where each step uses a successively lower temperature than the previous one (Figure 2.7). In this way, a single high temperature resource may supply a mixed electricity generating plant (with a Carnot or Rankine cycle coupled to a binary fluid power plant) and thereafter a heating application that, in itself, may be designed for cascading use. Extraction of chemicals or other raw materials from thermal waters may form part of such a cascade. Examples include the following.

- In Iceland, at Svartsengi, a binary-fluid power plant is installed at the back end of a steam power plant, producing both electricity and heat for a district heating system. The condensate is discharged into the popular warm bathing pool (the Blue Lagoon) and, as an added bonus, a silica gel is precipitated from the water onto the lagoon floor which, when applied to the bathers' skin, is believed to have a therapeutic value.
- In France, in the Paris region, most of the thermal water networks have cascades with radiators, floor heating and heat pumps.
- In Italy, at Larderello, electricity generation used to be combined with boron extraction from thermal waters.

3

Hydrogeochemistry and origin of mineral waters

> *The amount of minerals you get in a glass of water is probably equivalent to the nutrition gained from a scraping of carrot.*
>
> Liz Edwards, 1994

3.1 INTRODUCTION

Many people regard mineral waters as something extraordinary but, in most cases, they (and here we include thermal waters) acquire their characteristic chemistry in the same way that any groundwater does. Much of the character of mineral water comes from the dissolution or leaching of components from minerals, but that is not the whole story, so let's start from the beginning.

Taking a short step back, we need to know a little about the occurrence and flow of groundwater – the science of hydrogeology. The purpose of this book is not to provide an introduction to this topic and we assume that most readers are familiar with the basics of this subject. For those who are not, there are many excellent introductory textbooks, of which those by Freeze and Cherry (1979), Todd (1980), Driscoll (1986), Domenico and Schwartz (1990), Fetter (1994) and Price (1996) are among the best. Briefer introductions have been provided by Price (1991) and D. Banks (1992). If you do not have these to hand, here are a couple of basic hydrogeological principles to bear in mind while reading on.

- Recharge. Groundwater is not mysterious. Most groundwater systems are ultimately recharged by precipitation (rain and snow) falling on permeable and porous strata and percolating down to the water table.
- Head. Groundwater flows from areas of high head to areas of low head. Head is a measure of groundwater potential energy – it takes into account

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M. Albu, D. Banks and H. Nash.
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both the pressure and elevation of the water. It can be easily understood by considering a typical plumbing system. A header tank in your loft will provide a potential energy 'drive' to distribute water to lower points in your house. Alternatively, an enclosed pressure tank at ground level can do the same job.

The relative densities of water bodies will also have an effect on head. For most groundwater, the density of water is taken to be constant at 1 kg/l and it is not necessary to consider this effect. With mineral and thermal waters, high salinity, elevated temperature or exsolution of gas may lead to differential density effects and thus to a 'buoyancy'-related potential energy (or head), which may assist in powering circulation in groundwater systems.

3.2 CHEMICAL EVOLUTION OF GROUNDWATER

As most groundwater is ultimately derived from rainfall, let's follow that rainfall down into the ground and find out where it picks up the chemical components that make it unique.

3.2.1 Rainfall quality

Rainfall is not just distilled water. It has a small, but finite, component of chemicals dissolved in it. These include:

- salts derived from sea spray, typically sodium and chloride; the rainwater concentrations of these chemicals will decrease with increasing distance from the coast and this will be reflected in shallow groundwater composition (Figure 3.1);
- minerals dissolved from windblown dust and particulate contaminants;
- natural and anthropogenic gases.

In hot climates, evaporation of rainfall before it reaches the ground will result in a higher concentration of solutes.

Acid rain

Gases such as SO_x, NO_x and HCl are produced naturally (particularly nitrogen oxides, produced by the action of lightning on atmospheric nitrogen). They are also produced as emissions from industry, power stations and internal combustion engines, causing the phenomenon of acid rain (Pearce, 1987; Glenny, 1987). Two prominent contaminants are SO_2 and NO_x. These are oxidized and hydrolysed in the atmosphere, and then dissolved in raindrops as sulphuric and nitric acid. The reactions can be expressed, in highly simplified form, as:

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \tag{3.1}$$

$$SO_3 + H_2O \rightleftharpoons 2H^+ + SO_4^{2-} \tag{3.2}$$

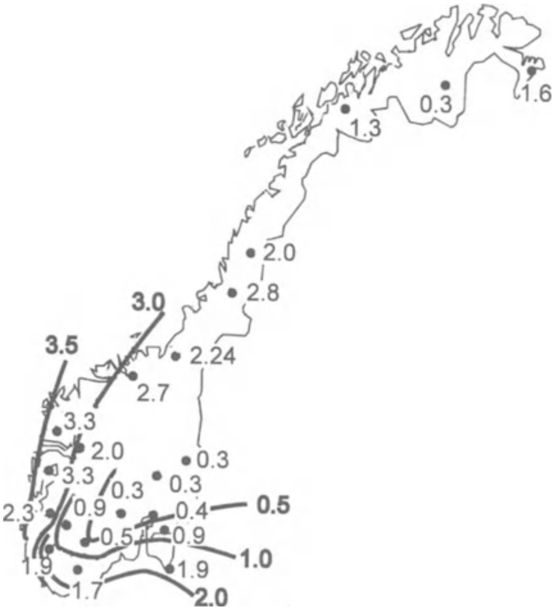


Figure 3.1 Map of Norway illustrating contours of chloride concentration (mg/l) in precipitation, modified after Storrø (1990).

The oxidation of nitrogen oxides is more complex as several differing oxidations states are possible, but one pathway is:

$$2NO_2 + H_2O \rightleftharpoons 2H^+ + NO_3^- + NO_2^- \qquad (3.3)$$

$$2H^+ + 2NO_2^- + O_2 \rightleftharpoons 2H^+ + 2NO_3^- \qquad (3.4)$$

The acids will react with silicates (such as feldspars) and carbonates in the ground:

$$\underset{\text{albite}}{2NaAlSi_3O_8} + \underset{\substack{\text{sulphuric}\\ \text{acid}}}{2H^+ + SO_4^{2-}} + \underset{\text{water}}{H_2O} \rightleftharpoons \underset{\text{sodium}}{2Na^+} + \underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} + \underset{\text{sulphate}}{SO_4^{2-}} + \underset{\text{silica}}{4SiO_2} \qquad (3.5)$$

$$\underset{\text{calcite}}{Ca^{2+}CO_3^{2-}} + \underset{\substack{\text{nitric}\\ \text{acid}}}{H^+ + NO_3^-} \rightleftharpoons \underset{\text{calcium}}{Ca^{2+}} + \underset{\text{bicarbonate}}{HCO_3^-} + \underset{\text{nitrate}}{NO_3^-} \qquad (3.6)$$

Signs that groundwaters are being affected by acid rain are thus increased sulphate and nitrate concentrations, and increased base cations and total dissolved solids, as can be observed in some locations in Scandinavia and Central Europe (Chapter 14). The acid (H^+) will tend to be buffered by

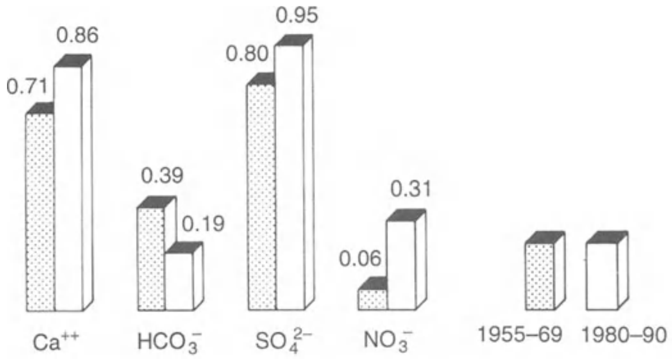


Figure 3.2 Changes in calcium, bicarbonate, sulphate and nitrate concentrations (meq/l) in bedrock groundwater (as sampled from springs) between the periods 1955–1969 and 1980–1990 in the Krusné Hory mountains of Bohemia. (Reproduced with permission from Hrkal, 1992.)

basic minerals in the ground and hence groundwaters will not (at least in theory) exhibit decreased pH values until the buffering capacity has been used up. The main buffering minerals are basic silicates and carbonates. The alkalinity (e.g. bicarbonate) of groundwater will also have a buffering effect.

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3 \rightleftharpoons H_2O + CO_2 \qquad (3.7)$$

Areas that are underlain by rocks composed of leucocratic minerals, poor in basic minerals, (e.g. Southern Norway and parts of the Czech Republic) will tend to be much more vulnerable to acidification (e.g. Krám and Hruška, 1994). It might be thought that the influence of rainfall composition on anything other than very shallow groundwaters would be minimal, but in some heavily polluted areas, groundwaters in crystalline bedrock have exhibited significant decreases in alkalinity and increases in sulphate, nitrate and total mineralization (e.g. Figure 3.2, from the Krusné Hory mountains of Bohemia; Hrkal, 1992).

3.2.2 Vegetation and the soil zone

When rain falls on a forest or other vegetation, some will fall directly onto the ground, but much will fall on the foliage. This will then be retained and subject to evaporation. The effect of this evaporation will be to concentrate the solutes in the rainwater, or throughfall as it becomes when it has passed through the vegetation canopy. The throughflow may also pick up solutes derived from the plant material itself. Natural dust and particulate contaminants may settle out on leaves. These may then be readily dissolved and mobilized by rainfall, leading to further input of solutes to the throughfall.

When throughfall infiltrates into the soil it becomes soil moisture. Many chemical changes occur because of biological processes. Plants will suck up water from the soil to be evapotranspired, leaving the soil water further concentrated in solutes. The plants will also remove some nutrients from the soil. In particular, nitrate and potassium can be very effectively removed (although acid rain or excessive fertilizer application may load the soil with more nitrogen than can be usefully removed by plants).

Additionally, other cations will be removed, being effectively exchanged for protons (acid) by the plants. If dead vegetation is allowed to rot back into the soil, the nutrients will be returned to the soil and only a limited net change will take place. If, however, vegetation is harvested (as food crops, for example, or timber) the nutrients will be removed and there may be a tendency to soil acidification. Thus, artificial fertilizer and lime may need to be applied to re-establish the nutrient and chemical balance.

Some vegetation, particularly coniferous forest, appears to be very effective in (1) concentrating solutes by evapotranspiration (2) removing base cations and acidifying the soil (3) producing acidic tree litter, resulting in the generation of humic acids, which add to the acid load of groundwater. In fact, some geochemists, notably Ivan Rosenqvist of Oslo, have argued that acidification episodes in lakes and watercourses can be correlated with reafforestation following depopulation events such as the Black Death in the Middle Ages and the mass emigration of Norwegians to the USA in the first half of the 20th century (Rosenqvist, 1978; Skeffington, 1987).

A huge amount of biological and, particularly, microbiological activity occurs in the soil zone. Much of it is decomposition of vegetable matter involving respiring organisms. These excrete carbon dioxide, which dissolves in the groundwater to form an acidic solution.

3.2.3 Water–rock interaction

Groundwaters will begin to react with rocks or sediments as soon as they enter the unsaturated zone, and will continue to react, to a greater or lesser extent, in the saturated zone.

Strömberg and Banwart (1994) proposed a very simple and elegant model of groundwater chemistry (Figure 3.3). They point out that the atmosphere and biosphere are essentially acidic (e.g. natural CO_2 and anthropogenic acid rain) and oxidizing (O_2, nitrates, sulphates, etc.). The geosphere, in contrast, is essentially basic (carbonates and silicates) and reducing (sulphides, organic carbon and methane). Groundwater is the medium that transports acidic, oxidizing species into the geological environment. Recently recharged groundwater will contain CO_2 and oxygen. Thus, in the zone of groundwater circulation, it is not surprising that the dominant reactions are acid–base and redox reactions.

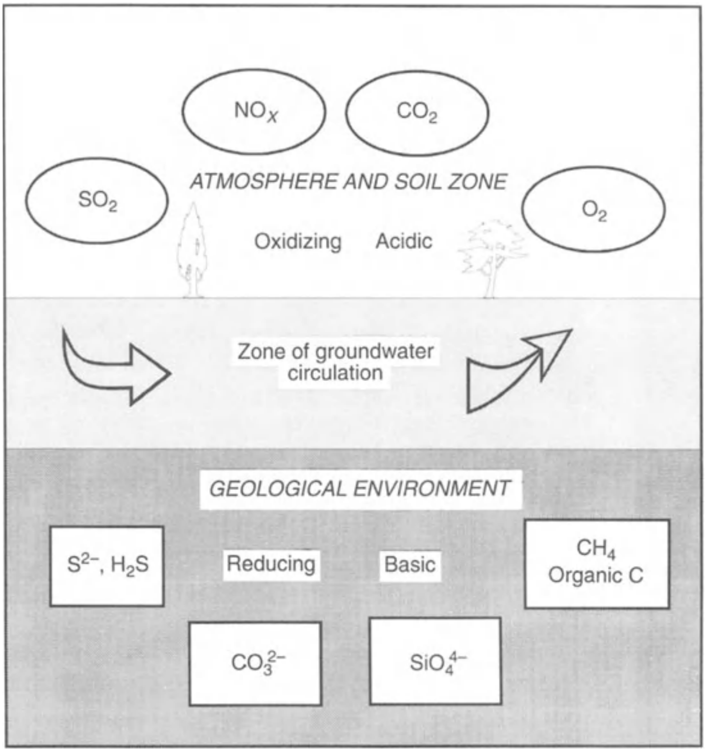


Figure 3.3 The Strömberg and Banwart (1994) model of hydrogeochemistry.

Examples of acid–base (type 1) reactions, include the dissolution of carbonates

$$Ca^{2+}CO_3^{2-} + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^- \qquad (3.8)$$

or the weathering of silicates (e.g. feldspars)

$$2NaAlSi_3O_8 + 2CO_2 + 3H_2O \rightleftharpoons 2Na^+ + 2HCO_3^- + Al_2Si_2O_5(OH)_4 + 4SiO_2 \qquad (3.9)$$

$$CaAl_2Si_2O_8 + 2CO_2 + 3H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^- + Al_2Si_2O_5(OH)_4 \qquad (3.10)$$

The outcome of these reactions is the consumption of acid or CO_2, the elevation of groundwater pH, the production of alkalinity in the form of bicarbonate (HCO_3^-), and the release of base cations and silica to solution. These reactions dominate in the early stages of groundwater evolution.

Examples of redox reactions (type 2) include the oxidation of pyrite

$$\begin{array}{l} 2FeS_2 + 2H_2O + 7O_2 \rightleftharpoons 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \\ \text{pyrite} + \text{water} + \text{oxygen} \rightleftharpoons \text{iron(II)} + \text{sulphate} + \text{acid} \end{array} \tag{3.11}$$

and the oxidation of organic carbon or carbohydrates (nominal formula CH_2O) by oxygen or other oxidizing species

$$CH_2O + O_2 \rightleftharpoons HCO_3^- + H^+ \tag{3.12}$$

It will be noted that many (but not all) oxidation reactions produce acid (protons) which will be consumed in further acid–base reactions of type (1). The oxidation of pyrite typically produces ferruginous sulphate-rich waters. These are characteristic, for example, of waters derived from the pyritic Millstone Grit shales of the UK, such as Harrogate, Allen Hill Spaw in Matlock and the Chalybeate Spa of Buxton (Chapter 10). An even more extreme case is found at the aptly named 'acid springs' feeding the Rio Vinagre in South America (Bailey *et al.*, 1902), where pyrite oxidation resulted in an estimated daily flux of 37 tonnes of 'vitriol' (sulphuric acid).

Other reactions may also be significant: ion exchange reactions (type 3), e.g. cation exchange on clays

$$\text{Ca-clay} + 2Na^+ \rightleftharpoons (Na)_2\text{-clay} + Ca^{2+} \tag{3.13}$$

or straight dissolution reactions (type 4), e.g. the dissolution of fluorite

$$Ca^{2+}(F^-)_2 \rightleftharpoons Ca^{2+} + 2F^-. \tag{3.14}$$

All of the above reactions add 'mineral salts' or solutes to the groundwater (although it should be noted that precipitation and adsorption reactions may also be important, particularly at later stages of groundwater evolution). Many sedimentary aquifers are rich in calcium carbonate, which is commonly present in the cement; thus circulating groundwater in such aquifers typically exhibits a high pH and is dominated by calcium and bicarbonate, through reaction (3.8). In granite aquifers, the dominant reaction may be the dissolution of sodic plagioclase (reaction (3.9) above) and the water chemistry will thus be dominated by sodium and bicarbonate. In non-calcareous, inert rocks (e.g. pure sands and gravels or leucocratic granites), particularly if there is a fast throughflow of groundwater and very low residence time, there will be little water–rock interaction. The groundwater will retain an atmospheric 'signature', e.g. in coastal areas it will be dominated by sodium chloride from sea spray.

Many geochemical and hydrochemical reactions are catalysed by bacteria. Perhaps the best known are those related to sulphate reduction, metal (especially iron) and sulphide oxidation (e.g. *Leptospirillum ferrooxidans*, *Thiobacillus thiooxidans*, *Thiobacillus ferrooxidans* and *Sulfobacillus thermosulfidooxidans*) and metal oxidation, precipitation and immobilization (e.g. the genera *Gallionella*, *Leptothrix*, *Metallogenium*, *Siderocapsa* and

Sphaerotilus). For further background on these groups of bacteria, the reader is referred to Cullimore and McCann (1977), Howsam (1988) and S.B. Banks (1992). Despite the emphasis placed on bacterial involvement in metal, nitrogen and sulphur redox reactions and, of course, on reactions involving organic carbon, there is growing evidence that bacteria may be involved in most geochemical processes, from silicate weathering to evaporite formation (Norton *et al.*, 1993). A taste of the growing science of geohydromicrobiochemistry can be obtained by referring to ISSM (1993), Pedersen (1993) or Chappelle (1993).

Highly evolved waters

If the groundwater resides for a long time in an aquifer, for example if it follows a deep flow path or enters a confined part of an aquifer system, other reactions may become important. Ion exchange may take place; some of the calcium derived from calcium carbonate dissolution may be replaced by sodium (reaction (3.13)), giving the water a sodium bicarbonate character. In addition, reactions such as (3.11) and (3.12) above, often catalysed by bacterial involvement, will tend to consume the dissolved oxygen and the groundwater will gradually become more reducing. Organic carbon may begin to consume and reduce other oxidized species, such as iron(III), manganese(IV), nitrate and sulphate:

$$CH_2O + 7H^+ + 4Fe(OH)_{3(s)} \rightleftharpoons 4Fe^{2+} + 10H_2O + HCO_3^- \qquad (3.15)$$

$$CH_2O + 3H^+ + 2MnO_{2(s)} \rightleftharpoons 2Mn^{2+} + 2H_2O + HCO_3^- \qquad (3.16)$$

$$NO_3^- + 2CH_2O + H_2O \rightleftharpoons NH_4^+ + 2HCO_3^- \qquad (3.17)$$

$$2CH_2O + SO_4^{2-} \rightleftharpoons H_2S + 2HCO_3^- \qquad (3.18)$$

Such deep, reducing waters will thus tend to be alkaline (many reduction reactions consume protons and produce bicarbonate), poor in oxidized species such as sulphate and nitrate, and may smell of hydrogen sulphide. They may also be rich in iron and manganese (and possibly other heavy metals) as the reduction of immobile oxides of these metals produces mobile free ions (equations (3.15) and (3.16)). At high pH values, however, even these reduced species of metals may become immobile again.

3.2.4 Mixing

Once in the aquifer, the groundwater may mix with other water types, such as seawater, connate waters, formation or diagenetic waters (section 3.7.3). During its ascent to a discharge point, a mineral water may even mix with shallower, fresh groundwater.

In coastal areas, an aquifer may be in contact with the sea and the seawater may penetrate into the aquifer. This is particularly likely if a pumping well is situated near the coast, as saline water may be drawn towards the well. The terrestrial groundwater will then mix with intrusive saline water and acquire a character dominated by seawater composition, i.e. sodium chloride.

Connate waters are waters that have remained in a sediment's pore space since deposition. The connate water may be quite recent. For example, in Norway, deposits of marine silts and clays date from the end of the last ice age (some 10 000 years ago). The sodium chloride-dominated character of Farris mineral water is thought to be derived from the leaching of saline pore waters from Quaternary marine sediments. Other connate waters may be much more ancient and may be found, for example, deep in the confined parts of sedimentary aquifers, where there has never been any fresh groundwater throughflow to flush out the pore waters.

When a highly evolved mineral water reaches the end of its flow path it may emerge at the surface. It may emerge via rapid ascent along a fault system, by a discrete fissure pathway to a spring or by natural hydraulic discharge pathways to an influent river valley. During its journey to the surface, the water may be subject to differing degrees of mixing with shallower, less evolved, often less saline waters. These differing degrees of mixing with shallower waters are likely to be responsible for the wide variety of salinities in springs found in spa towns such as Harrogate in the UK (Chapter 10) and Druskininkai in Lithuania (Chapter 11).

3.3 HYDROCHEMICAL PRINCIPLES

3.3.1 Main constituents

The composition of most groundwaters is dominated by a limited number of major ions. These are usually the cations Ca^{2+}, Na^+, Mg^{2+}, K^+ and the anions, Cl^-, HCO_3^-, SO_4^{2-} (and NO_3^- in contaminated areas).

Subsidiary to these, but still important from a therapeutic viewpoint, are the minor constituents: iron (Fe), manganese (Mn), fluoride (F^-), bromide (Br^-), silicon (Si), strontium (Sr^{2+}), barium (Ba^{2+}) and possibly ammonium (NH_4^+). Other constituents, including heavy metals, are normally referred to as trace constituents.

From the point of view of spas, several gaseous species are also important, including carbon dioxide (CO_2), hydrogen sulphide (H_2S) and radon (Rn). In high temperature geothermal systems, CO_2, H_2S, NH_3 and N_2 tend to be the dominant gases, while CO_2, H_2S, N_2, CH_4, He and Ar predominate in low temperature geothermal systems (Czernichowski-Lauriol and Fouillac, 1991).

3.3.2 Moles and equivalents

A mole is equal to 6.02×10^{23} atoms, ions or molecules. This strange number, Avogadro's constant, is chosen such that the mass of 1 mole (mol) of particles is equal to its atomic/molecular weight in grams. For example, one atom of ^{12}C has a mass of 12 atomic mass units (AMU). One mole of ^{12}C has a mass of 12 g. Similarly, one mole of calcium ions (Ca^{2+}) has a mass of 40.08 g, one mole of sulphate ions has an approximate mass of $(32 + 4 \times 16)\,g = 96\,g$ and one mole of hydrogen sulphide has a mass of 34.1 g.

This concept is useful as it allows us to say that a mineral water with 40.08 mg/l dissolved calcium and 22.99 mg/l sodium actually contains equal numbers of dissolved sodium and calcium ions (namely 1 mmol/l of each).

It has been seen that sodium and calcium can be subject to ion exchange:

$$\text{Ca-clay} + 2Na^+ \rightleftharpoons (Na)_2\text{-clay} + Ca^{2+} \tag{3.13}$$

and that carbon dioxide will weather both albite and anorthite feldspars:

$$\begin{aligned} 2NaAlSi_3O_8 + 2CO_2 + 3H_2O \rightleftharpoons 2Na^+ + 2HCO_3^- \\ + Al_2Si_2O_5(OH)_4 + 4SiO_2 \end{aligned} \tag{3.9}$$

$$CaAl_2Si_2O_8 + 2CO_2 + 3H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^- + Al_2Si_2O_5(OH)_4 \tag{3.10}$$

It will be noted that one calcium ion is exchanged for two sodium ions in (3.13), and that 1 molecule of carbon dioxide releases twice as many sodium ions from a sodic feldspar as calcium from a calcic one. Thus, in a sense, one ion of calcium is equivalent to two ions of sodium. This is due to the fact that Ca^{2+} has an oxidation state (or, more simply, charge) of 2, while sodium ions have only one charge. One equivalent is thus defined as one mole of charge.

Thus, one equivalent (1 eq) of sodium ions is equal to 1 mole of sodium ions; however, 1 eq calcium is only equal to 0.5 moles. For any species:

$$\text{concentration (meq/l)} = \frac{\text{concentration (mg/l)} \times \text{charge (meq/mmol)}}{\text{molar mass (mg/mmol)}}$$

3.3.3 Ionic balance and the presentation of hydrochemical data

Any solution should be electrically neutral. Thus all positively charged cations should be balanced by negatively charged ones. In other words:

$$\Sigma\ (\text{cations}) = \Sigma\ (\text{anions})$$

where Σ denotes the sum of the concentrations in meq/l. In practice, it is usual to calculate the ionic balance from the major ions. The error in the ionic balance is calculated as:

$$\text{error} = \frac{\Sigma\ \text{cations} - \Sigma\ \text{anions}}{(\Sigma\ \text{cations} + \Sigma\ \text{anions})} \times 100\%$$

The error should not be greater than 5%. If a significant error is encountered, it may be necessary to include minor or trace ions or to carry out speciation modelling (see below). If the error persists, it may be due to

- inaccuracies in analysis;
- the presence (possibly due to contamination) of unknown species.

Examples of calculation of ionic balances are given in Table 3.1. It should be noted that an accurate ion balance does not necessarily mean that the analysis is an accurate measurement of the groundwater chemistry: a representative sample, sampling technique, field measurements of unstable parameters and preservation of the sample are all important.

The existence of the ionic balance and the concept of equivalence lends itself to several presentation methods, mostly based on the major ion chemistry. These include the following.

The Kurlov formula

This method is mainly used in Central and Eastern Europe whereas, in the West, graphical methods are usually preferred. The Kurlov formula does, however, concisely summarize the dominant hydrochemistry of water. It typically takes the form:

$$M_{1.2}\frac{\mathrm{Na}72\,\mathrm{Ca}20\,\mathrm{Mg}6\,\mathrm{K}2}{\mathrm{Cl}75\,\mathrm{SO_4}18\,\mathrm{HCO_3}7}$$

where the total dissolved solids are 1.2 g/l, 72% of the cation milliequivalents are sodium, 20% are calcium, and so on. Of the anions, 75% of the milliequivalents are chloride, etc.

Line diagram

In the Schoeller diagram, concentrations are plotted on the y-axis against the ion species on the x-axis (Figure 3.4). Another common line diagram is the Stiff diagram (Fetter, 1993).

Pie diagrams

Here the equivalent percentages of the major anions and cations are plotted as slices of a pie. The radius of the pie itself can be related to the total ionic content of the water. Cations and anions should occupy half of the pie each (Figure 3.5).

Piper and Durov diagrams

In these diagrams the major cations and major anions are plotted on ternary diagrams as percentages of Σ cations and Σ anions (as milliequivalents per litre). On the cation ternary diagram, the apices are occupied by

Table 3.1 Analyses of various waters (rainfall, runoff, groundwater types I–IV and seawater) from the granitic Hvaler area of southeastern Norway. See section 3.5.1 for further explanation of evolution of the water types

	Units	*Rainfall*	*Runoff*	*Type I Berg borehole*	*Type II Skartlien*	*Type III Sandbrekke*	*Type IV Bore 38B*	*Standard Seawater*
Na$^+$	mg/l	1.2	23.8	3.12	21.81	80.20	313	10 500
	meq/l	0.052	1.04	0.136	0.95	3.49	13.6	456
	%	34.90	60.70	50.26	57.77	75.33	77.52	76.45
K$^+$	mg/l	0.47	0.65	0.15	0.87	4.07	6.66	380
	meq/l	0.012	0.017	0.004	0.02	0.10	0.17	9.72
	%	8.02	0.97	1.42	1.35	2.25	0.97	1.63
Mg^{2+}	mg/l	0.21	3.11	0.54	2.09	4.15	16.68	1350
	meq/l	0.017	0.26	0.044	0.17	0.34	1.37	111
	%	11.57	15.00	16.45	10.47	7.37	7.81	18.59
Ca^{2+}	mg/l	0.36	2.06	1.16	10.01	13.97	48.21	400
	meq/l	0.018	0.10	0.058	0.50	0.70	2.41	20.0
	%	12.01	6.03	21.43	30.41	15.05	13.70	3.34
pH		(4.3)[a]	3.53	4.55	6.86	7.87	7.47	–
H$^+$	meq/l	0.050	0.295	0.028	0.00014	0.000013	0.000034	–
	%	33.50	17.30	10.44	Trace	Trace	Trace	–
Total cations	meq/l	0.150	1.71	0.270	1.64	4.63	17.55	597
SO$_4^{2-}$	mg/l	2.03	16.8	5.8	17.8	12.4	70.1	2700
	meq/l	0.042	0.35	0.118	0.37	0.26	1.46	56.2
	%	22.23	22.57	50.48	23.37	6.16	8.43	9.45
NO$_3^-$	mg/l	4.01	0.22	–	<0.05	<0.05	<0.05	–
	meq/l	0.065	0.0035	–	<0.0008	<0.0008	<0.0008	–
	%	34.01	0.23	–	–	–	–	–
Cl$^-$	mg/l	2.95	41.8	4.2	30.9	34.5	468	19 000
	meq/l	0.083	1.18	0.121	0.87	0.97	13.2	536
	%	43.76	76.08	49.52	54.98	23.22	76.24	90.14
F$^-$	mg/l	<0.1	0.33	–	0.25	2.86	4.1	1.3
	meq/l	<0.005	0.017	–	0.01	0.15	0.22	0.07
	%	–	1.12	–	0.83	3.59	1.25	0.01
Alkalinity	mg/l	0	0	c.0	20.1	171	149	142
as HCO$_3^-$	meq/l	0	0	c.0	0.33	2.81	2.44	2.33
	%	0	0	c.0	20.81	67.03	14.09	0.39
Total anions	meq/l	0.190	1.55	0.239	1.58	4.19	17.32	595
Ionic balance error	%	−11.8	+4.9	+6.1	+1.9	+5.0	+0.7	+0.2
Si	mg/l	<0.02	2.42	–	4.54	7.41	6.10	3.0
Electrical conductivity	μS/cm	–	274	45.7	179	388	1840	–

[a] Average value for area.

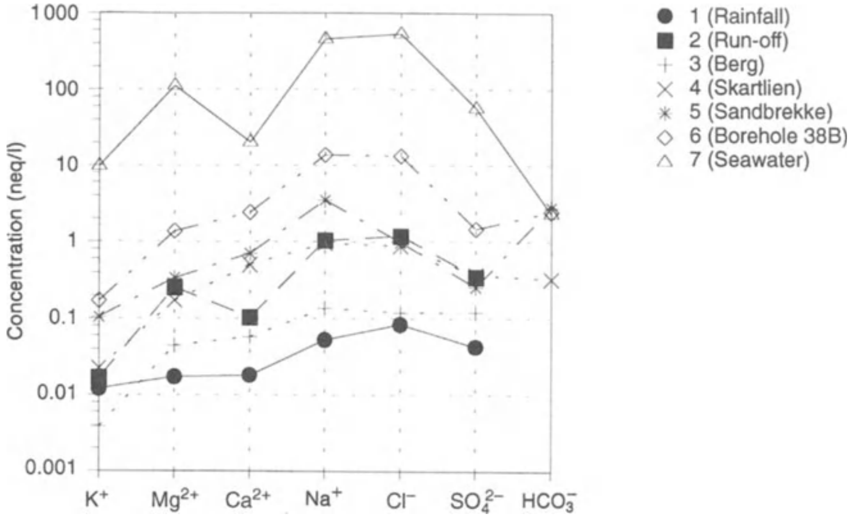


Figure 3.4 Schoeller diagram illustrating the chemical composition of waters from Hvaler (Table 3.1).

Ca^{2+}, Mg^{2+} and $(Na^+ + K^+)$ and on the anion diagram by SO_4^{2-}, HCO_3^- (or alkalinity) and $Cl^-(+NO_3^-)$.

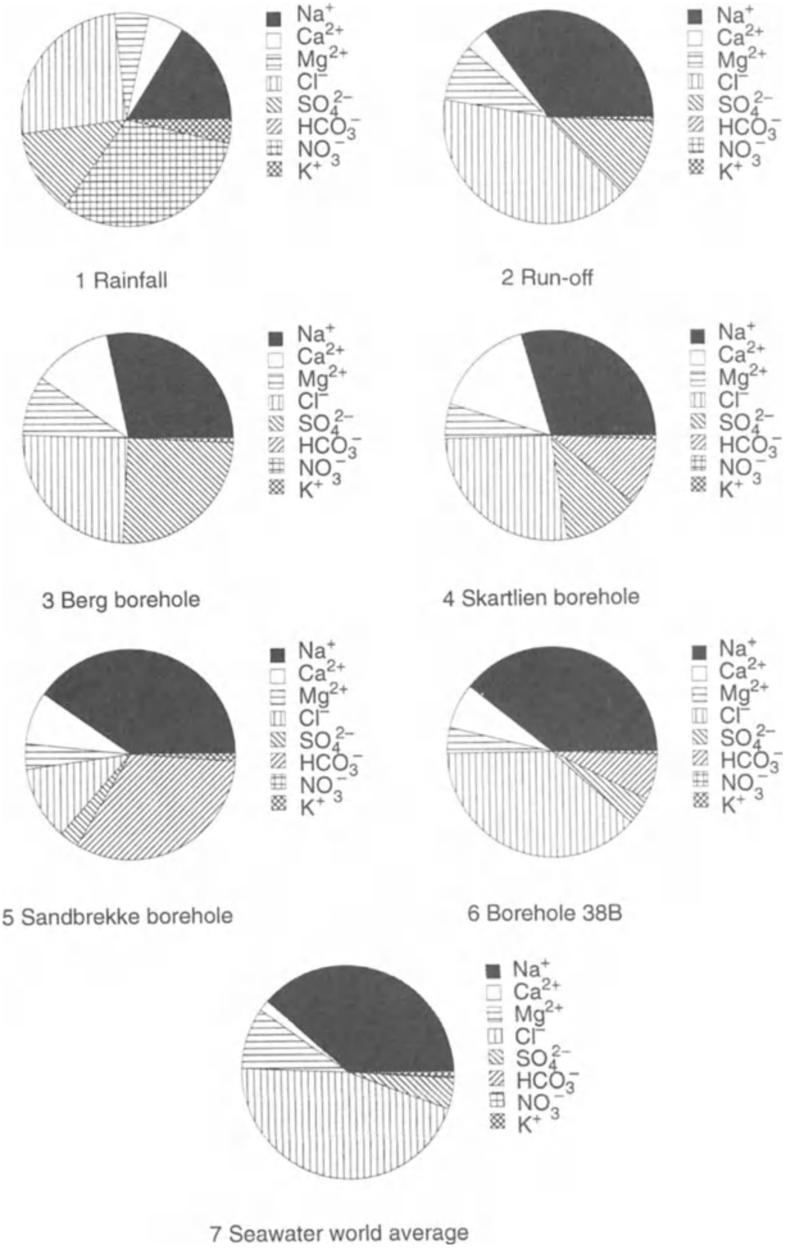
These two ternary diagrams are then projected onto a central diamond (Piper; Figure 3.6) or square (Durov, Figure 3.7) field, allowing the ready identification of different hydrogeochemical water types (or facies). For example, on a Durov diagram, typical fresh groundwaters in a carbonate-rich sedimentary aquifer will plot in the Ca^{2+}–HCO_3^- field at the top left. The points may be plotted as symbols of radius related to total ionic content. Waters dominated by saline connate or seawater intrusion components will plot in the Na^+–Cl^- field at the lower right. Granitic waters or ion-exchanged Na^+–HCO_3^- waters will plot in the lower left field.

The compositions of a number of well known and rather obscure mineral waters are plotted on a Durov diagram in Figure 13.8.

3.3.4 Total dissolved solids and electrical conductivity

Total dissolved solids (TDS) is reported either as the residue left after evaporating a unit volume of water at a given temperature, or as the sum of all the constituents analysed. Some impression of the TDS content can be gained by measuring the solution's electrical conductivity (EC). The EC will increase with the number of charged ions in solution, although it will be to some extent dependent on the type of ion, as some are more effective transporters of charge than others. As a rough guide:

$$\text{EC } (\mu\text{S/cm}) \times 0.640 \approx \text{TDS (mg/l)}$$



1 Rainfall

2 Run-off

3 Berg borehole

4 Skartlien borehole

5 Sandbrekke borehole

6 Borehole 38B

7 Seawater world average

Figure 3.5 Pie diagrams illustrating the chemical composition of waters from Hvaler (Table 3.1). Note that the pie diagram for rainfall appears not to balance as hydronium ions ($H^+_{(aq)}$) have been omitted.

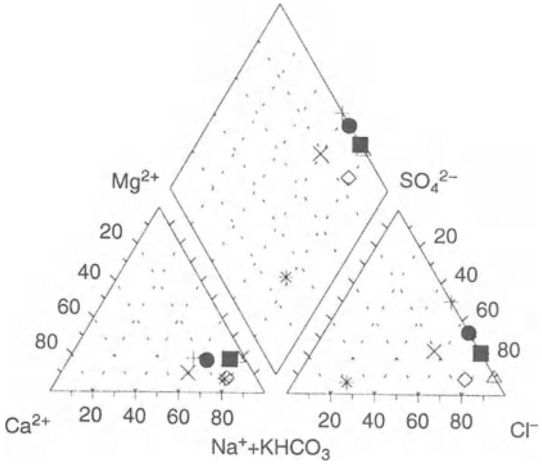


Figure 3.6 Piper diagram illustrating the chemical composition of waters from Hvaler (Table 3.1). Key as for Figure 3.4.

3.3.5 Activity and concentration

In very dilute solutions, ions will be awash in a large volume of pure water and will not interact greatly with each other. In more concentrated solutions, they will encounter each other and tend to interact electrostatically. This impedes their reaction dynamics and thus their 'thermodynamically effective

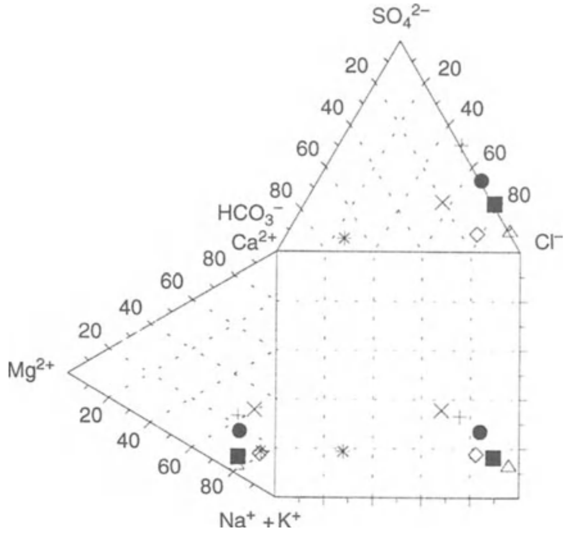


Figure 3.7 Durov diagram illustrating the chemical composition of waters from Hvaler (Table 3.1). Key as for Figure 3.4.

concentration', or activity tends to appear less than the actual concentration. Activity is measured, like concentration, in mmol/l and is calculated for an ion Y (Domenico and Schwartz, 1990) by:

$$[\mathrm{Y}] = \gamma_{\mathrm{Y}}(\mathrm{Y})$$

where [Y] is the activity of Y (mol/l), γ_{Y} is an activity coefficient (typically a little less than 1) and (Y) is the concentration of Y (mol/l).

γ_{Y} will depend on the salinity of solution, the type of ion and its charge. Several models are available for calculating γ_{Y}, of which one of the most used is the Debye–Hückel model:

$$\log \gamma_{\mathrm{Y}} = \frac{-\mathrm{A} z_{\mathrm{Y}}^2 (I)^{0.5}}{1 + \mathrm{B} a_{\mathrm{Y}} (I)^{0.5}}$$

where A and B are constants depending on temperature, I is the ionic strength of the solution in mol/l, z_{Y} is the ionic charge on Y and a_{Y} is the radius of the hydrated ion (cm). I is calculated by:

$$I = 0.5 \Sigma M_i z_i^2$$

where M_i is the molar concentration of each ionic species (i) in solution.

In dilute solutions, the lower part of the Debye–Hückel equation is approximately equal to one and

$$\log \gamma_{\mathrm{Y}} = -\mathrm{A} z_{\mathrm{Y}}^2 (I)^{0.5}$$

3.3.6 pH, acidity and alkalinity

The pH of water is related to the activity of hydrogen ions (or protons) in solution:

$$\mathrm{pH} = -\log_{10}[\mathrm{H}^+]$$

The notation 'p' denotes $-\log_{10}$, so similarly:

$$\mathrm{pOH} = -\log_{10}[\mathrm{OH}^-]$$

Water molecules have a slight tendency to dissociate into hydrogen and hydroxide ions:

$$\mathrm{H_2O} \rightleftharpoons \mathrm{H}^+ + \mathrm{OH}^- \qquad (3.19)$$

This is an equilibrium reaction and it turns out that:

$$[\mathrm{H}^+][\mathrm{OH}^-] = K_{\mathrm{w}}$$

where K_{w} is a temperature-dependent constant, with value $10^{-14}\,\mathrm{mol^2/l^2}$ at standard temperature (25°C).

Thus, in a neutral solution at 25°C, where $[\mathrm{H}^+] = [\mathrm{OH}^-]$, both the pH and pOH will be equal to 7. An excess of acid (H^+) will result in a pH less than 7.

Acidity and alkalinity

Strictly speaking, pH and pOH should be referred to as proton acidity and hydroxide alkalinity. An acid can be defined as any species that reacts or complexes with a base such as OH^-, to remove it from solution. Likewise, a base can be regarded as anything that reacts with an acid, such as hydrogen ions.

We can thus regard other ionic species as potential mineral acids (Hedin *et al.*, 1994; Younger, 1995); these might include Fe^{2+} or Fe^{3+}, Al^{3+} or Mn^{2+}, e.g.

$$Al^{3+} + 3OH^- \rightleftharpoons Al(OH)_3 \qquad (3.20)$$

Mineral alkalis or bases include CO_3^{2-}, HCO_3^-, S^{2-}, HS^- as well as OH^-, e.g.

$$HCO_3^- + H^+ \rightleftharpoons H_2O + CO_2 \qquad (3.21)$$

In practice, the alkalinity of most groundwaters is dominated by bicarbonate ions (HCO_3^-) and the term is often assumed to represent the concentration of bicarbonate. Alkalinity is usually measured by field or laboratory titration as the amount of strong acid (in mmol/l or meq/l) required to neutralize the alkalinity and lower the pH value to 4.5. It is thus also a direct measure of the acid-buffering capacity of the groundwater. Similarly, acidity is measured by titration against a strong base (e.g. sodium hydroxide) to an endpoint of (typically) pH 8.3.

It should be noted that many (but not all) oxidation reactions tend to result in the net production of acidity, and reduction reactions in the production of bicarbonate alkalinity.

3.3.7 Equilibria and speciation

The law of mass action

A fundamental chemical principle, known as the law of mass action, states that, for reactions which occur under equilibrium conditions, the product of the activities of the product species divided by the product of the activities of the reactant species is a temperature-dependent equilibrium constant K.

For example for the reaction

$$aA + bB \leftrightarrows yY + zZ \qquad (3.22)$$

$$K = \frac{[Y]^y[Z]^z}{[A]^a[B]^b}$$

and for example the dissolution of fluorite:

$$Ca^{2+}(F^-)_2 \rightleftharpoons Ca^{2+} + 2F^- \qquad (3.14)$$

$$K = \frac{[Ca^{2+}][F^-]^2}{[Ca^{2+}(F^-)_2]}$$

The activity of a solid phase is conventionally taken to be 1, thus:

$$K_s = [Ca^{2+}][F^-]^2$$

where K_s is the solubility constant for fluorite.

Speciation

Several solutes, such as carbonates, sulphides or silicates, may exist in solution in differing forms:

$$\underset{\substack{\text{carbon}\\\text{dioxide}}}{CO_2 + H_2O} \rightleftharpoons \underset{\substack{\text{carbonic}\\\text{acid}}}{H_2CO_3} \rightleftharpoons \underset{\text{bicarbonate}}{H^+ + HCO_3^-} \rightleftharpoons \underset{\text{carbonate}}{2H^+ + CO_3^-} \qquad (3.23)$$

$$H_2S \rightleftharpoons H^+ + HS^- \rightleftharpoons 2H^+ + S^{2-} \qquad (3.24)$$

$$SiO_2 + 2H_2O \rightleftharpoons H_4SiO_4 \rightleftharpoons H^+ + H_3SiO_4^- \rightleftharpoons 2H^+ + H_2SiO_4^{2-} \text{ etc.} \qquad (3.25)$$

The most important of these is the carbonate system. For each step, we can write an equilibrium activity equation; e.g. for the bicarbonate/carbonate step:

$$K = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]}$$

It thus follows that the lower the pH and the higher the $[H^+]$, the lower the concentration of carbonate and the higher the concentration of bicarbonate. The speciation chain is thus pH dependent. The lower the pH, the further to the left of the reaction series lies the equilibrium condition (Figure 3.8). In most typical groundwaters, with a nearly neutral pH, the dominant inorganic carbon species is bicarbonate.

3.3.8 Saturation

Consider again the dissolution of fluorite:

$$Ca^{2+}(F^-)_2 \rightleftharpoons Ca^{2+} + 2F^- \qquad (3.14)$$

$$K_s = [Ca^{2+}][F^-]^2$$

This equation should be true at equilibrium conditions (i.e. where the solution is in equilibrium with solid-phase fluorite). If only fluorite is present, and dissolves in pure water, $[F^-] \approx 2[Ca^{2+}]$ by stoichiometry. Thus the equation becomes:

$$K_s = 0.5[F^-]^3$$

Taking Krauskopf's (1979) value of K_s ($pK_s = -\log_{10} K_s = 10.4$ at 25°C), this means that the fluoride activity resulting from fluorite dissolution would be about 0.43 mmol/l or 8.2 mg/l at 25°C.

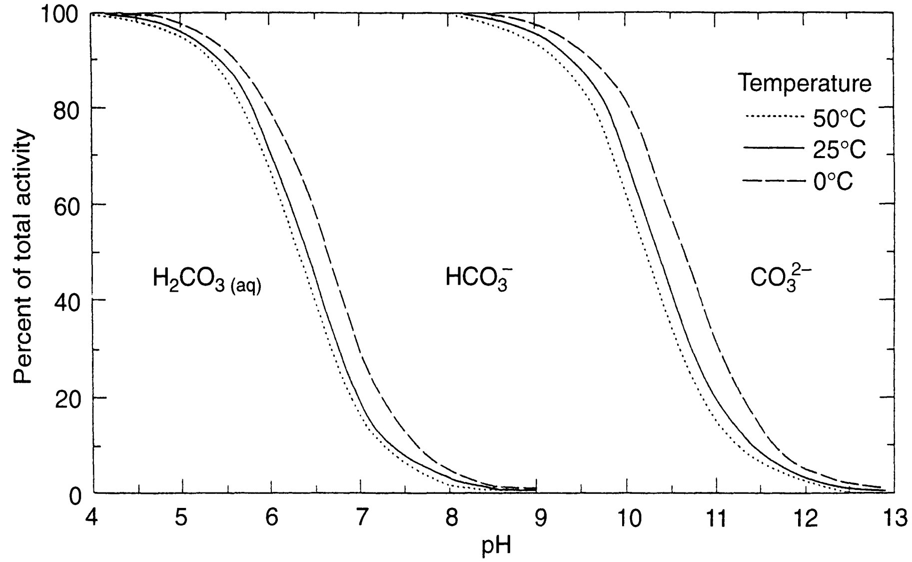


Figure 3.8 Distribution of major species of dissolved inorganic carbon. (Source: Hem, 1989.)

In practice, however, dissolved calcium will generally already be present in the groundwater, possibly derived from calcite dissolution or the weathering of anorthite feldspar. Thus, in order to maintain the equilibrium constant in (3.14) above, only a very much smaller amount of fluoride need be present in the system. In fact, if the calcium activity is 80.2 mg/l = 2 mmol/l, only 0.14 mmol/l or 2.7 mg/l fluoride activity can be present in the water. The presence of calcium in the water thus decreases the solubility of fluoride by what is known as the common ion effect.

Suppose that two waters mix; one of them a fluoride-rich water and one of them a calcium-rich water, such that the ion activity product (IAP) exceeds K_s:

$$\mathrm{IAP} = [\mathrm{Ca}^{2+}][\mathrm{F}^-]^2 > K_s$$

The water is then said to be supersaturated with respect to fluorite. There will be a tendency for fluorite to precipitate, removing calcium and fluoride ions from solution, until the water is just saturated and the equilibrium condition is satisfied.

A water where

$$\mathrm{IAP} = [\mathrm{Ca}^{2+}][\mathrm{F}^-]^2 < K_s$$

is said to be undersaturated with respect to fluorite. It has the capacity to dissolve fluorite, if present in the aquifer.

A saturation index (SI) can be defined:

$$\mathrm{SI} = \log_{10}\frac{\mathrm{IAP}}{K_s} = \log_{10}\frac{[\mathrm{Ca}^{2+}][\mathrm{F}^-]^2}{K_s}$$

If SI < 0 the solution is undersaturated; if SI > 0 the solution is supersaturated with respect to the mineral.

Fluorite is a simple example, but similar saturation conditions exist for all other minerals. The most important is probably saturation with respect to calcite, governed by:

$$\mathrm{Ca}^{2+}\mathrm{CO}_3^{2-} \rightleftharpoons \mathrm{Ca}^{2+} + \mathrm{CO}_3^{2-} \tag{3.26}$$

$$K_s = [\mathrm{Ca}^{2+}][\mathrm{CO}_3^{2-}]$$

However, carbonate concentrations, as we have seen above, are heavily pH dependent. Carbonate is also very difficult to analyse directly in a solution of near-neutral groundwater. It is standard practice to measure the alkalinity by titration and then calculate the carbonate concentration from knowledge of the carbonate speciation chain and pH conditions.

3.3.9 Kinetics

The equations above merely describe the concentration profile of dissolved species under equilibrium conditions. Another consideration to be taken into account is kinetic factors. Reactions progress at a given rate governed by

- temperature and pressure;
- concentrations of species present;
- a given rate constant, k', for each reaction.

A mineral will only dissolve in groundwater to yield a solution saturated with respect to that mineral if enough time is available for that reaction to proceed to equilibrium conditions. In many fast-flowing groundwater systems this is not necessarily the case. For example, in southern Norway high topographic gradients prevail in dominantly acidic silicate lithologies. Groundwater throughflow is rapid, while silicate weathering reactions are typically slow. Thus equilibrium conditions may not be reached and shallow groundwaters (on discharge at a well or spring) are typically low in minerals. In contrast, groundwaters in calcareous aquifers (e.g. chalk) in the UK tend to be more mineral rich: residence times are usually longer and the dissolution of carbonates occurs rapidly. As a third example, one can consider deep groundwaters in Scandinavia or Canada in areas of acidic crystalline basement. At depth, groundwater throughflow is very slow and residence times are long. Under such circumstances, silicate weathering reactions can proceed to their logical conclusion and groundwaters will typically have a high mineralization (section 3.5.2).

3.3.10 Effect of temperature

Two factors are temperature dependent.

- Reaction rates. These will typically increase with temperature (T), according to the Arrhenius equation:

$$\ln k' = \ln \mathrm{A} - E_a/RT$$

where A and E_a (activation energy) are constants and R is the gas constant.
- Equilibrium constants of reactions. These may increase or decrease with increasing temperature, according to the Van't Hoff equation:

$$\ln \frac{K(T_2)}{K(T_1)} = \frac{-\Delta H^\ominus}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where $\Delta H^\ominus$ = change in enthalpy of reaction; $K(T_1)$ = equilibrium constant at temperature T_1 and R = gas constant.

The temperature dependence thus hinges on the value of $\Delta H^\ominus$. For an endothermic reaction, where $\Delta H^\ominus$ is positive, K will increase with increasing temperature. If the reaction is exothermic (produces heat), $\Delta H^\ominus$ will be negative and K will decrease with increasing temperature. As many (but not all) mineral dissolution reactions are endothermic, many minerals will become more soluble as temperature increases.

This bald statement can, however, be misleading in cases where dissolution is dependent on a gaseous phase, such as carbon dioxide:

$$\mathrm{Ca^{2+}CO_3^{2-} + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^-} \qquad (3.27)$$

Carbon dioxide is less soluble in water at elevated temperatures, this being one reason why calcium carbonate solubility is greater at low temperatures. This partially accounts for the particularly intensive karst development often found to have occurred under periglacial conditions.

3.3.11 Redox potential

The final hydrogeochemical parameter to familiarize oneself with before embarking on a fuller assessment of the origin of mineral waters is redox potential or Eh. Redox reactions involve the transfer of electrons. Reduction involves the acquisition of electrons to result in a lower oxidation state, while oxidation involves the loss of electrons (e.g. the oxidation of ammonium to nitrate by oxygen):

$$\mathrm{NH_4^+ + 3H_2O \rightleftharpoons 10H^+ + NO_3^- + 8e^-}\ \text{(oxidation)} \qquad (3.28)$$

$$\mathrm{O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O}\ \text{(reduction)} \qquad (3.29)$$

where e^- is an electron. Together, these reactions form a redox couple:

$$\mathrm{NH_4^+ + 2O_2 \rightleftharpoons H_2O + 2H^+ + NO_3^-} \qquad (3.30)$$

For a standard reduction half-reaction, where ‘Ox’ is the oxidized species and ‘Red’ is the reduced species:

$$\mathrm{Ox} + \mathrm{e}^- \rightleftharpoons \mathrm{Red} \tag{3.31}$$

an equilibrium constant can be defined:

$$K = \frac{[\mathrm{Red}]}{[\mathrm{Ox}][\mathrm{e}^-]}$$

Thus, one can define pe, where pe = $-\log[\mathrm{e}^-]$, the negative logarithm of the electron activity:

$$\mathrm{pe} = \log K - \log\frac{[\mathrm{Red}]}{[\mathrm{Ox}]}$$

The electron activity in a groundwater can be measured by an electrode, giving an objective measure of how reducing or oxidizing the water is. The electrode typically gives a reading in millivolts, which we term Eh. Eh is converted to pe by:

$$\mathrm{Eh} = \frac{2.3RT}{F}\mathrm{pe}$$

where F is the charge on 1 mole of electrons (96 487 coulombs). From the equation for pe, above, it will be seen that a reduction reaction will occur to an appreciable degree (i.e. the product concentrations are equal to those of the reactants) when pe is of the same order of magnitude or lower than $\log K$. The lower $\log K$ is, the lower the value of pe and hence Eh required to provide enough electrons to allow the reaction to occur. It will, however, be noted that most redox reactions involve the transfer of protons. The oxidation states of species in a solution will thus depend not only on Eh, but also on pH and the activities of all other species involved in the reaction. All $\log K$ values are measured against the standard reduction of H^+ to H_2 (Table 3.2).

Groundwaters tend to become progressively more reducing along a flow path as organic carbon, carbohydrates and other reducing agents are

Table 3.2 Log*K* and equivalent Eh values for selected redox half-reactions (modified after Domenico and Schwartz, 1990)

Reaction	*log K*	*Equivalent Eh* $(= E^\ominus)$ *(mV)*
$H^+ + e^- = \frac{1}{2}H_{2(g)}$	0	0
$\frac{1}{8}SO_4^{2-} + \frac{5}{4}H^+ + e^- = \frac{1}{8}H_2S_{(aq)} + \frac{1}{2}H_2O$	+ 5.13	303
$\frac{1}{8}NO_3^- + \frac{5}{4}H^+ + e^- = \frac{1}{8}NH_4^+ + \frac{3}{8}H_2O$	+14.9	879
$\frac{1}{2}MnO_2(s) + 2H^+ + e^- = \frac{1}{2}Mn^{2+} + H_2O$	+20.8	1230
$Fe^{3+} + e^- = Fe^{2+}$	+13.0	767

oxidized. A series of reactions will take place with the most potent oxidizing agents being reduced first, under the highest Eh conditions. Dissolved oxygen disappears first, followed by Fe(III), nitrate and sulphate. In highly reducing waters, methane may be generated:

$$CH_2O + 7H^+ + 4Fe(OH)_{3(s)} \rightleftharpoons 4Fe^{2+} + 10H_2O + HCO_3^- \qquad (3.32)$$

$$5CH_2O + 4NO_3^- \rightleftharpoons 2N_2 + 2H_2O + 5HCO_3^- + H^+ \qquad (3.33)$$

$$NO_3^- + 2CH_2O + H_2O \rightleftharpoons NH_4^+ + 2HCO_3^- \qquad (3.34)$$

$$2CH_2O + SO_4^{2-} \rightleftharpoons H_2S + 2HCO_3^- \qquad (3.35)$$

$$2CH_2O + H_2O \rightleftharpoons CH_4 + HCO_3^- + H^+ \qquad (3.36)$$

A dynamic equilibrium will often be established in the aquifer, involving a so-called redox barrier. Up gradient of the barrier, oxidized species will dominate, while down gradient, reduced species dominate.

3.4 EVOLUTION OF GROUNDWATER IN A STRATABOUND AQUIFER

3.4.1 A stratabound aquifer – the Lincolnshire Limestone

The Lincolnshire Limestone is one of the United Kingdom's best studied aquifer units (e.g. Downing and Williams, 1969; Edmunds, 1981; Rushton, 1981; Lawrence and Foster, 1986). It is also the source of a number of mineral water spas, albeit now closed down.

Like many stratabound aquifers, the Jurassic Lincolnshire Limestone consists of unconfined and confined parts. The unconfined part lies in the west and is open to recharge from rain falling on its outcrop. The recharged rainfall becomes groundwater and flows through the unconfined zone, eventually discharging via (1) scarp slope springs (2) dip slope springs or (3) wells and boreholes. The confined part of the aquifer is shut in by the overlying low permeability Upper Estuarine Series, comprising silts and clays, although some direct recharge takes place via swallow holes. There are few natural outlets for groundwater flow from the confined aquifer (although some artesian springs or 'blow wells' are known to have existed) and the groundwater in the deeper parts is relatively old, having been resident in the aquifer for periods of time which are geologically significant. The deep confined water in the east has thus had time to acquire a higher degree of mineralization than that in the unconfined and shallow confined areas. In the deepest parts of the aquifer, highly saline groundwaters are found, possibly representing connate or diagenetic waters dating from the time of deposition and burial of the sediments (Figure 3.9).

Under natural conditions there was only a limited amount of throughflow in the confined aquifer. The little that there was, was due to (4) some degree

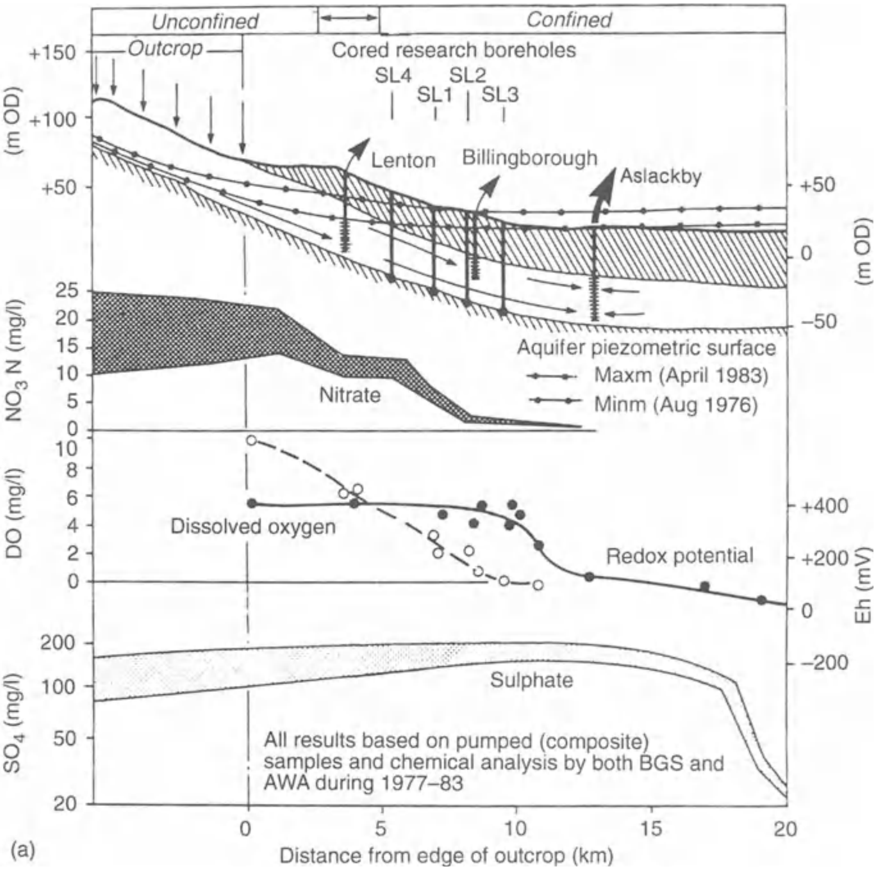


Figure 3.9 Cross-section through the Lincolnshire Limestone, illustrating changes in chemical composition down-dip. (Reproduced with permission from Lawrence and Foster, 1986, and Edmunds, 1981.)

of leakage up through the confining low-permeability strata, partially via artesian springs or 'blow wells' and (5) possibly leakage to deeply incised river valleys or buried glacial valleys. In more recent times, however, the drilling of deep water wells into the confined aquifer and the abstraction of groundwater (6) have induced a greater degree of flow from the unconfined into the confined part.

The confined aquifer is particularly permeable in south Lincolnshire; for example, east of Stamford, transmissivity values can reach several thousand m^2/d. Consequently, saline water has been flushed from the aquifer more efficiently in the south and the interface with saline formation water lies farther to the east than in north Lincolnshire.

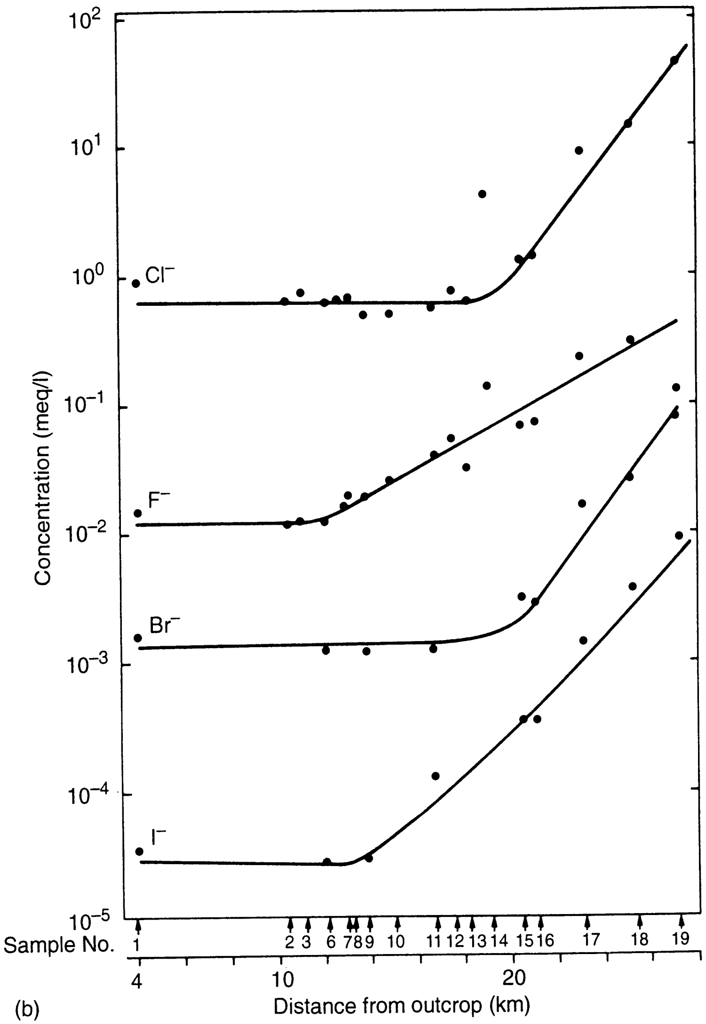


Figure 3.9 Continued.

3.4.2 Hydrochemical facies

Three types of water (or hydrochemical facies) can be distinguished in the aquifer as one progresses down dip.

Type I water is dominated by calcium and bicarbonate. This water is found largely in the unconfined aquifer. It rapidly becomes saturated with respect to calcite, limiting further dissolution. The calcium and bicarbonate concentrations thus remain approximately constant. The water is generally oxidizing and contains relatively high nitrate and sulphate concentrations, derived from agriculture, indicating that it is actively circulating water derived from recent recharge.

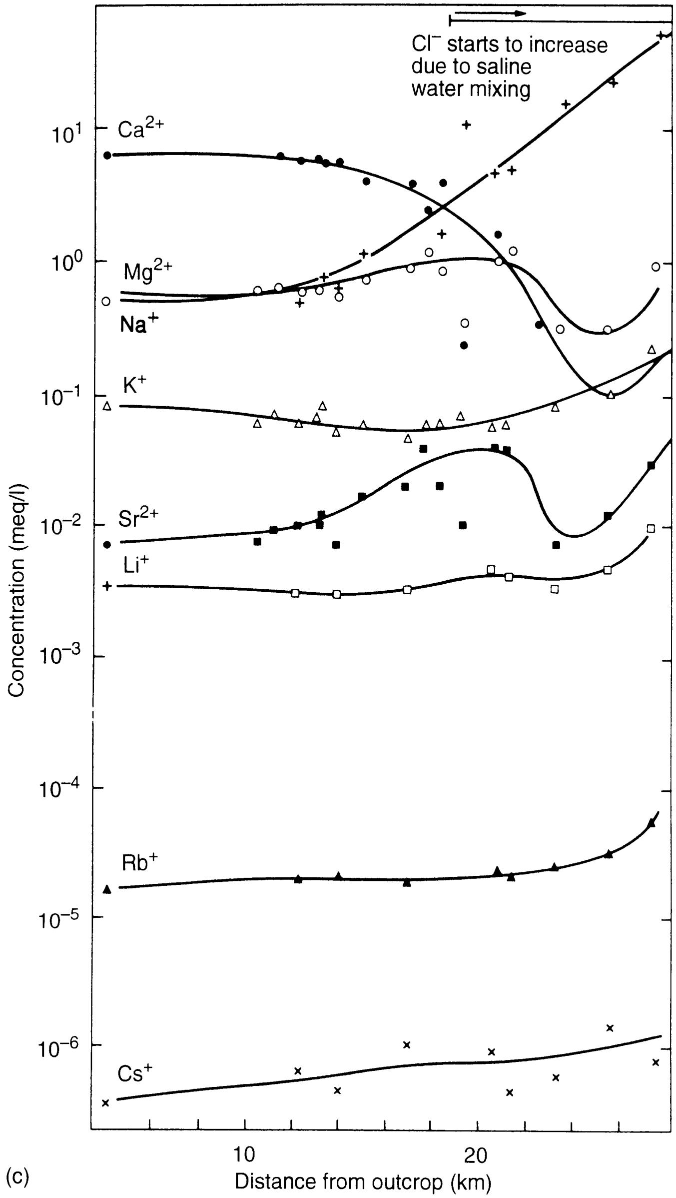


Figure 3.9 Continued.

Type II is dominated by sodium and bicarbonate, where the sodium is derived from ion exchange for calcium on clays or other surface-active media:

$$Ca^{2+} + (Na^+)_2\text{-clay} \rightleftharpoons 2Na^+ + Ca^{2+}\text{-clay} \tag{3.37}$$

The removal of calcium from solution leaves the groundwater free to dissolve fluoride from the aquifer without exceeding the fluorite solubility product. Thus fluoride increases towards the east. The type II facies contains a redox barrier. Towards the east sulphate decreases, as it is bacterially reduced to sulphide by the organic material in the aquifer:

$$2CH_2O + SO_4^{2-} \rightleftharpoons 2HCO_3^- + H_2S \qquad (3.18)$$

Also, as dissolved oxygen is consumed, the redox potential (Eh) falls and pH rises (due to production of alkalinity by e.g. sulphate reduction; see above). It has been suggested that ion exchange only commences in the reducing conditions of type II waters due to (reduced) iron sulphide and organic matter acting as ion exchange sites (Edmunds, 1981).

Type III waters, occurring at depth in the confined aquifer, are ancient 'fossil', possibly connate, saline waters of sodium chloride type, with rather low calcium concentrations and high fluoride concentrations (permitted by the lack of calcium).

Source of chloride

It will be noted that chloride has a tendency to act conservatively. It is not generally released by rock–water interaction in great quantities and, once in solution, it is very stable and does not precipitate out. In type I water, the chloride is probably derived from:

- chloride in precipitation;
- chloride from agriculture.

In type III it is derived from mixing with fossil saline water.

3.4.3 Mineral water spas

The chemical changes down the dip of the Lincolnshire Limestone have long been known. As early as 1904, Woodward described the increase in salinity (Table 3.3). Woodward (1904) also noted the sodium chloride, with minor bicarbonate, character of the deeper saline waters, together with the absence

Table 3.3 Salinity of groundwater from wells in the Lincolnshire Limestone (after Woodward, 1904)

Location	*Distance from outcrop (km)*	*Depth (m)*	*TDS (mg/l)*	*Cl^- (mg/l)*
Barn	3	30	393	20
Tongue End	8	61	633	152
Littleworth	14	107	2480	862
Crowland	21	183	2850	1500

of calcium: 'It is not easy to understand how (the water) gets rid of the carbonate and sulphate of lime'. As noted above, the problem has been partially solved by postulating ion exchange and possibly precipitation of calcite.

Catley and Braceborough Spas

Among the spas noted by Woodward (1904) was Catley, believed to produce the only British mineral water at the time which was aerated and bottled. At Braceborough Spa a valley has been incised down through the overlying Upper Estuarine Series almost to the top of the confined Lincolnshire Limestone. As a consequence, water has been able to find its way under pressure through the valley floor to form natural springs of saline water. The water seems to have been transitional in character, containing bicarbonate, sulphate and chloride anions, with calcium and sodium as dominant cations. Dissolved gases included CO_2, O_2 and N_2.

Woodhall Spa

Woodhall Spa was perhaps the most famous of the Lincolnshire spas (for locations see Figure 10.2). It consisted of wells sunk to the deep confined limestone. The first shaft was sunk in around 1820 as a 'wildcat' exploratory shaft for coal, in an attempt to locate the continuation of the productive Nottinghamshire and Derbyshire coalfields down dip. The diggers are reported to have carried small fragments of coal down the shaft at the beginning of each shift and 'found' them during the day's work in an attempt to keep the entrepreneur's hopes alive and themselves in employment. They continued to 840 ft (256 m) without finding coal and then constructed a borehole in the base of the shaft to 1200 ft (366 m) total, still without success. At 510–530 ft (155–162 m) a water-bearing rock, presumed to be the Lincolnshire Limestone, was struck. After the water was found to have a high mineral content (of sodium chloride type, *c.* 13 500 mg/l Cl^-), rumours of its health-giving properties spread and an inn was constructed by the shaft. In 1834 a new well was dug, a bathhouse and hotel constructed and the water systematically analysed. It was found to contain significant levels of iodide (5.7 mg/l) and bromide (47 mg/l). A steam engine is reported to have been used to haul buckets of mineral water up from the well (Woodhall Spa, 1994), although Woodward (1904) notes the use of a proper pump, yielding 1100 gallons (5000 l) per hour. The spa enjoyed a brief and prosperous life before it fell victim to the popularity of rival seaside resorts such as Skegness. The buildings are now owned by the Woodhall Spa Baths Trust and, until recently, were still used by the British National Health Service as a rheumatism clinic.

3.5 EVOLUTION OF GROUNDWATER IN CRYSTALLINE ROCKS

Crystalline bedrocks have been subject to detailed exploration at considerable depths during investigations for nuclear waste disposal. Two of the more interesting studies, from a hydrogeochemical point of view, have been performed in Canada (Gascoyne and Kamineni, 1994) and at Stripa, Sweden (Nelson *et al.*, 1983; Andrews *et al.*, 1989; Nordstrom *et al.*, 1989), where considerable light has been shed on the formation of the deep-seated brines commonly found at depth in such rocks. The evolution of shallow groundwaters has been subject to somewhat less detailed study. One study worth mentioning was carried out by Banks *et al.* (1992, 1993) on a shallow aquifer in Precambrian granite at Hvaler, southeastern Norway, and the results are discussed below.

3.5.1 Shallow groundwater

On the island of Kirkeøy, Hvaler, the groundwater can be divided into three main groups on an evolutionary pathway, by plotting silicon against chloride and sodium/chloride against chloride (Table 3.1). Type I waters were defined as rainfall composition.

Type II groundwaters had low silicon concentrations and similar sodium/chloride ratios to seawater and rainfall. The absolute concentrations of many solutes (including Na^+ and Cl^-) were 3–4 times greater than for rainfall. These waters were interpreted essentially as recently recharged coastal rainfall which had been concentrated by evapotranspiration, with the addition of some sea salts. Sulphate levels were elevated with respect to a seawater dilution line due to contamination by 'acid rain'. Very little evidence of extensive water–rock interaction was seen and the waters were dominated by Na^+ and Cl^-, reflecting the marine-dominated coastal rainfall.

Type III groundwaters were typically sodium bicarbonate waters, reflecting a significant degree of water–rock interaction. The sodium/chloride ratios and silicon concentrations were significantly higher than in rainfall or seawater, reflecting the weathering of sodic feldspars.

Type IV groundwaters were typically sodium chloride waters. They are believed to be due to mixing of type II or III waters with intruding sea water at depth in the aquifer. They typically reapproached the seawater dilution line for most elements, and the sodium/chloride ratio also approached that for seawater.

Banks *et al.* (1995a) also examined the minor ion chemistry of the granitic groundwaters of Hvaler and noted the following points.

- The granite groundwater was typically rich in fluoride (up to 6 mg/l), reflecting both the occurrence of fluorite as a vein mineral in the granite and the general paucity of calcium. Thus fluoride was able to achieve high concentrations without the fluorite saturation control being invoked.

- The groundwaters were richer in many heavy metals than were other Norwegian bedrock groundwaters, probably due to lower alkalinities (allowing metals to dissolve unhindered by carbonate saturation controls) and lower pH values than other bedrock waters.
- The groundwaters were rich in radioelements such as radon (up to 8500 Bq/l) and uranium (up to 0.17 mg/l), due to the generally elevated concentrations of uranium in the granitic host rock and the presence of uranium-rich pegmatites.

3.5.2 Evolution of deep crystalline rock groundwaters

Gascoyne and Kamineni (1994) summarized the findings of Canadian teams working on the hydrogeochemical evolution of deep groundwaters in crystalline bedrock. Like Banks *et al.* (1992, 1993) they found that shallow groundwaters were typically of Ca–Na–HCO_3 composition. At greater depths of up to several hundred metres, the waters evolved in the following manner:

- increasing salinity;
- increasing pH;
- gradual dominance of Na over Ca with depth (with the exception of a tendency to calcium chloride brines at the greatest depths).

The increased salinity is believed to be due to a wide variety of rock–water interactions involving dissolution and alteration of silicates. The increasing pH reflects the consumption of carbon dioxide and acids in the weathering process and possibly the production of alkalinity by reduction reactions. Magnesium and potassium concentrations are typically held at low levels due to ion exchange reactions on clays and the low solubility of their silicates, hydroxy- and carbonate species at a high pH.

At greater depths, chloride becomes the dominant anion, and sulphate also becomes apparent, possibly derived from the oxidation of sulphide minerals. At depth in many crystalline basement areas, concentrated sodium or even calcium chloride brines can be found, and the origin of these has been the subject of much debate. Two main arguments have been put forward:

- that they are fossil seawaters which have intruded into the crystalline bedrock, possibly at times when the sea level was higher than it is today;
- that they are hydrogeologically evolved waters; the origin of sodium and calcium can be explained easily enough by the weathering of calcic or sodic silicates, but where did the chloride come from?

For the origin of deep chlorides, Nordstrom *et al.* (1989) and Edmunds and Savage (1991) proposed several models, including

- leaching of chloride-containing fluid inclusions in crystals;
- radiogenesis of chloride;

- weathering of chloride from amphiboles and micas, where it may be present as a minor constituent;
- fossil seawater;
- juvenile fluids.

Of these, probably the most favoured model is that involving a combination of leaching of fluid inclusions and weathering of chloride from silicates.

3.6 RADIOACTIVE MINERAL WATERS

In most groundwaters the most significant radioelement in terms of activity is usually radon (^{222}Rn), followed by radium, uranium and thorium (Table 3.4). Much of the radioactive decay of such heavy nuclei takes place by the emission of alpha particles, i.e. helium nuclei, ^{4}He. This is the origin of much of the dissolved helium gas in deep mineral and thermal waters (Andrews, 1991), e.g.

$$^{238}\mathrm{U} \rightarrow {}^{234}\mathrm{Th} + {}^{4}\mathrm{He}$$

3.6.1 The natural occurrence of radon, radium, uranium and thorium

Natural radioactive elements form part of one of three radioactive decay chains, those commencing with ^{238}U, ^{235}U and ^{232}Th. Isotopes of radon (Rn), radium (Ra), uranium (U) and thorium (Th) occur as members of all of these decay chains. An element may have several isotopes, all with almost identical chemical behaviour but very different radioactive behaviour and differing atomic masses, due to the differing numbers of neutrons in the

Table 3.4 Global abundances and half-lives of the commonest U, Th and Rn isotopes, with typical U and Th contents in bulk continental crust, granites and granodiorites (after Killeen and Heier, 1975, and Banks *et al.*, 1995b)

Radionuclide	*Abundance*	*Half-life*	*Continental crust (ppm)*	*Typical granodiorites (ppm)*	*Typical granites (ppm)*
^{234}U	0.0056%	2.5×10^5 years	2.7–3.0	2.6	4–5
^{235}U	0.720%	7.0×10^8 years			
^{238}U	99.276%	4.5×10^9 years			
^{228}Th	Trace	1.91 years	10–11	9.0	17–20
^{230}Th	Trace	7.7×10^4 years			
^{232}Th	100%	1.4×10^{10} years			
^{234}Th	Trace	24.1 d			
^{219}Rn	–	3.92 s			
^{220}Rn	–	54.5 s			
^{222}Rn	–	3.8 d			

nuclei. Examples are ^{238}U (the isotope of uranium with mass number 238) and ^{235}U, which behave almost identically chemically but have very different half-lives and specific activities.

Uranium, thorium, radium and radon occur in many of the same rock types. Both thorium and uranium tend to be concentrated in highly fractionated magmas and hydrothermal solution and are thus found in acidic igneous rocks (e.g. granites), pegmatites and hydrothermal deposits (Killeen and Heier, 1975). As Ra and Rn are derived from the decay chains of U and Th, they may also be concentrated in these rocks.

In sedimentary and metamorphic rocks, radioactive elements can be concentrated in authigenic minerals such as glauconite, at weathering surfaces and by a variety of processes such as:

- hydrothermal activity along fault zones or other discontinuities;
- immobilization at palaeo-redox fronts;
- immobilization in organic-rich material in reducing environments; e.g. oil reservoirs and black shales such as the Scandinavian Alum Shales or the black shales of the Namurian of the English Peak District.

Uranium

Uranium has three isotopes (Table 3.5) occurring naturally in significant amounts, but over 99% of the global mass consists of ^{238}U. The shorter lived daughter ^{234}U is derived from ^{238}U via ^{234}Th and ^{234}Pa. In a single decay chain, if all nuclides are at equilibrium, the activities (in becquerels) of all member nuclides should be the same. However, in a dynamic system such as groundwater, equilibrium conditions will not necessarily pertain and deviations can tell us much about the hydrogeological system. For example, although negligible in terms of mass, the shorter lived daughter isotope ^{234}U is often dominant over ^{238}U in groundwater in terms of activity (i.e. Bq/l). This may be partly due to preferential dissolution of the lighter isotope, which Andrews (1991) believes can account for activity ratios ($^{234}U/^{238}U$) of as much as 1.5, but is often largely due to preferential alpha recoil from fracture surfaces (Milvy and Cothern 1990), particularly if these have been enriched in uranium by precipitation under reducing conditions. For example, the following activity ratios have been recorded:

- 3–11 in the groundwater of the granitic rocks at Stripa Mine, Sweden (Andrews *et al.*, 1989);
- 1–4 in bedrock groundwaters around Helsinki (Asikainen and Kahlos, 1979);
- 2.8–3.6 in the thermal waters of Bath, UK (Andrews, 1991);
- 1.69 at Buxton thermal spa, UK (Andrews, 1991);
- 2.56 at Matlock spa, UK (Andrews, 1991).

Table 3.5 Concentrations of Rn, U and Th in groundwaters, summary of selected previous studies

Location	*Radon*	*Uranium*	*Thorium*	^{226}*Ra*	^{4}*He*^{a}	*Reference*
UK Chalk groundwater	1.5–19 Bq/l	–	–	–	–	Younger and Elliot (1995)
USA groundwaters	–	–	^{232}Th rarely >0.004 Bq/l; up to 0.0004 Bq/l in drinking water ^{230}Th up to 0.015 Bq/l^{b}; up to 0.0015 Bq/l in drinking water	–	–	Barnes (1986)
Granite groundwaters, Main USA	Mean = 8200 Bq/l Maximum = 55 000 Bq/l	–	–	–	–	Michel (1990)
Groundwaters and mine waters, Carnmenellis Granite, UK	110–740 Bq/l	–	–	–	–	Ball *et al.* (1991)
Vimmerby, Sweden	>740 Bq/l in granite Maximum 2660 Bq/l	–	–	–	–	Snihs (1973)
Sweden (national mapping of groundwater supplies)	Typically 0–500 Bq/l in shallow crystalline bedrock; maximum thus far = 3400 Bq/l in Södermanland County	–	–	–	–	Published hydrogeological map descriptions by: Engqvist and Fogdestam (1984) Karlqvist *et al.* (1985) Pousette *et al.* (1981, 1983, 1984, 1989) Söderholm *et al.* (1987) Wikner *et al.* (1991)
Stripa deep mine waters (quartz monzonite rock)	Up to 74 000 Bq/kg	Up to 90 ppb	–	–	–	Andrews *et al.* (1989)
Finland (shallow bedrock boreholes, mainly in southern Finland)	Geometric mean = 240 Bq/l Arithmetic mean = 1020 Bq/l Maximum = 77 000 Bq/l	Median = 5 μg/l Arithmetic mean = 73 μg/l	–	–	–	Salonen (1988) (radon, 2065 boreholes) Lahermo and Juntunen (1991) (uranium, 1388 boreholes)

Finland (961 wells and springs in Quaternary deposits)	Geometric mean = 31 Bq/l Arithmetic mean = 92 Bq/l Maximum = 3800 Bq/l	–	–	–	–	Salonen (1988)
Uraniferous granites, Helsinki area, Finland	–	Maximum = 14 900 μg/l	–	–	–	Asikainen and Kahlos (1979)
Granite groundwaters, Hvaler, South Norway	Median = 2500 Bq/l Maximum = 8500 Bq/l	Median = 15 μg/l Maximum = 170 μg/l	Median = 0.38 μg/l Maximum = 2.2 μg/l	–	–	Banks *et al.* (1995b)
Non-thermal Carboniferous Limestone groundwater, Gurney Slade, UK	6 Bq/l	0.42 μg/l ^{238}U	–	0.0074 Bq/l	4	Andrews (1991)
King's Spring thermal water (45.5°C), Bath, UK (Carboniferous Limestone)	86 Bq/l	0.06 μg/l ^{238}U	–	0.38 Bq/l	1080	Andrews (1991)
Buxton Spa, thermal water (28°C), UK (Carboniferous Limestone)	77 Bq/l	2.78 μg/l ^{238}U	–	0.034 Bq/l	50	Andrews (1991)
Matlock, low temperature thermal water (20°C), UK (Carboniferous Limestone)	89 Bq/l	1.78 μg/l ^{238}U	–	–	75	Andrews (1991)
Hotwells thermal spring (24.3°C), Bristol, UK (Carboniferous Limestone)	43 Bq/l	0.85 μg/l ^{238}U	–	0.036 Bq/l	410	Andrews (1991)

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[a] Units of 10^{-8} cm^3 STP/cm^3 H_2O.

[b] Near U mineralizations in New Mexico.

The activity (Bq/l) represented by a given concentration (μg/l) of U in water will depend on the isotopic composition of the dissolved uranium and daughter isotopes, and conversion factors based on equilibrium assumptions can lead to an underestimation of activity. It can be shown that $1\,\mu g = 1.2 \times 10^{-2}\,Bq\,^{238}U$ and, assuming equilibrium, a conversion factor of $1\,\mu g = 2.5 \times 10^{-2}\,Bq\,[^{234}U + {}^{238}U]$ is thus commonly used (Barnes, 1986; Milvy and Cothern, 1990).

Thorium

In terms of mass, naturally occurring thorium consists almost entirely of ^{232}Th, and $1\,\mu g = 4 \times 10^{-3}\,Bq\,^{232}Th$. It decays, via ^{228}Ra and ^{228}Ac, to the short-lived ^{228}Th (half-life 1.91 years), and the activity (Bq) of the latter radionuclide in groundwater may exceed that due to ^{232}Th. The short-lived ^{234}Th (half-life 24.1 d) is produced by alpha decay of ^{238}U, itself decaying rapidly to ^{234}U. ^{230}Th (half-life 77 000 years) is also part of the ^{238}U decay series.

Radium and radon

Radium is an alkaline earth (group II) metal with similar chemical properties to its chemical analogues, calcium, barium and strontium. Radon is a chemically inert gas.

Both elements exist as isotopes which form parts of all three radioactive decay chains.

- ^{235}U decays, via intermediaries, to form ^{223}Ra, which in turn decays to release ^{219}Rn (also known as actinon). The ^{235}U decay series has a lower terrestrial abundance than the other series, due to its shorter half-lives. Thus ^{223}Ra and ^{219}Rn are typically present in negligible amounts in natural waters.
- The ^{232}Th series produces ^{228}Ra and ^{224}Ra and thence ^{220}Rn (thoron). The radium isotopes can be important in groundwater. The half-life of ^{220}Rn is rather short and, unless thorium concentrations are particularly high in the aquifer rocks and groundwater transport times are very rapid, it is seldom present in groundwater in large quantities.
- The corresponding members of the ^{238}U decay series are ^{226}Ra (half-life 1620 years) and ^{222}Rn (isotope half-life 3.8 d).

^{228}Ra is produced by the decay of ^{232}Th, while ^{226}Ra is produced by the analogous decay of ^{230}Th, a daughter of ^{238}U. The activity ratio of ^{226}Ra/^{228}Ra in groundwater would be expected to reflect the relative contents of ^{238}U and ^{232}Th in the host rocks, all things being equal. In the thermal water of Bath (derived from Carboniferous Limestone), however, the ^{226}Ra/^{228}Ra activity ratio of 13.4 considerably exceeds the expected value based on whole rock chemistry. This indicates, as do the elevated $^{234}U/^{238}U$ activity ratios, the enrichment of limestone fracture surfaces in uranium by precipitation under reducing conditions (Andrews, 1991).

Radon may be produced by *in situ* radioactive decay of radium in the rock, ejection across the rock–water interface during decay or by decay of dissolved radium. ^{222}Rn, during its half-life of 3.8 d, may travel limited distances (up to tens to hundreds of metres) in the groundwater of a fractured aquifer before decaying to ^{218}Po, ^{214}Pb, ^{214}Bi and ^{214}Po (the so-called radon daughters).

3.6.2 Hydrochemistry of uranium, thorium, radium and radon

Uranium

The hydrochemistry of uranium is particularly complex. For a detailed description, the reader is referred to Garrels and Christ (1965), Krauskopf (1979) and Drever (1988). The main features are as follows:

- uranium can occur in several oxidation states, but only +IV and +VI are hydrochemically important;
- The oxidation from uranous state (U^{4+}) to uranyl (UO_2^{2+}) has a redox potential of +330 mV, placing it in the normal hydrogeochemical range;
- The reduced (uranous) ion forms a highly insoluble hydroxide in water, even at low pH values;
- The UO_2^{2+} (uranyl) ion (and its hydroxide) is rather soluble.

Uranium is rather insoluble in reducing environments, but can be highly soluble in oxidizing, and particularly acidic, conditions. The solubility of oxidized uranium may be further enhanced by complexation with hydroxide (in highly alkaline conditions), carbonate, phosphate, organic/humic species (Higgo *et al.*, 1989) and perhaps even chloride (Nguyen-Trung *et al.*, 1991). Other species such as fluoride and sulphide can be important for solubility.

Ingested uranium adversely affects bone and kidney. As the specific radioactivity of uranium is relatively low, it is thought that the chemical and physiological toxicity of the element may outweigh the radiotoxic effects (Milvy and Cothern, 1990).

Thorium

In contrast to uranium, thorium is highly insoluble under all conditions. It exists almost exclusively in an oxidation state of +IV. Thus, although the content of thorium in most rocks exceeds that of uranium, uranium concentrations nearly always exceed those of thorium in groundwater.

Radon

Radon is a chemically inert but soluble gas. Its concentration in groundwater is believed to be directly controlled by (1) hydrodynamic factors, (2) geometric factors (fracture aperture and shape), (3) the uranium or, more precisely, radium content of rocks and groundwater (Michel, 1990) and (4) the uranium and radium mineralogy within the host rock (Ball *et al.*, 1991). Radon concentrations may vary with meteorological factors such as atmospheric pressure, heavy rainfall, snowmelt or frost cover events. Radon concentrations have been used as a diagnostic tool for predicting earthquake events, locating fracture zones and even estimating fracture apertures (Nelson *et al.*, 1983; Younger and Elliot, 1995). Andrews (1991) used radon concentrations to estimate fracture apertures of around 0.07 mm in the Carboniferous Limestone aquifer at Bath, UK. The relationship between groundwater radon and aperture depends on

- the flux F (Bq/m^2), of radon from a host rock across a fracture surface to groundwater;
- the assumption that groundwater flow is sufficiently slow to allow an equilibrium to be established;
- assumptions about fracture geometry.

For a plane parallel fracture, of aperture w (m), the activity of radon in the fracture groundwater [Rn] (Bq/m^3) can be estimated by

$$[\mathrm{Rn}] = 2F/w$$

Radium

Radium has analogous hydrochemical properties to its fellow group II elements calcium, barium and strontium. It is typically rather insoluble in most groundwaters, its solubility being limited by (Andrews, 1991)

- solubility limits of its carbonate and sulphate;
- coprecipitation with calcium carbonate;
- adsorption on iron and manganese oxides and hydroxides.

Under highly reducing conditions (reducing and mobilizing oxidized Fe and Mn) and in sodium chloride waters, these controls are to some extent negated and radium can be mobilized. Thus the hydrogeochemical behaviour is almost the opposite of that of uranium. As Andrews (1991) points out, the deep thermal waters of the limestone at Bath have elevated radium concentrations but low uranium concentrations compared with shallow groundwaters from the same Carboniferous Limestone aquifer lithology.

3.6.3 Radioelements in groundwater

One does not need to look to deep thermal or mineral waters to find high levels of dissolved radioelements. Granitic lithologies, with high host rock concentrations of U and Th, tend to yield groundwater with high U, Th and Rn concentrations in standard domestic wells and boreholes. Even in relatively shallow granitic groundwaters, concentrations of up to 77 000 Bq/l Rn and 14.9 mg/l U (in groundwater from boreholes in Finland) have been recorded. The Finnish Geological Survey have compiled hydrogeochemical maps of radionuclides and statistically analysed the data (Lahermo and Juntunen, 1991). The Geological Survey of Norway compared the content of Rn, U and Th in crystalline bedrock groundwaters from three lithology groups (Banks *et al.*, 1995b):

- the Precambrian Iddefjord Granite of Hvaler;
- the Permian lavas and Precambrian gneisses around Oslofjord;
- the Caledonian metamorphics and Precambrian gneisses of Trøndelag.

The highest concentrations, up to 8500 Bq/l Rn, 170 μg/l U and 2.2 μg/l Th, were found in waters from the U and Th rich Iddefjord granite of South

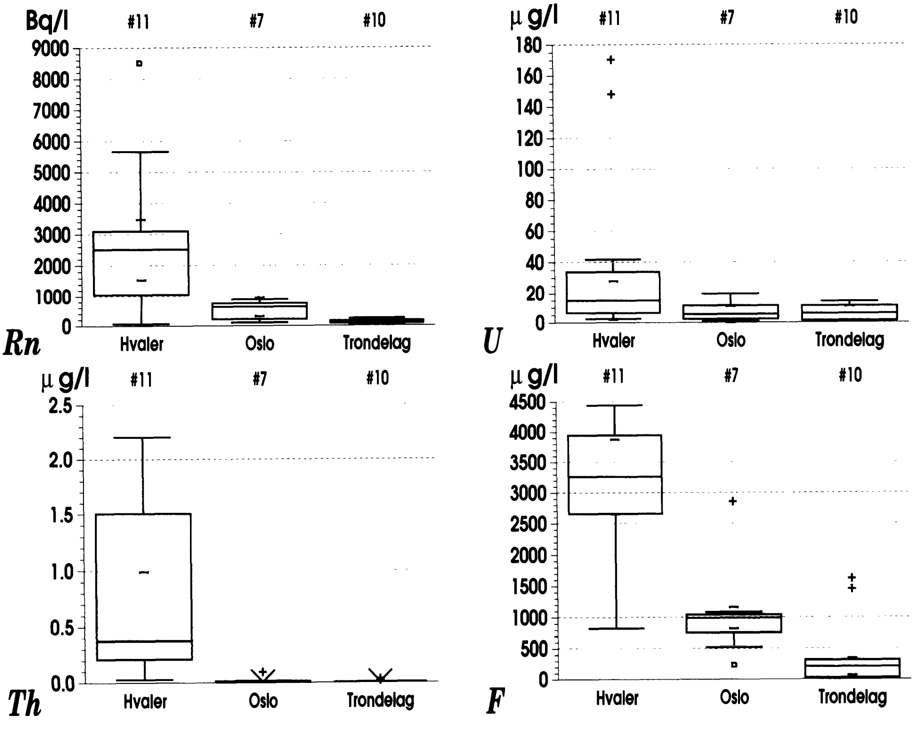

Figure 3.10 Concentrations of U, Th, Rn and F in groundwaters in the Iddefjord Granite of Hvaler, the gneisses and basalts around Oslofjord and the gneisses and metasediments of Trøndelag, Norway. (After data from Banks *et al.*, 1995a,b.)

Norway (Figure 3.10). A significant correlation was found between dissolved radon and fluoride, both at concentrations which exceed the typical drinking water health limits for these parameters of 500 Bq/l and 1.5 mg/l respectively (Figure 3.11). Surprisingly, Banks *et al.* (1995b) concluded that 'the correlations between U, Th and Rn themselves are rather weak, particularly within one lithology, indicating that hydrodynamic factors, complexing, pH and redox conditions, and solution/recoil phenomena are the major controlling factors for radioelement concentration, often masking the effect of mere

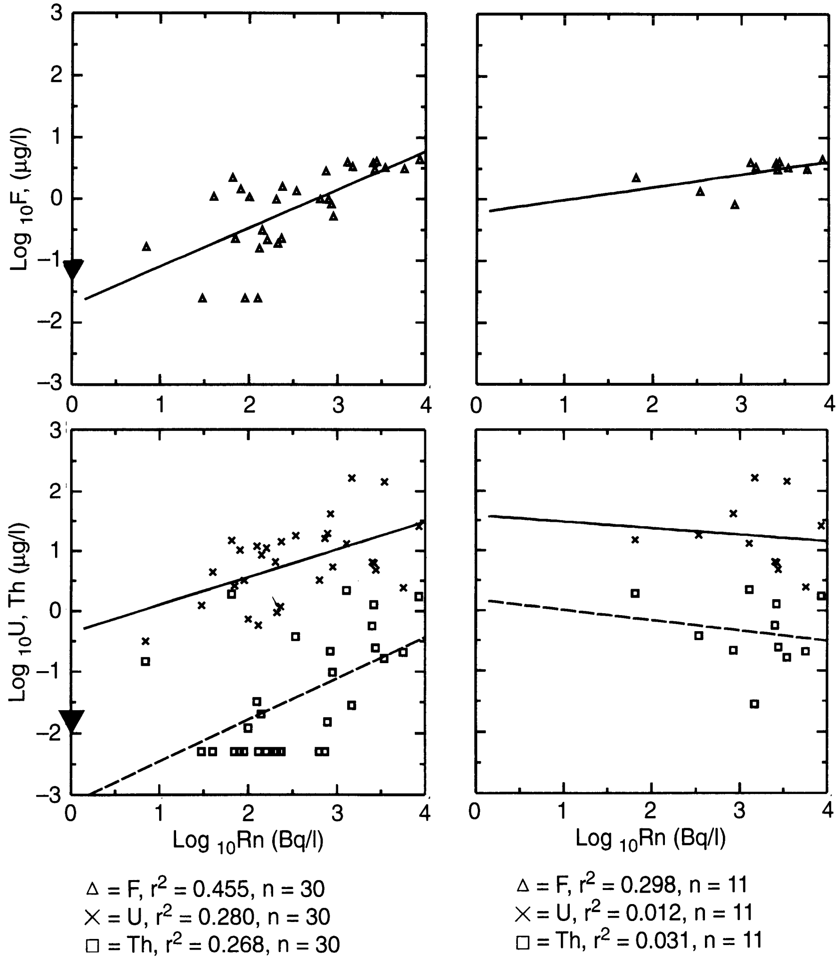

Figure 3.11 Correlations of Rn with U, Th and F for (left) the entire Norwegian data set ($n = 30$) used in Figure 3.10 and (right) the data set ($n = 11$) from the Iddefjord granite only (using data from Banks *et al.*, 1995b). Inverted black triangles show limits of detection for Th and F^- (concentrations below detection limit are arbitrarily set to half this value for the purposes of statistical analysis).

radioelement concentrations in the bedrock'. The results of selected investigations are presented in Table 3.5.

3.7 CATEGORIES OF MINERAL WATERS

A tentative categorization of mineral waters has been developed based on the mode of origin of the mineral composition and the mode of ascent to the surface. Needless to say, a large degree of overlap occurs between some of the classes listed below and very many mineral waters contain features of several of the categories:

- evolutionary waters – produced by normal hydrogeochemical reaction processes;
- marine waters – derived from intruded or entrapped sea water:
  - intrusive (modern day seawater intrusion);
  - connate (marine pore water dating from sedimentary deposition);
  - fossil (seawater intruded and entrapped during earlier period of saline intrusion);
  - leached (saline pore waters leached from overlying marine sediments);
- formation or diagenetic waters;
- mineral-related waters – derived from specific mineral occurrences:
  - pyrite waters (e.g. London Clay);
  - mine drainage waters;
  - evaporite brines;
- geothermal waters – mineral content enhanced by elevated temperature.

Modes of occurrence at surface

The waters may then rise to the surface by one or more of the following pathways:

- hydrostratigraphic (dip slope springs);
- confined incisional (incised river valleys);
- abstracted (wells, boreholes);
- injectional (fracture zone, flow pipe).

3.7.1 Evolutionary waters

The majority of mineral waters are believed to be derived by natural hydrogeothermal evolutionary processes. There will, of course, be a grey area between evolutionary waters and marine waters, as connate or fossil waters often occur at depth in many aquifers. In the UK the waters of Braceborough, Harrogate, Boston Spa and Tunbridge Wells are examples of evolutionary waters. Figure 3.12 also illustrates the four different modes of occurrence of the waters.

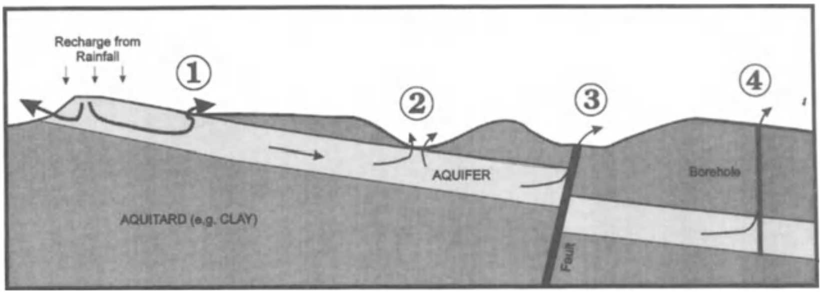

Figure 3.12 Modes of occurrence of evolutionary waters. (1) Spring at the feather edge of an overlying confining stratum; (2) valley incised through confining layer to aquifer; (3) fault-controlled spring; (4) abstraction from deep confined strata via a well or borehole.

Hydrostratigraphic occurrences

The feather edge of confining strata overlying the dip-slopes of aquifer units provide favourable locations for mineral water springs (Figure 3.12). The flow profile illustrates that these springs will typically receive the deepest water of the unconfined aquifer, i.e. that water which has had the longest residence time and is thus likely to be most evolved. It may also have had some contact with the waters of the confined aquifer. Mineral waters which occur in this stratigraphic position include Boston Spa and, to some extent, Leamington Spa (Chapter 10).

Both Bath and Harrogate are examples of another type of mineral water occurrence whose location is constrained by hydrostratigraphic factors. The Harrogate waters occur near the faulted core of an anticlinal structure and those at Bath occur above the subcrop of the rising limb of the Carboniferous Limestone in the Radstock Syncline. The rising limbs convey highly evolved waters residing in deep strata up to the surface. In both cases the ascent is assisted by faulting.

Incisional confined

In the case of Braceborough Spa, a river valley has eroded down towards the top of a confined aquifer containing highly evolved water. The mineral water has discharged in the base of the valley under pressure.

Abstraction

Woodhall Spa provides an example of a deeply confined mineral water resource with no natural outlet to the surface. The only way of tapping the resource was via a deep artificial shaft.

Injectional

The mineral water may alternatively reach the surface from depth by being 'injected' upwards along a discrete flowpath, typically a fracture zone or washout pipe. Fracture controls on mineral water occurrence are found in the spas of the White Peak (Buxton and Matlock) and, to some extent, at Bath and Harrogate.

3.7.2 Marine waters

Examples of these waters include the type IV waters at Hvaler (section 3.5.1), which are derived by various degrees of mixing with intruding seawaters.

Woodhall Spa provides an example of a mineral water whose salinity is, in all probability, derived from modified connate water trapped in a confined aquifer.

In contrast, the Norwegian mineral water, Farris, is a relatively shallow water derived from rocks overlain by Quaternary marine deposits raised above the land surface by isostatic rebound at the end of the last glaciation. The marine sediments have therefore only been exposed for the past few thousand years. Their marine porewater is still slowly being leached out into the underlying strata.

3.7.3 Formation and diagenetic waters

Saline or hypersaline brines are often observed in the deep confined parts of many sedimentary aquifers. It is, of course, possible that these could be derived from meteoric waters subject to long residence times and extensive water–rock interaction. In many cases, however, it is thought that these brines represent original porewaters, which would have been saline in the case of marine sediments, further modified by processes of diagenesis and water–rock interaction. Deep brines may alternatively be derived from leaching of evaporite deposits or from highly saline groundwaters dating from the time of evaporite formation. Finally, they may be derived from the compression-induced migration of highly saline waters, formed by any of the above processes, from adjacent or underlying formations during sedimentary compaction.

After sediments are deposited, they will very often be overlain by an accumulating pile of later sediments and be buried as part of a subsiding sedimentary basin. As the sediments become increasingly deeply buried, they will tend to become compacted and lose water. This water, termed diagenetic water, may migrate laterally or vertically into overlying sediments. Diagenetic waters may have a significant ionic solute loading and characteristic chemical signature related, for example, to the geochemical and mineralogical alteration of clay minerals. Under compaction, lithostatic pressure will often exceed hydrostatic pressure, particularly if the more permeable sediments (e.g. sands) are interbedded with less permeable clays and shales. The sediments may thus become overpressured and the pore waters will tend to squeeze out through the low permeability horizons. This may produce an 'ion filtration' effect, with diagenetic water slowly escaping from the formation, but many of the solutes being retained within the compacting sediment. This retention may be due to the passage of anions being impeded by negatively charged clay particles, or to adsorption of ionic solutes on clay surfaces (Downing, 1967). Such formation waters can thus become highly mineralized hypersaline brines under such conditions.

As formation waters and diagenetic waters are likely to be derived from connate pore waters, the distinction between the three water denominations is often rather blurred.

Two British examples serve to illustrate the importance of such processes. In the Wessex Basin of Southern England, compaction-induced flows are thought to have dominated over gravity-driven groundwater flow during Jurassic and Cretaceous times (Downing and Penn, 1992). Salinity signatures of groundwaters in the Triassic and Jurassic strata of the Wessex Basin are believed, on the basis of, among other factors, Br/Cl ratios and isotopic signatures, to be derived either from leaching of Triassic evaporite deposits or from relict groundwaters dating from the time of evaporite formation. These saline waters have subsequently been partially mobilized into overlying strata by compaction-induced flow. Ion filtration may have been responsible for some of the characteristic isotopic signatures observed (Edmunds, 1986).

The brines prevalent in the deep Carboniferous strata of the East Pennines coalfields (Anderson, 1945; Downing, 1967; Downing and Howitt, 1969) have been interpreted as owing much of their character to ion filtration effects. Recently, however, alternative models for these brines have been put forward; in particular, models proposing their derivation by downwards migration or diffusion of brines from overlying Permo-Triassic evaporitic sediments. Brine concentrations in the East Midlands Coalfield can exceed 200 g/l salinity, although the salinity is generally highest in the Westphalian Coal Measures strata, less in the Namurian Millstone Grit and lowest in the underlying Carboniferous Limestone (Edmunds, 1986). This decreasing salinity profile has been interpreted as evidence for downward migration of evaporite-derived brines from the overlying Permo-Triass, but other possible interpretations include (Downing and Howitt, 1969):

- flushing of the Carboniferous complex from below by relatively fresh meteoric water flowing down-dip along the more permeable Carboniferous Limestone strata;
- the progressive compaction of the sedimentary pile expelling waters upwards, resulting in accumulating ion filtration effects and increasing salinity in an upward direction;
- differences in clay mineralogy between the formations.

3.7.4 Mineral-related waters

These waters are related to specific mineralogies in rocks or sediments. Although the hydrochemical processes of rock–water interaction may be quite conventional, the mineral water occurrence is related to the presence of anomalous rock types. The most obvious examples of this water type are the evaporite-related brines, specifically derived from subcrops of halite or other easily soluble minerals. Such waters occur, in the UK, in Cheshire and near Droitwich, derived from evaporite deposits in the Mercia Mudstone. Leaching of gypsum from the same formation is also thought to account partly for the mineral content of the waters at Leamington Spa (Chapter 10).

The mineral waters formerly abstracted from the London Clay may also be construed as falling into this category. Epsom salts (magnesium sulphate) owes its origin to the oxidation of pyrite, which occurs in considerable quantities in the London Clay. The magnesium is likely to be derived from ion exchange reactions, for example, of iron released by pyrite oxidation, for magnesium on silicates. Pyrite oxidation is also responsible for the highly ochreous waters emerging from many metal sulphide mines and coal mines. Coal mine waters in particular exhibit many similarities to sulphate–chalybeate (iron-rich) waters such as are found at Harrogate, UK (Chapter 10), and may conceivably be regarded as mineral waters. The waters from many metal sulphide mines are, however, too laden with toxic heavy metals to be regarded as suitable for human consumption.

3.7.5 Geothermal waters

As we have seen, most reaction rates increase with increasing temperature and the equilibrium constants of endothermic dissolution reactions show a similar increase. Thus geothermal waters, by nature of the fact that they are high temperature, will usually have elevated concentrations of dissolved minerals.

They typically occur in tectonically active regions of the earth such as volcanic belts or rift situations; e.g. Iceland, the East African Rift or the North Bohemian Rift Valley. These represent deep-seated discontinuities in the earth's crust along which brines or fluids such as CO_2, SO_2, H_2S, HF or HCl might be injected (Chapter 4). In such situations it is important to note that the water itself is dominantly deep-circulating meteoric water. This water may mix with ascending gases which then dissolve, resulting in excess mineralization. The gases named above are acidic (e.g. CO_2) and will convey an additional aggressivity to the water enabling further mineral weathering and dissolution. Such waters will also typically be hot due to the high geothermal gradient over rift areas and to the hot ascending fluids. Examples of this type of water are common in Iceland and also exist in, for example, the Czech Republic (Karlovy Vary and Soos), the Neogene volcanic zones of Romania, the Rhenish Massif of Germany (May *et al.*, 1933) and Portugal (Almeida and Calado, 1993; Carvalho, 1993).

3.8 ISOTOPE HYDROCHEMISTRY, WATER ORIGINS AND GROUNDWATER DATING

Although an examination of groundwater chemistry will reveal many facets of the origin of mineral and thermal waters, it may not reveal all. A complementary tool used by hydrogeologists is the study of stable and radioactive isotopes (Evans *et al.*, 1979). These often provide a characteristic 'fingerprint' of the origin of the element in question. For example, an examination of sulphur isotopes may reveal whether the sulphur is juvenile, is derived from dissolution of sulphate deposits or from the oxidation of sulphides. Likewise, carbon isotopes will give clues as to the source of carbon; whether from soil gas carbon dioxide, non-marine or marine carbonate dissolution.

3.8.1 Isotope terminology

The concentration of a given isotope is normally quoted as a ratio; the denominator being the concentration of the most common isotope of that element. In most materials this ratio will be approximately constant, but fractionation, due to dissolution, precipitation, evaporation or microbiological processes, may lead to a small enrichment or depletion of a given isotope. Such enrichment or depletions are quoted as a permille (‰) deviation (δ) from an arbitrarily defined standard. For example, for ^{18}O:

$$\delta^{18}\mathrm{O} = \frac{(^{18}\mathrm{O}/^{16}\mathrm{O})_{\mathrm{sample}} - (^{18}\mathrm{O}/^{16}\mathrm{O})_{\mathrm{standard}}}{(^{18}\mathrm{O}/^{16}\mathrm{O})_{\mathrm{standard}}} \times 1000$$

The standard in the case of ^{18}O is standard mean ocean water (SMOW).

3.8.2 Oxygen and hydrogen stable isotopes

The stable isotopes of oxygen and hydrogen, the two component atoms in the water molecule, are among the most revealing isotopes in hydrogeological studies.

^{16}O is the most abundant oxygen isotope, accounting for 99.76% of all oxygen (Table 3.6). ^{18}O is next most abundant at 0.20%. For hydrogen, ^{1}H is the most common, accounting for 99.985% of hydrogen abundance, while ^{2}H (or deuterium; D) accounts for a mere 0.015%. δ^{18}O is defined in section 3.8.1, while δ^{2}H or δD is defined as follows:

$$\delta^{2}\mathrm{H} = \frac{(^{2}\mathrm{H}/^{1}\mathrm{H})_{\mathrm{sample}} - (^{2}\mathrm{H}/^{1}\mathrm{H})_{\mathrm{standard}}}{(^{2}\mathrm{H}/^{1}\mathrm{H})_{\mathrm{standard}}} \times 1000$$

Table 3.6 The abundance of naturally occurring isotopes of hydrogen, carbon, nitrogen, oxygen and sulphur

Hydrogen		*Carbon*		*Nitrogen*	
Isotope	*Abundance (%)*	*Isotope*	*Abundance (%)*	*Isotope*	*Abundance (%)*
^{1}H	99.985	^{12}C	98.90	^{14}N	99.63
^{2}H	0.015	^{13}C	1.10	^{15}N	0.37
^{3}H	Trace	^{14}C	Trace		

Oxygen		*Sulphur*	
Isotope	*Abundance (%)*	*Isotope*	*Abundance (%)*
^{16}O	99.76	^{32}S	95.02
^{17}O	0.048	^{33}S	0.75
^{18}O	0.20	^{34}S	4.21
		^{36}S	0.02

In the cases of both ^{18}O and ^{2}H, the relevant standard is SMOW. This choice of standard reflects the fact that ocean water is the isotopically homogeneous point of origin of nearly all terrestrial waters. Ocean water evaporates to form water vapour. This vapour has a tendency to be depleted in the heavier, less volatile isotopes, the degree of depletion being temperature, and thus latitude, dependent. The water vapour will eventually condense as rainfall or snow. The first precipitation to condense will have an isotopic composition similar to that of the vapour. However, the precipitation will have a tendency to remove progressively the heavier isotopes, leaving the vapour gradually more depleted as the air mass moves inland. In summary, the higher the latitude, the higher the altitude and the more distant from the ocean, the more depleted will be the rainfall in the heavy isotopes ^{18}O and ^{2}H. The various fractionation processes tend to operate proportionally on both oxygen and hydrogen, and meteoric waters tend to obey the linear relation:

$$\delta^{2}H = 8\delta^{18}O + 10‰$$

On a plot of $\delta^{2}H$ versus $\delta^{18}O$, this results in a straight line named the meteoric water line. Equatorial, coastal precipitation plots towards the top right of the line. Points towards the lower left indicate precipitation in high latitude or continental areas. Thus the climatic or palaeogeographical conditions of recharge of groundwaters can be assessed by plotting them on the diagram. Deviation from the meteoric water line will occur if the groundwaters have been affected by any of the following factors (Figure 3.13).

- Mixing with non-meteoric waters, e.g. diagenetic water.
- Evaporation of surface waters and very shallow groundwaters.

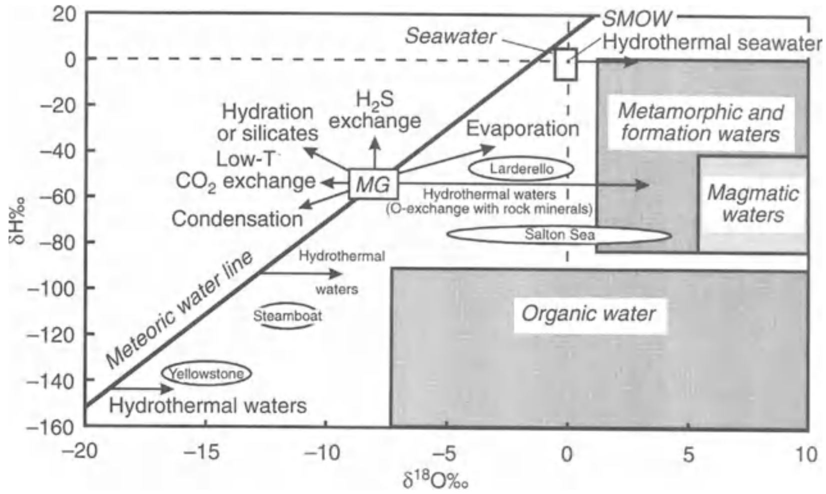

Figure 3.13 Diagram illustrating possible shifts away from the world meteoric line for δ^2H versus δ^{18}O plots. The arrows indicate shifts away from a typical meteorically derived groundwater (MG) lying on the world meteoric line. Ellipses show positions of hydrothermal waters from Larderello, Salton Sea, Steamboat Springs and Yellowstone, illustrating a shift to the right relative to the meteoric line. (Based on data from Leosson, 1993, Truesdell and Hulston, 1980, and Domenico and Schwartz, 1990.)

- Mineral exchange reactions, which may be important in high temperature geothermal systems. In geothermal waters, for example, there will be a shift towards a higher δ^{18}O composition, due to exchange with oxygen in isotopically heavier silicates. A similar shift in hydrogen is not observed due to the relative paucity of hydrogen in most minerals (Truesdell and Hulston, 1980; Kharaka and Carothers, 1986).

Hydrogen and oxygen isotopes have been applied in the studies of thermal waters at Bath (Figure 3.14; Chapter 10) and mineral waters at Harrogate (Figure 10.14). In both cases the waters were found to plot on the meteoric line in a similar position to present-day rainfall. This indicates a non-exotic origin for the waters, i.e. recharge under similar climatic conditions to today's. The groundwaters are thus presumed to be younger than the last ice age – i.e. less than 10 000 years old.

3.8.3 Carbon isotopes

There are three carbon isotopes of significance; ^{12}C (98.89% abundance) and ^{13}C (1.11%), which are both stable, and ^{14}C (about 10^{-10}%), which is radioactive, with a half-life of 5730 years. Carbon isotope ratios are usually measured on the dissolved bicarbonate fraction of groundwater following precipitation as carbonate. δ^{13}C enrichment is typically quoted relative to

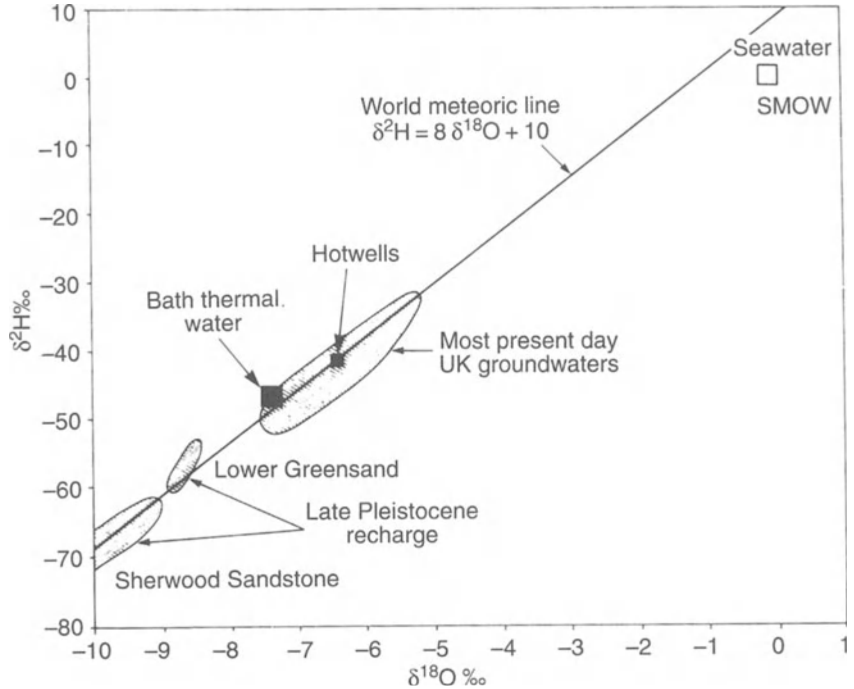

Figure 3.14 The use of δ^2H versus $\delta^{18}O$ plots to discern the palaeogeographic conditions of recharge of the thermal mineral waters of Bath and Hotwells (Bristol). The isotopic data indicate the waters have been recharged under climatic conditions similar to today's, in contrast to some other UK groundwaters, whose light isotopic signature indicates recharge under more glacially dominated conditions (late Pleistocene). (After Edmunds and Miles, 1991. Copyright Bath City Council, reproduced with permission.)

the calcite of a specific fossil marine belemnite of the Pee Dee Formation in South Carolina, USA, known as PDB. The study of carbon isotopes is more complex than that of oxygen or hydrogen, due to the existence of a number of different sources of carbon. The commonest model for bicarbonate generation in groundwaters is the dissolution of calcium carbonate by carbon dioxide.

$$CO_2 + H_2O + Ca^{2+}CO_3^{2-} \rightleftharpoons Ca^{2+} + 2HCO_3^-$$

Thus half the dissolved carbon is derived from the CO_2 and half from the calcium carbonate of the aquifer. In temperate climates the CO_2 derived from soil gas typically has a $\delta^{13}C$ of −26‰, while most marine carbonates have a $\delta^{13}C$ of around zero. Thus groundwaters evolving according to this model would be expected to exhibit a $\delta^{13}C$ of about −13‰. Deviations from this value might be due to:

- bicarbonate derived from oxidation of organic or other reduced carbon;
- bicarbonate being primarily derived from weathering of silicates by CO_2;
- non-marine or isotopically deviant aquifer calcium carbonate;
- carbon isotope exchange or incongruent precipitation/dissolution reactions in an aquifer.

As an example of the use of ^{13}C, thermal groundwaters from Bath, UK, were found to exhibit a $\delta^{13}C$ value of about $-1.5‰$, i.e. nearly in equilibrium with the marine Carboniferous Limestone aquifer with $\delta^{13}C = 0‰$. This was taken to indicate either carbon exchange or incongruent aquifer reactions. Such processes are thought to occur only very slowly, even in high temperature conditions. This implies a considerable residence time in the aquifers, as long as several thousand years, for an isotopic equilibrium to be established (Edmunds and Miles, 1991).

^{14}C is a powerful dating tool for archaeological remains where a single organic source of carbon is known. In groundwaters, according to the simple model described above, only 50% of bicarbonate carbon is recent and derived from biogenic CO_2, the rest is derived from aquifer carbonate, which will normally be far older than the half-life of 5730 years and will therefore have a negligible ^{14}C content. Thus the biogenic ^{14}C has been diluted by a factor of two and a correction will need to be applied before an age for the recharge of the groundwater can be calculated.

Such a model for ^{14}C has been apparently successfully applied in several limestone lithologies, but a clear understanding of bicarbonate genesis is a prerequisite. An example of a situation where ^{14}C dating was found to be highly problematic, due to the potential presence of recent marine aquifer carbonate (i.e. with non-negligible ^{14}C content) and other complicating factors, can be found in an article by Hilmo *et al.* (1992). In the case of Bath, UK (Edmunds and Miles, 1991), the anomalous $\delta^{13}C$ values led to great difficulties (Evans *et al.*, 1979) in developing a suitable model for ^{14}C, although a maximum age of 20 000 years for the thermal waters was inferred (Edmunds, 1986). The combination of evidence from ^{14}C, ^{13}C, ^{2}H and ^{18}O at Bath led Edmunds and Miles (1991) to constrain the probable age of the water to be between 4000 and 8000 years.

In some systems the addition of dead carbon from CO_2 and CH_4, together with the other complicating factors, often makes the interpretation of ^{14}C data in terms of water age difficult, not to say impossible. In these cases the simple model described above, without further correction for all these factors, gives a relative age that can at least help to define the flow direction (Mook, 1980).

3.8.4 Sulphur isotopes

Sulphur isotopes are usually measured on either the dissolved sulphate or sulphide systems of a groundwater. There are four stable isotopes of sulphur, as detailed in Table 3.6. The isotope which is typically measured as a 'variable' relative to ^{32}S is ^{34}S.

$$\delta^{34}S = \frac{(^{34}S/^{32}S)_{\text{sample}} - (^{34}S/^{32}S)_{\text{standard}}}{(^{34}S/^{32}S)_{\text{standard}}} \times 1000$$

The accepted standard is the ratio 1/22.22 of ^{34}S/^{32}S in the mineral troilite in the Cañon Diablo Meteorite (CDT). δ^{34}S in seawater is about +20‰, in evaporitic sulphates +4 to +36‰, while sedimentary sulphides typically yield more negative values between +10 and −50‰.

The isotopic composition of sulphur species in solution depends to a large extent on the source of sulphur: sulphate minerals (e.g. gypsum), sulphide minerals (e.g. pyrite), organic sulphur (coal or peat) or even marine or atmospheric sulphur. The various sources of sulphur typically have very characteristic isotopic signatures. These will also vary with age, depending on global sulphur fluxes at the time of deposition. From Figure 3.15 it can be seen that sulphate derived from dissolution of Ordovician evaporitic gypsum will be isotopically very different from that derived from Permian gypsum. For example, the measured δ^{34}S of +19‰ for the thermal waters of Bath, UK, indicates a Carboniferous source, rather than the alternative, stratigraphically plausible, Triassic source (Edmunds and Miles, 1991).

The main process which can affect sulphur isotope ratios in aqueous solutions is the sulphate–sulphide redox couple. The reaction rate of reduction of $^{32}SO_4^{2-}$ is faster than that of $^{34}SO_4^{2-}$, thus the product (sulphide) will be enriched in ^{32}S, while the reactant sulphate will become enriched in ^{34}S during the process. Oxidation of sulphide produces a similar effect, the product (sulphate) being enriched in ^{32}S. Obviously, fractionation will only be observed in waters if the reaction is incomplete or if some of the product (e.g. the early product) is removed from solution by precipitation. If the reaction goes to completion, fully in solution, all the reacting sulphur will end up in the product and the isotopic signature will be the same.

As an example of the complexity of sulphur isotope interpretation in a system where several potential sources of sulphur exist and where redox reactions are known to occur, one can take Leosson's (1993) study of the Harrogate mineral waters (UK). His primary (i.e. highly saline, sulphide rich) waters and secondary (less saline, sulphide free, mixed character) waters had δ^{34}S values, as shown in Table 3.7, compared with possible mineral sources of dissolved sulphur.

The data presented in Table 3.7 do not permit unequivocal interpretation. Leosson (1993) was of the opinion that the sulphate in the secondary waters was largely derived from relatively straightforward oxidation of disseminated sedimentary sulphides (and, to a lesser extent, due to their lesser volumetric significance, pyrite nodules) in the Carboniferous succession. Carboniferous sulphates were ruled out as a source due to their observed scarcity in the Harrogate area.

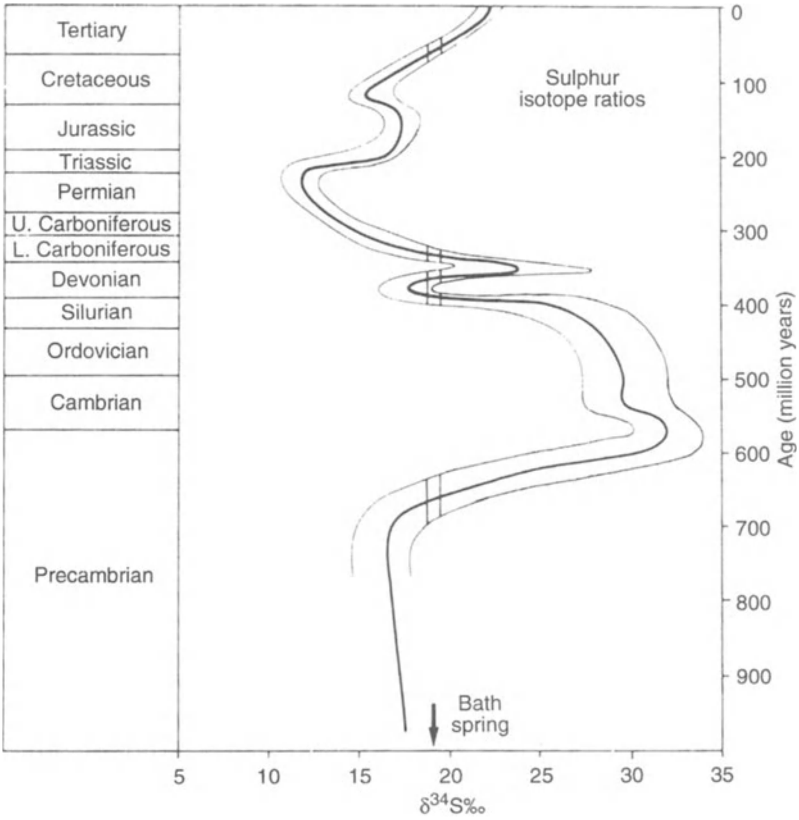

Figure 3.15 Sulphur isotope age curve for sulphate, showing the composition of King's Spring, Bath. (After Edmunds and Miles, 1991. Copyright Bath City Council, reproduced with permission.)

The (rather unaptly named) primary groundwaters were thought to have been derived by deep circulation of these sulphate-rich waters, followed by microbial reduction of sulphate to sulphide at depth, accounting for the H_2S concentrations in the primary waters. Leosson postulates that the first-formed, isotopically light sulphide is precipitated as FeS and removed from the system, resulting in overall enrichment of dissolved sulphide in ^{34}S. These isotopically heavy sulphide waters, of postulated composition +20 to +23‰, rise to the surface at Harrogate spa and significant reoxidation of sulphide to sulphate only takes near the surface and in the vicinity of wells.

3.8.5 Tritium and other dating techniques

Tritium is a radioactive isotope of hydrogen (^3H), measured in tritium units (TU), where $1\,TU = 1$ atom ^3H per 10^{18} atoms of ^1H. It occurs naturally in

Table 3.7 Sulphur isotope analyses for mineral waters at Harrogate, compared with values for various locally occurring lithologies (data from Leosson, 1993)

Sample	*$\delta^{34}S$ (sulphate) (‰)*	*$\delta^{32}S$ (sulphide) (‰)*
Primary mineral waters	+17.0 to +30	+19.7 to +25.5
Secondary mineral waters	−6.4 to +19.2	No sulphide
Disseminated sulphide, local Carboniferous mudstones	–	−36.8 to +6.9
Macrocrystalline pyrite nodules, local Carboniferous mudstones	–	+13.6 to +29
Carboniferous sedimentary sulphates/ connate Carboniferous seawater	Average +15.5	–

rainfall at levels of less than 20 TU. Between 1952 and 1963, atmospheric testing of fusion bombs (hydrogen bombs) produced large quantities of tritium such that rainfall often contained levels of over 1000 TU (Figure 3.16). Tritium in rainfall peaked in about 1963, after which atmospheric testing was forbidden by international treaty. Since then, tritium in rainfall has declined, although in many places modern rainfall still contains tritium at levels above natural background. Seasonal and latitudinal variations can be observed, and these are recorded in a network of stations worldwide.

As hydrogen does not exchange or undergo significant mineral reaction in the geological environment, high tritium levels have been particularly effective tracers of modern rainfall. In other words, groundwaters displaying

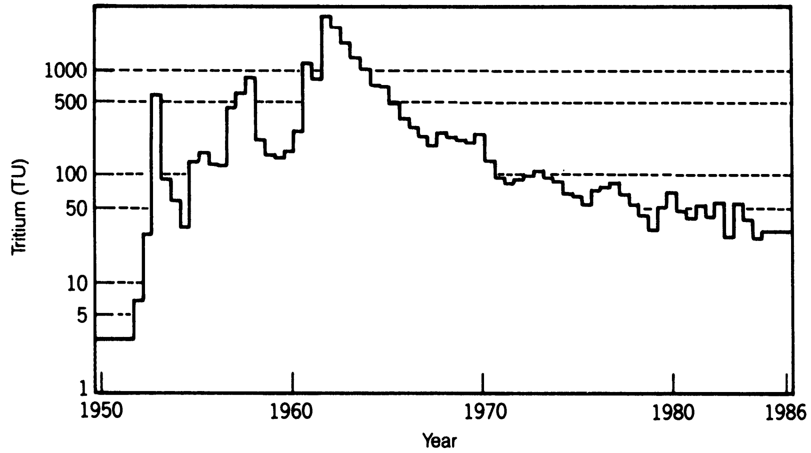

Figure 3.16 The content of tritium in precipitation (1950–1986) at Ottawa, Ontario, Canada. (After Domenico and Schwartz, 1990. Copyright American Geophysical Union.)

>1 TU (allowing for radioactive decay since 1952) can be said to have been recharged during the last four decades. As time goes on, the usefulness of tritium as a dating tool is declining, for two reasons:

- tritium in rainfall is again approaching natural background levels;
- the short half-life (12.3 years) of tritium means, as Domenico and Schwartz (1990) observe, that a 30 TU groundwater sampled in the 1980s could be interpreted as late 1950s recharge which has decayed through three half-lives or as 1970s recharge (originally 75 TU) which has decayed through one half-life.

Chlorinated fluorocarbons

It is possible that tritium's role may eventually be overtaken by chlorinated fluorocarbons (CFC). CFCs are stable and unreactive in the hydrogeological environment, but they are also anthropogenic. They have been used as solvents, cooling agents and aerosol agents during the last few decades and, despite recent bans on CFC products in some Western countries, their atmospheric concentrations show no sign of decline. Groundwater containing CFCs will not only be evidence of modern recharge, but comparison with the CFC content of rainfall may also allow dating to within a few years.

Other radioactive isotopes

Other isotopes used for groundwater dating include ^{36}Cl (half-life 301 000 years) and ^{39}Ar (269 years), described by Oeschger *et al.* (1974), Bentley *et al.* (1986) and Florkowski and Rózanski (1986).

4

Thermal water systems

> *While the red fires of smouldering clouds out-brake...*
> *The oped Earth, aghast*
> *With terror of that blast*
> *Shall from the surface to the centre shake.*
> Hymn – On the Morning of Christ's Nativity, Milton, 1645

4.1 HEAT PRODUCTION AND HEAT FLOW

The temperature of groundwater is influenced by air temperature to depths of about 50 m. Below this, additional heat is obtained from the rocks with which the water is in contact. The total amount of heat stored in the top 10 km of the earth's crust represents more than 5000 times the thermal energy available in world coal resources (Bouwer, 1978), but only a fraction of this is accessible.

The main source of heat is the earth's mantle, but heat from the decay of radioactive materials in the crust is also important (Table 4.1). Heat production due to radioactive decay may be estimated from concentrations of uranium (U), thorium (Th) and potassium (K) according to the empirical relationship:

$$A = 0.097[\mathrm{K}] + 0.261[\mathrm{U}] + 0.072[\mathrm{Th}]$$

(Birch, 1954), where A = heat production ($\mu\mathrm{W\,m^{-3}}$). Potassium is given as a percentage while U and Th are concentrations in ppm. This method was used by Vasseur *et al.* (1991) to evaluate heat production in fractured gneisses in the Massif Central of France, giving an average value of $2\,\mu\mathrm{W\,m^{-3}}$.

Rock and water temperatures increase gradually with depth in the earth's crust, by an average on land of about 3°C $(100\,\mathrm{m})^{-1}$. This temperature gradient, usually referred to as the geothermal gradient, results in the flow of heat from the earth's surface, averaging about $0.06\,\mathrm{W\,m^{-2}}$ (Table 4.2).

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Table 4.1 Production of heat from radioactive minerals in crustal rocks (from Sass, 1977)

	U (ppm)	*Th (ppm)*	*K (%)*	*Heat production (A) ($\mu W m^{-3}$)*
Silicic igneous rocks	4.0	16.0	3.3	2.5
Mafic igneous rocks	0.5	1.5	0.5	0.3
Shales	4.0	12.0	2.7	2.1
Carbonates	2.2	1.7	0.3	0.7
Beach sands	3.0	6.0	0.3	1.2

The heat flow is calculated as

$$q = \tilde{\kappa}\,\mathrm{grad}\,T$$

where q is the heat flow [$\mathrm{W\,m^{-2}}$], $\tilde{\kappa}$ is the thermal conductivity of rocks measured in the laboratory [$\mathrm{W\,(m\,K)^{-1}}$] and grad T is the temperature gradient [$\mathrm{K\,m^{-1}}$] measured in boreholes.

The highest heat flows are associated with seismically active belts (Figure 4.1), which include the oceanic rifts, the western coasts of North and South America, the main folded mountain chains of Alpine activity (Alps, Carpathians, Caucasians and Himalayas) and intercontinental rifts such as the Red Sea and East African rifts, where the earth's crust is relatively thin and where there is upwards convection in the mantle. Many of these belts mark the boundaries of crustal plates which move relative to each other (Figure 4.2), often giving rise to volcanism. Elsewhere a significant thermal potential may be found where the subcrustal or intracrustal heat flow is high, often in areas of crustal thinning, or where aquifers are deep enough for the water to be heated under a 'normal' geothermal gradient.

Table 4.2 Heat flow from various tectonic regions (from Sass, 1977)

Tectonic region	*Number of data*	*Mean heat flow (q) ($mW m^{-2}$)*	*Standard deviation*
All continents	597	61.0	19
Precambrian shields	214	41	10
Post-Precambrian non-orogenic areas	96	62	17
Palaeozoic orogenic areas	88	60	17
Mesozoic-Cenozoic orogenic areas	159	74	24
All oceans	2530	61.4	33
Ocean basins	683	53	22
Mid-oceanic ridges	1065	80	62
Ocean trenches	78	49	29
Continental margins	642	75	39
World	3127	61.4	31

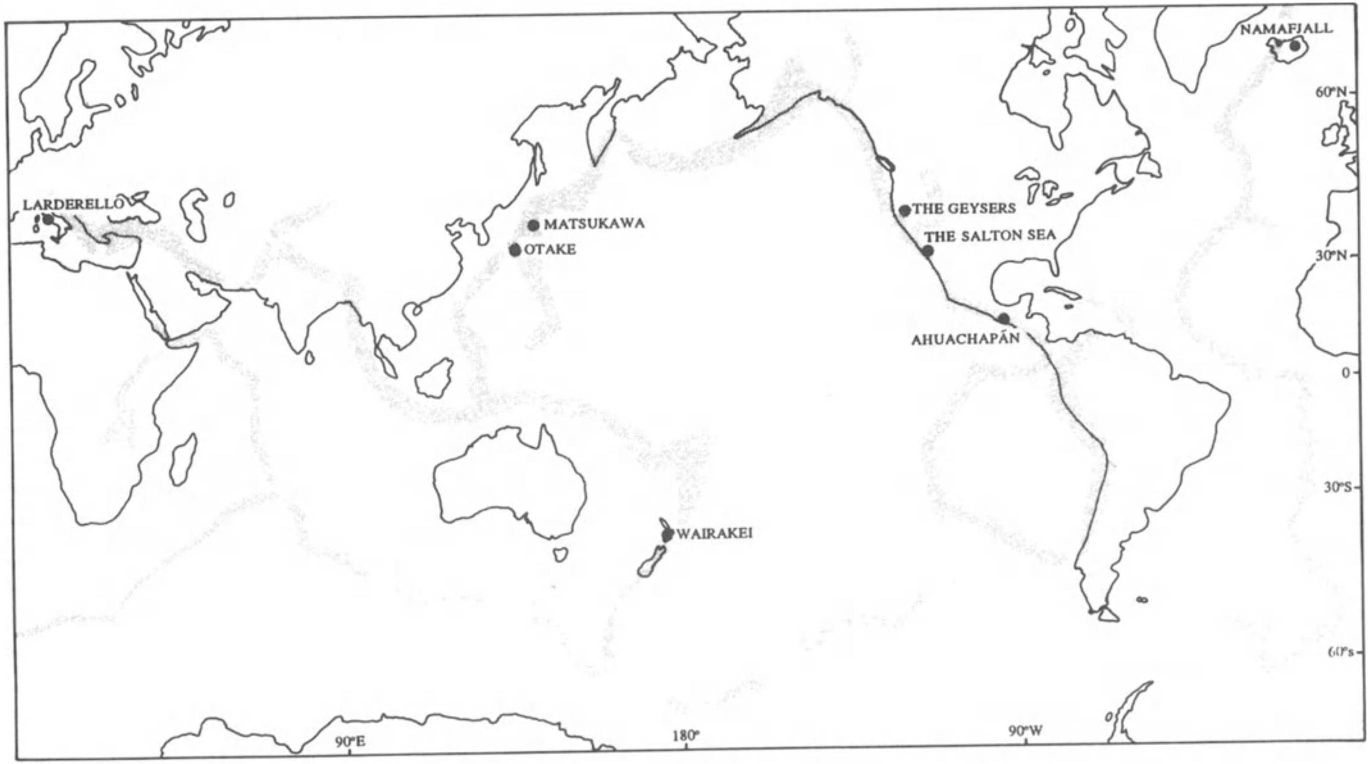

Figure 4.1 Map showing seismic zones of the Earth (modified from Baranzangi and Dorman, 1969; with permission from the Seismological Society of America) and some high temperature geothermal systems.

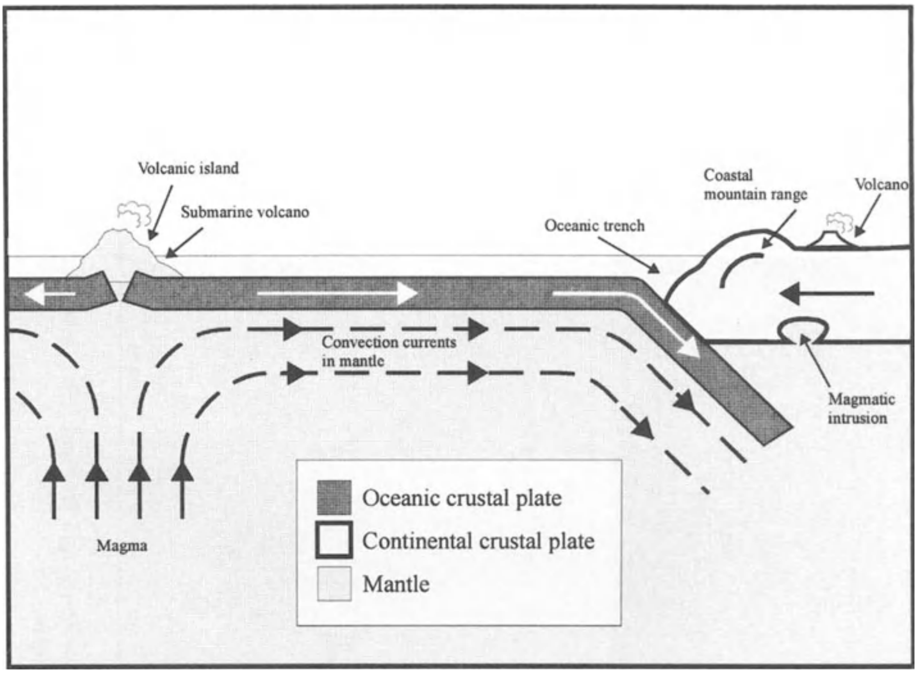

Figure 4.2 Schematic diagram of crustal movement, mantle convection and subduction. (From Armstead, 1983.)

4.2 HEAT TRANSPORT

Heat is transported in thermal water systems by conduction and convection. Conduction is the transfer of heat through a substance without any detectable motion of the substance taking place, while convection is the transfer of heat by the motion of fluids.

Heat transfer by conduction is the product of the thermal conductivity of the medium and the temperature gradient. Since fluids are generally poor conductors, conduction is often only significant in the rock matrix and is roughly approximated by the measured heat flow. However, the temperature gradient and hence the heat flow is affected by convection. Convection plays an important part in heat transport in aquifers of any extent (e.g. Bodri, 1995) and may be caused both by density variations due to temperature gradients (free convection) and by groundwater movement according to Darcy's law (forced convection or advection). A schematic diagram of conductive and convective heat transport is shown in Figure 4.3.

The conductive–convective equation for heat transport in homogeneous media is given by

$$\tilde{\rho}\tilde{c}\,\frac{\partial T}{\partial t} = \mathrm{div}(\tilde{\kappa}\,\mathrm{grad}\,T) - \rho c m \vec{u}\,\mathrm{grad}\,T \qquad (4.1)$$

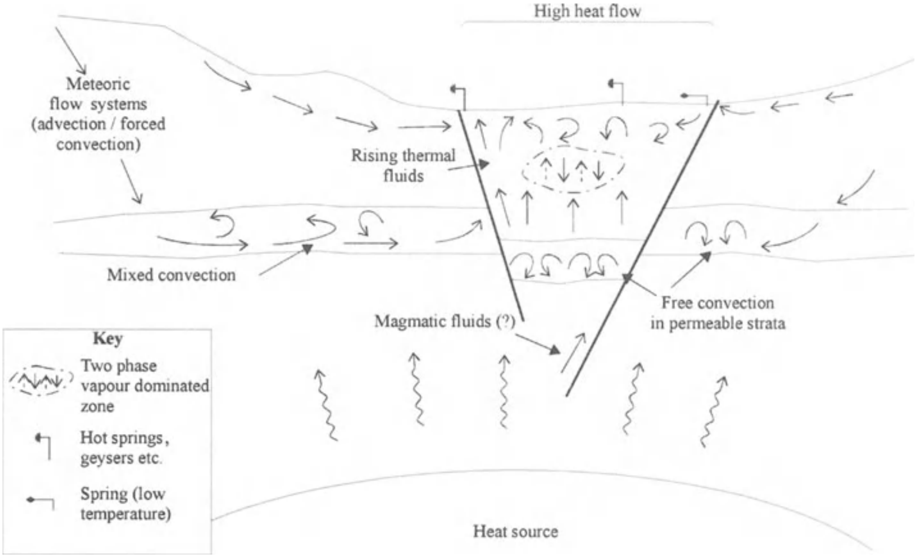

Figure 4.3 Schematic diagram showing heat transport. (From Domenico and Schwartz, 1990; based on Sharp and Kyle, 1988.)

where $\tilde{\rho}$ = density of water-bearing rock [kg m^{-3}], $\tilde{c}$ = specific heat of water-bearing rock [J(kg K)$^{-1}$], T = temperature [K], t = time [s], $\partial/\partial t$ = partial derivative in respect of time [s^{-1}], div = divergence operator [m^{-1}], $\tilde{\kappa}$ = thermal conductivity of water-bearing rock [W(m K)$^{-1}$], grad = vector gradient operator [m^{-1}], ρ = density of water [kg m^{-3}], c = specific heat of water [J(kg K)$^{-1}$], m = kinematic porosity [dimensionless] and $\vec{u}$ = effective velocity of water [m s^{-1}].

4.3 GEOTHERMAL SYSTEMS

4.3.1 Classification of systems

A general classification of geothermal systems (Albu, 1987), which includes thermal water systems, gives the following main divisions.

- According to the manner of heat transport, into conductive and convective systems.
- According to the mobility of the components, into systems with mobile components (water, gases and even magma), and those without mobile components (hot dry rock).
- According to the nature of the components, into hot dry rock systems, magmatic systems and thermal water systems.
- According to the state of the components into systems of solid components, systems of magmatic melts with and without gases and vapour,

high enthalpy systems (generally dominated by steam) and low enthalpy systems, with liquid water.
- According to the hydraulic closure of the components, into closed systems and open systems. In closed systems the thermal fluid is confined by strata of low permeability, recharge of water is slow and over long distances the discharge of water or steam is intermittent. In open systems the water flows from an area of recharge to one of discharge and is not confined by a low permeability layer.

Since hot dry rock (HDR) and magmatic systems are not water systems, and economic prototypes have yet to be developed to utilize their resources, they are mentioned only briefly here.

4.3.2 Hot dry rock systems

Hot dry rock systems are intended to exploit the heat contained in rock at significant depths. In effect this includes a large proportion of the earth's crust, and such systems may contain 100 to 1000 times the energy potential of thermal water systems (Bouwer, 1978), but the rocks have a low intrinsic permeability and do not contain water or other fluid to transport the heat to the surface. Utilization of the heat would rely on creating a reservoir at depth such that injected water could be heated and recovered. Research into heat recovery from hot dry rock systems has been carried out at Los Alamos (USA), Camborne (UK), Soultz-sous-Forêts (France and Germany), Le Mayet de Montagne (France), Falkenberg and Urach (Germany), Russkie-Komarovtsy (USSR), Fjällbacka (Sweden) and at Yakedake, Hijiori and Akinomiya (Japan). The technology required to create reservoirs by fracturing the rocks, and to circulate the water efficiently is still insufficiently developed for the heat to be extracted economically (Bernard and Evano, 1975; McFarland and Murphy, 1976; Nicholson *et al.*, 1984; Yamaguchi *et al.*, 1984; Downing and Gray, 1986; Downing and Wilkinson, 1991).

At Camborne, UK, a granite batholith has a surface heat flow of about $120\,\mathrm{mW\,m^{-2}}$, double that of the surrounding rocks, and the highest temperature gradients in the UK, of $3.5°\mathrm{C}\,(100\,\mathrm{m})^{-1}$. Commercial exploitation would require creation of a reservoir at 6 km depth, where rock temperatures are expected to be more than 200°C. A pilot project to create a test reservoir at a depth of 2 km failed, partly because of the poor recovery of the injected water. Here, as at other sites of HDR research, it is not considered feasible to extrapolate the results to design a much deeper reservoir (Parker, 1990).

4.3.3 Magmatic systems

Magmatic systems occur as plutonic or volcanic systems. Plutonic systems are associated with the initial or terminal stages of magmatism, where

Table 4.3 Composition of gas from Ushu volcano, Japan (from Carmichael *et al.*, 1974)

Fumarole	*T* *(°C)*	CO_2	CH_4	NH_3	H_2	*HCl* *(ppm)*	*HF*	H_2S	SO_2	P_4O_{10}	*Total active gases (%)*	H_2O *(%)*
A-1 (9081)	750	4700	5.8	4.3	1808	389	199	7.2	120	0.0016	0.723	99.25
C-4	430	3230	6.2	–	1400	669	230	45	89	0.0053	0.567	99.41
C-3	194	1970	4.1	0.26	351	120	11	110	13	–	0.258	99.72

magma is maintained in the molten state, without emissions of gas and vapour. To extract heat from a magmatic melt, boreholes would have to be drilled using specialized drilling and cooling equipment into hot rock near the surface of the magma. Water would be pumped down tubing inside the borehole casing and the heated water would return to the surface between the tubing and casing (Carson and Allen, 1984).

Volcanic systems are associated with eruptive phases of magmatism, where molten matter erupts at the earth's surface as lavas, releasing gases. Water vapour, usually of meteoric origin, is also given off, in fumaroles (temperatures >200°C), solfataras (temperatures of 40–200°C) or mofettes (temperatures <40°C). The gas and vapour emissions are normally considered as part of the water systems, while the magmatic system is the lava body itself.

Water vapour is the dominant component of volcanic gases, usually accounting for over 99% of the volume, but a proportion of this will be meteoric in origin. Of the subsidiary components CO_2 usually predominates, with accessory CH_4, SO_2, H_2S, HCl, HF, H_2, NH_3 and compounds of B, P and S. Some systematic variations with temperature can be identified, the ratio HF/HCl falling with decreasing temperature. At low temperatures H_2S may predominate over SO_2. The presence of O_2 and N_2 in volcanic gases is usually assumed to be indicative of atmospheric contamination (Carmichael *et al.*, 1974). The composition of gas from one volcano is shown in Table 4.3.

4.4 THERMAL WATER SYSTEMS

The commercial use of thermal waters is directly related to their quantity of usable heat. Systems are often classified as being of high or low enthalpy according to their temperature and potential use. Enthalpy is defined as the heat content of a substance:

$$H = \varepsilon + pV$$

where H = enthalpy [J], ε = internal energy [J], p = pressure [$\mathrm{N\,m^{-2}}$] and V = volume [$\mathrm{m^3}$].

High enthalpy systems are those with fluids at temperatures high enough to be utilized for electric power generation: currently this implies temperatures of over about 150°C. Lower temperature fluids cannot generally compete with other sources of power but they are of value in more direct use, for example for space heating (Chapter 2).

4.4.1 High enthalpy systems

High enthalpy (i.e. high temperature) systems may produce saturated steam (steam with water), dry steam or superheated steam. The dominant phase in any system depends on the temperature and pressure. The state of water for different temperatures and pressures is shown in Figure 4.4.

Such vapour-dominated systems often contain hot liquid at depth, where pressures are greatest, and steam at shallower depths. The hot liquid is generally accepted to be a boiling brine from which steam moves upwards along fractures. Condensation may take place at the top of the reservoir and also laterally, the condensate flowing back down by gravity to replenish the brine (e.g. Ellis and Mahon, 1977). As wells are constructed, pressures drop and the steam produced becomes increasingly dry and then superheated,

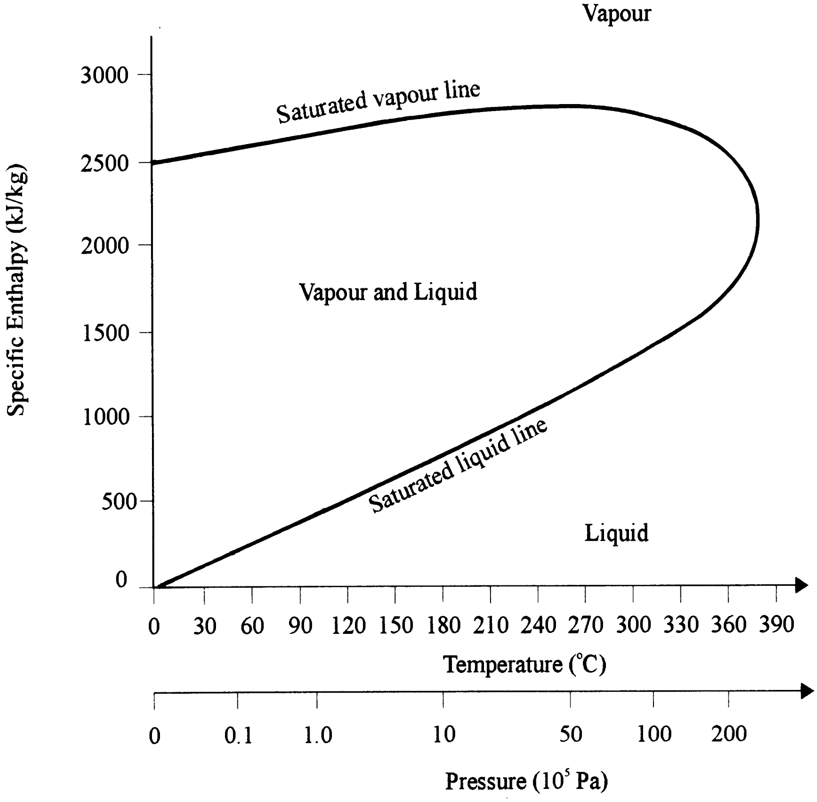

Figure 4.4 State of water for different pressures and temperatures.

especially where the porosity is low. One explanation for superheating is that as fluid is removed, the water–steam boundary is lowered, leaving a large volume of effectively dry rock that retains its heat at a higher temperature than the steam formed by boiling at depth. This heat is released to the dry steam as it travels towards and up the well, causing superheating (Ellis and Mahon, 1977; Armstead, 1983).

The aquifers are generally confined by overlying rocks of low permeability so that steam will normally only reach the surface through fractures or boreholes. Under natural conditions, undisturbed by boreholes, it appears that discharge from many systems associated with recent volcanism would be intermittent: as flow to the surface takes place, the pressure in the reservoir is lowered and deposition of silica and calcite blocks the pathways. A long period of no discharge follows until tectonic activity or movement due to high pressures cause new pathways to the surface to be opened (Ellis and Mahon, 1977). Such discharge takes place from geysers, where water boils near the surface (Figure 4.5), hot springs and fumaroles, for example.

A few features of some of these systems are given to illustrate their diversity. Systems producing dry and sometimes superheated steam, together with other gases such as CO_2, are found in the USA at The Geysers (California), Mount Lassen (California) and Valdes Caldera (New Mexico), in Italy at Larderello and Monte Amiata, and in Japan at Matsukawa and in other places.

The Geysers are located to the north of San Francisco in fractured greywackes of Jurassic to Cretaceous age, with a temperature of 240°C at a depth of only 1500 m (McLaughlin and Donnelly-Nolan, 1981; Grew, 1984). The steam at the wellhead is superheated by about 12°C (Armstead, 1983). The region is part of the Clear Lake volcanic zone, where a body of siliceous magma at about 7 km depth provides the heat source for a geothermal field covering an area of about 36 km^2.

Mount Lassen is a National Park with volcanic manifestations in the Cascade Province of California, and includes a system of dry steam at a temperature of 240°C which is situated above an intrusion of dacite (Grew, 1984).

At Larderello, dry and superheated (by 70°C; Armstead, 1983) steam are released to wells from fractured limestones, dolomites, evaporites, and quartzites of Jurassic to Triassic age. Overlying shales and clays provide a confining 'cap' with natural discharge comprising fumaroles and hot springs where the cap is thin. The average temperature of the system is 220°C, with an average well depth of 600 m (Bouwer, 1978).

The system at Matsukawa is in fractured Miocene sandstones and Pleistocene andesites (Kappelmeyer, 1979). It produces steam with a temperature of 220°C from an average well depth of 1000 m (Bouwer, 1978). As with some other systems, saturated steam (with up to 25% water) was produced at first but later discharges became dry (Ellis and Mahon, 1977).

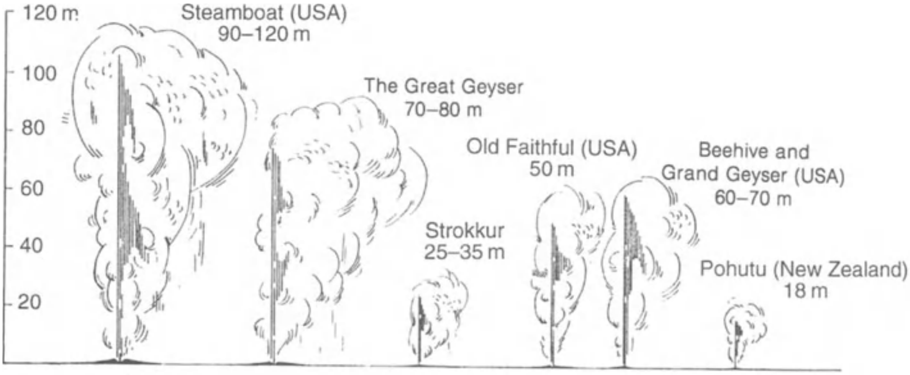

Figure 4.5 (a) Spouting heights of geysers around the world (from Torfason, 1985); (b) a geyser from Iceland (photographs by Benedikt Steingrímsson).

Systems producing saturated steam occur in the USA at Mono-Long Valley, Coso Hot Springs and Imperial Valley (California) as well as at Yellowstone (Wyoming); in Mexico at Cerro Prieto, in El Salvador at Ahuachapán; in New Zealand at Wairakei and Broadlands; in Japan at Otake; in Iceland at Namafjall (Chapter 9) and in many other places. These systems are dominated (flashes) to steam when brought to the surface, if the temperature is over about 200°C.

The Mono-Long Valley is situated east of the Sierra Nevada and includes a system of saturated steam where the temperature is probably between 210 and 280°C. The steam is found in the Bishop Tuff Formation, associated with rhyolites which erupted 700 000 years ago (Hermance, 1983). South-southeast of Mono-Long Valley, also east of the Sierra Nevada, is the geothermal zone of Coso Hot Springs. This occurs in an oval structure, probably a caldera, with numerous adjacent rhyolitic bodies, including a system of saturated steam at a temperature of 205–240°C in altered and fractured granites and metamorphic rocks (Moore and Austin, 1983).

Imperial Valley is at the southern extremity of the state of California. Here geothermal zones with systems of saturated steam at temperatures between 120 and 360°C (Rintoul, 1983; Grew, 1984) are associated with basic intrusive rocks overlain by metamorphosed sedimentary rocks (Fuis *et al.*, 1981; Johnson *et al.*, 1982). The most northerly of these is located at the Salton Sea where the temperature reaches 365°C at a depth of 2000 m. The geothermal zone of Cerro Prieto is considered to be a southwards extension of the Imperial Valley region, and its system of saturated steam is developed in an argillaceous deltaic sandstone at 650–900 m depth, overlain by thick clays. It has a basement of fractured granite at a depth of about 2500 m, which provides the heat source (Gupta, 1980; Grew, 1984; Read, 1984). The temperature reaches 375°C in a central upflow zone, reducing as the hot water flows laterally in the sandstone. This results in a temperature inversion at the edges of the system, a frequent phenomenon in high temperature fields (see Figure 4.6 for an example).

The Ahuachapán geothermal field is associated with Quaternary volcanic activity. The reservoir is in fractured andesites of Pliocene to Pleistocene age, containing saline water with temperatures of about 230°C. Although the andesites are up to 300 m thick, the permeable zones are usually found near the top of the formation (Cuéllar *et al.*, 1981). The caprock comprises some 400 m of well cemented volcanic agglomerate.

At Wairakei, in the Taupo volcanic zone of North Island, New Zealand, pumice and tuff breccias contain saturated steam with a temperature of 260°C (Kappelmeyer, 1979). At Broadlands, also in New Zealand, there is a system of saturated steam in a pumice breccia, with a temperature of 271°C (Macdonald, 1976). A conceptual model of the Wairakei system, based on information from boreholes, indicates that hot water rises in a narrow plume from considerable depths and then spreads laterally in the main aquifer (Figure 4.6).

The main reservoir at Otake consists of tuff breccias and overlying fractured andesites of Pleistocene age, at depths of 200–400 m. The andesites also form the caprock (Ellis and Mahon, 1977). The northwest-trending faulting gives rise to several hot springs and fumaroles and temperatures in

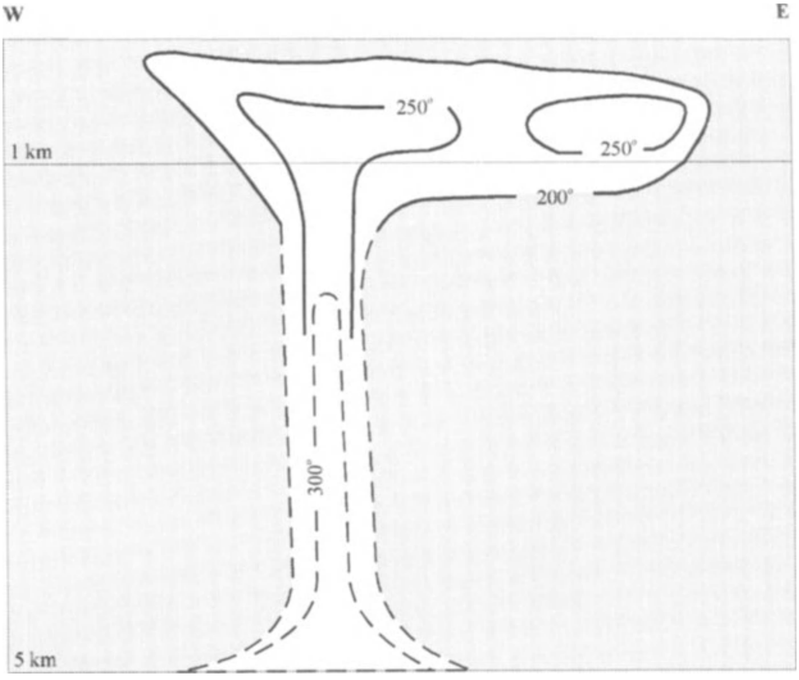

Figure 4.6 Mushroom-shaped heat distribution in the Wairakei system. (From Ellis and Mahon, 1977; after Elder, 1965.)

wells range from 215 to 250°C in the north of the area, increasing to 290°C in the south, over a distance of about 4 km.

4.4.2 Low enthalpy systems

Low enthalpy systems are widespread compared to those of high enthalpy because their occurrence only requires the presence of aquifers at a great enough depth, or at a small enough distance from a source of geothermal energy, to be heated by the local heat flux. Such systems have been identified in many countries including Algeria, Austria, Chile, Colombia, Costa Rica, the Czech Republic, Djibouti, Ecuador, El Salvador, Ethiopia, France, Germany, Greece, Guadeloupe, Guatemala, Honduras, Hungary, India, Indonesia, Iran, Israel, Italy, Japan, Kenya, Mexico, Montserrat, Netherlands, New Zealand, Nicaragua, Panama, Philippines, Poland, Portugal, Romania, Russia, Slovakia, Spain, Switzerland, Taiwan, Thailand, Turkey, The United Kingdom, the USA and former Yugoslavia (e.g. Kruger and Otte, 1973; Suter, 1980; Armstead, 1983).

The Commission of the European Communities (Haenel and Staroste, 1988) has published an atlas of the geothermal resources of many West

European countries. The atlas gives a summary of the occurrence of thermal water systems, most of them of low enthalpy but also including the high enthalpy systems of Italy. Geological maps and sections are given, together with temperature and salinity contours and maps of estimated resources (Chapter 5).

From a hydrodynamic point of view, low enthalpy systems can be closed or open. Closed systems are effectively isolated from present day recharge and discharge, while open systems are part of active flow regimes. As a rule, closed systems have hydrostatic pressures much greater than that corresponding to their depth, while open systems have hydrostatic pressures corresponding to their depth.

Closed systems include geopressured systems which are found in deep sedimentary basins. These are caused by differential subsidence of alternating sand and clay strata such that some compartments become closed. The water becomes locked in, and as the compartments sink and become more deeply buried, temperatures rise and very high pressures result, tending to approach lithostatic pressure. Known pressurized systems are often associated with oil fields and have been recognized in the USA as well as in Hungary and Romania. In the USA they are located in the sedimentary formations north of the Gulf of Mexico, especially in the states of Louisiana and Texas where, at a depth of about 3000 m, the liquid has a temperature of 150–180°C and contains significant quantities of dissolved combustible gases (Armstead, 1983; Kappelmeyer, 1979). In Hungary and Romania, geopressured systems are found in post-Miocene sedimentary formations of the Pannonian Basin, where the temperature reaches 117–135°C at depths of 1700–2500 m (Horvàth *et al.*, 1979; Albu, 1987). The water in these systems is generally highly mineralized.

Many low enthalpy thermal water systems are hydrodynamically open and relatively accessible. Examples are found (Burgess *et al.*, 1980; Andrews *et al.*, 1982; Albu, 1987; Downing and Wilkinson, 1991; Downing *et al.*, 1991):

- at Sofia in Bulgaria, in Neogene sands and sandstones;
- in France near Paris, in the Dogger Formation;
- in Greece, at Eleochoria, in Mesozoic limestones and at Sousaki–Athens in Mesozoic limestones and Neogene conglomerates;
- in Romania, at Oradea, in Triassic limestones and dolomites, near Bucharest in Jurassic limestones and dolomites, and in western Banat in Neogene sands;
- in the United Kingdom at Southampton in Permo-Triassic sandstones and at Bath, Bristol, Taff's Well and in Derbyshire, all in Carboniferous formations.

France is probably the furthest advanced country in Western Europe in utilizing its low temperature geothermal resources. The most important system in France is the Middle Jurassic Dogger Limestone (Figure 4.7).

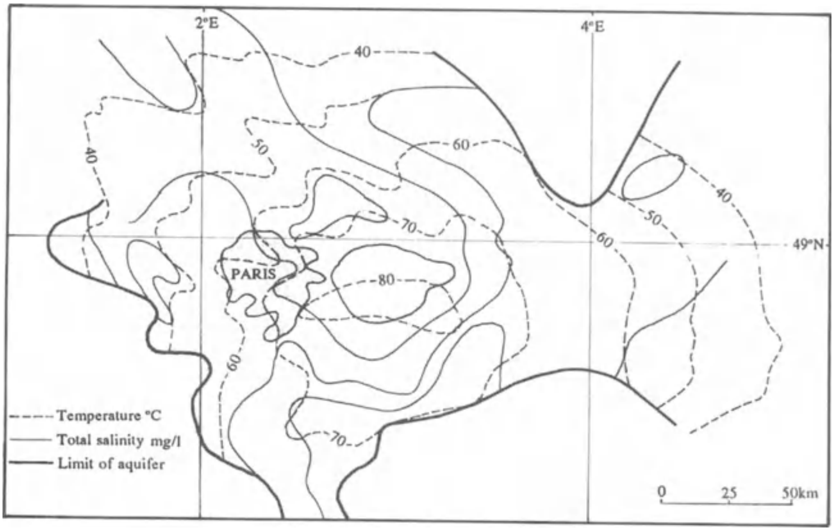

Figure 4.7 Temperature and salinity contours for the Middle Jurassic Dogger Limestone, Paris Basin, France. (From Haenel and Staroste, 1988. Copyright ESC, EEC, EAEC.)

Up to 300 $m^3 h^{-1}$ of water at more than 80°C can be obtained from the centre of the basin, which is close to Paris. The water is saline, with a total salinity of more than 30 g/l in the centre of the basin, necessitating reinjection of the water after use.

Many such sedimentary basins contain warm water at depth because of an average, or slightly above average, geothermal gradient. In the western Canadian sedimentary basin, for example, the gradient is around 2.5°C $(100\,m)^{-1}$, but this is sufficient to give temperatures of 100°C at a depth of 3.5 km (Jones and Majorowicz, 1987). In this case, the areal distribution of heat flow has been clearly demonstrated to be due to regional groundwater movement from recharge zones, with low heat flow, to discharge zones with a high heat flow. In recharge areas the geothermal gradient in the region of downwards vertical flow is reduced by the influx of cool water, while in discharge areas it is increased.

Many thermal waters are found where high relief exerts a driving head such that recharge water circulates to a depth where elevated temperatures are encountered, because of normal geothermal gradients. Where faults enable the water to rise quickly to the surface, warm springs may be encountered. This situation is shown schematically in Figure 4.8.

In the Gulf of Suez it has been estimated that the circulation of water giving rise to thermal and mineral springs could reach depths of 5 km (Shata, 1990). A similar depth of circulation of spring waters, based on temperatures of about 200°C estimated from geothermometers and the

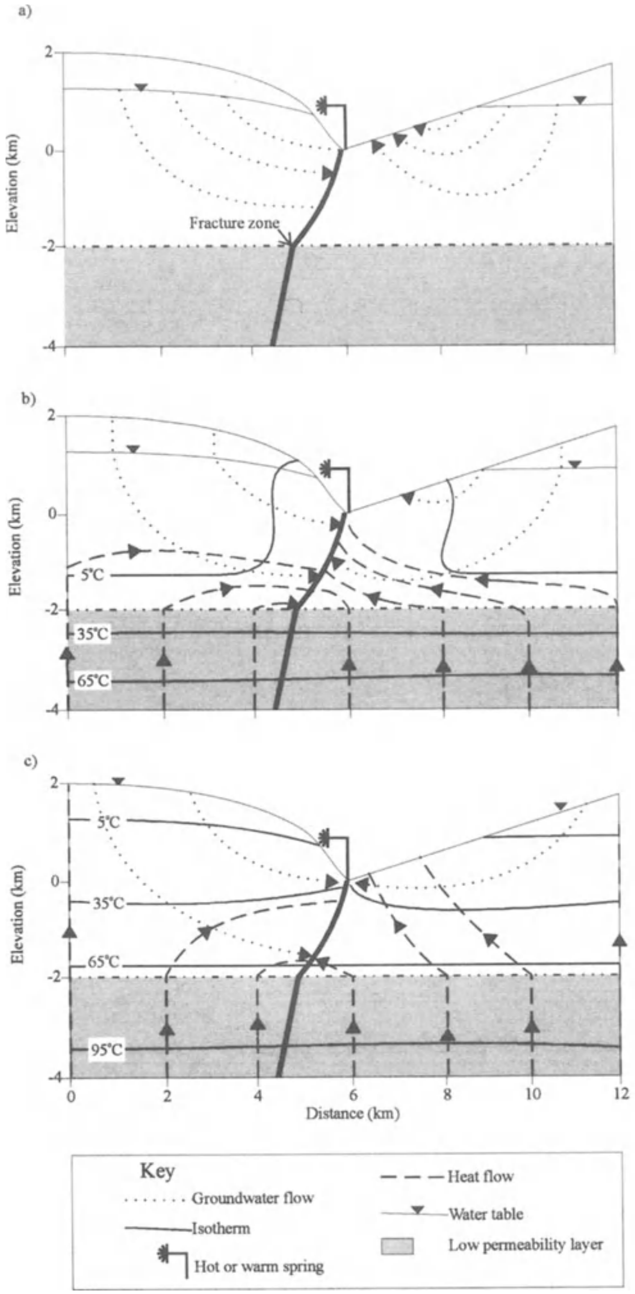

Figure 4.8 Schematic diagram showing the influence of a steeply dipping fault zone on the occurrence of (a) groundwater flow patterns, (b) thermal regime calculated when the bulk permeability is 10^{-15} m^2 and (c) thermal regime for a bulk permeability of 10^{-6} m^2. (Based on Forster and Smith, 1989. Copyright American Geophysical Union.)

Table 4.4 A selection of chemical analyses of thermal waters in the USA (from Hem, 1985)

Constituent (mg/l)	*1* *Clifton Hot Springs, Arizona*	*2* *Spring NW1/4 Custer Co., Idaho*	*3* *Lemonade Spring, Sulfur Springs, New Mexico*	*4* *Brine well 3 Munroe, Midland, Michigan*	*5* *Spring in Upper Geyser Basin, Yellowstone National Park, Wyoming*	*6* *Nevada Thermal Well 4, Steamboat Springs, Nevada*
Temperature (°C)	43.4	57.2	65.6	46.1	94	186
SiO_2	58	75	213	130	363	314
Al	–	–	56	–	0.2	0.22
Fe	0.19	0.05	33	41	0.06	0.52
Mn	0.08	–	3.3	–	0	0
Ca	860	1.3	185	93 500	0.8	3.6
Mg	41	0.3	52	12 100	0	0
Na	2670	72	6.7	28 100	352	660
K	142	2.4	24	11 700	24	65
HCO_3	109	20	0	0	≈0	312
CO_3	–	38	0	–	≈0	–
SO_4	153	32	1570	17	23	108
Cl	5800	6.5	3.5	255 000	405	874
F	3	16	1.1	–	25	2.6
NO_3	7.5	0	0	–	1.8	2.7
Sr	–	–	–	3 480	–	0.67
Br	–	–	–	3 720	1.5	–
I	–	–	–	48	0.3	–
B	–	–	–	–	4.4	48
Li	–	–	–	–	5.2	7
As	–	–	–	–	–	4
TDS	9750	254	2213	408 000	1310	2240
pH (in pH units)	–	9.4	1.9	–	9.6	8.9
Date	Jan. 1944	Sep. 1954	Aug. 1949	Mar. 1952	Oct. 1957	Sep. 1960

Rock types: 2, quartz monzonite; 3, volcanics; 4, sandstone.

Table 4.5 Composition of steam from fumaroles and wells (from Ellis and Mahon, 1977)

Source	*Source depth (m)*	*Temp. (°C)*	*Pressure for composition (bar abs.)*	*Steam fraction in discharge at pressure*	*Total gas in steam (mol%)*	*Gas composition (mol%)*							
						CO_2	H_2S	$\overline{HC}$[a]	H_2	$N_2 + Ar$	O_2	NH_3	H_3BO_3
Italy													
Fumaroles, Larderello	0	100	1	1.00	3	92.3	2.06	1.4	2.6	1.07	0.05	–	0.5
Average well, Larderello	500	200	1	1.00	2.0	94.1	1.6	1.2	2.3	0.8	–	0.8	0.33
USA													
Average well, The Geysers	200–2000	230	1	1.00	0.59	55	4.8	9.5	15	3.0	–	12.5	0.25
Wells, Salton Sea	1500–1800	300–350	16	0.18	0.1–1.0	90		— Remainder mainly H_2S + minor $\overline{HC}$ and H_2 —					
New Zealand													
Karapiti fumarole, Wairakei	0	115	1	1.00	0.17	94.6	2.3	0.74	1.0	1.1	–	0.26	–
Average well, Wairakei	650	260	1	0.32	0.063	91.7	4.4	0.9	0.8	1.5	–	0.6	0.05
Well 11, Broadlands	760	260	1	0.355	0.61	94.8	2.1	1.2	0.2	1.5	–	0.2	–
Well 1, Ngawha	585	228	1	0.33	20	93.9	0.7	4.1	0.5	0.8	–	0.04	–
Chile													
Well 5, Mexicali	1285	340	1	0.44	0.54	81.4	3.6	7.0	0.5	7.0	0.4	–	–
Fumarole, El Tatio	0	86.6	0.6	1.00	0.10	75	0.6	0.1	0.0	19.4	4.9	–	–
Well 2, El Tatio	650	220	0.9	0.24	0.11	99	0.7	0.01	0.03	0.2	–	–	–
El Salvador													
Well 1, Ahuachapan	1195	230	1	0.23	0.007	50–80	4	–	10–40	2–10	–	–	–
Japan													
Well 7, Otake	350	230	3.0	0.215	0.10	96.7	0.65	——— Remainder 2.7% ———					

[a] Total hydrocarbon gases.

geothermal gradient, is likely in the Cézallier region of France (Turpaul *et al.*, 1987), an area of important volcanic activity in the Miocene–Pliocene. The thermally induced differences in fluid density produce a buoyancy-driven component of fluid flow that enhances the vertical movement of water. Reduced fluid viscosity in the higher temperature regions also contributes to an increased fluid flux (Smith and Forster, 1990).

4.5 ORIGINS AND CHEMISTRY OF THERMAL WATERS

The water in thermal water systems has been shown, largely by isotope analyses of ^{18}O and ^{2}H (e.g. Truesdell and Hulston, 1980; Crăciun *et al.*, 1989; Figure 3.13), to be meteoric in origin in most instances. This does not mean that the waters are always derived from modern recharge, as circulation times can be in the order of hundreds or even thousands of years.

Since the dissolution of many minerals is accelerated at higher temperatures, thermal waters can be highly mineralized and may sometimes be considered as a subset of mineral waters. The evolution of the chemistry of such waters is described in some detail in Chapter 3: differences in temperature, contact times with different rock types and mixing with non-thermal waters give rise to a wide variety of thermal water types of which a few examples are given in Table 4.4. The more mineralized waters often have a high silica content and relatively high levels of minor constituents such as boron, lithium, rubidium and caesium (Ellis and Mahon, 1977).

Hot or warm groundwater may contain significant amounts of dissolved gases. H_2S and CO_2 are more soluble in water than the other gases and may be found in many groundwater systems. Much of the H_2S in mineral waters may originate from dissolved sulphate or the decomposition of organic matter (Chapter 3), but degassing of magma or the Earth's mantle is important in some high temperature thermal systems such as The Geysers. The presence of large quantities of CO_2 is generally linked with thermal activity, the main source being thermal alteration of carbonate rocks, with degassing of the mantle as a possible minor contributor (e.g. Greber, 1994; Chiodini *et al.*, 1995). In addition to these, NH_3, H_2, N_2, O_2 and CH_4 are often found in high temperature waters (Table 4.5).

5

Investigation of mineral and thermal water systems

> *It is a great mistake to theorise before one has data. Insensibly one begins to twist facts to suit theories, instead of theories to suit facts.*
>
> Sir Arthur Conan Doyle. A Scandal in Bohemia

The evaluation of mineral and thermal water systems embraces many activities, including exploration and investigation, determining whether a resource can be economically developed and monitoring both the system and its economic viability. It is emphasized that cost effective evaluation, in all its stages, must be carried out within the framework of a conceptual model of the system, which is improved as more information is collected. The activities involved often overlap in an iterative process and can rarely be separated in practice, although for reasons of length modelling of systems and exploitation of resources are discussed in Chapters 6 and 7.

5.1 STAGES OF INVESTIGATION

The investigation of mineral and thermal water systems takes place in progressive stages which frequently overlap. In order these are incipient and advanced basic research, preliminary and detailed prospecting, preliminary and detailed exploration, and experimental and industrial development (Table 5.1). Each stage of investigation involves a number of operations to obtain, process and interpret field and laboratory data, with a precision corresponding to the degree of knowledge achieved. Because of the expense of certain investigation methods such as geophysical surveys and drilling of deep basins, it is always recommended that investigations should proceed step by step.

Mineral and Thermal Groundwater Resources
M. Albu, D. Banks and H. Nash.
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Table 5.1 Stages of investigation

<table>
<tr><th colspan="2">*Stage of investigation*</th><th>*Degree of knowledge*</th><th>*Degree of assurance*</th><th colspan="5">*Resources*</th></tr>
<tr><td rowspan="2">Basic research</td><td>Incipient</td><td>0–0.0625</td><td>$0–10^{-7}$</td><td colspan="5">*Not evaluated*</td></tr>
<tr><td>Advanced</td><td>0.0625–0.25</td><td>$10^{-7}–1.8 \times 10^{-2}$</td><td>$P_3$</td><td colspan="3" rowspan="3">Forecast</td><td rowspan="3">Unidentified</td></tr>
<tr><td rowspan="2">Prospection</td><td>Preliminary</td><td>0.25–0.05</td><td>0.018–0.135</td><td>P_2</td></tr>
<tr><td>Detailed</td><td>0.5–1</td><td>0.135–0.368</td><td>P_1</td></tr>
<tr><td rowspan="2">Exploration</td><td>Preliminary</td><td>1–2</td><td>0.368–0.607</td><td>C_2</td><td>Possible</td><td colspan="2">Inferred</td><td rowspan="4">Identified</td></tr>
<tr><td>Detailed</td><td>2–4</td><td>0.607–0.779</td><td>C_1</td><td>Probable</td><td>Indicated</td><td rowspan="3">Demonstrated</td></tr>
<tr><td rowspan="2">Development</td><td>Experimental</td><td>4–16</td><td>0.779–0.939</td><td>B</td><td>Roughly proven</td><td rowspan="2">Measured</td></tr>
<tr><td>Industrial</td><td>>16</td><td>0.939–1</td><td>A</td><td>Accurately proven</td></tr>
</table>

The accuracy with which mineral and thermal water systems are defined and resources determined may be described by means of a degree of assurance $\hat{A}$ which has a value between 0 and 1. $\hat{A}$ depends on the degree of knowledge $\hat{K}$ according to the function $\hat{A} = \exp(-\hat{K}^{-1})$, so that as $\hat{A}$ tends to 0, $\hat{K}$ tends to 0, while as $\hat{A}$ tends to 1 so $\hat{K}$ tends to infinity (Albu, 1984). The stages of investigation and the classification of mineral and thermal water systems and resources depending on the degree of assurance achieved in these stages are presented in Table 5.1.

5.2 THE RESOURCE BASE

This categorization of resources may appear academic; however, the system of lettering (A, B, C and P) is used by the USGS (White and Williams, 1975) to present a general picture of the state of knowledge of resources. This is used to estimate the resources which may become available in the future and the scale and costs of investigation required to reach the development stage. In theory this classification system can be used to compare the state of knowledge of resources between different countries, but not all countries use exactly the same system (e.g. Chapter 11).

Depending on the technical, technological, economic and social conditions of development and of use, the identified resources (A, B, C_1 and C_2) are classified as subeconomic and economic resources. The label 'subeconomic' means that current market conditions do not make it worthwhile to exploit the resource. The term 'reserves' is normally restricted to identified economic resources, that is resources which are recoverable at competitive costs (McKelvey, 1972; Muffler and Cataldi, 1978; Albu, 1987; MCOuat, 1993).

McKelvey developed a diagram to show the state of knowledge of mineral resources, depending both on the state of knowledge and on the economic feasibility of utilizing them. The diagram is often used in relation to geothermal resources, as in Figure 5.1, which defines the terms 'resource' and 'reserve' more clearly than many of the available texts. Some methods for estimating resources of mineral waters and energy from thermal waters are given below in sections 5.4 and 5.5.

5.3 EXPLORATION

5.3.1 Tools for investigation

The presence of mineral and thermal groundwaters may often be known initially from surface expressions such as springs. However, many important resources, such as the thermal waters of the Pannonian and Baltic basins, do not show at the surface but were located during drilling, often for oil rather than for water. Once a resource is located, investigations are, or should be, carried out to define the configuration of aquifers and especially their

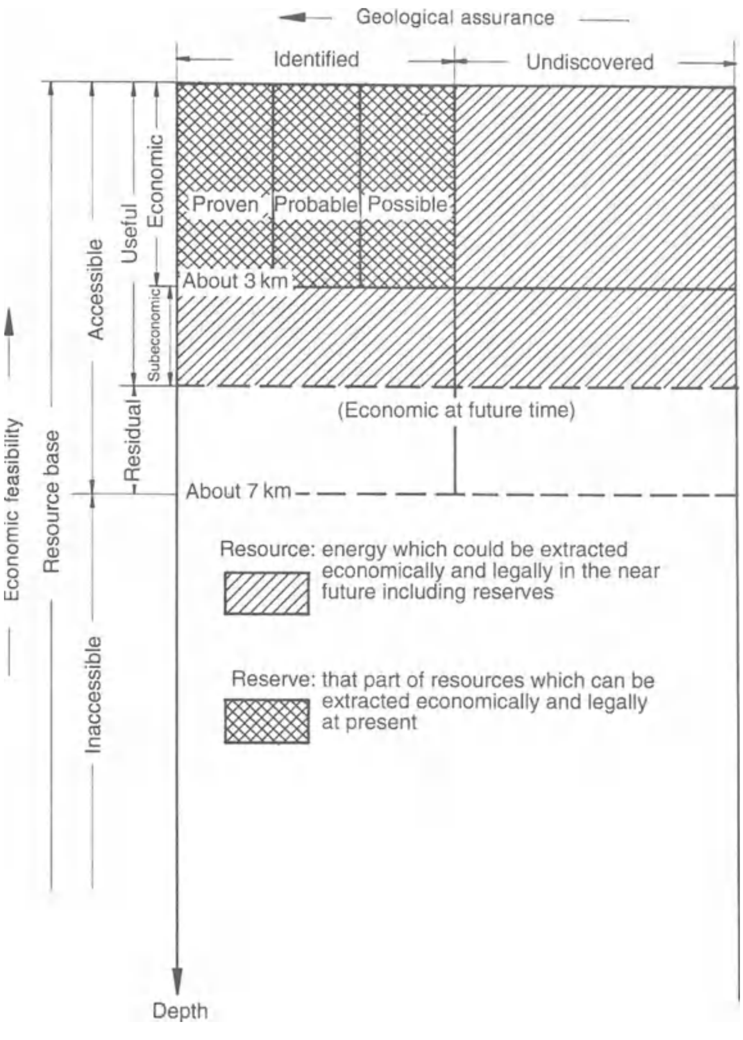


Figure 5.1 The McKelvey diagram.

boundaries, the quality of the resources, the conditions under which they occur and the technical and economic feasibility of exploiting them.

Hydrogeological investigations are carried out in much the same way as for non-mineralized and non-thermal waters and have been described in many texts, such as Driscoll (1986). Additionally, techniques used more commonly in oil exploration, such as seismic surveys, are important in defining deep structures of interest both for the geothermal potential and the production of carbon dioxide. A few other tools used specifically for the evaluation of thermal and mineral water resources are also described in this section.

5.3.2 Initial stages: mapping and inventory

Geological mapping, either from remote sensing or field determinations is essential as an operational basis for the investigation of mineral and thermal water systems. Logs made of boreholes during drilling, usually comprising lithology, fracture zones, water strikes and pressures, are an essential tool in correlating different strata and locating aquifers of interest.

Remote sensing is most commonly used to define the geological structure, which is then interpreted in terms of groundwater occurrence. Vertical black and white photography and satellite imagery from the Landsat and SPOT programmes are the main tools. Such imagery is also useful for the delineation of surface thermal phenomena such as steaming ground and changes in vegetation, which can be related to changes in shallow water temperatures (United Nations, 1964). Aerial scanning of infrared radiation is directly applicable to areas with anomalous heat flow at or near the surface (Moxham, 1969; Pálmason *et al.*, 1970; Hase, 1971).

Together with geological mapping, the initial investigation generally comprises a desk study and an inventory of points of access to groundwaters and surface waters. At this stage it is usual to carry out a field survey, recording observations of water levels, flow and temperature. On-site measurements of electrical conductivity, pH, alkalinity, redox potential and gas content may also be carried out and samples collected for laboratory analysis of chemical constituents (Castany, 1968).

An investigation of parts of the rift valley of Kenya was carried out by the British Geological Survey in the late 1980s (Dunkley *et al.*, 1993). The presence of volcanoes and emissions of hot water and gases indicated the possibility of locating steam with a minimum temperature of 200°C for the generation of electricity. The region of interest was initially identified from regional geological mapping. This was followed by detailed mapping of six centres, together with the collection of samples of hot water, gases and rocks for laboratory analysis. Hydrogeological information obtained from an inventory of boreholes and dug wells was used to produce a conceptual model of groundwater flow within the region. Stable isotope analyses (^{18}O and ^{2}H) were carried out on all water sources: rainfall, surface waters, groundwater, hot springs and steam. These results were incorporated in the model and indicate that there is sufficient recharge to sustain exploitation of the geothermal systems. Two areas were found to have the greatest geothermal potential and these have been recommended for further investigation, largely by geophysical methods.

Field work in this type of region is not as easy as it may sound in theory. The steam jets on one mountain summit are sacred to the inhabitants, who only granted access when the field team supplied a source of drinking water by constructing a condenser. In another area, equally territorial lions forced a retreat of the survey team (Dunkley, 1991).

5.3.3 Surface geophysics

The data from the above activities may be sufficient to define the areas of interest and to plan a geophysical survey. The most important surface geophysical methods are electrical resistivity sounding and horizontal profiling, seismic reflection and refraction, ground-penetrating radar and electromagnetic, magnetometer, gravity and aeromagnetic surveys. These provide information about the position, extent and physical properties of aquifers and the groundwater within them (Zohdy *et al.*, 1974; Ward, 1990).

Seismic refraction surveys are often used to clarify the deep structure and can locate areas of crustal thinning, indicative of a potential for thermal energy. Many such surveys are carried out for oil exploration and may lead indirectly to the identification of mineral and thermal waters. Aeromagnetic and gravity surveys detect anomalies which can be related to those in areas known to be productive for geothermal energy.

The electrical resistivity method in particular has been widely used for exploration of both mineral and thermal waters. The resistivities likely to be found in different types of system are shown in Figure 5.2. Resistivity generally decreases with increasing mineralization and temperature. High temperatures also result in increased pore space, further lowering the resistivity. At Wairakei, New Zealand, resistivity surveys carried out in the

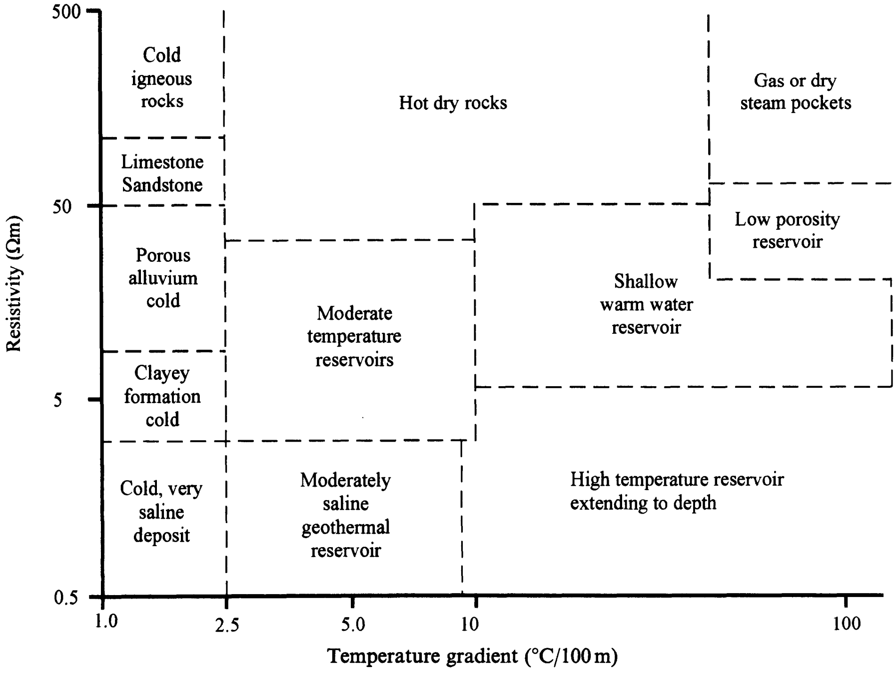


Figure 5.2 Types of reservoir indicated by varying resistivities and temperature gradients. (After Meidar and Tonani, 1976.)

1960s were instrumental in locating a new area for exploitation. Two low resistivity areas, with resistivities less than 10 Ωm, were located, the northern zone was the Wairakei geyser valley, already known for its geothermal power production. A test well was drilled in the southern Taupo zone and located water with a temperature of 220°C at a depth of 256 m (Zohdy *et al.*, 1974).

However in some vapour dominated systems, or where water contains large quantities of carbon dioxide, the resistivity is increased and this tool is less useful. Also, sediments containing a high proportion of clayed sands may have low resistivities, regardless of the quality or temperature of the water, making the survey data more difficult to interpret.

In most cases further drilling will be required both to provide sufficient control for interpretation of the geophysical data and for exploration and testing of the system. The cost of drilling often determines that exploratory boreholes are utilized for production purposes (Costache and Găvan, 1986). Of 20 boreholes drilled to investigate the part of the Pannonian Basin in Slovakia in 1984, 19 were put into use and only one was kept as a monitoring point (Franko *et al.*, 1989). There is therefore often little difference in the construction of exploratory and production boreholes, and this topic is dealt with in more detail in Chapter 7.

5.3.4 Borehole geophysics

Geophysical well logging may include caliper, fluid and temperature logs, conductivity and single-point resistance, resistivity, spontaneous potential and nuclear logging (natural gamma radiation, neutron logging, gamma–gamma radiation) and acoustic logs. The application of these logs, their interpretation in terms of the position, thickness and physical properties of aquifers, and the chemistry and temperature of groundwater are described in Keys (1990) and Ward (1990). The properties that can be measured by different types of log, together with limitations on their use, are given in Table 5.2 and some typical forms of different logs are shown in Figure 5.3. Television cameras may also be used to look at borehole walls. This is only feasible in clear water and, since many boreholes are drilled with and logged in mud, this tool is more often used to examine the state of borehole screen and casing some time after their installation, or for open holes in consolidated rocks.

5.3.5 Well testing

Hydrodynamic testing generally comprises pumping, or sometimes injection, tests in boreholes or occasionally in mine workings. Where artesian flow occurs, pumping may not be necessary. Observation wells, usually of a smaller diameter than the test well, may also be used to determine the effects

Table 5.2 Types of borehole log: applications and limitations (from Keys, 1990)

Type of log	*Properties measured*	*Potential applications*	*Required hole conditions*	*Other limitations*
Spontaneous potential	Electric potential caused by salinity differences in borehole and interstitial fluids	Lithology, shale content, water quality	Uncased hole filled with conductive fluid	Salinity difference needed between borehole fluid and interstitial fluids correct only for NaCl fluids
Single-point resistance	Resistance of rock, saturating fluid, and borehole fluid	High-resolution lithology, fracture location by differential probe	Uncased hole filled with conductive fluid	Not quantitative; hole diameter effects significant
Multi-electrode	Resistivity, in ohm-metres, of rock and saturating fluids	Quantitative data on salinity of interstitial water; lithology	Uncased hole filled with conductive fluid	Normals provide incorrect values and thicknesses in thin beds
Gamma	Gamma radiation from natural or artificial radioisotopes	Lithology – may be related to clay and silt content and permeability	Any hole conditions, except very large diameter, or several strings of casing and cement	
Gamma–gamma	Electron density	Bulk density, porosity, moisture content, lithology	Optimum results in uncased; qualitative through casing or drill stem	Severe hole diameter effects
Neutron	Hydrogen (i.e. water) content	Saturated porosity, moisture content, activation analysis, lithology	Optimum results in uncased holes; can be calibrated for casing	Hole diameter and chemical effects
Acoustic velocity	Compressional wave velocity	Porosity, lithology, fracture location and character, cement bond	Fluid-filled, uncased, except cement bond	Does not see secondary porosity; cement bond and wave form require expert analysis

Acoustic televiewer	Acoustic reflectivity of borehole wall	Location, orientation, and character of fractures and solution openings, strike and dip of bedding, casing inspection	Fluid-filled, 3 to 16 inch diameter	Heavy mud or mud cake attenuate signal; very slow log
Caliper	Hole or casing diameter	Hole diameter corrections to other logs; lithology, fractures, hole volume for cementing	Any conditions	Deviated holes limit some tools; significant resolution difference between tools
Fluid temperature	Temperature of fluid near sensor	Geothermal gradient, in-hole flow, location of injected water, correction of other logs, curing cement	Fluid filled	Accuracy and resolution of tools varies
Fluid conductivity	Most measure resistivity of fluid in hole	Quality of borehole fluid, in-hole flow, location of contaminant plumes	Fluid filled	Accuracy varies, requires temperature correction
Flow	Measures up- or down-hole fluid velocity by impeller or heat pulse	In-hole flow, location and apparent hydraulic conductivity of permeable interval	Fluid filled	Impellers require higher velocities. Needs to be centralized and calibrated

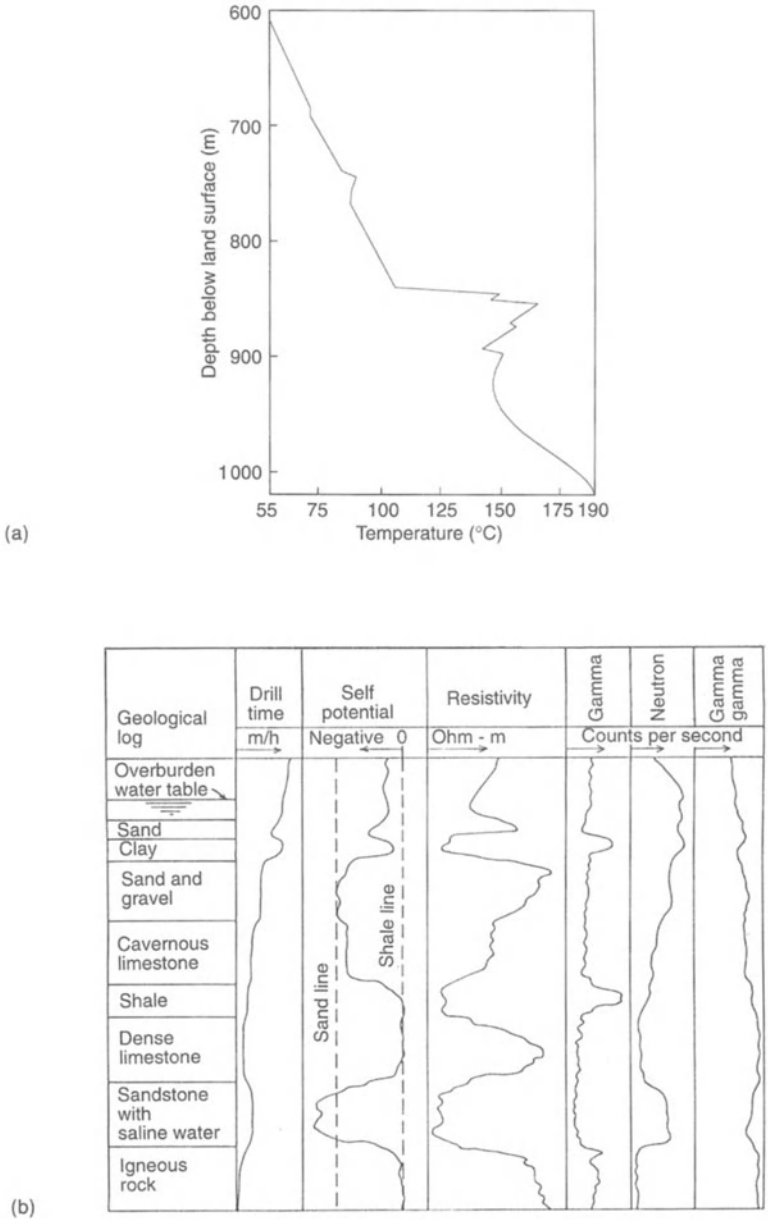


Figure 5.3 Schematic geophysical borehole logs: (a) is a temperature log from a geothermal well at Roosevelt Hot Springs, Utah, and indicates an inflow of hot water from fracture zones below 850 m (from Keys, 1990), while (b) shows the impact of lithology, permeability and salinity on different types of logs. (From Bouwer, 1978, with permission of the McGraw-Hill Companies.)

of pumping on the aquifer rather than within the pumping borehole (Burgess and Dottridge, 1992). In a single phase (water) system, the piezometric head or pressure in the aquifers is measured as it varies with the flow rate, time and distance, both in the pumping or injection boreholes and especially in observation holes or piezometers. The presence of gas reduces the fluid density and the fluid levels measured are correspondingly higher. This can lead to apparently anomalous head changes during testing, as described in Chapter 16.

The interpretation of such tests to determine aquifer transmissivity and storage and well performance characteristics is discussed in, for example, De Wiest (1965), Albu (1981) and Domenico and Schwartz (1990). Kruseman and de Ridder (1991) provide the most comprehensive guide to determining the hydraulic characteristics of aquifers from such tests, including some methods for systems where fracture flow is important. However they do not deal with two-phase fluids or heat flow.

5.3.6 Tracing

Tracing may be used to determine, at least locally, the direction and velocity of groundwater flow (Avramescu *et al.*, 1971). The tracers used most frequently are dyes such as fluorescein, rhodamine and eosin, radionuclides (^{82}Br, ^{131}I, ^{24}Na, ^{36}Cl, ^{60}Co and ^{90}Sr), soluble salts (sodium chloride, sodium dichromate and sodium nitrite) and particles such as lycopodium spores. Some of these substances are not acceptable in water used for drinking supplies; they can also pollute surface waters and their use may therefore be restricted by law.

Such investigations are most often applied in fissured or karstic aquifers where predictions of flowpaths from measurements of hydraulic head may not be applicable. The recharge areas of springs are often determined this way and the arrival times of tracers can be useful in estimating the frequency and dimensions of fractures.

5.3.7 Geothermometers

Chapter 3 discusses the chemistry of mineral and thermal waters and the processes by which they evolve. The chemistry of groundwater also provides a guide to the temperature at the depth from which the water is derived.

Where the effective permeability is relatively high and water residence times are long, water and rock reach chemical equilibrium quite fast, in the order of months to years, especially where temperatures exceed 200°C. Chemical reaction rates are generally slower at lower temperatures and the concentrations of dissolved silica, sodium, potassium and calcium and some isotopes stay relatively constant as the water cools on its way to the

Table 5.3 A selection of geothermometers (based on Fournier, 1981)

Geothermometer	*Equation*	*Restrictions*
Quartz: no loss of steam	$T\,(\mathrm{K}) = \dfrac{1309}{5.19 - \log C}$	$T = 273\text{–}523\,\mathrm{K}$ (0–250°C)
Quartz: maximum loss of steam	$T\,(\mathrm{K}) = \dfrac{1522}{5.75 - \log C}$	$T = 273\text{–}523\,\mathrm{K}$ (0–250°C)
Chalcedony	$T\,(\mathrm{K}) = \dfrac{1032}{4.69 - \log C}$	$T = 273\text{–}523\,\mathrm{K}$ (0–250°C)
α-Cristobalite	$T\,(\mathrm{K}) = \dfrac{1000}{4.78 - \log C}$	$T = 273\text{–}523\,\mathrm{K}$ (0–250°C)
β-Cristobalite	$T\,(\mathrm{K}) = \dfrac{781}{4.51 - \log C}$	$T = 273\text{–}523\,\mathrm{K}$ (0–250°C)
Amorphous silica	$T\,(\mathrm{K}) = \dfrac{731}{4.52 - \log C}$	$T = 273\text{–}523\,\mathrm{K}$ (0–250°C)
Na/K (Fournier)	$T\,(\mathrm{K}) = \dfrac{1217}{\log(\mathrm{Na/K}) + 1.483}$	$T > 423\,\mathrm{K}$ (>150°C)
Na–K–Ca	$\dfrac{1647}{\log(\mathrm{Na/K}) + \beta[\log((\mathrm{Ca})^{1/2}/\mathrm{Na}) + 2.06] + 2.47}$	See text
$\Delta^{18}\mathrm{O}(\mathrm{SO_4^{2-}} - \mathrm{H_2O})$	$10^3 \ln\left[\dfrac{10^3 + \delta^{18}\mathrm{O}(\mathrm{HSO_4^-})}{10^3 + \delta^{18}\mathrm{O}(\mathrm{H_2O})}\right] = 2.88\,(10^6\,T(\mathrm{K})^{-2}) - 4.1$	

C = Concentration of dissolved Si (SiO_2). All concentrations are in mg/kg.

surface, and can be used to estimate the temperature of the system (Truesdell and Fournier, 1976).

The relationships between chemistry and temperature shown in Table 5.3 have been determined empirically from a large number of temperature measurements in boreholes and are valid only for the stated temperature ranges. The quartz geothermometer is most accurate for well waters where subsurface temperatures are above about 150°C, but it is affected by steam separation since the silica remains in the residual liquid and becomes more concentrated. The relationship for quartz/maximum steam loss is therefore used for boiling springs with a high flow rate. Where flow rates are low and there is some conductive heat loss during steam formation, the relationship will lie between the two quartz geothermometers. For springs at high altitudes, steam formation occurs at lower temperatures and the maximum steam loss relationship will give a high estimate of the temperatures. Dissolved silica in geothermal systems is usually in equilibrium with quartz. However, where other more soluble species are present, they will control the solution of silica. Chalcedony for example can control the solution of silica up to temperatures of 180°C in some basalt systems and at temperatures of less than 90°C in some granite areas.

Where thermal water is diluted with cooler water, the silica content will be reduced and it is necessary to correct the figures before the quartz geothermometer can be applied.

The Na/K geothermometer generally gives good results with waters from environments with temperatures more than 80°C and is best for waters of more than 180°C. It can be useful for diluted waters where the cool water is less mineralized and low in Na and K, so that the Na/K ratio is not significantly affected (Fournier, 1981). However, the temperatures calculated for calcium-rich waters are sometimes too high and the Na–K–Ca geothermometer then becomes applicable (Fournier and Truesdell, 1973). The calculation is a bit more complicated: the temperature is first calculated with a value for the constant β of $\frac{4}{3}$ (Table 5.3). If the calculated temperature is more than 100°C or $\log(\sqrt{Ca}/Na) + 2.06$ is negative, then $\beta = \frac{1}{3}$ is used to calculate the temperature. This geothermometer is affected by boiling and dilution. Boiling results in the loss of CO_2 and precipitation of $CaCO_3$, while dilution may also result in too low Ca values being used in the calculation. Both effects result in an overestimation of the temperature. Corrections are also necessary if the waters are rich in Mg (Fournier and Potter, 1979).

The distribution of ^{18}O between dissolved sulphate and water is a function of temperature. The ^{18}O–sulphate geothermometer (Lloyd, 1968) can be applied provided that no additional sources of sulphate are encountered during flow from the reservoir to the sampling point. The most likely additional source is from oxidation of H_2S and can be checked from the ^{34}S content of the water and variations in the Cl/SO_4 ratio (Fournier, 1981). Steam formation results in fractionation of the oxygen isotopes and corrections have to be made for this, as well as for any mixing. These and several other geothermometers are discussed by Truesdell and Hulston (1980), who provide a comparison of estimated temperatures for different sources of water (Table 5.4).

Because mixing of water affects the various geothermometers differently, comparison of their results may be used to recognize mixed waters. Some can be used to estimate the temperature of the reservoir soon after drilling, while the hole is still affected by drilling fluids. An example is given by Fournier (1981) of a geothermal exploration well in which the temperature of the water immediately after drilling was 165°C. Water samples collected during well stimulation indicated aquifer temperatures of 195°C, a temperature which was not reached by the sampled water until 4 months after completion.

Water from non-thermal springs may have a different water chemistry to adjacent shallow groundwater, indicating a different flow history with the possibility that the water has been heated at depth. In the French Massif Central, for example, cation geothermometers indicate that cold CO_2-rich mineral springs have reached temperatures of around 200°C (Vasseur *et al.*, 1991).

Table 5.4 Temperatures (°C) observed and calculated by different geothermometers (from Truesdell and Hulston, 1980)

	Observed reservoir temperatures	*Chalcedony saturation*	*Quartz saturation*	*Na–K*	*Na–K–Ca*	$\Delta^{18}O$ SO_4-H_2O
Useful temperature ranges and equilibration rates						
Useful temperature range (°C)	–	50–150	130–300	100–350	50–350	80–350
Estimated $t_{1/2}$ at 250°C (years)	–	0.02	0.02	0.1	0.1	1
Indicated temperatures in geothermal systems						
System:						
Seltjarnarnes, Iceland spring	119	115	140	68	109	142
Raft River, Idaho, shallow wells	147	110	137	90	139	180–280
Ohtake, Japan, wells	195	–	195–238	220	230	–
Hveragerdi, Iceland springs, well G-8	220	–	174–212	–	–	–
Wairakei, New Zealand, well 44	248	–	248	255	259	303
Broadlands, New Zealand, springs well 8	273	–	203–278	311	218–302	–
Salton Sea, California, IID No. 2	300	–	230	354	308	–
Larderello, Italy, steam wells	180–260	–	–	–	–	152–329
The Geysers, California, steam wells	240–250	–	–	–	–	232

5.3.8 Thermodynamics

The study of thermodynamics involves measurement of the temperature, pressure and density of the fluids to determine the enthalpy of the system (Keenan *et al.*, 1969).

The collection of rock and water samples during drilling is important both for effective well design and assessment of the economic value of the resource (Iordache, 1977). Coring is especially necessary for investigation of rock–water equilibrium. The thermal conductivity of the rocks must be measured in the laboratory and thin sections analysed for mineral assemblages. The analysis of hydrothermal alteration products in rock cores (Ellis and Mahon, 1977; Fournier, 1981) helps to define the number of phases of active hydrothermalism and its intensity.

In the sedimentary Pannonian Basin, the thermal conductivity has been found to increase with depth and with increasing sand content. Clays by contrast have a relatively low thermal conductivity (Franko *et al.*, 1989). Average conductivities are estimated from the samples, and from the clay fraction determined from gamma logging where appropriate. The heat flow (Chapter 4) is calculated from the thermal conductivity of rocks and the temperature gradient over the interval of interest.

Maps of heat flow (e.g. Figure 5.4), either at the earth's surface or at depth, often at 1–2 km, give a good indication of regions with a higher thermal potential. They are usually based on temperature gradient measurements in many boreholes and petroleum exploration wells are often used for this purpose. Maps of temperature at set depths or temperature gradients give similar information, but are less directly related to the quantity of usable heat.

In the Prairies Basin of western Canada, measurements of temperature have been made at different depths in some 36 000 petroleum exploration wells (Jones and Majorowicz, 1987), enabling a conceptual model of regional heat flow to be developed. However, Allen *et al.* (1985) found that the most accurate temperature data are obtained from boreholes drilled for the purpose. Heat is transported in the drilling fluid and measurements made shortly after drilling do not always represent formation temperatures: as mentioned above, it can take several months for thermal equilibrium to be reached.

5.3.9 Technique and technology

The methods of the technique and technology of abstraction and use of mineral and thermal waters are applied in the final stage of investigation, in which the possibilities of development and conservation of the resources and the economic feasibility of their utilization are tested. They include pumping and injection well tests in boreholes and drainage of mine workings, by production, injection and recovery tests. Testing the economic feasibility

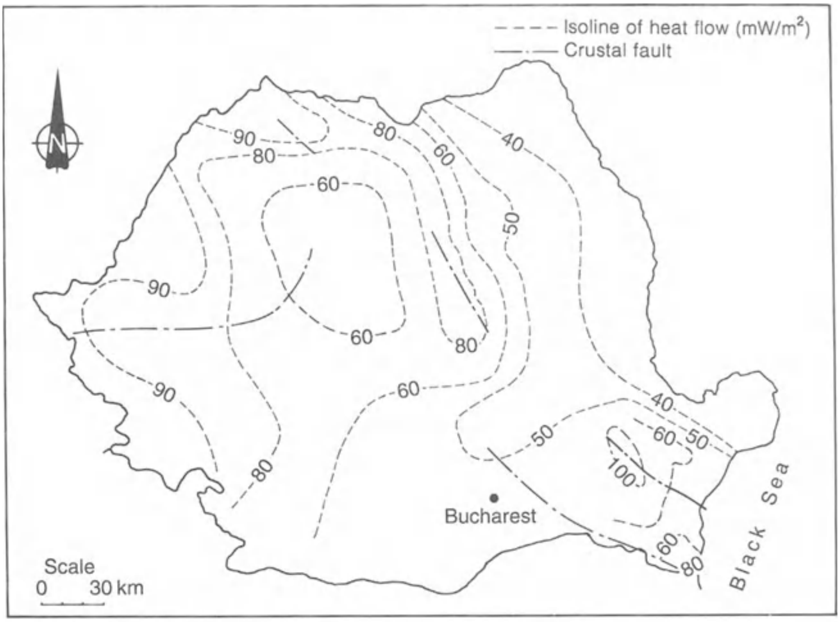


Figure 5.4 Heat flow map of Romania. (From Gheorghe and Crăciun, 1993. Copyright Elsevier Science, with permission.)

of utilizing the resources comprises pilot tests for balneal treatment or other medical purposes, the extraction of useful components, the bottling as mineral water for table use or for consumption under medical supervision, and the use for energy or industrial purposes of the identified resources. On the basis of these tests the most effective means of processing of and uses for the mineral and thermal waters are determined.

5.4 ESTIMATION OF THE POTENTIAL YIELD OF MINERAL WATERS

The following simplistic methods are often used from the early stages of investigation to check the potential yield of resources and decide whether further investigation or development of the system is economically justified.

5.4.1 Productivity method

The productivity method is useful for extensive, relatively uniform aquifers where the data collected are representative of large volumes, but where the behaviour of the system as a whole is not well known.

On the basis of hydrodynamic tests on sources such as boreholes, wells or springs, component blocks may be distinguished within the mineral water system. These are characterized by the volume productivity Q_i^y/V_i, which is the ratio of the optimal yield Q_i^y to the volume V_i of aquifer contributing to each source i for which exploitation is being considered.

The optimum yield of water is determined from the results of steady or near-steady state tests, from which correlations between the rate of flow and the drawdown, as well as between the rate of flow and the content of different chemical components, are determined (Albu and Hînculov, 1975; Albu and Radu, 1984). This takes into account the condition that the velocity of water should not exceed that at which sediment will enter the source, and that the chemical content is maintained within the quality limits required for the use of the water (Figure 5.5).

The volume V_i of the domain of influence can be expressed as the product of the thickness H_i of the system and the area of influence A_i. The thickness is established from direct measurements or on the grounds of geological structure, and the area of influence is determined from interpretation of the test data. Hence the volume productivity may be written in the form

$$\frac{Q_i^y}{V_i} = \frac{1}{H_i}\frac{Q_i^y}{A_i}$$

Thus the assemblage of n component blocks is characterized by the average volume productivity

$$\sum_{i=1}^{n} Q_i^y \Big/ \sum_{i=1}^{n} V_i$$

or, in the case of a system of relatively uniform thickness, with an average value of $\tilde{H}$, by the average surface productivity

$$\sum_{i=1}^{n} Q_i^y \Big/ \sum_{i=1}^{n} A_i = \tilde{H} \sum_{i=1}^{n} Q_i^y \Big/ \sum_{i=1}^{n} V_i$$

Corresponding to these two cases, the total resources Q^y of the system are evaluated by the relationships

$$Q^y = V\frac{\sum_{i=1}^{n} Q_i^y}{\sum_{i=1}^{n} V_i} \qquad \text{or} \qquad Q^y = A\frac{\sum_{i=1}^{n} Q_i^y}{\sum_{i=1}^{n} A_i} \tag{5.1}$$

respectively, and include, depending on the degree of knowledge about the system, both the measured and the inferred resources (Table 5.1).

This method has been applied for the determination of mineral water resources at Bazna, Sângeorgiu de Mureş, Călacea and Vatra Dornei in Romania.

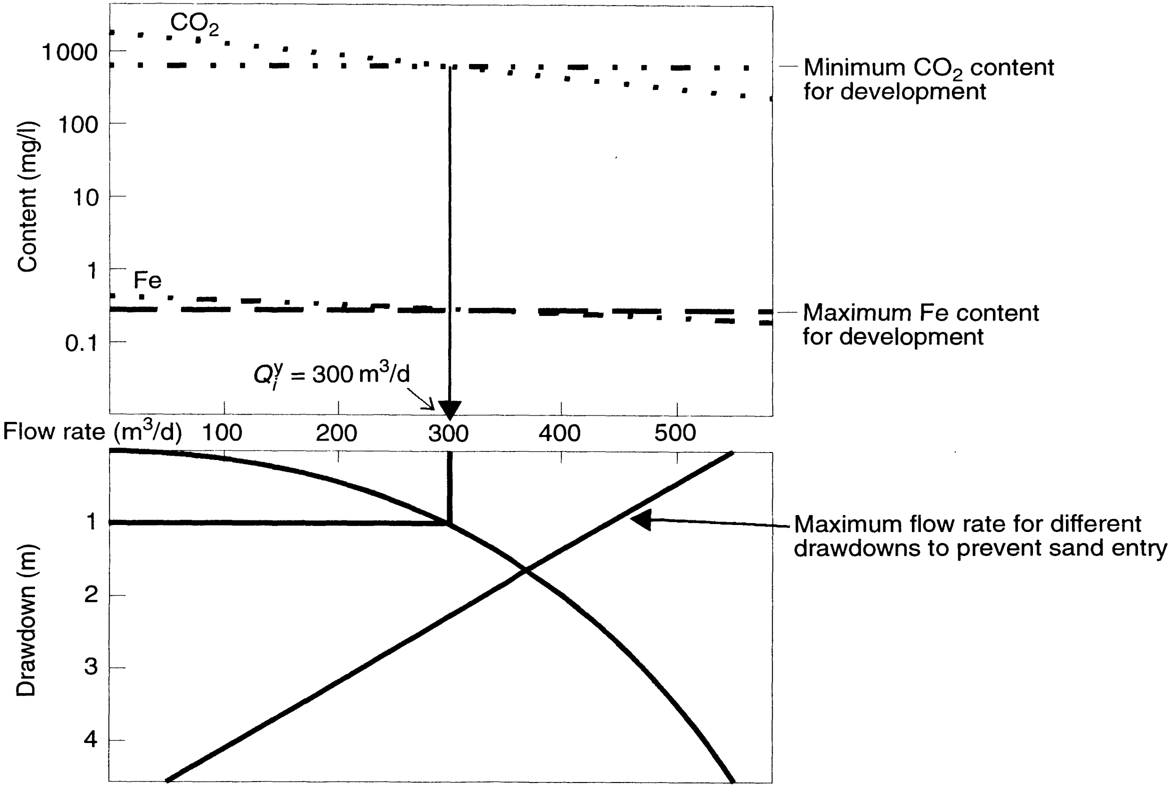


Figure 5.5 Determination of the optimal yield of mineral water for acceptable CO$_2$ and Fe$_2$ content without sand entry.

5.4.2 Step test method

The step test method is usually applied to a system of limited extent, with relatively few points of investigation but for which the behaviour of the system as a whole is well known.

The system is tested as a whole, simultaneously at all possible sources or groups of sources. A constant flow rate is maintained for a period of time, usually for several days or more, and then increased in steps, each for the same period of time, until the influence on natural sources such as springs or on observation points installed at the extremities of the system can be measured. To ensure the maintenance of natural conditions, such as spring flow or recharge, the discharge rate below which no adverse influence is measured represents the total available resources Q^y (Albu and Radu, 1984). This method was applied to a naturally carbonated mineral water system at Sângeorz in Romania.

5.4.3 Gasohydrodynamic method

This method is used for two-phase systems (gas and liquid) where the gas, usually carbon dioxide, has an upward movement while the liquid can move laterally. It is particularly useful for determining resources of gases but requires detailed field investigations to obtain sufficient data for its application. The method was developed in Romania (Albu, 1976) and is relatively little known. For this reason the mathematical detail is given in full.

Carbonated mineral water systems extend along or close to fractures in the basement, which provide access to aquifers for carbon dioxide associated with the latter stages of volcanic activity. The flow of the two-phase fluid in a carbonate mineral water system (Albu, 1976; Roco, 1993) may be characterized by the vectorial function

$$\boldsymbol{v} = \frac{\rho_\alpha}{\rho}\boldsymbol{v}_\alpha + K\left(\frac{\rho_\alpha}{\rho} - 1\right)\operatorname{grad} z \tag{5.2}$$

where grad = vector gradient operator [m^{-1}], h = hydraulic head of the fluid as a whole [m], K = hydraulic conductivity of the aquifer [$\mathrm{m\,d}^{-1}$], $\boldsymbol{v} = -K\,\mathrm{grad\,h}$ = specific discharge vector of the fluid as a whole [$\mathrm{m\,d}^{-1}$], $\boldsymbol{v}_\alpha$ = specific discharge vector of liquid phase [$\mathrm{m\,d}^{-1}$], z = elevation above a given datum [m], ρ = mass density of the fluid as a whole [$\mathrm{kg\,m}^{-3}$] and ρ_α = mass density of the liquid phase [$\mathrm{kg\,m}^{-3}$].

Such systems usually include at least one subdomain of volume V where the concentration C_β of the gaseous phase is always positive. This subdomain is bounded, as illustrated in Figure 5.6, by the surface S, enclosed below by a surface of area A_1 of impervious basement and above by the surface A_2 of the water table, and laterally by the surface Ω, which is the boundary of concentration $C_\beta = 0$, or possibly by an impermeable surface Σ.

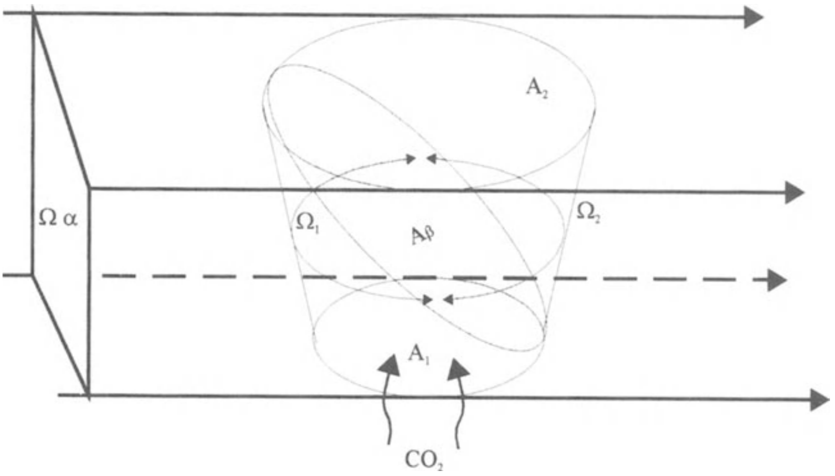


Figure 5.6 Components of the gasohydrodynamic method; for explanation see text.

Because function (5.3) is defined for volume V as a vectorial field $\boldsymbol{v}$, given by the sum of the fields $(\rho_\alpha/\rho)\boldsymbol{v}_\alpha$ and $K(\rho_\alpha/\rho - 1)\,\text{grad}\,z$, it follows that the integral of this function on the closed surface S represents the total flux of the vectorial field $\boldsymbol{v}$ through S, in keeping with the expression

$$\oint_S \boldsymbol{v}\,\mathrm{d}\boldsymbol{S} = \oint_S \frac{\rho_\alpha}{\rho}\boldsymbol{v}_\alpha\,\mathrm{d}\boldsymbol{S} + \oint_S \left[K\left(\frac{\rho_\alpha}{\rho} - 1\right)\text{grad}\,z\right]\mathrm{d}\boldsymbol{S} \tag{5.3}$$

A_1 and A_2 are the field surfaces for $(\rho_\alpha/\rho)\boldsymbol{v}_\alpha$, Ω is the surface on which $(\rho_\alpha/\rho)\boldsymbol{v}_\alpha = \boldsymbol{v} = -K\,\text{grad}\,h$ and $K(\rho_\alpha/\rho - 1)\,\text{grad}\,z = 0$ because $C_\beta = 0$, while Σ, if present, is the field surface both for $(\rho_\alpha/\rho)\boldsymbol{v}_\alpha$ and for $K(\rho_\alpha/\rho - 1)\,\text{grad}\,z$. From this it is deduced that the flux of the field $(\rho_\alpha/\rho)\boldsymbol{v}_\alpha$ through S represents the difference between the inflow through side Ω_1 and outflow through side Ω_2 of the surface Ω, while the flux of the field $K(\rho_\alpha/\rho - 1)\,\text{grad}\,z$ through S represents the difference between the inflow through surface A_1 and outflow through surface A_2, i.e.

$$\oint_S \frac{\rho_\alpha}{\rho}\boldsymbol{v}_\alpha\,\mathrm{d}\boldsymbol{S} = \int_{\Omega_1} (-K\,\text{grad}\,h)\,\mathrm{d}\boldsymbol{S} - \int_{\Omega_2} (-K\,\text{grad}\,h)\,\mathrm{d}\boldsymbol{S} \tag{5.4}$$

$$\oint_S \left[K\left(\frac{\rho_\alpha}{\rho} - 1\right)\text{grad}\,z\right]\mathrm{d}S = \int_{A_1} \left[K\left(\frac{\rho_\alpha}{\rho} - 1\right)\text{grad}\,z\right]\mathrm{d}\boldsymbol{S} - \int_{A_2} \left[K\left(\frac{\rho_\alpha}{\rho} - 1\right)\text{grad}\,z\right]\mathrm{d}\boldsymbol{S} \tag{5.5}$$

Although these fluxes vary in time, their net variation over a number of years can generally be assumed to be nil, provided the system is in equilibrium. Consequently the terms on the left side of equations (5.4) and (5.5) vanish, giving the more or less constant conservative fluxes

$$\int_{\Omega_1} (-K \operatorname{grad} h)\, \mathrm{d}\boldsymbol{S} = \int_{\Omega_2} (-K \operatorname{grad} h)\, \mathrm{d}\boldsymbol{S} = \int_{\Omega_\alpha} (-K \operatorname{grad} h)\, \mathrm{d}\boldsymbol{\Omega}_\alpha \tag{5.6}$$

and

$$\begin{aligned}\int_{A_1} \left[K\left(\frac{\rho_\alpha}{\rho} - 1\right) \operatorname{grad} z\right] \mathrm{d}\boldsymbol{S} &= \int_{A_2} \left[K\left(\frac{\rho_\alpha}{\rho} - 1\right) \operatorname{grad} z\right] \mathrm{d}\boldsymbol{S} \\ &= \int_{A_\beta} \left[K\left(\frac{\rho_\alpha}{\rho} - 1\right) \operatorname{grad} z\right] \mathrm{d}\boldsymbol{A}_\beta \end{aligned} \tag{5.7}$$

where Ω_α is a section through the stream tube V; Ω_1 and Ω_2 are respectively the sections at the entrance and exit of V, while A_β is a section through volume V between A_1 and A_2 (Figure 5.6).

If the fluxes (5.6) and (5.7) are known, then the average perennial yield Q^{py} of carbonated water within volume V can be determined from the relationship

$$Q^{py} = \int_{\Omega_\alpha} (-K \operatorname{grad} h)\, \mathrm{d}\boldsymbol{\Omega}_\alpha + \int_{A_\beta} \left[K\left(\frac{\rho_\alpha}{\rho} - 1\right) \operatorname{grad} z\right] \mathrm{d}\boldsymbol{A}_\beta \tag{5.8}$$

Since $-\operatorname{grad} h = -(\partial h/\partial n)\boldsymbol{n} = i \cdot \boldsymbol{n}$, where $-(\partial h/\partial n) = i$ is the hydraulic gradient and $\boldsymbol{n}$ is the unit vector of the normal n to the surface of constant level h which crosses through a considered point on section Ω_α, and $\operatorname{grad} z = \boldsymbol{k}$, where $\boldsymbol{k}$ is the unit vector of the upward pressure gradient, relationship (5.8) can be written

$$Q^{py} = \int_{\Omega_\alpha} K i \boldsymbol{n}\, \mathrm{d}\boldsymbol{\Omega}_\alpha + \int_{A_\beta} K\left(\frac{\rho_\alpha}{\rho} - 1\right) \boldsymbol{k}\, \mathrm{d}\boldsymbol{A}_\beta \tag{5.9}$$

Because the products $K \cdot i$ and $K(\rho_\alpha/\rho - 1)$ on sections Ω_α and A_β have respectively the average values

$$\overline{(Ki)}_{\Omega_\alpha} = \frac{1}{\Omega_\alpha^*} \int_{\Omega_\alpha} K i \boldsymbol{n}\, \mathrm{d}\boldsymbol{\Omega}_\alpha \tag{5.10}$$

and

$$\overline{\left[K\left(\frac{\rho_\alpha}{\rho} - 1\right)\right]}_{A_\beta} = \frac{1}{A_\beta^*} \int_{A_\beta} K\left(\frac{\rho_\alpha}{\rho} - 1\right) \boldsymbol{k}\, \mathrm{d}\boldsymbol{A}_\beta \tag{5.11}$$

it follows that the average perennial yield of carbonated waters from the volume V can be calculated as

$$Q^{py} = \overline{(Ki)}_{\Omega_\alpha} \Omega_\alpha^* + \overline{\left[K\left(\frac{\rho_\alpha}{\rho} - 1\right)\right]}_{A_\beta} A_\beta^* \tag{5.12}$$

Here

$$\Omega_\alpha^* = \int_{\Omega_\alpha} \boldsymbol{n}\,\mathrm{d}\boldsymbol{\Omega}_\alpha$$

is the area of the projection of section Ω_α on the surface of constant level h which crosses through the centre of this section (the area of the cross-section of the stream tube laterally bounded by the outline of section Ω_α) and

$$A_\beta^* = \int_{A_\beta} \boldsymbol{k}\,\mathrm{d}A_\beta$$

is the area of the projection of section A_β on a horizontal plane.

Corresponding to expression (5.12), the average perennial yield Q^{py} of carbonated water from volume V comprises the sum of the dynamic throughflow of water (support resources)

$$\overline{(Ki)}_{\Omega_\alpha}\Omega_\alpha^*$$

and the available resources of carbonated water

$$Q^y = \overline{\left[K\left(\frac{\rho_\alpha}{\rho} - 1\right)\right]}_{A_\beta} A_\beta^* \tag{5.13}$$

The conditions for utilization of carbonated water impose a minimum value C_β on the concentration of the gaseous phase. It follows that Q^y must be calculated separately as resources Q_{I}^y of carbonated water with a concentration $C_\beta \geq C_\beta^{\min}$ and Q_{II}^y with the concentration $C_\beta < C_\beta^{\min}$.

If section A_β is made up of $A_{\beta\mathrm{I}}$ where $C_\beta \geq C_\beta^{\min}$, and $A_{\beta\mathrm{II}}$ where $C_\beta < C_\beta^{\min}$, then

$$Q_{\mathrm{I}}^y = \overline{\left[K\left(\frac{\rho_\alpha}{\rho} - 1\right)\right]}_{A_{\beta\mathrm{I}}} A_{\beta\mathrm{I}}^* \tag{5.14}$$

which are the resources of interest for utilization, and

$$Q_{\mathrm{II}}^y = \overline{\left[K\left(\frac{\rho_\alpha}{\rho} - 1\right)\right]}_{A_{\beta\mathrm{II}}} A_{\beta\mathrm{II}}^* \tag{5.15}$$

which are not, where $\overline{[K(\rho_\alpha/\rho - 1)]}_{A_{\beta\mathrm{I}}}$ and $\overline{[K(\rho_\alpha/\rho - 1)]}_{A_{\beta\mathrm{II}}}$ are the average values of the product $K(\rho_\alpha/\rho - 1)$ on $A_{\beta\mathrm{I}}$ and $A_{\beta\mathrm{II}}$ respectively, and $A_{\beta\mathrm{I}}^*$ and $A_{\beta\mathrm{II}}^*$ are the areas of the projections of the corresponding portions $A_{\beta\mathrm{I}}$ and $A_{\beta\mathrm{II}}$ on a horizontal plane.

This method was used to estimate the naturally carbonated mineral water at Busiaş and Borsec in Romania, using average values for aquifer parameters determined from field tests. The data used and the results are given in Table 5.5.

Table 5.5 Estimates of parameters of naturally carbonated mineral water at Buziaş and Borsec, Romania (average values of parameters)

	Mineral water system					
	Buziaş (granular aquifer)			*Borsec (fissured aquifer)*		
	$C_\beta = 0$	$C_\beta > 0$	$C_\beta \geq C_\beta^{\min}$	$C_\beta = 0$	$C_\beta > 0$	$C_\beta \geq C_\beta^{\min}$
Groundwater flow						
Horizontal hydraulic conductivity $\bar{\kappa}_{\Omega_\alpha}$ (m/d)	6.0	–	–	1.9	–	–
Hydraulic gradient ($\bar{i}_{\Omega_\alpha}$)	0.001	–	–	0.002	–	–
Width of flowpath cross-section $\bar{l}^*$ (m)	750	–	–	1000	–	–
Height of flowpath cross-section $\bar{H}^*$ (m)	110	–	–	170	–	–
Upward flux of carbonated water						
Vertical hydraulic conductivity (m/d)	–	1.5 ($\bar{K}_{A_\beta}$)	1.5 ($\bar{K}_{A_{\beta\mathrm{I}}}$)	–	1.0 ($\bar{K}_{A_\beta}$)	1.9 ($\bar{K}_{A_{\beta\mathrm{I}}}$)
Ratio of liquid density to density of two-phase fluid	–	1.0005 $\overline{(\rho_\alpha/\rho)}_{A_\beta}$	– $\overline{(\rho_\alpha/\rho)}_{A_{\beta\mathrm{I}}}$	–	1.0007 $\overline{(\rho_\alpha/\rho)}_{A_\beta}$	1.0015 $\overline{(\rho_\alpha/\rho)}_{A_{\beta\mathrm{I}}}$
Horizontal area (m^2)	–	1 374 700 A_β^*	394 400 $A_{\beta\mathrm{I}}^*$	–	1 641 430 A_β^*	312 630 $A_{\beta\mathrm{I}}^*$

$\bar{l}^* \times \bar{H}^* = \bar{\Omega}^*$ (m^2).

Since $Q^{\rho y} = \bar{K}_{\Omega_\alpha} \cdot \bar{i}_{\Omega_\alpha} \cdot \bar{l}^* \cdot \bar{H}^* + \bar{K}_{A_\beta}[\overline{(\rho_\alpha/\rho)}_{A_\beta} - 1] \cdot A_\beta^*$, for Buziaş

$$Q^{\rho y} = 6 \times 0.001 \times 750 \times 110 + 1.5 \times (1.0005 - 1) \times 1\,374\,700\,\mathrm{m^3\,d^{-1}}$$

$$= 495 + 1031 = 1526\,\mathrm{m^3\,d^{-1}}, \text{ and for Borsec}$$

$$Q^{\rho y} = 1.9 \times 0.002 \times 1000 \times 170 + 1.0 \times (1.0007 - 1) \times 1\,641\,430\,\mathrm{m^3\,d^{-1}}$$

$$= 646 + 1149 = 1795\,\mathrm{m^3\,d^{-1}}.$$

$Q^y = \bar{K}_{A_\beta} \cdot [\overline{(\rho_\alpha/\rho)}_{A_\beta} - 1] \cdot A_\beta^* = 1031\,\mathrm{m^3\,d^{-1}}$ for Buziaş and $1149\,\mathrm{m^3\,d^{-1}}$ for Borsec, and the resources where the carbon dioxide is equal to or more than that required for exploitation.

$Q_\mathrm{I}^y = \bar{K}_{A_{\beta\mathrm{I}}} \cdot [\overline{(\rho_\alpha/\rho)}_{\mathrm{A}_{\beta\mathrm{I}}} - 1] \cdot A_{\beta\mathrm{I}}^* = 1.5 \times 0.0013 \times 394\,400 = 769\,\mathrm{m^3\,d^{-1}}$ for Buziaş and $1.9 \times 0.0015 \times 312\,630 = 891\,\mathrm{m^3\,d^{-1}}$ for Borsec.

5.5 METHODS FOR ESTIMATING THE QUANTITY OF HEAT STORED IN THERMAL WATER SYSTEMS

5.5.1 General

There are many methods for the evaluation of geothermal resources, beginning with old methods such as that of planar fracture (Böðvarsson and Bolton, 1971; Böðvarsson, 1974; Nathenson, 1975) and some methods of questionable use such as that of the magmatic heat budget (Noguchi, 1970; Smith and Shaw, 1975). At present, estimates of the size of geothermal resources are usually based on volume calculations of reservoir heat content, together with empirical assumptions regarding the rate at which energy can be withdrawn from the reservoir (Bowen, 1989).

Thermal water resources can sometimes be evaluated using the productivity or step test methods described in section 5.4. In other situations the heat discharge and volumetric methods described below may be applied. Both of these treat heat as a non-renewable resource, with negligible natural regeneration of heat.

All of these methods are used to estimate the quantity of heat stored in a system. Only a relatively small quantity of heat can be recovered from the geothermal resources thus calculated. The recoverable resources can be estimated by applying a recovery factor, generally less than 0.25 (Muffler and Cataldi, 1978; Table 7.2), which depends on the geological and thermodynamic features of the system, as well as on technological and economic conditions.

Due to their complexity, evaluation of thermal water resources usually involves the application of numerical modelling, these methods now being common practice (Faust and Mercer, 1975; Downing *et al.*, 1984; Ranganathan and Hamor, 1987; Burgess *et al.*, 1991).

5.5.2 Heat discharge method

The variation in time of the quantity of heat in a volume V is equal to the difference between the power corresponding to the heat sources inside the volume and the total heat flux through the surface S which encloses this volume. For a thermal water system, the surface S generally comprises a bottom surface A_b, a lateral surface Ω and a top surface A_t. Assuming that the internal generation of heat, the flux through the bottom of the system and the flux through its lateral surface can be neglected for a duration $\Delta t = t - t_0$ of heat extraction, short in comparison with the time taken for natural heat regeneration, then the variation of the quantity of heat in time is due only to the heat loss through the top surface, and the geothermal resources are estimated from the natural thermal power of the surface A_t multiplied by the interval of time Δt (Muffler and Cataldi, 1978).

If the temperature at the top surface A_t has the average value T_t, the upward conductive heat discharge is given by an average heat flow $\tilde{q}_t$, and the upward convective heat discharge is produced by outlets $i = 1, 2, ..., n$ which can be fumaroles, solfataras, mofettes, springs or wells, characterized by the average values $(\rho Q)_i$, c_i and T_i for the mass flow rate, specific heat and temperatures of the discharged fluids, then the geothermal resources are calculated from the expression

$$\left[\tilde{q}_t A_t + \sum_{i=1}^{n} (\rho Q)_i c_i (T_i - T_t)\right] \Delta t$$

The likely duration and amount of convective heat discharge as thermal water can be appreciated by analogy with other geothermal systems for which the evolution in time is better known. Some such systems can supply heat quantities of four to over ten times the geothermal energy estimated by the heat discharge method (White, 1965). This is because the method does not take into account the recharge of water, regeneration of heat and the storage capacity of the system.

The heat discharge method is known for its application to evaluate the geothermal resources of the systems of Wairakei in New Zealand (Banwell, 1963), Tatunshan in Taiwan (Chen, 1970) and Takinoue in Japan (Suyama *et al.*, 1975).

5.5.3 Volumetric method

This method is used to estimate the quantity of heat stored in the system between the reservoir temperature T and a reference temperature T_{ref} below which the thermal resources are not of any commercial interest. If the system is divided into n blocks of volume V_i, which have an average heat capacity per unit volume $(\tilde{\rho}\tilde{c})_i$ and an average temperature T_i, then the quantity of heat above T_{ref} is calculated as

$$\sum_{i=1}^{n} (\tilde{\rho}\tilde{c})_i (T_i - T_{\text{ref}}) V_i$$

This type of calculation is optimally suited to numerical solution by the finite element method.

Considering a thermal water system with blocks of kinematic porosity m_i, of heat capacity per unit volume $(\rho c)_i$ for free water and $(\rho^* c^*)_i$ for solid material together with adhesive water, the total quantity of heat in the system on cooling to T_{ref} can be calculated as

$$\sum_{i=1}^{n} (\rho c)_i (T_i - T_{\text{ref}}) m_i V_i + \sum_{i=1}^{n} (\rho^* c^*)_i (T_i - T_{\text{ref}})(1 - m_i) V_i$$

Since the kinematic porosity is often around 10%, the quantity of heat is distributed in the proportion of about 90% in the solid material together with adhesive water, and only about 10% in free water. This distribution may vary considerably; for example, the porosities used for calculating the amount of heat stored in water in Late Jurassic systems in France range from 5 to 20% (Haenel and Staroste, 1988).

The volumetric method is frequently used to evaluate resources, as in the models adopted for the systems of Wairakei, Broadlands and Kawerau in New Zealand (Banwell, 1967; Macdonald and Muffler, 1972; Macdonald, 1976), Ahuachapán in El Salvador (Böðvarsson and Bolton, 1971; Cataldi, 1974), Paujetzk in Kamchatka, Russia (Sugrobov, 1970), and

Takinoue in Japan (Suyama *et al.*, 1975), as well as for other systems in Italy (Barelli *et al.*, 1975), the USA (White and Williams, 1975) and New Zealand (Bolton, 1976).

This method is also widely used for low enthalpy systems (e.g. in Haenel and Staroste, 1988).

6

Modelling of groundwater systems

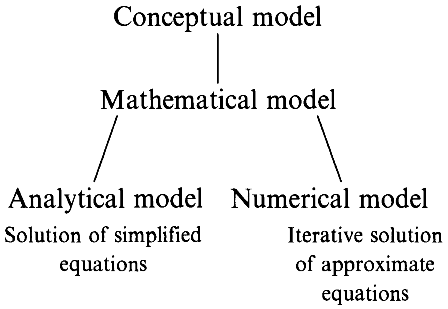
Everything flows and nothing stays.

Heraclitus c. 540–480 BC

6.1 CONCEPTUAL MODELS

At an early stage in exploration it is necessary to develop a conceptual model of the system (e.g. Figure 6.1). This provides a framework within which to plan investigations and hypotheses against which to test the data collected, as well as to plan exploitation. The usefulness of any model depends on whether it meets the users' requirements and these must be clearly defined so that the conceptual model can be developed accordingly.

Once a conceptual model has been formulated, it can be represented mathematically. Mathematical models may be solved analytically or numerically but can only be successful if the conceptual model used represents the system realistically. Analytical solutions are used for very simple conditions or as a rough check on the results of numerical modelling. Numerical modelling with the use of iterative calculations performed by a computer can cope with more complex situations and allows a closer approximation to real conditions.



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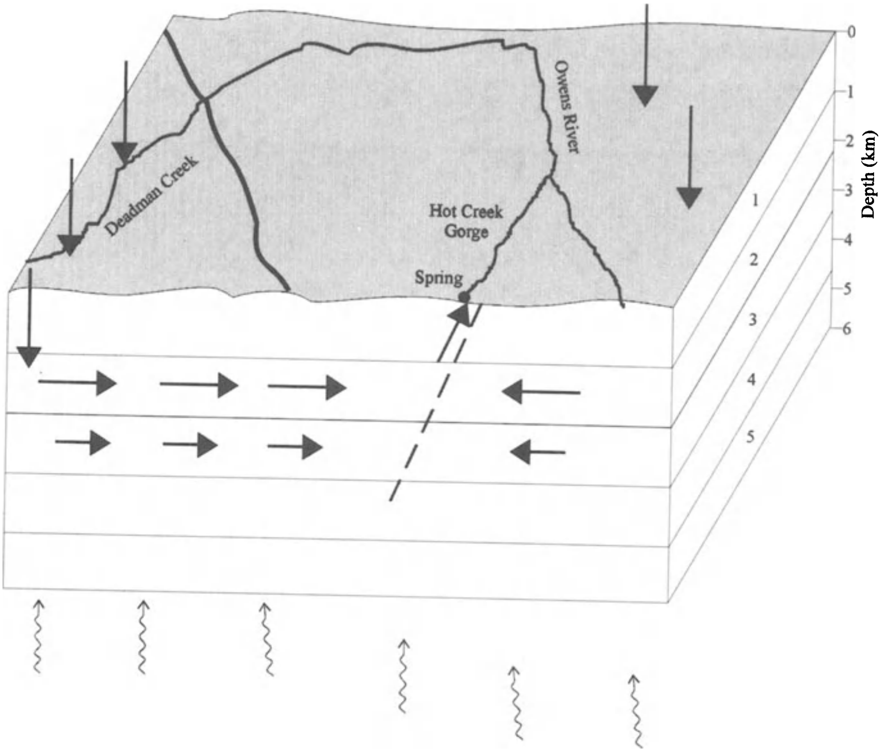


Figure 6.1 Conceptual model of the hydrothermal system of Long Valley caldera, California. (From Garg and Kassoy, 1981; after Sorey, 1976. Copyright John Wiley and Sons, with permission.)

6.2 CONSTRUCTING A MODEL

The following steps are usually followed in developing and utilizing mathematical models:

- defining the conceptual model and its boundaries;
- setting up the base for modelling and preparation of the model;
- estimation of the hydraulic or other parameters;
- calibration of the model;
- sensitivity testing;
- simulation of the evolution of the system in different possible variants;
- choosing the optimal variant for development and applying it to the development of the system; and
- improving the model as more data become available.

It should be noted that these steps are iterative to a large extent, and the conceptual model and even the boundaries may need to be modified as the understanding of the system improves.

Both analytical and numerical models should follow these steps, but in practice analytical solutions are often limited to fairly simplistic solutions and much of the description below therefore relates to numerical modelling. Depending on the type of system, the data base requires initial values and variations in time of:

- hydraulic head;
- the content of chemical components and of gases;
- temperature;
- pressure.

The first is sufficient to model groundwater flow where it is unaffected by temperature or gas content. The chemical content is needed for modelling the evolution of groundwater chemistry, while gas contents are required for some mineral systems. Temperature and pressure are necessary to model heat flow.

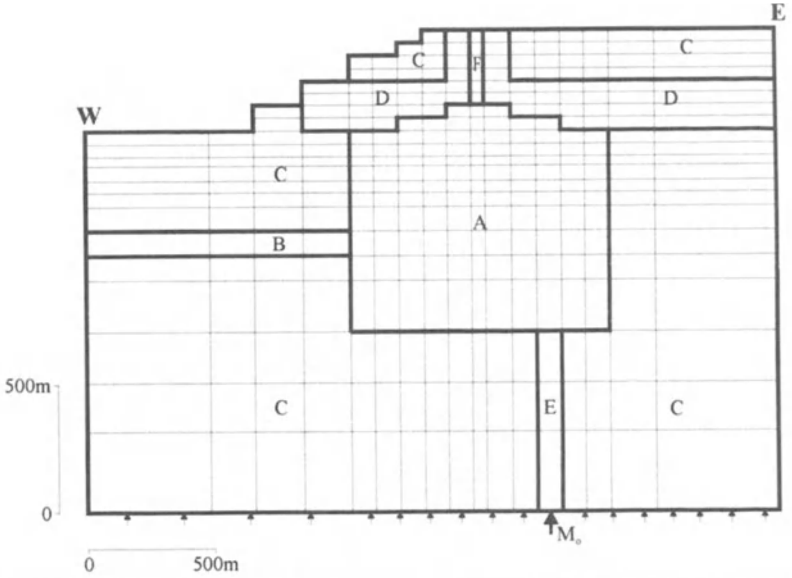
Maps are drawn up with isolines of known or estimated hydraulic head or pressure, mineralization and temperature at different times. The spatial variations of these parameters or their values at specific points and times are used for calibration of the model.

Boundary conditions of the system are established. The boundaries may be physical, such as impermeable strata, or they can be represented by constant values or fluxes of the parameters listed above. The definition of appropriate boundary conditions is possibly the step in model design that is most open to serious error (Franke *et al.*, 1987). A practical guide to setting up boundaries for modelling groundwater flow and advective transport is provided by Anderson and Woessner (1992).

The hydraulic conductivity or transmissivity, specific yield or storage coefficients, advection–diffusion and heat transmission (the characteristic parameters) are estimated, usually from aquifer test data. Space and time are discretized and are allocated data values to be used in the calculation. Figure 6.2 illustrates the discretization of space as a grid for numerical modelling.

The best estimates of the characteristic parameters are used to simulate the system, providing calculated values of head, pressure etc. The model is then calibrated by comparing the results of the simulation with the data base, preferably with data obtained by direct observation. The values for the input parameters are modified accordingly and the discretization of time and space may also be altered to allow convergence and stability of numerical solutions. The boundary conditions of the system are also validated by reference to known conditions at set times.

Once reasonable correspondence to the data values set for calibration is achieved, the model is run with different values of the characteristic parameters to determine the sensitivity of the model. For ease of interpretation, the parameters are normally altered one at a time. If the simulation results



Dimensions			
	Width (m)	Height (m)	Thickness (m)
Entire system	2850	1900	500
Reservoir (A)	1050	800	500
Fracture (F)	50	300	500
Deep conduit (E)	100	700	500
Horizontal conduit (B)	1100	100	500

Rock properties

Unit	Intrinsic permeability (m^2)	Porosity
A	1.0×10^{-13}	0.1
B	4.0×10^{-14}	0.1
C	1.0×10^{-15}	0.01
D	2.0×10^{-17}	0.01
E	1.0×10^{-13}	0.1
F	1.0×10^{-13}	0.1

Relative permeability (linear functions)
Residual liquid saturation = 0.3
Residual steam saturation = 0.05
Rock heat capacity = 1000 J/kg °C
Rock thermal conductivity = 2.5 W/m °C
Rock density = 2700 kg/m^3

Boundary conditions

Lateral	Closed to heat and mass flow, except at end of conduit B (P_1 = 4.6 MPa, constant)
Top	Open to heat and mass flow. Constant pressure = 0.1013 MPa; constant temperature (10°C, except at the top of fracture F which is kept at 100°C, reflecting the shallow soil temperatures measured around the fumaroles)
Bottom	Open to conductive heat flux of 5 HFU, except at the inlet of deep conduit E, and 2 HFU for 1100 m on the bottom west side. Mass input through conduit E: M_0 (kg/s) of T_0 (°C) fluid

Figure 6.2 Computational grid used in numerical modelling of the Ginyu reservoir, Japan. (From Yano and Ishido, 1995.)

do not change significantly then the accuracy of that parameter is not critical. If they do change significantly, the results of modelling may have to be qualified according to the degree of uncertainty in the input parameters. It must always be borne in mind that a model which gives a good calibration is not necessarily correct, nor a unique solution.

When the user is convinced that the model represents the system as accurately as is needed, predictive modelling can be carried out, forecasting the evolution of the system for a range of possible variants of development. The fundamental equations are integrated, and the resources of the system and the possible duration of development in the selected variants are estimated. The results are used to select the most economically efficient variant. Maps of prognosis are drawn up with isolines of hydraulic head, mineralization and temperature to represent the evolution of the system in the optimal variant of development. This variant is applied to the system and the behaviour of the system during development is observed. Periodically the real and simulated evolutions are compared and the model is tuned to the behaviour of the system during development (Albu, 1987).

6.3 FUNDAMENTAL EQUATIONS

In mineral and thermal water systems the processes of flow, solute transport and heat transport operate in accordance with the law of mass conservation (continuity principle), the first law of thermodynamics (law of conservation of energy) and the laws of transmission of energy, i.e. Darcy's law, Fick's first law and Fourier's law respectively, which are derived from the second law of thermodynamics. On the basis of these laws, the equations can be deduced for flow,

$$S\frac{\partial h}{\partial t} = \mathrm{div}(KH\,\mathrm{grad}\,h) + w \tag{6.1}$$

solute transport

$$m\frac{\partial(C\rho)}{\partial t} = \mathrm{div}[mD\,\mathrm{grad}(C\rho)] - m\vec{u}\,\mathrm{grad}(C\rho) + N \tag{6.2}$$

and heat transport

$$\tilde{\rho}\tilde{c}\frac{\partial T}{\partial t} = \mathrm{div}(\tilde{\kappa}\,\mathrm{grad}\,T) - \rho c m\vec{u}\,\mathrm{grad}\,T \tag{6.3}$$

where S = storage coefficient [dimensionless], $\partial/\partial t$ = partial derivative in respect of time [d^{-1}], t = time [d], h = hydraulic head [m], div = divergence operator [m^{-1}], K = hydraulic conductivity [$\mathrm{m\,d}^{-1}$], H = saturated thickness [m], grad = vector gradient operator [m^{-1}], w = rate of accumulation (e.g. recharge) [$\mathrm{m\,d}^{-1}$], m = kinematic porosity [dimensionless], C = relative solute concentration [dimensionless], ρ = density of water [$\mathrm{kg\,m}^{-3}$], $C\rho$ = solute concentration [$\mathrm{kg\,m}^{-3}$], D = coefficient of hydrodynamic dispersion [$\mathrm{m}^2\,\mathrm{d}^{-1}$], $\vec{u}$ = velocity of water [$\mathrm{m\,d}^{-1}$], N = mass productivity of solute

$[\mathrm{kg\,(m^3\,d)^{-1}}]$, $\tilde{\rho}$ = density of water-bearing rock $[\mathrm{kg\,m^{-3}}]$, $\tilde{c}$ = specific heat of water-bearing rock $[\mathrm{J\,(kg\,K)^{-1}}]$, T = temperature [K], $\tilde{\kappa}$ = thermal conductivity of water-bearing rock $[\mathrm{W\,(m\,K)^{-1}}]$ and c = specific heat of water $[\mathrm{J\,(kg\,K)^{-1}}]$. These equations correspond to hydraulic diffusion (groundwater flow), dispersion (advection–diffusion) and conduction–convection, which for homogeneous media are given by the particular forms

$$\frac{\partial h}{\partial t} = a\,\mathrm{div}\,\mathrm{grad}\,h + \frac{w}{S} \tag{6.4}$$

$$\frac{\partial (C\rho)}{\partial t} = D\,\mathrm{div}\,\mathrm{grad}(C\rho) - \vec{u}\,\mathrm{grad}(C\rho) + \frac{N}{m} \tag{6.5}$$

and

$$\frac{\partial T}{\partial t} = \tilde{\chi}\,\mathrm{div}\,\mathrm{grad}\,T - \frac{\rho c}{\tilde{\rho}\tilde{c}} m\vec{u}\,\mathrm{grad}\,T \tag{6.6}$$

where $a = KH/S$ = hydraulic diffusivity $[\mathrm{m^2\,d^{-1}}]$, $\tilde{\chi} = \tilde{\kappa}/(\tilde{\rho}\tilde{c})$ = thermal diffusivity of water-bearing rock $[\mathrm{m^2\,d^{-1}}]$.

Flow, solute transport and heat transport in mineral and thermal water systems may be determined by analytical or numerical integration of the fundamental equations (e.g. Hubbert, 1940; Boulton, 1954; Carslaw and Jaeger, 1959; Hantush, 1959; Scheidegger, 1960; De Josselin de Jong and Bossen, 1961; Bondarev and Nikolaevskij, 1962; De Weist, 1965; Luikov, 1966; Bear, 1969; Tye, 1969; Meixner, 1970; Holst and Aziz, 1972; Liw, 1972; Aladiev *et al.*, 1975; Garg *et al.*, 1975; Gringarten and Sauty, 1975; Renner *et al.*, 1975; Albu and Enăchescu, 1985). These solutions use values for initial conditions given by the functions $h = h(t, P)$, $C\rho = C\rho(t, P)$ and $T = T(t, P)$, where $t = 0$ (zero time) and P is the point in the system, together with set conditions on the boundaries of the system, given by

- values of the functions (Dirichlet conditions); or
- values their normal derivatives, i.e. their gradients or fluxes across the boundary (Neumann conditions); or
- values of a linear combination of the functions and their normal derivatives (Fourier conditions).

An exact determination of the evolution of the system would require values of the functions h, $C\rho$ and T at each instant and every point for the whole duration of evolution. However, in real life the values of the functions can only be known for a finite number of instants and points and elsewhere must be approximated from known values of initial and boundary conditions and from the coefficients of the fundamental equations. The calculated values comply better with reality as the known values increase in number and distribution both temporally and spatially, and as the initial and boundary conditions and coefficients of the fundamental equations are more accurately represented.

6.4 ANALYTICAL MODELLING

For homogeneous and isotropic conditions, the hydraulic diffusivity, dispersion and conductive–convection equations are presented in the forms (6.4), (6.5) and (6.6) respectively. These equations may be analytically integrated under restricted initial and boundary conditions and solutions for different conditions are given in Theis (1935), Muskat (1946), Jacob (1950), Hantush and Jacob (1955), Scheidegger (1961), Stallman (1962), Boulton (1963), Hantush (1964), De Wiest (1969), Bear (1972), Fetter (1994) and elsewhere.

A range of analytical solutions applied to hydrodynamic test data to determine aquifer characteristics is described in Krusemann and de Ridder (1991). The methods for evaluating resources and for determining the recoverability of heat, given in Chapters 5 and 7, are also analytical models.

6.5 NUMERICAL MODELLING

As with analytical solutions, numerical modelling is based on a conceptual model, analogous to the mathematical model adopted for the evolution and extent of the mineral or thermal water system. The equations of flow, solute transport and heat transport, as well as the initial and boundary conditions, are usually transformed into analogous finite difference or finite element equations and into the analogous conditions respectively. These are used in the first instance to calculate the coefficients of the equations for known values of the functions h, $C\rho$ and T for certain points and times within the system and on its boundaries.

Once a reasonable correspondence between the calculated and measured values of the coefficients is reached, it is considered that the model is calibrated and that it can be used for simulation of the system. The direct problem can then be solved numerically, predicting the evolution in time of the functions $h = h(t, P)$, $C\rho = C\rho(t, P)$ and $T = T(t, P)$.

6.5.1 Finite difference method

To present the finite difference method in the case of horizontal (two-dimensional) propagation (e.g. Peaceman and Rachford, 1955; Richtmyer, 1957; Collatz, 1960; Forsythe and Wasow, 1960; Douglas, 1961; Lax, 1965; Isaacson and Keller, 1966; Godunov and Reabenkii, 1973; Albu and Enăchescu, 1981; Garçon, 1981; Enăchescu and Albu, 1982; Albu and Drăghici, 1984; Albu and Enăchescu, 1985; Domenico and Schwartz, 1990), it is convenient to express equations (6.4), (6.5) and (6.6) as

$$\frac{\partial h}{\partial t}=a\left(\frac{\partial^2 h}{\partial x^2}+\frac{\partial^2 h}{\partial y^2}\right)+\frac{w}{S} \tag{6.7}$$

$$\frac{\partial(C\rho)}{\partial t}=D\left[\frac{\partial^2(C\rho)}{\partial x^2}+\frac{\partial^2(C\rho)}{\partial y^2}\right]+\frac{K}{m}\left[\frac{\partial h}{\partial x}\frac{\partial(C\rho)}{\partial x}+\frac{\partial h}{\partial y}\frac{\partial(C\rho)}{\partial y}\right]+\frac{N}{m} \tag{6.8}$$

and

$$\frac{\partial T}{\partial t}=\tilde{\chi}\left(\frac{\partial^2 T}{\partial x^2}+\frac{\partial^2 T}{\partial y^2}\right)+\frac{\rho c}{\tilde{\rho}\tilde{c}}K\left(\frac{\partial h}{\partial x}\frac{\partial T}{\partial x}+\frac{\partial h}{\partial y}\frac{\partial T}{\partial y}\right) \tag{6.9}$$

respectively, where w/S and N/m are, in general, functions of time and position. If time is discretized into steps of equal length $\Delta t=\tau$ and the domain into a square grid with intervals of $\Delta x=\Delta y=\lambda$, the values of hydraulic head, solute concentration and temperature at the nth instant and at point (i,j) can be written as $h_{n,i,j}=h(n\tau,i\lambda,j\lambda)$; $C\rho_{n,i,j}=C\rho(n\tau,i\lambda,j\lambda)$ and $T_{n,i,j}=T(n\tau,i\lambda,j\lambda)$, then the partial differential equations (6.7), (6.8) and (6.9) can be given in the form of the finite difference equations

$$\begin{aligned}h_{n+1,i,j}&-\left(1-\frac{4\tau}{\lambda^2}a_{n,i,j}\right)h_{n,i,j}\\&=\frac{\tau}{\lambda^2}a_{n,i,j}(h_{n,i-1,j}+h_{n,i+1,j}+h_{n,i,j-i}+h_{n,i,j+1})+\tau\left(\frac{w}{S}\right)_{n,i,j}\end{aligned} \tag{6.10}$$

$$\begin{aligned}C\rho_{n+1,i,j}&-\left(1-\frac{4\tau}{\lambda^2}D_{n,i,j}\right)C\rho_{n,i,j}\\&=\frac{\tau}{\lambda^2}D_{n,i,j}(C\rho_{n,i-1,j}+C\rho_{n,i+1,j}+C\rho_{n,i,j-i}+C\rho_{n,i,j+1})\\&\quad+\frac{\tau}{4\lambda^2}\left(\frac{K}{m}\right)_{n,i,j}[(h_{n,i+1,j}-h_{n,i-1,j})(C\rho_{n,i+1,j}-C\rho_{n,i-1,j})\\&\quad+(h_{n,i,j+1}-h_{n,i,j-1})(C\rho_{n,i,j+1}-C\rho_{n,i,j-1})]+\tau\left(\frac{N}{m}\right)_{n,i,j}\end{aligned} \tag{6.11}$$

and

$$\begin{aligned}T_{n+1,i,j}&-\left(1-\frac{4\tau}{\lambda^2}\tilde{\chi}_{n,i,j}\right)T_{n,i,j}\\&=\frac{\tau}{\lambda^2}\tilde{\chi}_{n,i,j}(T_{n,i-1,j}+T_{n,i+1,j}+T_{n,i,j-i}+T_{n,i,j+1})\\&\quad+\frac{\tau}{4\lambda^2}\left(\frac{\rho c}{\tilde{\rho}\tilde{c}}K\right)_{n,i,j}[(h_{n,i+1,j}-h_{n,i-1,j})(T_{n,i+1,j}-T_{n,i-1,j})\\&\quad+(h_{n,i,j+1}-h_{n,i,j-1})(T_{n,i,j+1}-T_{n,i,j-1})]\end{aligned} \tag{6.12}$$

To ensure the convergence and stability of the solutions of these three finite difference equations (Evans *et al.*, 1954; Douglas, 1956; Albu, 1984; Albu and Enăchescu, 1985) the values of τ and λ must be chosen to meet the conditions

$$0 \leq 1 - \frac{4\tau}{\lambda^2} a_{n,i,j} < 1, \quad 0 \leq 1 - \frac{4\tau}{\lambda^2} D_{n,i,j} < 1, \quad 0 \leq 1 - \frac{4\tau}{\lambda^2} \tilde{\chi}_{n,i,j} < 1 \qquad (6.13)$$

$$\begin{aligned} &0 \leq \frac{\tau}{\lambda^2}\left[D_{n,i,j} + \frac{1}{4}\left(\frac{K}{m}\right)_{n,i,j}(h_{n,i+1,j} - h_{n,i-1,j})\right] < 1, \\ &0 \leq \frac{\tau}{\lambda^2}\left[\tilde{\chi}_{n,i,j} + \frac{1}{4}\left(\frac{\rho c}{\tilde{\rho}\tilde{c}}K\right)_{n,i,j}(h_{n,i+1,j} - h_{n,i-1,j})\right] < 1 \end{aligned} \qquad (6.14)$$

and

$$\begin{aligned} &0 \leq \frac{\tau}{\lambda^2}\left[D_{n,i,j} + \frac{1}{4}\left(\frac{K}{m}\right)_{n,i,j}(h_{n,i,j+1} - h_{n,i,j-1})\right] < 1, \\ &0 \leq \frac{\tau}{\lambda^2}\left[\tilde{\chi}_{n,i,j} + \frac{1}{4}\left(\frac{\rho c}{\tilde{\rho}\tilde{c}}K\right)_{n,i,j}(h_{n,i,j+1} - h_{n,i,j-1})\right] < 1 \end{aligned} \qquad (6.15)$$

The coefficients $a_{n,i,j}$, $D_{n,i,j}$, $\tilde{\chi}_{n,i,j}$, $(K/m)_{n,i,j}$ and $(\rho c K/\tilde{\rho}\tilde{c})_{n,i,j}$, $(w/S)_{n,i,j}$ and $(N/m)_{n,i,j}$ may be estimated using the method of least squares by applying the finite difference equations (6.10), (6.11) and (6.12) repeatedly at the grid nodes at the times for which measurements or estimates of hydraulic head, solute concentration and temperature are available (numerical solution of the inverse problem).

The seven coefficients may be estimated for any unsteady state mineral or thermal water system from maps showing isolines of hydraulic head, mineralization and temperature. Maps for at least two different times are required for the finite difference equations to be applied.

After estimating the coefficients, the same equations may be used for the prognosis of values of the hydraulic head, solute concentration and temperature at any point in the system (numerical solution of the direct problem). Such forecasts are possible as long as they do not cause fundamental changes to conditions on the boundaries of the mineral or thermal water system. The solutions are not unique and must compare with the range of possible values determined by experience and from analytical solutions. By these means not only is the determination of the coefficients, and reconstituting and/or forecasting the evolution of the mineral or thermal water system in the given variant made possible, but also the simulation of its behaviour in other variants corresponding to different distributions of abstraction and injection wells and to different flow rates of wells (Lasseter and Witherspoon, 1975; Albu and Enăchescu, 1981; Albu and Drăghici, 1984; Merrit, 1993).

6.5.2 Finite element method

The hydraulic diffusivity, dispersion and conductive–convection equations generally comply with a functional equation of the type

$$\mathbf{A}\varphi = z \tag{6.16}$$

where the unknown function $\varphi = h$, $C\rho$, T must be determined to give the function z and the operator $\mathbf{A}$. In keeping with the fundamental Ritz theorem of existence and uniqueness (by the method of the extremes of quadratic functionals), if the operator $\mathbf{A}$ is positive, definite and therefore self-adjoint (satisfying the equality of the scalar products

$$\langle \mathbf{A}\varphi, z\rangle = \int_A (\mathbf{A}\varphi)z\,\mathrm{d}\mathbf{A} \qquad \text{and} \qquad \langle \varphi, \mathbf{A}z\rangle = \int_A \varphi\mathbf{A}z\,\mathrm{d}\mathbf{A}$$

for any φ and z) and at the same time linear, then the solution $\varphi = \varphi_\infty$ of equation (6.16) exists and minimizes the real quadratic functional

$$Z(\varphi) = \langle \mathbf{A}\varphi, \varphi\rangle - \langle \varphi, z\rangle - \langle z, \varphi\rangle$$

Equation (6.16) is usually solved by either the Galerkin or the Ritz method of approximation (Gutmann, 1965). The Galerkin method consists of finding the approximate solution

$$\varphi_n = \sum_{\alpha=1}^{n} \varphi_\alpha \xi_\alpha \approx \varphi_\infty = \sum_{\alpha=1}^{\infty} \varphi_\alpha \xi_\alpha \tag{6.17}$$

in a finite-dimensional subspace A_n of basis $(\xi_1, \xi_2, \ldots, \xi_n)$ of a space A of basis $(\xi_1, \xi_2, \ldots, \xi_n, \xi_{n+1}, \ldots)$ so that

$$\sum_{\alpha=1}^{n} \varphi_\alpha \mathbf{A}\xi_\alpha = z \tag{6.18}$$

Calculating the scalar products $\langle z, \xi_\beta\rangle$ for $\beta = 1, 2, \ldots, n, n+1, \ldots,$ and selecting the first n equations (for $\beta = 1, 2, \ldots, n$) from the infinite number of equations

$$\sum_{\alpha=1}^{n} \varphi_\alpha \langle \mathbf{A}\xi_\alpha, \xi_\beta\rangle = \langle z, \xi_\beta\rangle$$

the parameters $\varphi_1, \varphi_2, \ldots, \varphi_n$ may be obtained if the determinant $\|\langle \mathbf{A}\xi_\alpha, \xi_\beta\rangle\|$ is not zero, where $\alpha, \beta = 1, 2, \ldots, n$. The approximate solution

$$\varphi_n = \sum_{\alpha=1}^{n} \varphi_\alpha \xi_\alpha$$

represents the projection of the exact solution

$$\varphi_\infty = \sum_{\alpha=1}^{\infty} \varphi_\alpha \xi_\alpha$$

on the given subspace A_n.

The Ritz approximation method is based on his theorem of existence and uniqueness of the solution for equation (6.16). A sequence of functions (vectors)

$$\varphi_n = \sum_{\alpha=1}^{n} \varphi_\alpha \xi_\alpha$$

is determined for the minimum values of the functional $Z(\varphi_n) = f(\varphi_1, \varphi_2, \dots, \varphi_n)$, i.e.

$$\frac{\partial f}{\partial \varphi_\alpha} = 2\sum_{\beta=1}^{n} \langle \mathbf{A}\xi_\alpha, \xi_\beta \rangle \varphi_\beta - 2\langle z, \xi_\alpha \rangle = 0 \tag{6.19}$$

which gives unique values for φ_1, φ_2, ..., φ_n when the determinant $\|\langle \mathbf{A}\xi_\alpha, \xi_\beta \rangle\|$ is not zero. By means of the parameters thus calculated the approximate solution (6.17) is obtained. In particular, if

$$\langle \mathbf{A}\xi_\alpha, \xi_\beta \rangle = \delta_{\alpha\beta} = \begin{cases} 0 & \text{when } \alpha \neq \beta \\ 1 & \text{when } \alpha = \beta \end{cases} \tag{6.20}$$

where α, $\beta = 1, 2, \dots, n$, then

$$\sum_{\beta} \delta_{\alpha\beta} \varphi_\beta = \langle z, \xi_\alpha \rangle \tag{6.21}$$

and consequently

$$\varphi_\alpha = \langle z, \xi_\alpha \rangle \quad \text{and} \quad \varphi_n = \sum_{\alpha=1}^{n} \langle z, \xi_\alpha \rangle \xi_\alpha \tag{6.22}$$

The Galerkin and Ritz methods of approximation are the basis of the finite element method (Turner *et al.*, 1956; Clough, 1960; Taylor and Hood, 1973; Witherspoon and Neuman, 1973; Pinder and Gray, 1977; Brătianu, 1983; Marsily, 1986; Sudicky, 1989). This represents a systematic procedure to approximate a continuous function $h = h(t, P)$, $C\rho = C\rho(t, P)$ or $T = T(t, P)$ by a discrete model formed by a set of values of the function given for a finite number of selected times and points, together with the local approximation in portions of the domain of the function in a finite number of subdomains named finite elements. The local approximation of the function for each subdomain is defined in respect of its discrete values at the selected times and points.

In essence, the construction of a finite element model involves the identification of a finite number of times and points for which values of the function can be approximated. The points at which values of this function are specified are considered as nodes. Lines joining the nodes subdivide the domain into a number of spatial elements (finite elements) within which the function is approximated as a continuous function, uniquely defined in respect of the values of the function given for different times at the nodes of each element.

In the case of solute transport, without supplementary sources of mineralization, equation (6.2) may be presented in the form

$$m\frac{\partial(C\rho)}{\partial t} = \frac{\partial}{\partial x_i}\left[(mD)_{ij}\frac{\partial(C\rho)}{\partial x_j}\right] - (mu)_i\frac{\partial(C\rho)}{\partial x_i} \qquad (6.23)$$

with the initial condition $C\rho(0, x_i) = C\rho_0(x_i)$ inside A, and with boundary conditions $C\rho = C\rho_*$ on L_1 and $(mD)_{ij}[\partial(C\rho)/\partial x_j]n_i = -q(t, x_i)$ on L_2, where $(mD)_{ij}$ is the coefficient of dispersional conductivity, considered as a symmetrical and positive tensor $[(mD)_{ij} = (mD)_{ji} \geq 0]$ defined as

$$(mD)_{ij} = F[x_i, (mu)_i] = G_{ij}|mu|$$

with G_{ij} assumed constant; $(mu)_i$ is the density of convective flux (specific discharge), assumed dependent on point and independent of time; $\partial(C\rho)/\partial x_i$ is the gradient of the solute concentration;

In the case of heat transport, without interior sources of heat, equation (6.3) may be presented in the form

$$\tilde{\rho}\tilde{c}\frac{\partial T}{\partial t} = \frac{\partial}{\partial x_i}\left(\tilde{\kappa}_{ij}\frac{\partial T}{\partial x_j}\right) - (\rho cmu)_i\frac{\partial T}{\partial x_i} \qquad (6.23)$$

with the initial condition $T(0, x_i) = T_0(x_i)$ inside A, and with boundary conditions $T = T_*$ on L_1 and $\tilde{\kappa}_{ij}(\partial T/\partial x_j)n_i = -q(t, x_i)$ on L_2, where $\tilde{\kappa}_{ij}$ is the coefficient of thermal conductivity, considered as a symmetrical and positive tensor $(\tilde{\kappa}_{ij} = \tilde{\kappa}_{ji} \geq 0)$ defined as

$$\tilde{\kappa}_{ij} = F[x_i, (\rho cmu)_i] = G_{ij}|\rho cmu|$$

with G_{ij} assumed constant; $(\rho cmu)_i$ is the density of convective flux of caloric capacity assumed dependent on point and independent of time; $\partial T/\partial x_i$ is the gradient of the temperature;

n_i indicates the normal to the boundary $L = L_1 \cup L_2$ oriented outwards from the domain **A** of the mineral water system or thermal water system,

m is the kinematic porosity and q is the density of the flux of dispersion, where $i, j = 1, 2, 3$.

Applying the operator

$$\mathbf{A} \equiv m\frac{\partial}{\partial t} - \frac{\partial}{\partial x_i}\left[(mD)_{ij}\frac{\partial}{\partial x_j}\right] + (mu)_i\frac{\partial}{\partial x_i}$$

$\tilde{\rho}\tilde{c}$ is the average heat capacity per unit volume and q is the density of the flux of heat conduction, where $i, j = 1, 2, 3$.

Applying the operator

$$\mathbf{A} \equiv \tilde{\rho}\tilde{c}\frac{\partial}{\partial t} - \frac{\partial}{\partial x_i}\left(\tilde{\kappa}_{ij}\frac{\partial}{\partial x_j}\right) + (\rho cmu)_i\frac{\partial}{\partial x_i}$$

to the function $C\rho$, the expression

$$\mathbf{A}(C\rho) = m\frac{\partial(C\rho)}{\partial t} - \frac{\partial}{\partial x_i} \times \left[(mD)_{ij}\frac{\partial(C\rho)}{\partial x_j}\right] + (mu)_i\frac{\partial(C\rho)}{\partial x_i} \qquad (6.24)$$

to the function T, the expression

$$\mathbf{A}T \equiv \tilde{\rho}\tilde{c}\frac{\partial T}{\partial t} - \frac{\partial}{\partial x_i}\left(\tilde{\kappa}_{ij}\frac{\partial T}{\partial x_j}\right) + (\rho cmu)_i\frac{\partial T}{\partial x_i} \qquad (6.24)$$

is obtained. This expression is not self-adjoint and therefore is not suited to develop a variational principle in the sense of the Ritz method, but it may be represented by Galerkin's method of approximation. In keeping with the latter method, if the approximation

$$(C\rho)_n = \sum_{\alpha=1}^{n} C\rho_\alpha \xi_\alpha \qquad (6.25)$$

is used for the function $C\rho$,

$$T_n = \sum_{\alpha=1}^{n} T_\alpha \xi_\alpha \qquad (6.25)$$

is used for the function T,

where n is the number of nodes in the domain A, discretized into $e = 1, 2, \ldots$ finite elements, then equation (6.23) can be shown as the analogous tensorial equation

$$\sum_e \int_{\mathbf{A}^e} \left\{ -m\frac{\partial(C\rho)}{\partial t}\xi^e_\alpha + \frac{\partial}{\partial x_i} \times \left[(mD)_{ij}\frac{\partial \xi^e_\beta}{\partial x_j}\right] C\rho_\beta \xi^e_\alpha - (mu)_i \times \frac{\partial \xi^e_\beta}{\partial x_i} C\rho_\beta \xi^e_\alpha \right\} \mathrm{d}\mathbf{A} = 0 \qquad (6.26)$$

$$\sum_e \int_{\mathbf{A}^e} \left\{ -\tilde{\rho}\tilde{c}\frac{\partial(T)}{\partial t}\xi^e_\alpha + \frac{\partial}{\partial x_i} \times \left(\tilde{\kappa}_{ij}\frac{\partial \xi^e_\beta}{\partial x_j}\right) T_\beta \xi^e_\alpha - (\rho cmu)_i \times \frac{\partial \xi^e_\beta}{\partial x_i} T_\beta \xi^e_\alpha \right\} \mathrm{d}\mathbf{A} = 0 \qquad (6.26)$$

with the conversion of summation by $\beta = 1, 2, \ldots, n$, where the local derivative, kept in the initial form, is defined in each α node by the relationship

$$\left[\frac{\partial(C\rho)}{\partial t}\right]_\alpha = \frac{\sum_e \int_{\mathbf{A}^e} m\frac{\partial(C\rho)}{\partial t}\xi^e_\alpha \,\mathrm{d}\mathbf{A}}{\sum_e \int_{\mathbf{A}^e} m\xi^e_\alpha \,\mathrm{d}\mathbf{A}} \qquad (6.27)$$

$$\left(\frac{\partial T}{\partial t}\right)_\alpha = \frac{\sum_e \int_{\mathbf{A}^e} \tilde{\rho}\tilde{c}\frac{\partial T}{\partial t}\xi^e_\alpha \,\mathrm{d}\mathbf{A}}{\sum_e \int_{\mathbf{A}^e} \tilde{\rho}\tilde{c}\xi^e_\alpha \,\mathrm{d}\mathbf{A}} \qquad (6.27)$$

Assuming that the coefficients $(mD)_{ij}$ and $(mu)_i$ are constant in each element, and introducing the

Assuming that the coefficients $\tilde{\kappa}_{ij}$ and $(\rho cmu)_i$ are constant in each element, and introducing the notation

$$\sum_e \int_{\mathbf{A}^e} m\xi_\alpha^e \, \mathrm{d}\mathbf{A} = P_\alpha \qquad (6.28)$$

$$\sum_e \int_{\mathbf{A}^e} (mD)_{ij} \frac{\partial \xi_\alpha^e}{\partial x_j} \times \frac{\partial \xi_\beta^e}{\partial x_i} \, \mathrm{d}\mathbf{A} = \mathbf{A}Q_{\alpha\beta} \qquad (6.29)$$

$$\sum_e \int_{\mathbf{A}^e} (mu)_i \xi_\alpha^e \times \frac{\partial \xi_\beta^e}{\partial x_i} \, \mathrm{d}\mathbf{A} = R_{\alpha\beta} \qquad (6.30)$$

and

$$-\sum_e \int_{L_2^e} q\xi_\alpha^e \, \mathrm{d}L = S_\alpha \qquad (6.31)$$

the analogous equation (6.26) can be written as

$$P_\alpha \left[\frac{\partial (C\rho)}{\partial t}\right]_\alpha + (\mathbf{A}Q_{\alpha\beta} + R_{\alpha\beta}) C\rho_\beta = S_\alpha \qquad (6.32)$$

If the coefficients $(mD)_{ij}$ and $(mu)_i$ are not constant, but vary linearly within each element, they are replaced by the linear approximations

$$(mD)_{ij} = [(mD)_{ij}]_\beta^e \xi_\beta^\alpha$$

and

$$(mu)_i = [(mu)_i]_\beta^e \xi_\beta^e$$

notation

$$\sum_e \int_{\mathbf{A}^e} \tilde{\rho}\tilde{c}\xi_\alpha^e \, \mathrm{d}\mathbf{A} = P_\alpha \qquad (6.28)$$

$$\sum_e \int_{\mathbf{A}^e} \tilde{\kappa}_{ij} \frac{\partial \xi_\alpha^e}{\partial x_j} \times \frac{\partial \xi_\beta^e}{\partial x_i} \, \mathrm{d}\mathbf{A} = \mathbf{A}Q_{\alpha\beta} \qquad (6.29)$$

$$\sum_e \int_{\mathbf{A}^e} (\rho cmu)_i \xi_\alpha^e \times \frac{\partial \xi_\beta^e}{\partial x_i} \, \mathrm{d}\mathbf{A} = R_{\alpha\beta} \qquad (6.30)$$

and

$$-\sum_e \int_{L_2^e} q\xi_\alpha^e \, \mathrm{d}L = S_\alpha \qquad (6.31)$$

the analogous equation (6.26) can be written as

$$P_\alpha \left(\frac{\partial T}{\partial t}\right)_\alpha + (\mathbf{A}Q_{\alpha\beta} + R_{\alpha\beta}) T_\beta = S_\alpha \qquad (6.32)$$

If the coefficients $\tilde{\kappa}_{ij}$ and $(\rho cmu)_i$ are not constant, but vary linearly inside each element, they are replaced by the linear approximations

$$\tilde{\kappa}_{ij} = (\tilde{\kappa}_{ij})_\beta^e \xi_\beta^e$$

and

$$(\rho cmu)_i = [(\rho cmu)_i]_\beta^e \xi_\beta^e$$

The Ritz method of approximation may be used to solve the same problem, using the definitions

$$-\frac{\partial}{\partial x_i}\left[(mD)_{ij} \frac{\partial (C\rho)}{\partial x_j}\right] = \mathbf{A}(C\rho)$$

and

$$-m\frac{\partial (C\rho)}{\partial t} - (mu)_i \frac{\partial (C\rho)}{\partial x_i} = z$$

$$-\frac{\partial}{\partial x_i}\left(\tilde{\kappa}_{ij} \frac{\partial T}{\partial x_j}\right) = \mathbf{A}T$$

and

$$-\tilde{\rho}\tilde{c}\frac{\partial T}{\partial t} - (\rho cmu)_i \frac{\partial T}{\partial x_i} = z$$

and thus forming a functional equation of the type $\mathbf{A}(C\rho) = z$,	and thus forming a functional equation of the type $\mathbf{A}T = z$,

the numerical solution of which is equivalent to that obtained from the application of Galerkin's method of approximation (Witherspoon and Neuman, 1973).

As in the case of the finite difference method, the application of the finite element method aims to calibrate the model, to reconstitute and/or predict the evolution of the mineral or thermal water system in different variants, and establish the optimal variant for exploitation and regeneration.

6.6 COMPARISON OF MODELLING METHODS

The mathematical modelling of mineral and thermal water systems may be successfully achieved by analytical or numerical integration of the equations of flow, solute transport and heat transport. These methods can be adapted to concrete situations related to mineral and thermal water systems and allow satisfactory solutions to be obtained for the reconstruction and prediction of their evolution.

A concise comparative analysis of modelling methods and techniques, showing their advantages and disadvantages, is presented in Table 6.1.

Most managers or consultants will use commercially available software to solve their problems. There are now many models available, both finite

Table 6.1 Comparison of modelling methods and techniques

Model type	*Usual methods or techniques*	*Advantages*	*Disadvantages*
Analytical	Separation of variables, Fourier transforms, Laplace transform, Green's functions	Precise determination of parameters and functions	Simplifying conditions and restricted subdomains of applicability
Numerical	Finite difference, Monte Carlo, least squares	Satisfactory estimation of functions for the whole domain of application, very accessible technique of integration	Conditions for convergence and stability of the solutions, approximate tracing of boundaries and limits of non-homogeneity
	Finite element (Galerkin, Ritz)	Satisfactory estimation of functions for the whole domain of application, flexibility in tracing of boundaries and limits of non-homogeneity	Condition: to develop a variational principle, special techniques of integration required

difference and finite element. The performance of such calculation programs depends on the validity of the model adopted for simulation of the system. Most, such as the well-tried MODFLOW and PLASM (finite difference) and AQUIFEM and AQUA (finite element) aim mainly to simulate groundwater flow as continua in systems which are dominated by intergranular flow. This is not as limiting as it may at first appear. Many systems with significant fracture flow can be represented as intergranular flow continua if a large enough volume of the system, the representative elementary volume, is included in the model. How large such a volume should be, however, is still the subject of discussion and research and may not be the same for flow and solute transport (Guérin and Billaux, 1994).

Commercially available software capable of simulating two-phase flow and heat transport is still limited due to the complexity of the systems being investigated. USGS codes such as HT3D, and the code TOUGH are used to simulate heat transport; MUSHRM (Garg *et al.*, 1977) can treat multiphase, multispecies fluid flow in three dimensions. This model has been used to test different hypotheses concerning, for example, boundaries, temperature distribution, groundwater flow and convective flow in the Salton Sea geothermal field (Garg and Kassoy, 1981). TOUGH2 is a more recent model used for simulating multicomponent, multiphase fluids (Lai *et al.*, 1994), and has been applied to predict phase distribution in high temperature systems. By now there are doubtless many other models available commercially, however, for many problems computer codes have to be written from scratch to simulate the required conditions. An example of the use of numerical modelling to define expected thermal regimes is given in Figure 4.8. Two different bulk permeabilities are used, giving a guide as to what could be expected in a real situation.

Where a model cannot represent known conditions, it can still contribute to an understanding of the type and characteristics of the system. Wilson and Luheshi (1987) found that the thermal regime of the East Midlands aquifer system in the UK could not be simulated by a two-dimensional model. This helped to determine that the distribution of the measured heat anomaly was due to three-dimensional fluid and heat flow. Barker (Downing *et al.*, 1984) developed a three-layer model to simulate a pumping test carried out on a low enthalpy geothermal well at Southampton, UK. The model simulated drawdowns closely, but predicted levels 20–30 m higher than measured on recovery. This was taken to indicate that the transmissivity of the Permo-Triassic sandstone decreased away from the well.

7

Exploitation and management of mineral and thermal waters

> *Nos numerus sumus et finges consumere nati – We are just statistics, born to consume resources*
>
> Horace, Epistles Book 1, no. 2, 1.40

7.1 ABSTRACTION OF MINERAL WATERS

Mineral waters have traditionally been exploited at natural emergences such as springs, by wells or shafts up to tens of metres deep and more rarely by drainage galleries. Springs are often improved to protect the source and provide ready access to the water. Improvements may range in complexity from simple collection structures to the provision of storage tanks, gas bells to release gas pressure, housing built over the source (Figures I.1 and 12.1, for example) and piped reticulation systems.

Karstic limestone aquifers are still often exploited through natural springs, augmented in places with galleries and shafts to tap water from below the natural spring level. The quantity of water abstracted from these traditional sources is generally limited, and creates only a small to moderate disturbance of the natural state of the mineral water system.

In most sedimentary basins, mineral water sources today generally comprise boreholes of relatively great depth, often of hundreds of metres (Costache and Gavan, 1986). The use of boreholes to withdraw mineral waters can modify the natural state of the system quite severely since higher abstraction rates are often used compared to the discharge from other sources.

In the case of non-artesian carbonated waters it is necessary to avoid the use of air-lift pumping, which strips the carbon dioxide from the water.

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M. Albu, D. Banks and H. Nash.
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Submersible pumps should be lowered to below the depth where carbon dioxide is released from solution in order to retain the gas.

7.2 ABSTRACTION OF THERMAL WATERS

Thermal waters are extracted primarily for their heat content and only secondarily for their mineral content. High crustal temperatures and good aquifer permeability are the most important factors giving rise to thermal water systems from which heat can be obtained.

The heat is extracted from liquid water or steam, which may be brought to the surface at natural emergences such as fumaroles, solfataras, mofettes (Figure 14.11), geysers and springs, or via wells and boreholes, which may be several thousand metres deep in sedimentary basins.

Most high enthalpy and many low enthalpy thermal water systems are artesian in the initial state, however as pressures decline pumping equipment may be necessary. Even where artesian pressures are maintained, the use of pumps is recommended for high enthalpy systems (Bowen, 1989). In this case flashing (vaporization) and accompanying scaling within the well, and even sealing of the reservoir due to precipitation of silica, are reduced and the liquid or steam is obtained at a higher temperature, making exploitation more economically feasible. Although the yield of steam increases with decreasing pressure at the wellhead, the amount of electrical energy that can be generated decreases with decreasing steam pressure and it is necessary to optimize the operating pressure and yield of steam to give the maximum power generation (Bouwer, 1978).

To maintain hydraulic heads, or at least to minimize drawdowns, it is often necessary to reinject steam condensate and waste water (often brine) into productive horizons to maintain pressure in the system. Reinjection also improves the recovery of heat from the reservoir and reduces the risk of subsidence. In this way groups of positive and negative sources are used to optimize production. It is not always necessary to have one injection well to every production well as in Figure 7.1: at The Geysers, the ratio is about 1 to 14.

Reinjection is often a necessary requisite for exploitation of inland sites, since the disposal of poor quality water to the surface may be unacceptable. At Southampton, UK, the waste water could be disposed of to the sea; there was no need to go to the expense of drilling a second deep well, making exploitation of a low temperature, limited resource more viable.

The technique of reinjection generally has few problems and successful systems have operated for several years at Ahuachapán (El Salvador), Otopeni (Romania), in Italy, the USA and France. However, the disposal of large volumes of waste water presents greater difficulties (Böðvarsson, 1972) unless high quality water is injected. Filtering of particles $>5\,\mu m$, and ideally $>1\,\mu m$, removal of oxygen, chlorination and pH control of the

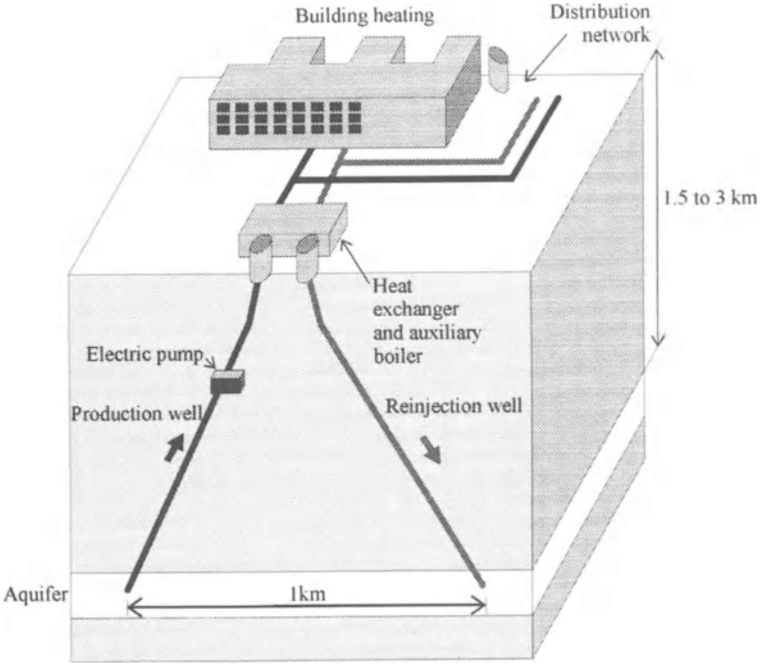

Figure 7.1 Schematic diagram of a doublet system: one production well and one injection well.

injected water are recommended to minimize corrosion, precipitation of silica and carbonates and clogging (British Geological Survey, 1988; Downing, 1986). It is common practice to use old production wells, which may be too shallow or in which pressures have declined, as injection wells.

7.3 DRILLING AND BOREHOLE CONSTRUCTION

Different types of drilling systems are described in Papuc (1965) and Driscoll (1986) amongst others. For the relatively shallow wells required for mineral waters, a variety of methods may be used but for deeper wells rotary drilling is the norm. The cost of drilling often determines that exploratory boreholes are utilized for production purposes and there is little difference in their construction (Costache and Găvan, 1986). In addition to production and injection wells, observation wells are also constructed in order to monitor the behaviour of the system during exploitation.

High temperatures and saline fluids affect the physical properties of drilling muds and the density has to be carefully controlled. Investigation of the Pannonian Basin by the Geological Survey of the Slovak Republic involved sampling of drilling mud every 5 m (Franko *et al.*, 1989), while in other countries continuous monitoring may be carried out. Sepiolite clay may be substituted for bentonite since it is less liable to flocculate at high temperatures; lignite or chrome may be added to the mud to give it greater stability. In vapour-dominated high temperature systems, air is often used in the productive zones to avoid sealing them with mud (Greene and Goodman, 1982). The collection of rock and water samples during drilling is essential for effective well design and assessment of the economic value of the resource (Iordache, 1977). If the water is to be bottled for consumption, continuous disinfection may be carried out while drilling.

Construction of production wells must ensure that screens with as great an open area as possible are set against the most productive horizons. The permeability of the aquifers of interest may be improved near the borehole by high velocity surging, acidification and other well development procedures in order to maximize the yield (Driscoll, 1986). Construction should allow the selective exploitation of individual horizons containing thermal water of specific temperatures, or mineral water of specific composition: mixed waters often cause problems with scaling. There should also be space for the introduction of intervention devices (for repair and maintenance, replacing screens and acidification) and monitoring equipment in addition to pumping equipment. A typical construction of a well for abstracting high temperature waters is shown in Figure 7.2, while another for low temperature water can be seen in Figure 16.10; this has an inner tubing to control artesian flow. The tubing collects much of the carbonate scale and, since it is removable, it provides a simple and economic means of cleaning the well.

Drilling in high temperature fields can cause hazards such as blowouts, possibly leading to landslides. Where the ground is unstable, as in parts of the Wairakei field, boreholes may be set at an angle, utilizing areas of stable ground at the surface. Angle drilling is also used, as in the Paris Basin of France, to reduce the cost of surface pipelines to and from injection wells and abstraction wells, as in Figure 7.1.

The corrosive nature of many mineral and thermal waters often dictates that non-reactive plastic casings and screens, sometimes reinforced with glass fibre (GRP), are used for relatively shallow depths, while different grades of stainless steel (Table 7.1) are necessary for deeper wells. At depths greater than about 1200–1500 m, cement casing is often installed and perforated by jetting. This gives the necessary strength at a lower cost than stainless steel; however, at even greater depths, as in the 2500 m deep boreholes in the Slovak part of the Pannonian Basin, perforated cement and slotted steel pipe may be used together to achieve the necessary strength (e.g. Franko *et al.*, 1989). An overview of casing design for geothermal wells is given by Rieke and Chillingar (1982), while Shyrock (1982) discusses the problems of cementing in well casings.

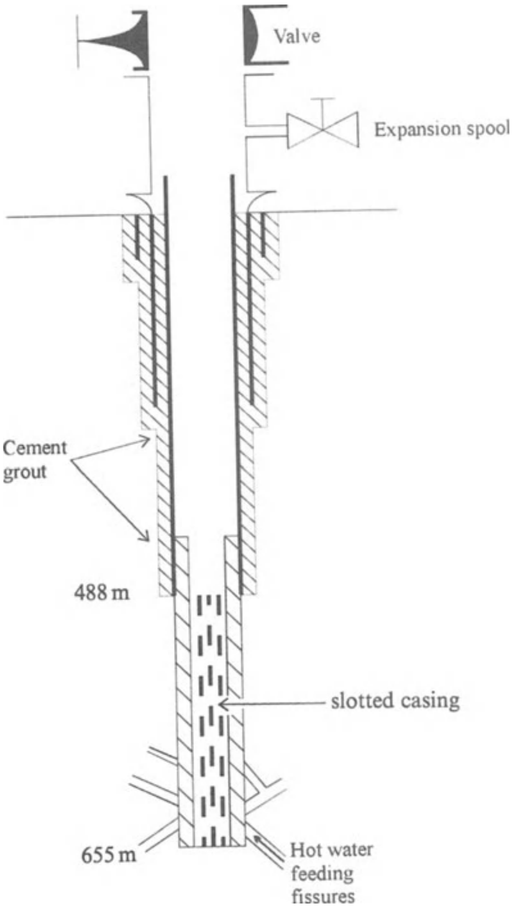

Figure 7.2 Well construction in fractured rocks, based on wells at Wairakei, New Zealand. (After Armstead, 1983.)

7.4 SCALING AND CORROSION

7.4.1 Scaling

Scaling (incrustation) due to the deposition of silica, calcite or other minerals in wells and pipelines is a problem in the exploitation of certain systems. This reduces flow to the well and in pipes and is to be avoided if possible. Silica deposition in wells causes problems in many high temperature systems. More commonly, calcium carbonate scale formation in wells or even within the aquifer may limit development of the system, as for example in Turkey and the Philippines. To minimize such effects, fresh water is sometimes used to carry the heat from a production loop via heat exchangers

Table 7.1 Grades of stainless steel for well construction in different types of water (from Driscoll, 1986)

Metal	*Composition*		*Suggested applications*
Low-carbon steel	Carbon	0.8% max	Not corrosion resistant. Will give satisfactory service life where waters are non-corrosive and non-incrusting
	Iron	Balance	
Type 405 stainless steel	Chromium	11.5% min	Moderate corrosion resistance. Applicable for potable waters of low to medium corrosivity. May exhibit slight surface rusting in oxygenated environments
	Aluminium	0.3% max	
	Iron	Balance	
Type 304 stainless steel	Chromium	18% min	Excellent corrosion resistance. Most widely used stainless steel material for water well screens. Occasionally specified for casing in high capacity wells in corrosive environments
	Nickel	8% min	
	Manganese	2% max	
	Carbon	0.08% max	
	Iron	Balance	
Type 316L stainless steel	Chromium	16% min	For use in groundwaters having a moderate salt content. Molybdenum content helps resist pitting and crevice corrosion in moderate saline solutions. Better resistance to stress-corrosion cracking than Type 304 stainless steel
	Nickel	10% min	
	Molybdenum	2% min	
	Carbon	0.03% max	
	Iron	Balance	
Carpenter 20Cb-3	Nickel	32% min	Strong resistance to stress-corrosion cracking, pitting and crevice corrosion. Will provide satisfactory service in very saline waters and at water temperatures over 100°F (38°C)
	Chromium	19% min	
	Copper	3% min	
	Molybdenum	2% min	
	Manganese	2% max	
	Iron	Balance	
Monel 400	Nickel (plus cobalt)	63% min	Will provide satisfactory service in seawater where a high sodium chloride content is combined with dissolved oxygen. Material is sensitive to hydrogen sulphide
	Copper	28% min	
	Iron	2.5% max	
	Manganese	2% max	
Incoloy 825	Nickel (plus cobalt)	38% min	Material has a low corrosion potential in high chloride water and resists cracking, pitting and crevice corrosion. Satisfactory for use in geothermal, oil and gas and injection wells
	Iron	22% min	
	Chromium	19.5% min	
	Molybdenum	2.5% min	
	Copper	1.5% min	
Inconel 600	Nickel (plus cobalt)	72% min	For use in geothermal, oil and gas and injection well applications. Strong resistance to stress-corrosion cracking
	Chromium	14% min	
	Iron	6–10%	
Hastelloy C	Nickel	51% min	Extremely corrosion-resistant alloy used only in most aggressive environments, such as brine, corrosive gases and where temperatures exceed 200°F (93°C). Used for geothermal, oil and gas and injection wells
	Molybdenum	15% min	
	Chromium	14.5% min	
	Iron	4% min	
	Tungsten	3% min	
	Cobalt	2.5% max	
	Vanadium	0.35% max	

(Chapter 2). The thermal water yields its heat to the fresh water which then goes to the distribution network. Systems with thermal water that is high in total carbonates are now regarded with suspicion for simple development.

Scaling is also a problem in wells supplying mineral waters. Changes in pressure and the loss of carbon dioxide may result in the deposition of calcium carbonate within the well, close to where the change of pressure takes place. The growth of bacterial slime is common in wells in iron-rich water, and may cause clogging of the aquifer and screen.

Scaling by carbonates is favoured by:

- a high pH;
- high carbonate hardness (>300 mg/l);
- reduction of pressure.

Incrustation and colonization of well screens, gravel packs and fractures by iron and other slime-forming bacteria are favoured by the following factors:

- where iron or manganese rich groundwater (i.e. >0.25 mg/l Fe or >0.2 mg/l Mn) encounters oxygenated or higher pH water (Driscoll, 1986);
- fluctuating pumping rates, resulting in repeated introduction of oxygen to the immediate vicinity of the well;
- drawdown of pumping water level below the well screen or yielding fractures;
- excessive inflow velocity caused by overpumping or insufficient screen open area, again a design problem.

7.4.2 Corrosion

Corrosion of metals (well casing and screen, pumps and rising mains, delivery pipes) is accelerated by many thermal and mineral waters. High temperature acidic waters found in some zones of active volcanism are particularly aggressive. The principal effects are sulphide and chloride stress corrosion of certain stainless and high strength steels, and rapid corrosion of copper-based alloys. In the Paris Basin of France, the action of sulphides in a chloride environment has resulted in severe corrosion of the metallic section of geothermal loops (Kelk, 1992).

Corrosion is favoured by the following factors (Driscoll, 1986):

- abrasion by rock particles, often due to poor well design;
- soft, aggressive water with low pH (<6.5);
- water with a high dissolved CO_2 content (>50 mg/l);
- saline water (i.e. $TDS > 1000$ mg/l, $Cl^- > 500$ mg/l), although a fully saturated sodium chloride brine is not corrosive;
- warm/thermal water;
- water containing hydrogen sulphide;
- water with a high dissolved oxygen content (>2 mg/l).

7.4.3 Well maintenance

Maintenance implies regular checking of the condition of surface fixtures, wellhead seals and pumps, as well as a rehabilitation programme for removing scale and any fine grains blocking the screen. In general about 10–12% of the capital cost of a well should be allocated annually for maintenance (Driscoll, 1986), although the exact amount needed will depend on the individual well, aquifer, water quality and operating regime.

It is clear that an appropriate well design, using non-corrosive materials and having an adequate open area for the design yield, can prevent many problems, but when incrustation and abrasion/corrosion problems are a risk, they can be minimized by the following operating procedures:

- not pumping the well above its design yield, and certainly not at such a rate that sediment enters the borehole; not drawing the water level down below the top of the well screen or the main yielding fracture;
- pumping the borehole at a steady rate rather than spasmodically;
- cathodic protection, e.g. using a sacrificial anode, in areas prone to corrosion;
- sterilizing all downhole equipment;
- instigating a programme of regular remediation when the specific yield falls to a trigger level;
- continuous in-hole disinfection using chlorine, although this may not be acceptable for many mineral water wells.

When the specific yield (yield divided by drawdown or drop in pressure) of a borehole drops below a target value (typically between 60 and 70% of the original value), rehabilitation should be carried out. If deterioration in the yield progresses too far, problems in the well become increasingly difficult to rectify.

Rehabilitation of a well for low temperature and many mineral waters generally comprises mechanical measures such as high pressure jetting, surging or wire brushing to remove incrustation. These measures are also useful for removing fine sediment from the vicinity of the screen. Different acids may be used, usually in conjunction with mechanical methods, to help remove carbonates and biofilms. Biocides such as chlorine can be useful in killing bacteria and dissolving biofilms (Howsam, 1988). In fractured rocks the use of hydraulic fracturing or explosives has enjoyed a degree of success, both for initial development of the well and for remediation (Driscoll, 1986).

Reaming is commonly used to remove silica and carbonate deposits from high temperature wells. In Iceland reaming of calcite scale with a drill bit allows wells to be cleaned with only a 2-day interruption in steam supply. This process has been carried out twice a year for 25 years with no decline in production (Orkustofnun, 1992).

In severe cases of corrosion, the installation of a secondary, inner casing string and well screen, possibly with a gravel pack, is an option, although this may result in a reduced yield. The old screen and casing may be removed and replaced, but this is often not possible for deep wells and in many cases a new well will be required.

7.5 TRANSPORT

The transport of waters is a significant factor in the development of resources. Pipelines carrying mineral water to therapeutic treatment centres or to bottling plants are at the most a few kilometres long, since greater distances cannot be justified economically, although once bottled, water may be distributed worldwide (Figure 7.3). Thermal steam, on the other hand, is commonly transported over distances of 1–2 km. The distance of transport is limited by heat loss and resulting condensation, and pipelines are rarely more than 3 km long, but can be up to about 10 km long for high flow rates. Figure 7.4 shows how the cost of transport drops as the flow rate of steam increases. Pipelines for hot water, for space heating for example, can be longer if insulation is effective: the pipeline carrying water with a temperature of 83°C from the Nesjaveelir plant to Reykjavík in Iceland is 27 km long (Orkustofnun, 1992).

7.6 HEAT RECOVERABILITY

7.6.1 Recovery factors

Fuel and non-fuel minerals can only be fully recovered in exceptional circumstances. At present the recovery of oil is about 32% by volume although with new developments in technology and recovery practice this could increase to up to 60% in the foreseeable future. The average quantity recovered from coal mines is about 50–60% and from metallic ores between about 75 and 95%. Current recovery factors for salt mines in Cheshire, England, are about 65% for rock salt and about 25% for salt obtained by controlled dissolution according to the mine management.

Geothermal energy is also a finite resource, since the capacity for regeneration of the resource through natural heat transport processes does not generally compensate for the energy abstracted. Only a relatively small quantity of heat can be recovered from the geothermal resources as calculated in section 5.5. The recoverable, or available, resources are estimated by multiplying the calculated quantity of stored heat by a recovery factor, which may be defined as the ratio of heat brought to the surface to the quantity of stored heat originally available in the system. Thus the recovery factor depends on the geological and thermodynamic features of the system, as well as on the manner and regime of discharge.

Figure 7.3 Mineral water labels for Borsec, Romania, for different markets.

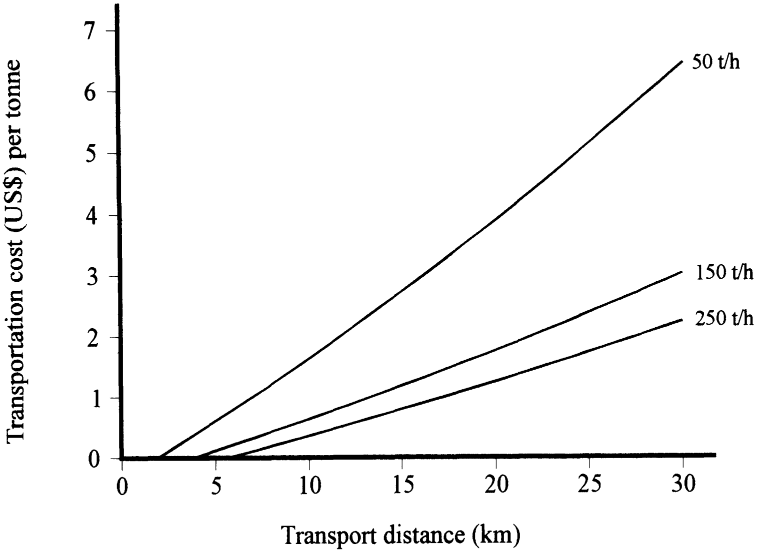

Figure 7.4 Transport costs related to the flow rate of steam. (From Orkustofnun (National Energy Authority of Iceland), 1992.)

The recovery factor for heat can have values between nearly zero and 25% (Muffler and Cataldi, 1978).

Recovery factors are evaluated differently depending on whether the systems are of high or low permeability and some examples are given below.

7.6.2 High permeability systems

In systems of high permeability, heat recoverability is calculated on the basis of four main models (Muffler and Cataldi, 1978):

- intergranular liquid flow;
- planar liquid flow;
- intergranular vaporization (boiling *in situ*) in an initially liquid system; and
- boiling in a steam system.

Intergranular liquid flow model

In the model of intergranular liquid flow (Böðvarsson, 1974; Nathenson, 1975) the system is considered to be porous and permeable, such that the liquid water has a very large surface of contact with the rock matrix and takes practically all the heat from it. The recovery factor therefore does not depend on a decrease of temperature during exploitation, and would eventually tend to 100%. However, in practice the recovery factor in such systems is frequently only 10% (Böðvarsson, 1974) and very exceptionally 25% (Nathenson and Muffler, 1975) because real systems do not generally satisfy the conditions either of full contact between the water and rock matrix or of high enough porosity and permeability to ensure efficient access to the systems by production and injection wells.

Planar liquid flow model

The model of planar liquid flow is based on the planar fracture method, by which so-called specific theoretical resources are calculated in megawatts per square metre of fracture surface (Böðvarsson, 1974). This value depends on the initial temperature T_i of the rock and on the ratio of the final temperature $(T_f - T_0)/(T_i - T_0)$, where T_0 and T_f are respectively the temperature of water when it enters the fracture and the final temperature of water when it leaves the fracture. From these theoretical resources it is possible to evaluate heat recovery factors for different times of production from successive parallel fractures, situated at the minimum distance d from each other at which thermal interference between them becomes negligible (Böðvarsson, 1974; Muffler and Cataldi, 1978). For example, considering a duration of production t_f of 100 years, an average thermal diffusivity $\tilde{\chi}$ of $10^{-6}\,\mathrm{m}^2/\mathrm{s}$ and a half-distance between fractures $d/2 \approx 3(\tilde{\chi} t_f)^{1/2}$ of 169 m, the recovery factors given in Table 7.2 are found. The recovery factors calculated on the basis of this model are always less than those obtained from real systems because fractures are not uniformly planar for their whole length and the surface area is underestimated.

Table 7.2 Theoretical heat recovery factors according to the model of planar liquid flow

Initial temperature of rock		*Duration of production (years)*		
(K)	*(°C)*	*25*	*50*	*100*
453	180	0.116	0.167	0.235
463	190	0.131	0.186	0.263
473	200	0.144	0.204	0.288
483	210	0.156	0.220	0.312
493	220	0.168	0.237	0.335
503	230	0.178	0.252	0.356
513	240	0.187	0.263	0.373
523	250	0.195	0.274	0.389
533	260	0.201	0.283	0.403
543	270	0.206	0.289	0.413
553	280	0.209	0.294	0.421
563	290	0.213	0.298	0.426
573	300	0.215	0.300	0.431

Calculated for a distance between planar fractures of 338 m; initial temperature of water entering the fractures of 40°C and the final temperature of water leaving the fracture of 162°C.

Intergranular vaporization model

The model of intergranular vaporization is used to evaluate heat recoverability depending on the total porosity and temperature of an ideal system. Some examples of these determinations are given below.

Reference temperature: 40°C
System temperature: 250°C

Total porosity (%)	1	2	5	10	15
Recovery factor (%)	3	8	19	40	61

Reference temperature: 40°C
Total porosity: 10%

System temperature (°C)	200	250	300
Recovery factor (%)	58	40	27

(after Böðvarsson, 1974)

Reference temperature: 15°C
Final pressure 2.5×10^5 N/m^2
System temperature: 250°C

Total porosity (%)	1	5	10	15
Recovery factor (%)	3	18	35	51

Total porosity: 10%

System temperature (°C)	200	250	300
Recovery factor (%)	46	35	26

(from Nathenson, 1975; Muffler and Cataldi, 1978)

For real systems, these theoretical factors must be reduced by two-thirds or three-quarters, due to the effects of anisotropy and variations in porosity and thermal properties (Böðvarsson, 1974).

The application of this model to the complex system of Larderello–Travale, where the total porosity is 15% for the carbonate–anhydrite formation and 4% for the covering sedimentary rocks, gives factors of heat recovery from rocks and stored water of 12.5 and 15% respectively (Barelli *et al.*, 1975) and the factor of heat recovery from the system as a whole has an average value of 13.3% (Muffler and Cataldi, 1978).

Boiling in steam system model

The model of boiling in a steam system is based on the work of White *et al.* (1971) and Truesdell and White (1973). This was used by Nathenson (1975) to evaluate heat recoverability on the hypothesis that the system initially contains a mixture of liquid and vapour, in which the vapour is maintained at a controllable pressure. A correspondence can be established between the model of intergranular vaporization and the model of boiling steam if the kinematic porosity rather than the total porosity of the rocks is considered. Applying this model to the thermal water systems of The Geysers, with a temperature of 240°C and a presumed kinematic porosity of 5%, Nathenson and Muffler (1975) estimated a recovery factor which would be 19.4% in theory but probably only 9.7% in practice because the water bearing rocks do not have the same porosity and permeability everywhere.

7.6.3 Low permeability systems

In the case of low permeability systems, heat recoverability can be estimated by extrapolation from high permeability systems which are generally better known, since the recovery factors generally decrease almost linearly with decreasing temperature and porosity and also with increasing depth (Barelli *et al.*, 1975).

In low permeability systems producing vapour, the recoverability does indeed decrease with decreasing porosity, especially kinematic porosity (Muffler and Cataldi, 1978), but it can sometimes increase with decreasing temperature (Böðvarsson, 1974; Nathenson, 1975). Independent of porosity and temperature, the recovery factor of heat from these systems depends on depth, because the enthalpy of the fluid brought to the surface is reduced by losses of potential and kinetic energy, by conductive heat transfer and by friction as it travels upwards in production wells. Thus, on the basis of measurements in well VC10 at Larderello (Nathenson, 1975), it is estimated that the enthalpy of the fluid is reduced by about 21 kJ/(kg km), and the temperature drops by about 5°C/km between the bottom and top of the well.

In low permeability systems producing liquid (hot water), it is accepted, at least as a first approximation, that the heat recoverability is a direct linear function of kinematic porosity (Muffler and Cataldi, 1978), and does not depend on the temperature of the system in conditions where the intergranular flow model is applicable (Böðvarsson, 1974; Nathenson, 1975).

7.7 HEAT REGENERATION

In the course of exploitation, the thermodynamic state within thermal water systems is modified by a decrease of temperature and pressure, relative to the undisturbed thermodynamic state outside. This generates local or zonal non-equilibrium conditions in the relatively stable distribution of energy in the terrestrial crust, resulting in a redistribution of energy to compensate for, or at least to diminish, the losses through exploitation, by the upward and lateral transfer of heat and mass (Albu and Enăchescu, 1985). Thus at the same time as exploitation some conductive and convective heat recharge is induced from outside the exploited system, resulting in heat regeneration inside the system.

The conductive regeneration of heat takes place at an average rate expressed as

$$\tilde{\boldsymbol{u}}_c = -\frac{\tilde{\kappa}\,\text{grad}\,T}{\tilde{\rho}\tilde{c}T}$$

where $\tilde{\rho}\tilde{c}$, T and $-\tilde{\kappa}\,\text{grad}\,T$ are the heat flow [W/m^2], the absolute temperature [K] and the average heat capacity per unit volume [J/(m^3 K)] respectively. Useful values for this rate of transmission, which depends on temperature and on heat flow (Albu, 1987), are given in Table 7.3.

The rate of heat transmission by conduction is very low, from 0.6 to 24.5 mm/year (only 0.06–2.45 m/century), and conductive regeneration of heat is thus very slow compared with the rate of extraction of heat during exploitation, which may take place over periods of 10–100 years. The power corresponding to this regeneration in a thermal water system is given by the flux of heat by conduction through the surface S bounding the system, i.e.

$$\int_S \tilde{\rho}\tilde{c}T\tilde{u}_c\,\mathrm{d}\boldsymbol{S} = \int_S (-\tilde{\kappa}\,\text{grad}\,T)\,\mathrm{d}\boldsymbol{S}$$

The convective regeneration of heat occurs due to transfer into the system of fluids, as a rule hot water or steam, with a temperature higher than that in the system being exploited. If these fluids are transferred with a mass flow rate ρQ, specific heat c and temperature $T + \Delta T$ higher than the temperature T inside the system, then the power corresponding to convective heat regeneration is expressed by the flux of heat convection $\rho Qc\,\Delta T$. To give an example, for the transfer of hot water with a volumetric flow rate of 1 l/s, and therefore a mass flow rate of about 1 kg/s, with a specific heat of 4.2 kJ/(kg K) and a temperature of 370 K (97°C) into a system with a temperature of 340 K (67°C), the convective heat flux has the value of 126 kW, which is more than the conductive heat flux resulting from a heat flow of 0.1 W/m^2 through an area of 1 km^2.

Bearing in mind the approximations which are necessary in the calculation of thermal water resources, it is generally accepted that heat regeneration in exploited systems can only be considered as significant if it is at least 10% of the heat recoverable from storage (Muffler and Cataldi, 1978).

Heat regeneration in thermal water systems can be evaluated by three main models: (a) model of regional conductive heat recharge; (b) model of conductive heat recharge from magmatic intrusions; and (c) model of lateral convective heat recharge (Muffler and Cataldi, 1978). To exemplify their use, a permeable system of area A, thickness b, average heat capacity per unit volume $\tilde{\rho}\tilde{c}$, temperature T (higher than the reference temperature T_{ref}) and recovery factor R_f is considered, so that the quantity of recoverable heat can be expressed as $R_f\tilde{\rho}\tilde{c}(T - T_{\text{ref}})Ab$.

Table 7.3 Rates of heat transmission (10^{-9} m/s) for different rock types

Rock type	*Average heat capacity per unit volume, $\tilde{\rho}\tilde{c}$ (10^6 J/(m^3 K))*	*Temperature, T (K)*	*Heat flow $-\tilde{\kappa}$ grad T (10^{-3} W/m^2)*					
			40	*60*	*80*	*100*	*120*	*140*
Volcanic rocks								
Basalt	2.5	300	0.0553	0.0800	0.1067	0.1333	0.1600	0.1867
		500	0.0320	0.0480	0.0640	0.0800	0.0960	0.1120
		800	0.0200	0.0300	0.0400	0.0500	0.0600	0.0700
Diorite	1.9	300	0.0702	0.1053	0.1404	0.1754	0.2105	0.2456
		500	0.0421	0.0632	0.0842	0.1053	0.1263	0.1474
		800	0.0263	0.0395	0.0526	0.0658	0.0789	0.0921
Gabbro	2.1	300	0.0635	0.0952	0.1270	0.1587	0.1905	0.2222
		500	0.0381	0.0571	0.0762	0.0952	0.1143	0.1333
		800	0.0238	0.0357	0.0476	0.0595	0.0714	0.0833
Granite	2.8	300	0.0476	0.0714	0.0952	0.1190	0.1429	0.1667
		500	0.0268	0.0429	0.0571	0.0714	0.0857	0.1000
		800	0.0179	0.0268	0.0357	0.0446	0.0536	0.0625
Pumice	0.6	300	0.2222	0.3333	0.4444	0.5556	0.6667	0.7778
		500	0.1333	0.2000	0.2667	0.3333	0.4000	0.4667
		800	0.0833	0.1250	0.1667	0.2083	0.2500	0.2917
Syenite	2.3	300	0.0580	0.0870	0.1159	0.1449	0.1739	0.2029
		500	0.0348	0.0522	0.0696	0.0870	0.1043	0.1217
		800	0.0217	0.0326	0.0435	0.0543	0.0652	0.0761
Tuff	1.4	300	0.0952	0.1429	0.1905	0.2381	0.2857	0.3333
		500	0.0571	0.0857	0.1143	0.1429	0.1714	0.2000
		800	0.0357	0.0536	0.0714	0.0893	0.1071	0.1250
Metamorphic rocks								
Crystalline schists	4.8	300	0.0741	0.1111	0.1481	0.1852	0.2222	0.2593
		500	0.0444	0.0667	0.0889	0.1111	0.1333	0.1556
		800	0.0278	0.0417	0.0556	0.0694	0.0833	0.0972
Gneiss	1.9	300	0.0702	0.1053	0.1404	0.1754	0.2105	0.2456
		500	0.0421	0.0632	0.0842	0.1053	0.1263	0.1474
		800	0.0263	0.0395	0.0526	0.0658	0.0789	0.0921
Marble	2.4	300	0.0556	0.0833	0.1111	0.1389	0.1667	0.1944
		500	0.0333	0.0500	0.0667	0.0833	0.1000	0.1167
		800	0.0208	0.0313	0.0417	0.0521	0.0625	0.0729
Sedimentary rocks								
Asphalt	1.2	300	0.1111	0.1667	0.2222	0.2778	0.3333	0.3889
		500	0.0667	0.1000	0.1333	0.1667	0.2000	0.2333
		800	0.0417	0.0625	0.0833	0.1042	0.1250	0.1485
Bituminous coal; clay	1.7	300	0.0784	0.1176	0.1569	0.1961	0.2353	0.2745
		500	0.0471	0.0706	0.0941	0.1176	0.1412	0.1647
		800	0.0294	0.0441	0.0588	0.0735	0.0882	0.1029

Table 7.3 Continued

Rock type	*Average heat capacity per unit volume, $\tilde{\rho}\tilde{c}$ (10^6 J/(m^3 K))*	*Temperature, T (K)*	*Heat flow $-\tilde{\kappa}$ grad T (10^{-3} W/m^2)*					
			40	*60*	*80*	*100*	*120*	*140*
Sedimentary rocks – continued								
Dolomite	2.6	300	0.0513	0.0769	0.1026	0.1282	0.1538	0.1795
		500	0.0308	0.0462	0.0615	0.0769	0.0923	0.1077
		800	0.0192	0.0288	0.0385	0.0481	0.0577	0.0673
Limestone; marl	2.1	300	0.0635	0.0952	0.1270	0.1587	0.1905	0.2222
		500	0.0381	0.0571	0.0762	0.0952	0.1143	0.1333
		800	0.0238	0.0357	0.0476	0.0595	0.0714	0.0833
Sand	1.6	300	0.0833	0.1250	0.1667	0.2083	0.2500	0.2917
		500	0.0500	0.0750	0.1000	0.1250	0.1500	0.1750
		800	0.0313	0.0469	0.0625	0.0781	0.0938	0.1094
Sandstone	1.9	300	0.0702	0.1053	0.1404	0.1754	0.2105	0.2456
		500	0.0421	0.0632	0.0842	0.1053	0.1263	0.1474
		800	0.0263	0.0395	0.0526	0.0658	0.0789	0.0921
Slate	2.0	300	0.0667	0.1000	0.1333	0.1667	0.2000	0.2333
		500	0.0400	0.0600	0.0800	0.1000	0.1200	0.1400
		800	0.0250	0.0375	0.0500	0.0625	0.0750	0.0875

Regional conductive heat recharge model

The model of regional conductive heat recharge evaluates heat regeneration in the case when the quantity of ascending heat from the regional flux of heat conduction in a time interval Δt, given as the heat flow $\tilde{q}$ through a horizontal surface of area A_* at the base of the thermal water system with a horizontal section of area $A \leq A_*$, is completely transferred into the system by horizontal convection (flow of water) on the surface of area A_*. Expressing the quantity of heat transferred into the system in the form $\tilde{q}A_*\Delta t$ and dividing it by the quantity of recoverable heat, $R_f\tilde{\rho}\tilde{c}(T - T_{\text{ref}})Ab$, the result must be at least 0.10 for heat regeneration to be considered at all significant, i.e.

$$\frac{\tilde{q}A_*\Delta t}{R_f\tilde{\rho}\tilde{c}(T - T_{\text{ref}})Ab} \geq 0.1$$

This condition means that the significance of heat regeneration increases with the regional flux of heat conduction and that heat flow is greater the larger the extent of the aquifer and the smaller the dimensions of the system. The model of regional conductive heat recharge has been applied to the complex system of Larderello–Travale. Using the data regarding heat flow (Calamai *et al.*, 1976), Muffler and Cataldi (1978) estimated that 0.177 × 10^{18} J of heat can be regenerated, which amounts to only 5% of the recoverable heat evaluated by Barelli *et al.* (1975) of 3.388 × 10^{18} J. By contrast, when this model is applied to the thermal water system of Oradea (for which it is assumed as a first approximation that $\tilde{q} = 80\,\mathrm{mW/m^2}$, $A_* = 100\,\mathrm{km}^2$, $\Delta t = 100$ years, $R_\mathrm{f} = 0.05$, $\tilde{\rho}\tilde{c} = 2500\,\mathrm{kJ/(m^3/K)}$, $T - T_\mathrm{ref} = 70\,\mathrm{K}$ (70°C), $A = 27\,\mathrm{km}^2$ and $b = 750\,\mathrm{m}$), the resulting quantity of heat that can be regenerated is 0.25×10^{17} J, which represents 14.1% of the recoverable heat estimated at 1.77×10^{17} J (Albu, 1987).

Conductive heat recharge model

The model of conductive heat recharge from a magmatic intrusion corresponds to the case in which heat is transmitted upwards by conduction from a magmatic body beneath the system to the basal surface of the system, and then horizontally by convection (flow of water) within the system. If a magmatic body with a temperature T_mag lies at a depth b_mag under the system and extends over an area A_mag through which the heat flow is $\tilde{q}$, then the quantity of heat transmitted to the basal surface of the system in an interval of time Δt is expressed in the form

$$\tilde{q} A_\mathrm{mag} \Delta t = \tilde{\kappa} \frac{T_\mathrm{mag} - T}{b_\mathrm{mag}} A_\mathrm{mag} \Delta t$$

where $\tilde{\kappa}$ is the average thermal conductivity of the rocks covering the magmatic body and T is the temperature at the base of the system. Assuming that all this heat is then transmitted horizontally by convection at the base of the system, dividing it by the quantity of recoverable heat $R_\mathrm{f}\tilde{\rho}\tilde{c}(T - T_\mathrm{ref})Ab$ and given the condition that heat regeneration should be significant, then

$$\frac{\tilde{\kappa}(T_\mathrm{mag} - T) A_\mathrm{mag} \Delta t}{b_\mathrm{mag} R_\mathrm{f} \tilde{\rho}\tilde{c}(T - T_\mathrm{ref}) A b} \geq 0.1$$

In this model, heat regeneration is more significant for a smaller system, for a greater extent of the magmatic body, and for shallower depths of the magma beneath the system. Applying the model to the system of The Geysers, the following data were used: $\tilde{\rho}\tilde{c} = 2500\,\mathrm{kJ/(m^3\,K)}$, $\tilde{\kappa} = 2.93\,\mathrm{W/(m\,K)}$ (Diment *et al.*, 1975), $T = 513\,\mathrm{K}$ (240°C), $A = 70\,\mathrm{km}^2$, $b = 2000\,\mathrm{m}$ (Renner *et al.*, 1975), $A_\mathrm{mag} = \pi(6.9)^2\mathrm{km}^2$ (Isherwood, 1976), $T_\mathrm{mag} = 873\,\mathrm{K}$ (600°C), $T_\mathrm{ref} = 288\,\mathrm{K}$ (15°C), $R_\mathrm{f} = 0.15$ and $\Delta t = 100$ years (Muffler and Cataldi, 1978). From these data it is calculated that heat regeneration would be significant only if the depth b_mag of the magmatic body below the base of the system was at most 0.42 km, i.e. at least eight times less than in reality (Isherwood, 1976).

Lateral convective heat recharge model

The model of lateral convective heat recharge is used when a system of high porosity and permeability regenerates heat by the transfer of hot water or steam from surrounding rocks of lower porosity and permeability. If the system and the surrounding rocks have volumes of V and V_*, average heat capacities per unit volume $\tilde{\rho}\tilde{c}$ and $(\tilde{\rho}\tilde{c})_*$, temperatures T and T_* and recovery factors R_f and R_{f^*} (where $R_f > R_{f^*}$), then for a reference temperature T_{ref}, the quantity of heat recoverable from the system and the quantity of heat transfer to the system from the surrounding rocks are determined respectively by the expressions $R_f\tilde{\rho}\tilde{c}(T - T_{\text{ref}})V$ and $R_{f*}\tilde{\rho}\tilde{c}_*(T_* - T_{\text{ref}})V_*$. Dividing the quantity of heat transferred into the system by the quantity of recoverable heat, and given that heat regeneration should be significant, then

$$\frac{R_{f*}\tilde{\rho}\tilde{c}_*(T_* - T_{\text{ref}})V_*}{R_f\tilde{\rho}\tilde{c}(T - T_{\text{ref}})V} \geq 0.1$$

which is satisfied as a rule, since $R_{f*}V_* \geq 0.1R_fV$ (Muffler and Cataldi, 1978).

Applications of the three models indicate that heat regeneration is negligible in systems such as The Geysers (Ramey, 1970; White *et al.*, 1971; Nathenson, 1975; Isherwood, 1977), Larderello (Nathenson, 1975) and Imperial Valley (Nathenson, 1975). However, it can be significant for some systems such as Wairakei (Nathenson, 1975; Hunt, 1977) and Oradea (Romania) among others.

The behaviour of thermal water systems during exploitation is essentially conditioned by the degree of hydraulic closure. In closed, or nearly closed, systems the evolution is characterized by a gradual drop of pressure and by a relatively well maintained temperature of the abstracted water, due to the lack of any significant recharge from lower temperature water from outside the system. Conversely, in open systems significant recharge with cooler water from outside the system can take place to compensate for abstraction, such that pressures are maintained even though temperatures will tend to drop.

Using a graph of time against the variation of flow rates of heat from wells, the optimal variant of exploitation must be chosen to obtain the maximum quantity of recoverable heat, during a period of time which is restricted for the closed or nearly closed systems and as long as possible (or even unlimited) for open systems. The thermal water resources of these systems can be regenerated over an unlimited period only if, during exploitation, the velocity of recharge of the water does not exceed the maximum velocity required to allow sufficient heating by the rocks through which it flows (Albu *et al.*, 1986).

7.8 RESOURCE MANAGEMENT

7.8.1 Management characteristics of mineral and thermal water resources

Interest in the commercial use of mineral water has been stimulated as a result of the perceived contamination of surface waters and groundwaters used for drinking water supplies. The development of spas is dependent on changes in cultural and social attitudes: achieving good health or curing illness without taking drugs is now an important aspect of the quality of life. The tourism potential of the locality is also an important economic factor in the viability of spas. The money spent on research and development of the use of thermal waters for heating and power generation fluctuates with the price of oil and was much enhanced by the oil crises of 1973 and 1979. More recently, the Rio agreement of 1992 to reduce greenhouse emissions has resulted in renewed interest in the use of geothermal energy, along with renewable resources such as hydro-power.

Both mineral and thermal water resources are often local and sometimes finite resources. They are considered as finite when the water or heat brought in by natural recharge processes does not compensate for that extracted. Consequently, strict management policies are called for to ensure the longest possible exploitation life at an acceptable operating cost. Such policies may include limiting the abstraction of mineral water to the level of the natural regeneration potential, reinjection of waste water and optimization of the sustainable flow from boreholes. A successful example of the first policy is given in the case study on Buziaş, Romania (Chapter 15).

In most cases these waters can be transported economically for only limited distances (section 7.5). The development of such resources is therefore justified only when certain conditions are met, such as guarantees that the quality and quantity are satisfactory, and that they are accessible at depths that are not too great, and not too distant for potential consumers or users. Whether or not their utilization is deemed profitable depends upon economic factors, which are closely dependent on the cost of alternative products and fuels, both at the time of development and as projected for the future. The variables that particularly influence cost are:

- exploration costs for hydrogeological and geophysical surveys, drilling and testing;
- development costs for pumping units, pipelines and any surface plant; and
- operating costs for maintenance, pumping, etc.

The capital investment required for exploration, together with development costs, can be high but operating costs are relatively low (Downing and Gray, 1986). A useful appraisal of the costs of such development and relevant financial analyses is given by Harrison *et al.* (1990).

7.8.2 Available resources and variants for their management

Any managerial activity has as its basis some available or readily available resources (Heyel, 1973). In a given period of time, the available mineral and thermal water resources comprise economically proven resources. These include added (e.g. newly identified), attracted (e.g. by inducing recharge)

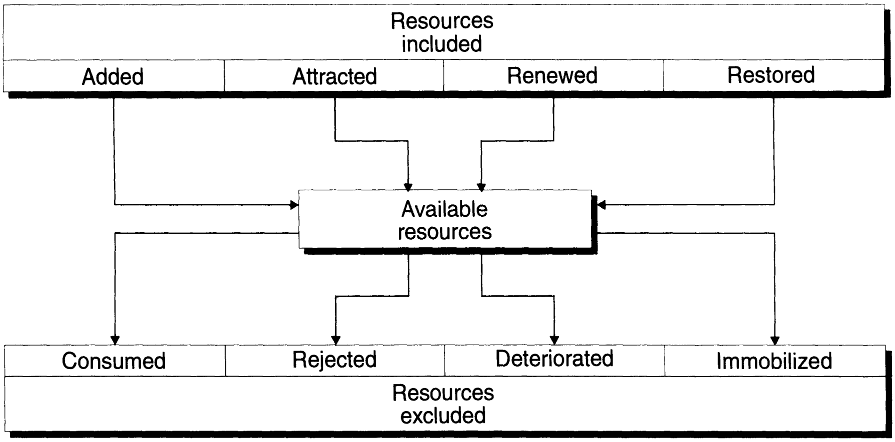

Figure 7.5 Schematic diagram of the make up of available resources.

and restored resources. They exclude consumed, rejected, deteriorated and immobilized resources, in keeping with the scheme presented in Figure 7.5.

The resources included in the 'available' category change as exploration proceeds and systems become better known or perhaps overutilized. In general, the available resources Q are expressed as included resources P and excluded resources R, corresponding to the equation of state

$$Q = Q(P, R) \tag{7.1}$$

which can be written in the differential form

$$\mathrm{d}Q = \left(\frac{\partial Q}{\partial P}\right)_R \mathrm{d}P + \left(\frac{\partial Q}{\partial R}\right)_P \mathrm{d}R \tag{7.2}$$

The rate of variation of available resources

$$\frac{\mathrm{d}Q}{Q} = \left[\frac{1}{Q}\left(\frac{\partial Q}{\partial P}\right)_R \mathrm{d}P\right] - \left[-\frac{1}{Q}\left(\frac{\partial Q}{\partial R}\right)_P \mathrm{d}R\right] \tag{7.3}$$

is calculated by subtracting the rate of exclusion

$$-\frac{1}{Q}\left(\frac{\partial Q}{\partial R}\right)_P \mathrm{d}R = r\,\mathrm{d}R \tag{7.4}$$

from the rate of inclusion

$$\frac{1}{Q}\left(\frac{\partial Q}{\partial P}\right)_R \mathrm{d}P = p\,\mathrm{d}P \tag{7.5}$$

where r and p represent the coefficients of exclusion and inclusion respectively.

If equation (7.3), expressed in the form

$$\frac{\mathrm{d}Q}{Q} = p\,\mathrm{d}P - r\,\mathrm{d}R \tag{7.6}$$

is integrated between an initial state $Q_0 = Q(P_0, R_0)$ and a subsequent state $Q = Q(P, R)$, i.e.

$$\int_{Q_0}^{Q} \frac{\mathrm{d}Q}{Q} = \int_{P_0}^{P} p\,\mathrm{d}P - \int_{R_0}^{R} r\,\mathrm{d}R$$

then the available resources are determined by the function

$$Q = Q_0 \exp\left(\int_{P_0}^{P} p\,\mathrm{d}P - \int_{R_0}^{R} r\,\mathrm{d}R\right) \tag{7.7}$$

Finally, calculating the average coefficient of inclusion

$$\tilde{p} = \frac{1}{P - P_0} \int_{P_0}^{P} p\,\mathrm{d}P \tag{7.8}$$

and the average coefficient of exclusion

$$\tilde{r} = \frac{1}{R - R_0} \int_{R_0}^{R} r\,\mathrm{d}R \tag{7.9}$$

function (7.7) is more in keeping with the form

$$Q = Q_0 \exp[\tilde{p}(P - P_0) - \tilde{r}(R - R_0)] \tag{7.10}$$

so that for small values of the argument $\tilde{p}(P - P_0) - \tilde{r}(R - R_0)$, the available resources and their rate of variation are estimated respectively by

$$Q = Q_0[1 + \tilde{p}(P - P_0) - \tilde{r}(R - R_0)] \tag{7.11}$$

and

$$\frac{Q - Q_0}{Q_0} = \tilde{p}(P - P_0) - \tilde{r}(R - R_0) \tag{7.12}$$

If, in a given period of time, the included, excluded and available resources vary such that $P - P_0 = \Delta P$, $R - R_0 = \Delta R$, and $Q - Q_0 = \Delta Q$ respectively, then the rate of variation of the available resources can be expressed as

$$\frac{\Delta Q}{Q_0} = \tilde{p}\,\Delta P - \tilde{r}\,\Delta R \tag{7.13}$$

This expression of rate can be used to define the following variants of available resource management:

- in deficit (i.e. available resources reducing over time)

$$\frac{\Delta Q}{Q_0} = \tilde{p}\,\Delta P - \tilde{r}\,\Delta R < 0 \tag{7.14}$$

- in equilibrium

$$\frac{\Delta Q}{Q_0} = \tilde{p}\,\Delta P - \tilde{r}\,\Delta R = 0 \tag{7.15}$$

- in excess (i.e. available resources increasing with time)

$$\frac{\Delta Q}{Q_0} = \tilde{p}\,\Delta P - \tilde{r}\,\Delta R > 0 \qquad (7.16)$$

As it tends towards certain limits, the management of available resources is characterized as:

- spendthrift management

$$\tilde{p}\,\Delta P \to 0 \quad \text{or} \quad \frac{\Delta Q}{Q_0} \to -\tilde{r}\,\mathrm{d}R \qquad (7.17)$$

  in which resources are quickly used up;
- conservative management

$$\tilde{p}\,\Delta P \to \tilde{r}\,\Delta R \quad \text{or} \quad \frac{\Delta Q}{Q_0} \to 0 \qquad (7.18)$$

  in which the available resources are maintained; and
- avaricious management

$$\tilde{r}\,\Delta R \to 0 \quad \text{or} \quad \frac{\Delta Q}{Q_0} \to \tilde{p}\,\Delta P \qquad (7.19)$$

  in which resources are hoarded and little utilized.

7.8.3 Basic analyses used in financial and economic appraisal

The project management of engineering services and development depending on mineral and thermal water resources can be financially and economically appraised using the project costs and benefits listed in Table 7.4 (Frankel, 1990).

Table 7.4 Project costs and benefits

Appraisal	*Financial*	*Economic*
Costs	Investment	Resources used for investment
	Operation	Operational resources used
	Capital repayment–depreciation	
	Maintenance	Maintenance resources used
	Overheads	
		Environmental/social costs/indirect/ external costs
Benefits	Revenues	Economic benefits
	Cost savings	Social benefits
		Environmental benefits
	Goodwill–market share/penetration	Indirect–intangible–external benefits

As in other areas of activity, some basic analyses can be applied to help make management decisions (Cook and Slack, 1984). These include cost–benefit (cost effectiveness) analysis, breakeven (cost–volume–profit) analysis and profit budget performance report–variance analysis.

Cost–benefit analysis evaluates projected schemes in terms of social outcomes as well as the usual profit and loss accounting. It begins with assessing the costs, benefits and drawbacks of the scheme, including side effects such as the generation of noise. Financial values are assigned to these, including qualities such as aesthetic appearance which are not usually associated with cost. As most major projects are developed over a long period of time, costs must reflect future conditions (Mayhew and Penny, 1992). A cost–benefit analysis has five principal steps (Heyel, 1973):

- identification of pertinent measures of effectiveness, i.e. benefits;
- description of alternatives;
- expression of both mission performance and cost as functions of the characteristics of each alternative;
- estimation of appropriate values for the equation parameters; and
- computation, analysis and presentation of results.

Breakeven (cost–volume–profit) analysis measures the functional relationships between the major factors affecting profits, and determines the profit structure of a firm (Heyel, 1973). Taking into account that

$$\text{profit} = \text{revenue} - \text{cost}$$

where total cost = fixed cost + variable cost (Evans *et al.*, 1987), this analysis can be represented by the balance of expenditure and sales income (Barker, 1989), as in Figure 7.6.

Profit budget performance report–variance analysis determines the variance from budgeted values (Lock, 1973) of the following parameters:

(a) sales volume, mix (changes in market mix, changes in product mix) and selling prices;
(b) product cost changes (material usage and prices, labour usage and rates, and overheads);
(c) carriage, freight and insurance;
(d) cost adjustments (factory overheads – activity and expenditure, inventory adjustments; and engineering overheads – activity and expenditure);
(e) overhead expenses (administration, selling and distribution);
(f) non-trading variances (discount allowed, agent's commission and interest).

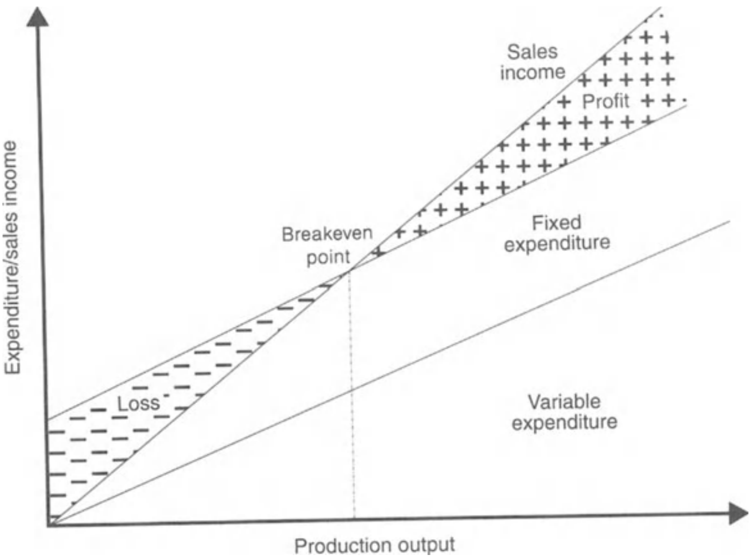

Figure 7.6 Components of breakeven analysis.

These are used to established the parameters

$$(a) - (b) - (c) = \text{gross margin}$$
$$(a) - (b) - (c) - (d) = \text{gross trading profit}$$
$$(a) - (b) - (c) - (d) - (e) = \text{net trading profit and}$$
$$(a) - (b) - (c) - (d) - (e) - (f) = \text{profit before tax}$$

Financial and economic evaluation in mineral and thermal water resource management can also be performed by current competitive logistics (Blanchard, 1992). This method is especially necessary in complex or highly developed situations and provides computer programmes for the evaluation.

7.8.4 Evaluation and maximization of profit

The first step in the evaluation of an investment opportunity is the calculation of the net cash flow, i.e. of the cash inflow and outflow, over a period of time. If the net cash flow is equivalent to profit plus depreciation, plus any other non-cash charges for a given period, usually taken as 1 year, then for the lth time increment the relationship

$$\begin{aligned}(\text{net cost flow})_l = (\text{gross revenue})_l - (\text{royalty})_l - (\text{taxes})_l \\ - (\text{operating cost})_l - (\text{investment})_l\end{aligned}$$

applies, taking into account that the net cash flow is defined on an after tax basis, since the investment represents money that has already passed through the tax system. Summing the net cash flow over a sequence of time intervals $N\,\Delta t = t$ gives the cumulative net cash flow, in the form

$$(\text{cumulative net cash flow})_t = \sum_{l=1}^{N} (\text{net cash flow})_l$$

The cash flow is generally negative during the development period. Taking into consideration that the income from production offsets costs at a time of maximum exposure, and the payout time, the project life is complete when the net cash flow rate reaches zero at a time t_f (Warren, 1992).

The manner of evaluating and maximizing revenue flow for the usage of ordinary groundwater resources in the water sales and agricultural produce markets (Douglas and Johnson, 1993) can be applied only in some special cases of mineral and thermal water resources.

A more interesting approach is to analyse the management of available resources in the successive phases of exploitation, delivery, utilization, trading and revenue for the different types of substance (mineral water, thermal water, mofettic carbon dioxide, sapropelic mud, etc.) and for different fields of use (baths, extraction of useful components, bottling, heating, etc.). For each type $i = 1, 2, \ldots, m$ of substance and for each field $j = 1, 2, \ldots, n$ of use, considered for a given time interval, these phases are characterized by the ratios

$$\alpha^i = \frac{\text{quantity exploited annually}}{\text{available resource}}$$

$$\beta_i^j = \frac{\text{quantity delivered annually}}{\text{quantity exploited annually}}$$

$$\gamma_j^i = \frac{\text{quantity utilized annually}}{\text{quantity delivered annually}}$$

$$\delta_i^j = \frac{\text{quantity traded annually}}{\text{quantity utilized annually}}$$

and

$$\varepsilon_{ij} = \frac{\text{annual profit}}{\text{quantity traded annually}}$$

named respectively the degree of exploitation [year^{-1}], factor of delivery [unitless], factor of utilization [unitless], factor of trading [unitless] and unitary profit [\$/m^3 or \$/tonne]. To these can be added the degree of trading:

$$c_i^j = \frac{\text{quantity traded annually}}{\text{quantity exploited annually}} - \delta_i^j \gamma_j^i \beta_i^j$$

Starting with the available resource Q^i [cubic metres or tonnes] and multiplying successively by the ratios corresponding to each phase, the various quantities can be expressed as follows, usually in units of m^3/year or tonnes/year:

quantity exploited annually, $\alpha^i Q^i$
quantity delivered annually, $\beta_i^j \alpha^i Q^i$
quantity utilized annually, $\gamma_j^i \beta_i^j \alpha^i Q^i$
quantity traded annually, $\delta_i^j \gamma_j^i \beta_i^j \alpha^i Q^i = c_i^j \alpha^i Q^i = b^{ij}$
annual profit, $\varepsilon_{ij} \delta_j^i \gamma_j^i \beta_i^j \alpha^i Q^i = \varepsilon_{ij} c_i^j \alpha^i Q^i = \varepsilon_{ij} b^{ij}$ [\$/year]

The annual profit varies as a result of changes of technology and other factors, including

- restrictions imposed for the protection and rational exploitation of resources and losses of exploitation;
- changes in the fields of use and losses of distribution;
- efficiency of utilization, technological losses and rejects;
- efficiency of trading, losses through transport, depreciation and refusals;
- changes in market forces, costs, etc.

Over a period of time, there will be a delay between the evolution of the functions $\varepsilon_{ij} = \varepsilon_{ij}(t)$ and $b^{ij} = b^{ij}(t)$, which appear in the expression of profit. If the evolution of these two functions is analysed in the time interval from the initial moment $t = 0$ to the current moment t, and an intermediate moment τ is considered, then $0 < \tau < t$. This expresses the delay between the values of one function of the argument τ and another function with an argument $t - \tau$, so that the profit in the whole time interval is presented, in keeping with the theorem of convolution, in the form of Borel's product of composition

$$\varepsilon_{ij}(t) * b^{ij}(t) = \int_0^t \varepsilon_{ij}(\tau) b^{ij}(t-\tau)\,\mathrm{d}\tau = \int_0^t \varepsilon_{ij}(t-\tau) b^{ij}(\tau)\,\mathrm{d}\tau \qquad (7.20)$$

Continuing the analysis for the time interval between the initial and current moments, as in profit budget performance report–variance analysis, a reduction of benefit according to an annual retraction rate $a = a(t)$ is noted. Integration of this rate with time gives the retraction of benefit

$$\int_0^t a(t)\,\mathrm{d}t$$

Consequently, in the time interval of analysis, the profit obtained before tax can be represented by the function

$$\beta(t) = \varepsilon_{ij}(t) * b^{ij}(t) - \int_0^t a(t)\,\mathrm{d}t \qquad (7.21)$$

that is submitted to taxation, multiplying by a coefficient $\zeta = \zeta(t)$, i.e. $\zeta(t)\beta(t)$, giving the final profit after tax of

$$B(t) = \beta(t) - \zeta(t)\beta(t) = [1 - \zeta(t)]\left[\varepsilon_{ij}(t) * b^{ij}(t) - \int_0^t a(t)\,\mathrm{d}t\right] \qquad (7.22)$$

As the function $\zeta = \zeta(t)$ is determined irrespectively of the managerial scheme adopted, it follows that the optimum usage of available resources should maximize the profit before tax by prescribing the conditions $\mathrm{d}\beta/\mathrm{d}t = \beta' = 0$ and $\mathrm{d}^2\beta/\mathrm{d}t^2 = \beta'' < 0$ or

$$[\varepsilon_{ij}(t) * b^{ij}(t)]' - a(t) = 0 \quad \text{and} \quad [\varepsilon_{ij}(t) * b^{ij}(t)]'' - a'(t) < 0 \qquad (7.23)$$

According to Duhamel's theorem, the derivatives of the product of composition are expressed as

$$[\varepsilon_{ij}(t) * b^{ij}(t)]' = \varepsilon_{ij}(0)b^{ij}(t) + \int_0^t \varepsilon'_{ij}(t-\tau)b^{ij}(\tau)\,\mathrm{d}\tau$$

and

$$[\varepsilon_{ij}(t) * b^{ij}(t)]'' = \varepsilon_{ij}(0)[b^{ij}(t)]' + \varepsilon'_{ij}(0)b^{ij}(t) + \int_0^t \varepsilon''_{ij}(t-\tau)b^{ij}(\tau)\,\mathrm{d}\tau.$$

Therefore the two conditions for maximizing the benefit before tax are of the forms

$$\varepsilon_{ij}(0)b^{ij}(t) + \int_0^t \varepsilon'_{ij}(t-\tau)b^{ij}(\tau)\,\mathrm{d}\tau - a(t) = 0 \qquad (7.24)$$

and

$$\varepsilon_{ij}(0)[b^{ij}(t)]' + \varepsilon'_{ij}(0)b^{ij}(t) + \int_0^t \varepsilon''_{ij}(t-\tau)b^{ij}(\tau)\,\mathrm{d}\tau - a'(t) < 0 \qquad (7.25)$$

The first of these, given with the notation $-1/\varepsilon_{ij}(0) = \lambda$ and $a(t)/\varepsilon_{ij}(0) = f(t)$, represents the Volterra equation of the second kind

$$b^{ij}(t) = \lambda \int_0^t \varepsilon'_{ij}(t-\tau)b^{ij}(\tau)\,\mathrm{d}\tau + f(t) \qquad (7.26)$$

which has a unique solution b^{ij} for every continuous f and every value of λ. Using the power series

$$b^{ij}(t) = b_0^{ij}(t) + \lambda b_1^{ij}(t) + \lambda^2 b_2^{ij}(t) + \cdots + \lambda^k b_k^{ij}(t) + \cdots \qquad (7.27)$$

in equation (7.26), the following solutions are obtained:

$$b_0^{ij}(t) = f(t),$$

$$b_1^{ij}(t) = \int_0^t \varepsilon_{ij}(t-\tau)f(\tau)\,\mathrm{d}\tau,$$

$$b_2^{ij}(t) = \int_0^t \varepsilon_{ij}(t-\tau)b_1^{ij}(\tau)\,\mathrm{d}\tau, \ldots,$$

$$b_k^{ij}(t) = \int_0^t \varepsilon_{ij}(t-\tau)b_{k-1}^{ij}(\tau)\,\mathrm{d}\tau, \ldots$$

For the time interval between the initial moment $t = 0$ and the final moment $t = t_{\mathrm{f}}$, where the functions $\varepsilon'_{ij}(t - \tau)$ are limited in their absolute value by $|\varepsilon'_{ij}(t - \tau)| \leq E$ and $|f(t)| \leq F$, the quantity traded annually must be of the dimensions

$$|b_k^{ij}(t)| \leq F\frac{E^k t^k}{k!} \leq F\frac{E^k t_f^k}{k}! \qquad (7.28)$$

The solution is given by the Neumann series, which is absolutely and uniformly convergent for any large, finite value of $|\lambda|$ and can be integrated term by term (Sąbac, 1965).

If the unitary profit and annual retraction rate are given by the functions $\varepsilon_{ij} = \varepsilon_{ij}(t)$ and $a = a(t)$ respectively, which are known for at least several discrete values, then the problem of maximization of profit before tax is reduced to determining the quantity traded annually as a function of time: $b^{ij} = b^{ij}(t)$. This problem is solved by operational calculus (Jaeger and Newstead, 1971; Ditkine and Proudnikov, 1978), using the Laplace transforms

$$\mathscr{L}[\varepsilon_{ij}(t)] = \int_0^{\infty} \varepsilon_{ij}(t)\,\mathrm{e}^{-pt}\,\mathrm{d}t = \varepsilon_{ij}^*(p),$$

$$\mathscr{L}[b^{ij}(t)] = \int_0^{\infty} b^{ij}(t)\,\mathrm{e}^{-pt}\,\mathrm{d}t = b_*^{ij}(p),$$

$$\mathscr{L}[a(t)] = \int_0^{\infty} a(t)\,\mathrm{e}^{-pt}\,\mathrm{d}t = a_*(p)$$

and transposing the condition $[\varepsilon_{ij}(t) * b^{ij}(t)]' - a(t) = 0$ into the operational equation

$$p\varepsilon_{ij}^*(p)b_*^{ij}(p) - a_*(p) = 0 \qquad (7.29)$$

that has the solution

$$b_*^{ij}(p) = \frac{a_*(p)}{p\varepsilon_{ij}^*(p)} \qquad (7.30)$$

The inverse transform

$$\mathscr{L}^{-1}[b_*^{ij}(p)] = b^{ij}(t) \qquad (7.31)$$

represents the original function to determine the quantity that should be traded annually to obtain the maximum profit before tax.

8

Environmental issues and conservation

> *If anyone be too lazy to keep his dam in proper condition, and does not keep it so; if then the dam breaks and all the fields are flooded, then shall he in whose dam the break occurred be sold for money and the money shall replace the corn which he has caused to be ruined.*
>
> Code of Hammurabi, 1760 BC

Environmental issues have to be addressed in the exploration and development of mineral and thermal waters. Several problems, such as over-abstraction and pollution have already been mentioned. Here some of these concerns are drawn together and the need for a holistic approach to the management of resources is emphasized.

8.1 ANTHROPOGENIC IMPACTS

Until the end of the 19th century, the natural conditions of mineral and thermal water systems had not been seriously degraded by human intervention. These resources had been utilized only locally and slowly, and these effects were generally compensated for by natural regeneration. In this century, and especially in the last few decades, these resources have become progressively more endangered, both in quantity and quality, by accelerated modification of their natural conditions. The causes of these modifications include the following.

- Intensive or uncontrolled exploitation by which the potential for natural regeneration was sometimes exceeded, resulting in a gradual reduction of available resources.

Mineral and Thermal Groundwater Resources
M. Albu, D. Banks and H. Nash.
Published in 1997 by Chapman & Hall, London. ISBN 0 412 61040 X.

- The numerous excavations, wells and especially boreholes which were used to abstract groundwater and associated gases, often without any control. On being closed and cemented they may constitute impermeable bodies. Conversely many abandoned wells are not sealed and can provide paths for movement of water between aquifers at different levels.
- Deforestation on steep slopes may lead to increased surface water runoff and correspondingly less groundwater recharge.
- Construction in the catchment area of waterworks, industrial estates, factories and other buildings, which alter the amount and distribution of recharge.
- Direct pollution from industrial, chemical and domestic wastes; from petroleum products and detergents as well as from the spreading of fertilizers and pesticides.
- Indirect pollution from precipitation and surface waters carrying impurities, toxic and radioactive substances from the atmosphere.
- Exploitation of other fuel or non-fuel mineral resources which causes dewatering and the deterioration of water quality in the mineral and thermal water systems.

At present, the degradation of many resources is aggravated alarmingly:

- large quantities of extracted mineral and thermal waters are wasted, without being utilized;
- rare and valuable mineral and thermal resources are consumed for ordinary use;
- pathogenic amoebae and bacteria may colonize therapeutic waters;
- mineral and thermal water sources having important religious, historic, scientific and cultural significance have disappeared or been altered or spoiled in terms of the qualities which made them important in the first place;
- relict forms of flora and fauna associated with certain thermal sources have been threatened with obliteration, as in the waters of Băile-1 Mai, Romania.

Such problems are common to many countries but in Central and Eastern Europe the deterioration of mineral and thermal water resources sometimes began as early as the investigation phase, when many boreholes were constructed unnecessarily, disturbing the natural regime. This unscientific type of investigation was carried out to avoid the more complex planning involved in tapping and equipping natural emergences, as well as to justify new funding for investment. At the same time, in the absence of an operational system to repair, clean and maintain existing wells, new boreholes were constructed.

The problems arising from utilization of many mineral waters and spa waters differ in some respects from those of utilizing high temperature thermal resources. Subsidence, noise and visual impacts on the environment for example are generally less severe, while maintaining the chemical quality of the water is more important than for geothermal waters. Spas are dependent both on temperature and water chemistry, but the conservation of their resources is allied to that of mineral waters, overabstraction and pollution of the resource being the main issues. Impacts on the environment are generally small compared to utilization of high temperature resources. The release of gases such as CH_4 and H_2S from springs or wells may cause a hazard to humans (Bélteky and Korim, 1974; Grayson *et al.*, 1990). This release is usually increased during exploitation and again is most severe in the case of high temperature waters. Thus the following sections on mineral and spa waters focus on pollution of the resource and protection of water quality while the section on geothermal waters is more concerned with the impact of exploitation on the environment.

8.2 CONCERNS OF MINERAL WATER EXPLOITATION

In contrast to other mineral resources, the chemistry of mineral waters can be unstable when natural conditions are interfered with during abstraction. Reduction of pressure can lead to loss of carbon dioxide and scaling, altering the chemical balance. Such disturbances are generally generated by arbitrary or negligent exploitation, such as that carried out formerly at Buziaş, Romania (Chapter 15). Buziaş is but one locality where the number of abstraction boreholes was increased without regard for recharge of water or the generation of carbon dioxide. This resulted in a reduction of carbon dioxide and an increase in salinity, derogating the spa until exploitation was controlled.

The use of spas is fraught with difficulties. In Budapest overabstraction has led both to a reduction in yields and to changes in water quality, a problem which has not yet been resolved. The growth of bacteria and amoebae is also problematical. There was a fatality in Bath from *Naegleria fowleri* in 1978 (Kilvington *et al.*, 1991); French spas are under scrutiny, due to a series of infections in patients (Patel, 1994). Some of the organisms implicated thrive in a warm, oxygenating environment. At Bath it has been necessary to drill a borehole to tap sterile waters at depth, rather than using the traditional springs. The proliferation of such biota is more common where warm waters are stored for a period (Legionnaire's disease, for example, is readily spread in such conditions) and a fast throughflow of water may be necessary to keep such problems at bay, possibly increasing the amount of water that has to be abstracted.

8.3 PROTECTION OF MINERAL WATER RESOURCES

8.3.1 Control of exploitation

To ensure optimal conditions of abstraction, regeneration and purity of mineral water resources (Commission du Codex Alimentarius, 1983; Albu, 1991), measures to regulate exploitation and protect the water quality are required, including

- giving priority to the maintenance, equipping and exploitation of traditional sources, especially those which are natural;
- limitation of drilling new production boreholes, and filling in of unexploited boreholes;
- adjustment of the abstraction regime such that flow rates are limited to those required by the uses and admissible losses, and the cumulative flow rate does not exceed the available resources;
- equipping and protecting the sources so as to exclude the risk of pollution or contamination;
- monitoring the exploitation, for both quantity and quality, as well as rectifying deficiencies which occur in the course of exploitation;
- periodic checks in keeping with regulations regarding the reasonable exploitation and protection of the mineral water systems.

Reductions in yields of water and heat are inevitable unless the abstraction is kept to the level of regeneration, which is often not possible for thermal waters used for heat and electricity generation.

8.3.2 Catchment protection

During its passage through the soil zone and shallow geological strata, groundwater may pick up anthropogenic contaminants. These may be from:

- dry deposition of atmospheric contaminants;
- regional application of fertilizers and pesticides (e.g. Saull, 1990; Parker *et al.*, 1991; Klimas and Paukštys, 1993);
- changes in land use, e.g. ploughing up grassland or pasture may result in a pulse of nitrate being leached from the soil zone (Addiscott, 1988);
- urban development, including sewerage, industry, roads (oils and salt), rail tracks (herbicides) and airport runways;
- spills of chemicals and persistent leakages from industrial sites.

Such contaminants may be held in the soil or unsaturated zone, where degradation of oils and other organics may take place and many of them have not caused serious harm to water resources. In England the greatest problem is from nitrate pollution from fertilizer application and from pesticides. In other countries, urbanization, sometimes related to the development of spas, is a threat, especially from sewage. Several wells in Budapest used for spa pools have been contaminated by sewage (Pearce, 1994). Industry is generally a lesser threat to direct contamination of mineral and thermal waters, but the burning of fossil fuel has led to carbon deposition over some towns, such as Karlovy Vary, where the aesthetic attraction of the spa has been damaged.

The investigation of many mineral water sources has been such that although the characteristics of the aquifers may be well known in the area of exploitation, the location of recharge areas and sensitivity of the sources to land use there are often poorly known. Generally, where an aquifer appears to be confined, it has been considered as well protected from surface activities. In many cases the flow paths of the water are poorly known, especially where there is circulation to great depths and along faults. In these systems the definition of recharge areas can be very difficult. For unconfined aquifers the catchment area is often relatively simple to define, flow times are often shorter and the effects of activities in the catchment area on the sources are easier to investigate. In these cases, the abstractor usually aims to control the land use to prevent pollution of the source.

Most countries have regulations restricting potentially polluting activities around a source or in its catchment (see Chapter 15 for an example). However, these regulations are not always easily implemented, especially in retrospect, and do not address all the potential problems. For example, they rarely apply to abstraction from other, usually overlying aquifers. Quarrying and dewatering in the limestones of the Mendip Hills in southwest England is thought to pose a risk to the thermal water sources at Bath, in the long term by possibly reducing recharge and in the shorter term by indirectly reducing pressure heads in the deep aquifer. This phenomenon has been identified in Budapest, and attempts are being made to restrict quarrying activities (Pearce, 1994).

8.4 IMPACTS OF EXPLOITATION OF THERMAL WATERS

8.4.1 General

The use of geothermal energy has often been promoted as an environmentally friendly technology. While it is often true that the environmental damage caused by its exploitation is less than that caused by most conventional energy sources, the environmental impacts can be significant. There is inevitably a degree of detrimental impact consisting of ground deformation, as well as noise and thermal and chemical pollution.

The hydrogeological regime is locally, and sometimes regionally, modified due to intensive and long term abstraction from wells. Decreasing the system pressure may cause boiling of water in the rocks, encroachment of cool water, or changes in water chemistry due to lowered temperatures and gas concentrations (Awerbuch *et al.*, 1984). The thermal field of Wairakei is one of several where uncontrolled abstraction has led to a rapid decline of temperature. Overabstraction in Iceland has led to similar problems, described in Chapter 10. Some physical and chemical changes occur in all exploited systems, and a good understanding of the hydrogeology is needed so that the flow rate of wells can be matched to their long term capacity to yield fluid (Banwell, 1974; Parker, 1983).

To avoid environmental harm, several solutions are available:

- treatment of water prior to discharge;
- controlled dilution by fresh water: in practice a dilution factor of at least 100 : 1 may be needed (Parker, 1983);
- reinjection of waste water to the reservoir;
- extraction and recovery of by-products;
- cascading use of heat in waste water (the final sink may be, for example, a fish farm where fish thrive in an elevated water temperature or a mineral bathing pool, such as at Svartsengi, Iceland).

8.4.2 Subsidence

Ground deformation is usually most severe above thermal water systems, since much larger volumes of fluid are withdrawn compared to most mineral water systems. The subsidence usually appears in the form of vertical settlement due to a pressure decrease after prolonged fluid withdrawal. Such effects are known from several systems which have been operating for a long time, for example in the Travale system in Italy (Kelk, 1992). Subsidence of up to 4.5 m and horizontal movements of up to 0.5 m have been measured at Wairakei in New Zealand (Williams, 1986). Production of steam from 64 boreholes has caused a pressure drop of over 2.4 MPa resulting in ground subsidence over an area of more than 30 km^2. Withdrawal of fluids has led to a general lowering of hydrostatic pressures in the reservoir and to the creation of a steam zone in the upper part within the production field, over an area of 2 km^2. The gradual decrease in temperature in this steam zone may be a major factor in controlling the magnitude and location of the subsidence (Pritchett, 1977). Another possible cause is that the pressure drop in the aquifer has allowed cool surface water to penetrate faults in the overlying aquitard (McNabb, 1977). The subsidence has disrupted steam pipelines and cracked drainage channels. The fact that the wells are cemented through the aquitard and that the casing does not protrude from the ground surface is taken to indicate that the subsidence is occurring within the aquifer, not in the overlying aquitard.

At The Geysers a pressure drop of 10 MPa was observed in the reservoir between 1969 and 1977, causing land deformation, with a maximum subsidence of 13 cm in the area of maximum fluid withdrawal. Here rates of subsidence are largest after new sources of steam are put on line, and gradually diminish as hydraulic gradients reach steady-state conditions. In other important geothermal reservoirs, such as Larderello, Italy, no subsidence has been reported although production has been on a relatively large scale over the last 40 years and water levels in parts of the reservoir have dropped by over 100 m (Williams, 1986).

8.4.3 Noise

Noise pollution is an inescapable part of exploitation of vapour-dominated thermal systems. Mufflers are used during air drilling at The Geysers to reduce noise levels (Greene and Goodman, 1982). A high noise level can arise from unsilenced discharging wells (up to 120 dB adjusted), but it can be attenuated to a large extent by insulation.

8.4.4 Visual impact

One negative effect of the exploitation of high temperature waters for electrical energy is the loss of surface expressions such as geysers and fumaroles. These are often tourist attractions, as in North Island, New Zealand, and in the rift system in Kenya, of aesthetic value to visitors and others who feel a sense of loss when these natural wonders disappear.

In the Whakarewarewa thermal system at Rotorua, about 150 active geysers were known in 1950 but by 1982 fewer than 15 remained, due largely to exploitation by hundreds of geothermal wells. This was the last remaining concentration of geysers in New Zealand, which had once covered a zone 250 km long, and such was the concern that the Geyser Preservation Society was founded. It was estimated that the continued uncontrolled use of geothermal resources could lose the area $NZ 160 million annually with the loss of 10 000 jobs in the tourist industry. However, it was not until the second half of the 1980s, by which time the total heat flow from the field had dropped by 50% and wells were drawing about twice the estimated natural recharge, that firm measures were taken by the Ministry of Energy to protect the system. Some boreholes were shut down, reinjection of waste waters was encouraged and the field has slowly been recovering since. The course of the struggle to achieve this end is graphically described by Andrews (1993). Now, however, there is a new threat: the Maoris are claiming the rights to the thermal resources and plan to develop more power stations.

8.4.5 Pollution from thermal waters

Many thermal waters (and some mineral waters) are rich in dissolved salts and gases, some of which may be environmentally harmful or toxic to humans. The chemistry of such waters is often highly reducing and thus incompatible with surface water. The waters may contain exceptional salinities (up to several hundred grams per litre) or concentrations of specific elements such as boron, arsenic, thallium, mercury or selenium, which would contaminate receiving surface waters and limit their use (Ellis and Mahon, 1977; Czernichowski-Lauriol and Fouillac, 1991). For example, waste water from the geothermal power plant at Kizildere in Turkey contains up to 30 mg/l boron. In addition, the elevated temperature of the waste water may prove detrimental to surface water ecology.

When power is generated from steam, about 75% of the steam is lost to the atmosphere (e.g. cover photograph), and the remaining 25% of condensate must be disposed of. In many cases this water is of poor quality, and not suitable for discharge to surface water. At The Geysers, reinjection provides a means of disposing of a condensate which is high in ammonia and boron, although it has increased levels of microseismicity (Williams, 1986).

The gases released by geothermal fluids may be undesirable due to their direct toxicity to animal and plant life (e.g. H_2S), their contribution to acid rain (H_2S, HCl), their radioactivity or their contribution as greenhouse gases (CO_2, CH_4). Czernichowski-Lauriol and Fouillac (1991) are, however, of the opinion that greenhouse gas emissions from geothermal plants are not significant at today's levels of usage. Currently, H_2S appears to be the most problematic gas: power stations at The Geysers (USA) were reported to emit some 28 tonnes H_2S per day (Ellis and Mahon, 1977) and in 1980 the figure would have been 50 tonnes per day without treatment. At Cerro Prietto an estimated 400 tonnes per day were being emitted in the early 1980s and at times the staff had to wear gas masks (Armstead, 1983). Chemical treatment both within the bore and at the surface is carried out at The Geysers to reduce H_2S emissions and this is likely to become common practice elsewhere in the world.

Most geothermal fluids carry a content of radionuclides, such as the gas ^{222}Rn, which may be discharged into the atmosphere. Releases may be significant: UNSCEAR (1982) relate that the Italian plants at Larderello (400 MW), Piancastagnaio (15 MW) and Bagnore (3 MW) release 110 TBq, 7 TBq and 1.5 TBq annually, respectively. This indicates, at least in the Italian context, a release of 400 TBq ^{222}Rn per GWa (gigawatt-annum). Assuming a population density of 100 per km^2 around the plant, this would lead to a collective effective dose of 6 person-Sv per GWa.

Even without human intervention, thermal waters have some impact on the environment. Thermal springs modify the climate locally and the gases given off, in mofettes for example, must have an influence on the chemical composition of air. The buildup of CO_2 beneath an impermeable cap can result in such a buildup of pressure that the cap may be ruptured, resulting in ground movement and creating potential hazard to humans (Chiodini *et al.*, 1995).

8.5 OPERATIONAL CHARACTERIZATION OF RESOURCE CONSERVATION

Mineral and thermal water resources, like any other renewable or nonrenewable natural resource, must be protected both quantitatively and qualitatively so that they remain available for exploitation and utilization for future generations. There is now a larger general interest, stimulated by social conscience and increasing environmental awareness, regarding the conservation of resources. The significance of resource conservation depends not only on time and place, but also on the background of the people involved in implementing management schemes. Thus the conservation of mineral and thermal water resources is represented for the hydrogeologist by avoiding overabstraction and protecting water quality among other activities; for the development engineer by avoiding abandonment and deterioration of the resources, as well as reducing extraction losses to a minimum; for the balneologist by ensuring the stability of therapeutic factors; for the economist by the planned distribution in time of the use and management of the resources. In all cases, conservation involves the sensible management and optimal use of resources.

In the absence of a satisfactory definition from all points of view, of the conservation of resources as a whole, it is necessary to resort to an operational (functional) characterization using certain measures of conservation such as maintenance, restoration, regeneration, increasing profitability, maximization, replacement, allocation and integrated management of resources (Cain, 1978; Albu *et al.*, 1989; Albu, 1991; Klee, 1991).

Maintenance is a measure to keep the resources, quantitatively and qualitatively, whilst avoiding their diminution, immobilization and deterioration. This is achieved by:

- keeping the natural conditions of the system, including:
  - the environmental conditions at the surface and in the zone of aeration (hydrogeological, pedological, microclimatic and biological);
  - initial conditions (geological, hydrological, peloidal and hydrochemical);
  - boundary conditions (of recharge, discharge, confinement, mineralization and heating);
- limitation and supervision of activities for prospecting, exploration and any other work that could cause a disturbance in the natural regime of mineral and thermal water systems;
- reduction to a minimum of immobilization and abandonment of resources;
- limiting the rate of extraction to the level of the actual possibilities for utilization;
- reduction of the minimum necessary number of access points (wells, boreholes, galleries, pipes, ditches, etc.) to the system;
- interdiction of any possible sources of direct pollution and reduction of the risks of indirect pollution.

Restoration of diminished, immobilized or deteriorated resources to normal conditions. Application of this involves:

- recovery of the natural conditions of the system;
- retrieval of immobilized and abandoned resources;

- return to the system, including reinjection, of some extracted resources which have been used and possibly reconditioned;
- removal, isolation or confinement of the sources of pollution;
- remediation of water quality.

Regeneration requires the renewal of resources to compensate for their consumption and deterioration. This involves:

- preservation or reactivation of the processes of formation and regeneration of resources (recharge, mineralization, heating, peloid formation);
- slowing down the processes of destruction and degeneration (discharge, dilution, alteration and contamination) of resources;
- attraction of resources of renewal.

Increasing profitability is a measure to increase the efficiency of exploitation and utilization of resources which can become profitable through technical and scientific progress. This measure is applied by:

- perfecting the techniques and technology of extraction and utilization of resources with difficult conditions for exploitation or of low quality (certain formation and oilfield waters, salt waters and mineral muds);
- identification or discovery of therapeutic properties;
- procedures of beneficiation or of administration, for attraction into the market of sub-profitable goods and services (for example, certain mineral waters, gases, peats, rocks and aerosols).

Maximization consists of avoiding waste, reducing losses and more efficient utilization, to obtain the maximum return from the resources. Application of this measure involves:

- reducing to a minimum losses occurring during extraction, transport, distribution, handling and use;
- increasing the level of trading by using the extracted resources as completely as possible (stocking, self-regulation, thrifty direction of capacities);
- observing the norms for specific consumption rates in different fields of use (balneal therapy, extraction of useful components, bottling, heating, etc.);
- multiple utilization in cascading applications or in steps of use (for example, thermal waters used successively for energy production and balneal or recreational purposes; carbonated mineral waters used first for extracting carbon dioxide and second for bathing or bottling, salt waters and muds used successively for bathing and for extracting useful components);
- obtaining extracts or concentrates with a high value of use (medicinal salts obtained by evaporation of mineral waters, pharmaceutical and cosmetic products prepared from extracts of sapropelic muds);
- extension of use at a distance (from the source) by bottling, or packing, transport and retailing of therapeutic mineral substances.

Replacement is a measure of saving resources of higher quality, or those which can only be regenerated slowly, by increasing the proportion used of lower quality or more easily regenerated. This involves:

- progressively fulfilling requests for goods and services from relatively more abundant and less valuable resources (for example, low temperature waters, formation or oilfield waters, salt and brine lakes, carbon dioxide in solution, mineral muds, peats);
- limiting consumption of high value or rare resources (certain mineral waters for medicinal use, heliothermal lakes, mofettic gases of high purity and sapropelic muds) as the proportion of use of replacement resources increases.

Allocation consists of regulating tariffs and prices depending on political, economic and social interests, governmental priorities, rationalization or share allocations. Application of this measure involves:

- financial support from state departments, municipalities, etc., or from commercial firms for the utilization of certain mineral and thermal water resources, with the aim of stimulating the activities of spas, tourism, bottling plants, etc.;
- provision of social assistance and humanitarian support to enable the aged or handicapped to benefit from using certain resources.

The integrated management of resources is a measure of conservation in that it maximizes in the long term the cumulative goods and services from which society as a whole can benefit. This measure is achieved by:

- harmonization of exploitation of the different mineral and thermal water resources, in accordance with their magnitude, importance and availability for multiple uses;
- protecting and guaranteeing the mineral and thermal resources against the disruptive effects of exploitation and utilization of other types of resources (of coals, hydrocarbons, ores, etc).

In summary, conservation can be defined as the maximization in the long term of net social benefits in goods and services from resources (Cain, 1978), against a background of general harmonization of conditions of the technology with those complementary social requirements (Carter *et al.*, 1977; Tindbergen, 1978).

8.5.1 Trends, institutionalization and strategy

At present there are three main trends in conservation of resources. The first trend is to subordinate the particular interests of intensive production from particular types of resources to the general interest of integrated management of all resources, and thereby to pass gradually from short term and local profitability, due to locally intensive and uncontrolled exploitation of certain resources, to long term and global profitability achieved by good organization of the utilization of the resources as a whole (Cain, 1978).

The second trend in conservation is manifested in integrated management of resources, so as to avoid the deterioration of some by the exploitation and utilization of others (Bonnefous, 1976).

The third trend is represented by the increasing role of social, political and economic factors in the integrated management of resources and in maintenance of ecological conditions, on the basis of a more thorough analysis of the social efforts and benefits, and the humanitarian purpose in utilization of resources (Commoner, 1980).

There are numerous national and international organizations which are concerned with the conservation of water resources. They are more or less effective depending on the laws or standards followed, and especially depending on their powers to enforce compliance. The main EC Directives which apply to the protection of groundwater quality are 91/676/EEC (on Diffuse Pollution by Nitrates) and 80/68/EEC (the Groundwater Directive). The former aims to protect groundwater from further pollution with nitrates, while the latter aims to control the release of toxic substances into water. Most countries restrict certain potentially polluting activities around a source used for water supply, and require abstractions to be licensed, permitting abstraction only if it will not affect existing sources. However, the existing legislation and practice is mostly concerned with the protection of drinking water supplies and does not usually directly address the conservation of mineral and thermal waters.

Current international practice indicates that the efficiency of conservation of resources on the whole can be ensured not only by conservation of different types of resources, but especially by the co-ordination of these activities. For the future development of resources an institutional basis must be established corresponding to the following strategy of conservation:

- correct re-estimation and systematic regeneration of resources according to rigorous scientific criteria;
- ensuring proper legislation for conservation of each type of resource and of resources as a whole;
- constituting institutional and educational bases for optimization and control of the use of resources, as well as for raising consciousness of the importance of conservation;
- subordination of the interests of intensive exploitation of certain preferential types of resources to the higher interest of equilibrated management of all resources;
- integrated management of resources and harmonization of technology with the complementary conditions of social order, methodically avoiding the deterioration of one resource by the exploitation and utilization of

others, as well as avoiding disharmony between economic and social trends;
- increasing the role of social, political and economic factors in the integrated management of resources and in the preservation of ecological conditions;
- gradual integration of national strategies into regional, continental and worldwide strategies of conservation of resources.

The development potential of every country is determined by the quantity and quality of its resources, both human (labour, skills, finance, capital and technology) and natural (fuel and non-fuel minerals, energy, water, flora and fauna, soil and air). If these resources are managed moderately, efficiently and harmoniously, to the advantage not only of the present but also for future generations, then a country thrives, becoming rich and strong in the long term. Otherwise, the country becomes impoverished and weakened, with increasingly uncontrollable crises which can even endanger the existence of future generations.

Part Two

Case Studies

9

Geothermal energy in Iceland

Hjalti Franzson, Jens Tómasson, Guðrún Sverrisdóttir and Freysteinn Sigurðsson

9.1 GEOLOGICAL OUTLINE

Iceland lies in the North Atlantic Ocean, just south of the Polar Circle. It is formed by the only major subaerial part of the Mid-Atlantic Ridge system (Figure 9.1) and has an area of some 100 000 km^2. The Mid-Atlantic Ridge is represented by the Reykjanes Ridge to the south and the Kolbeinsey Ridge to the north. The continuation of the ridge across Iceland is complex, but there are two main zones of rifting present. Of these, the western zone runs from Reykjanes northeast to Langjökull where it is connected by the Mid-Iceland volcanic zone to the eastern rift zone, which runs from Tjörnes in the northeast of Iceland to the Torfajökull area in the south. In addition, there is a WNW-trending volcanic fracture zone which runs from Snæfellsjökull to within 30 km of Langjökull. The whole island is volcanic in origin, the rocks being dominantly of basaltic composition. A mantle hot-spot is thought to lie beneath Iceland, on the grounds of the observed anomalous volcanic productivity, geochemical signature and indications from geophysical measurements of an underlying low density mantle plume (Sæmundsson, 1978).

The age of the geological formations generally increases away from the volcanic rift axis, reaching about 15 Ma on the east and northwest coasts. Similarly, the depth and degree of erosion increases away from the volcanic zones. Rifting occurs to a large extent within distinct fissure swarms, often containing a central volcano. Each fissure swarm, together with its central volcano, is termed a *volcanic system*.

The oldest rocks in the country are of Tertiary age (more specifically, early Miocene to early Pliocene) consisting of sequences of subhorizontal lava

Mineral and Thermal Groundwater Resources
M. Albu, D. Banks and H. Nash.
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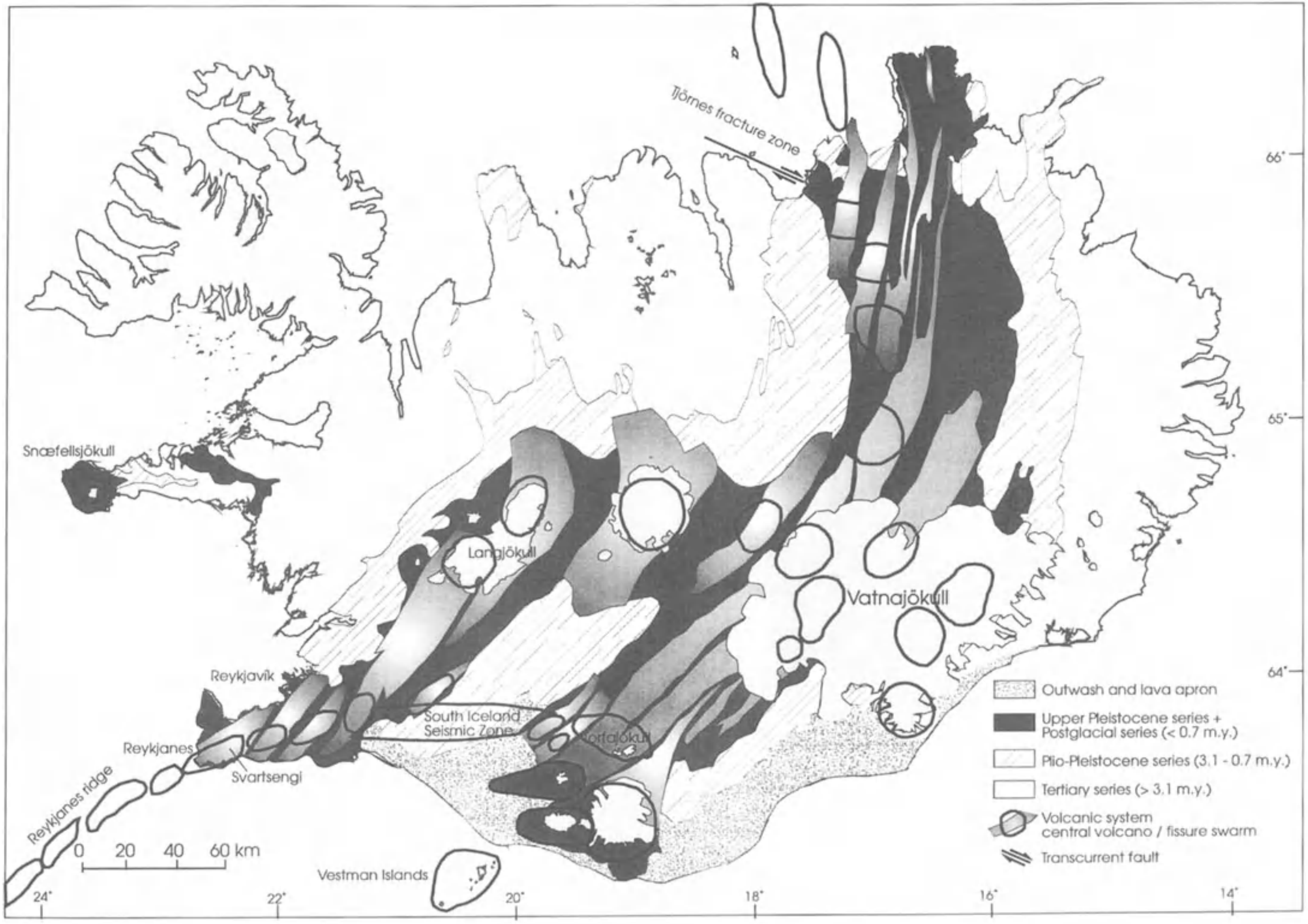

Tjörnes fracture zone
66°
65°
64°
Snæfellsjökull
Langjökull
Vatnajökull
Reykjavík
South Iceland Seismic Zone
Torfajökull
Reykjanes
Svartsengi
Reykjanes ridge
0 20 40 60 km
Vestman Islands
24°
22°
20°
18°
16°
14°
Outwash and lava apron
Upper Pleistocene series + Postglacial series (< 0.7 m.y.)
Plio-Pleistocene series (3.1 - 0.7 m.y.)
Tertiary series (> 3.1 m.y.)
Volcanic system central volcano / fissure swarm
Transcurrent fault

flows, interspersed with more irregularly structured central volcanoes. In the Plio-Pleistocene ('Early Quaternary', i.e. age 3.1–0.7 Ma) signs of glaciation, hyaloclastites and stronger erosion appear. In the Upper Pleistocene (0.7–0.01 Ma), subglacially formed mountains of hyaloclastites and pillow lavas alternate with subaerial, glacially scoured lava fields. In the recent volcanic zones, more than 20 active central volcanoes have been identified.

The structure of the central volcanoes is complex, with the occurrence of evolved rock types and common emplacement of shallow intrusions. The rocks in and around the central volcanoes show varying degrees of hydrothermal alteration. The central volcanoes are thought to be active for a typical duration of 0.5–1.5 Ma.

The fissure swarms in the current volcanic zones are tectonically active and some of them may extend into the older formations. The main volcanic zone is offset from the oceanic ridge by tectonic transform zones in southern Iceland, and on the north coast. This may conceivably be due to shifting of the position of the rift zone in relation to the assumed mantle hot-spot with time. Some volcanic activity occurs in the transform zones themselves, the chemistry of the related rocks being usually slightly alkaline. This complex and constantly changing tectonic regime is probably the cause of some of the observed rejuvenation or creation of fissure swarms in the older formations.

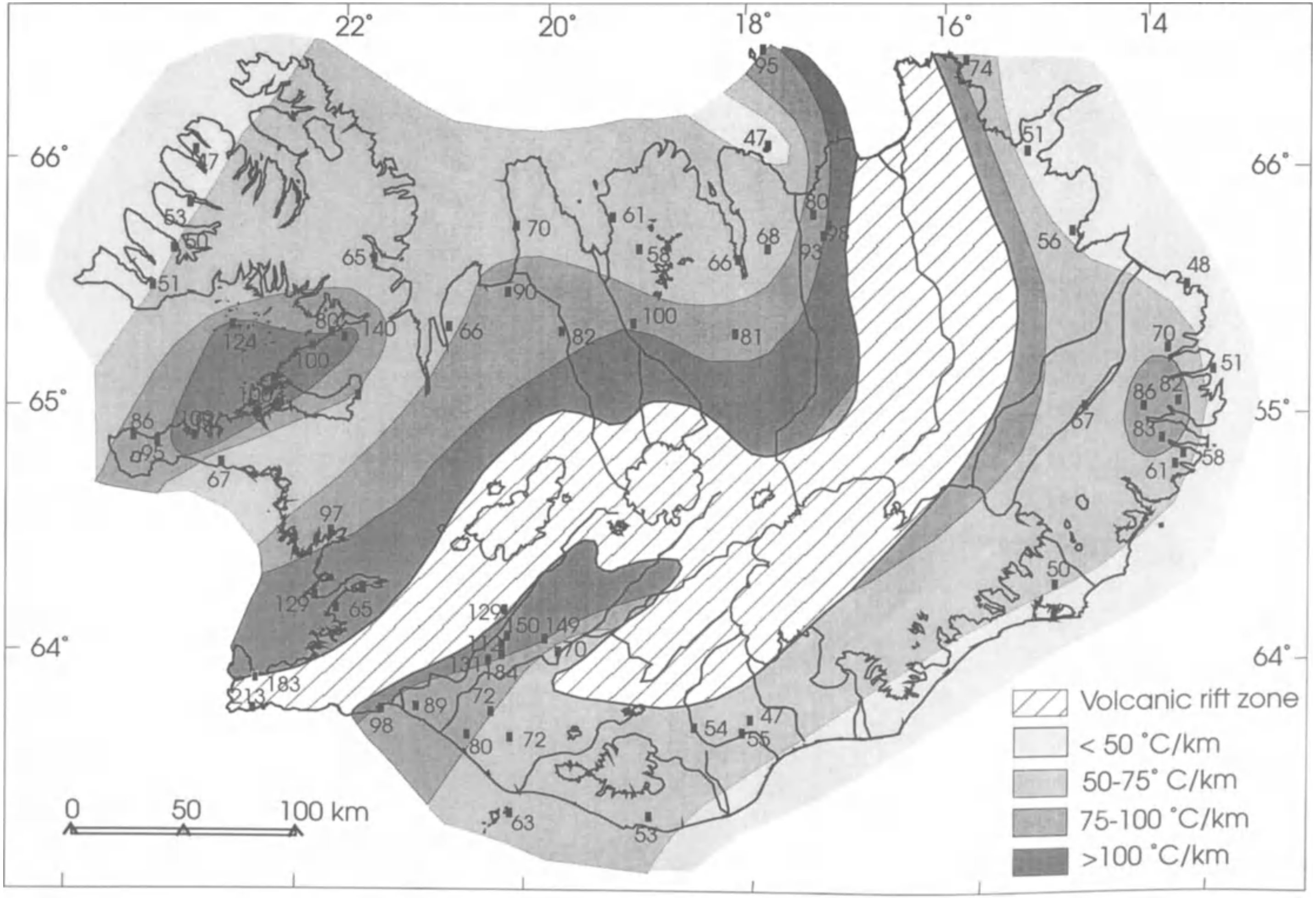
9.2 GEOTHERMAL ACTIVITY, HYDROGEOLOGY AND CHEMISTRY

Geophysical surveys indicate that the crustal thickness below Iceland is about 10–15 km (Flóvenz and Gunnarsson, 1991). This is about twice the thickness of typical oceanic crust, but much less than that found in continental crust. The thin crust results in a relatively high geothermal gradient. Figure 9.2 shows the distribution of the geothermal gradient within Iceland (outside active geothermal areas, the gradient is based on borehole data). The figure illustrates that the gradient increases towards the active volcanic zones, supporting the idea of crustal thinning below these zones. An appraisal of the thermal gradient within the volcanic zone itself is hampered by the effect of the substantial zone of active cold groundwater flow occupying the highly permeable top few hundred metres of the volcanic succession.

The crustal groundwater systems are divided into two main types: cold groundwater and geothermal systems.

The hydrogeology of the cold (fresh) groundwater is relatively simple (Sigurðsson, 1993). The older formations usually have a low permeability and exploitable groundwater is, as a rule, only found in surficial sediments,

Figure 9.1 Map showing the geological features and tectonic settings of Iceland. (Modified from Sæmundsson, 1978.)


22°
20°
18°
16°
14
66°
65°
64°
Volcanic rift zone
< 50 °C/km
50-75° C/km
75-100 °C/km
>100 °C/km
0
50
100 km

rejuvenated fissure zones and in occasional patches of unaltered rock. In the Upper Pleistocene and Holocene formations, however, very high permeabilities are found, particularly in recent lava fields, unaltered pillow lavas and in active fissure zones. These permeable formations yield fresh springwater, the springs having an estimated total flow rate of 600 m^3/s. The chemistry of the fresh groundwater is rather uniform, due to:

- the uniform rock chemistry;
- the cool climate (annual mean temperature about 5°C in the lowlands);
- sparse vegetation;
- sparse rural settlement.

The total dissolved solids (TDS) content of the waters is typically low (<100 ppm), the waters are very soft and the marine component from precipitation is significant (5–20 ppm chloride in the lowlands compared with 1–2 ppm in the central highlands).

Geothermal activity in Iceland is widespread and has been classified into (1) high temperature areas and (2) low temperature areas (Böðvarsson, 1961). Figure 9.3 shows the geothermal fields and their relationship to geological features. The high temperature fields are all found within the active volcanic zones and most of them are closely associated with the main volcanic centres and fissure swarms.

The heat source for the high temperature areas is related to magmatic activity, as indicated by their proximity to areas of active volcanism, their temperature and the chemical composition of the geothermal fluid and its dissolved gases. Shallow intrusions in the active rifting or volcanic zones give rise to a high thermal gradient and are probably the main contributors of heat in the high temperature systems. In these systems, by definition temperatures exceed 200°C at 1 km depth. The chemical composition of the geothermal fluids is characterized by a low pH and a high concentration of gases, mainly CO_2 and H_2S. As a result, hydrothermal alteration near the surface is extensive and visible in these areas. Table 9.1 shows examples of the composition of water in some high temperature geothermal fluids.

The low temperature areas are situated outside the main volcanic zones, in Plio-Pleistocene and Tertiary rock formations (Figure 9.3). Two main views prevail concerning their genesis, the flow path of their water and their heat source. The first hypothesis was presented by Einarsson (1942) and supported by Árnason (1976). This theory assumes that the precipitation falling on the highlands seeps down to deep levels in the crust where it is heated by the elevated geothermal gradient. It then returns to the surface by flow up permeable structures to emerge in lowland areas. The other hypothesis (Böðvarsson, 1982, 1983) proposes that the groundwater

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Figure 9.2 Distribution of the geothermal gradient in Iceland. (Source: Flóvenz and Sæmundsson, 1993.)

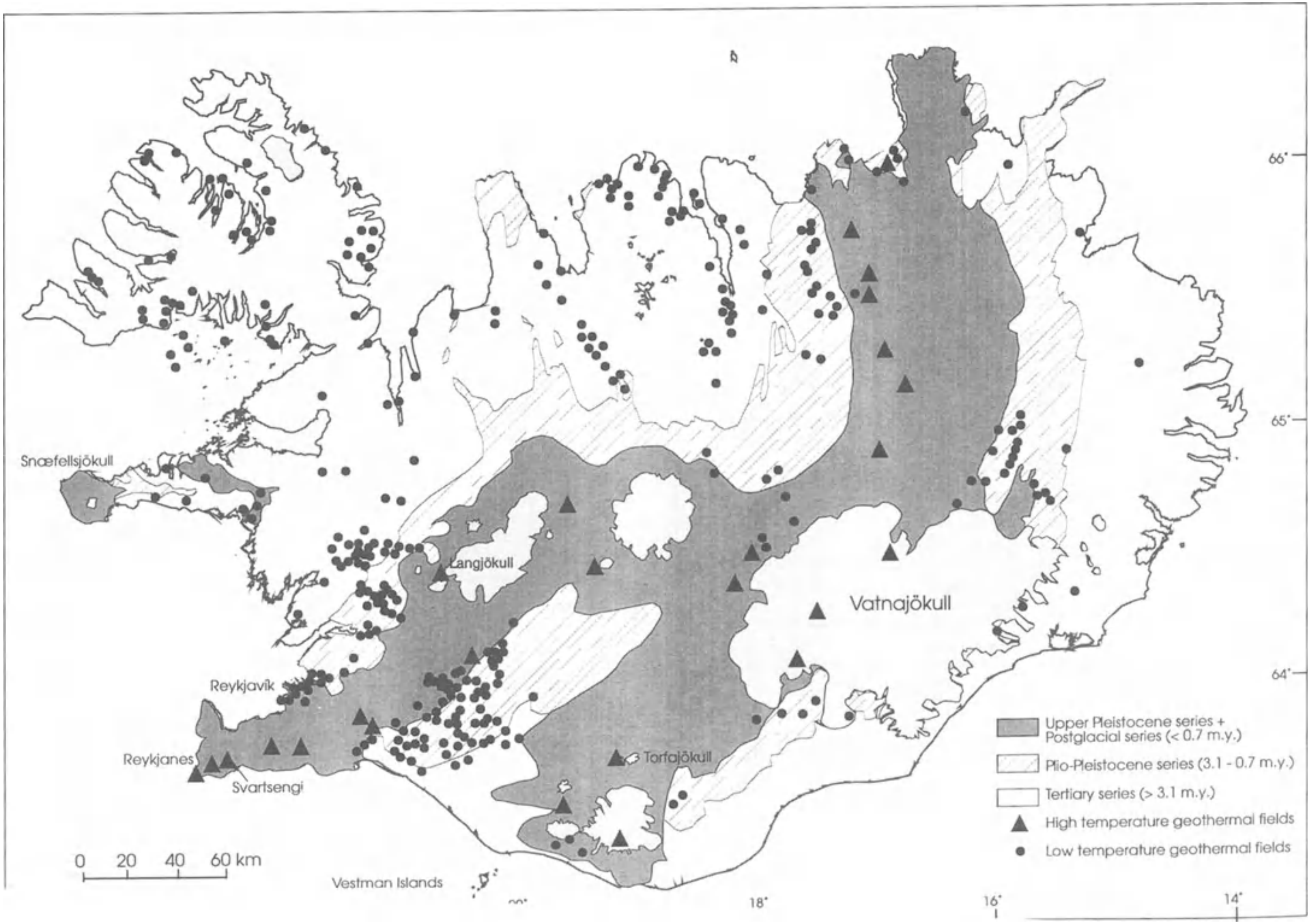
66°
65°
64°
18°
16°
14°
Snæfellsjökull
Langjökull
Vatnajökull
Torfajökull
Reykjavík
Reykjanes
Svartsengi
Vestman Islands
0 20 40 60 km
Upper Pleistocene series + Postglacial series (< 0.7 m.y.)
Plio-Pleistocene series (3.1 - 0.7 m.y.)
Tertiary series (> 3.1 m.y.)
High temperature geothermal fields
Low temperature geothermal fields

Table 9.1 Typical chemical composition of deep high temperature geothermal fluids (mg/l)

	Area		
	Reykjanes well 9	*Svartsengi well 8*	*Krafla well 7*
Temperature (°C)	295	238	277
P_s[a]	29.0	16.2	3.1
SiO_2	635	465	371
Na	9 400	6 360	152
K	1 390	970	27.3
Mg	0.9	0.59	0.02
Ca	1600	1 000	0.81
F	0.14	0.13	1.03
Cl	18 300	12 330	25.3
SO_4	14	28	126
TDS	32 300	21 400	1068
CO_2	1 670	330	173
H_2S	49	6.3	73
H_2	0.15	0.006	0.06
CH_4	0.08	0.03	0.01

[a] P_s = pressure at wellhead sampling point.

percolates to deep levels along near-vertical fracture systems where it is heated locally by the hot crust before returning to the surface. The latter theory is at present more generally accepted (Flóvenz and Sæmundsson, 1993). Characteristically, the temperature of water in low temperature areas does not exceed 150°C in the uppermost 1 km. The composition of the low temperature geothermal water is characterized by high pH (especially in waters with temperatures lower than 100°C), and low concentrations of gases. Most of the gas found in low temperature water is atmospheric nitrogen. Table 9.2 shows some representative analyses of low temperature geothermal waters ranging from fresh water with a high pH, through slightly brackish and brackish to saline water.

Most geothermal water in Iceland is of meteoric origin. It contains, in general, lower concentrations of dissolved solids than geothermal fluids of other countries. The low temperature waters normally contain TDS of 200–400 mg/l, while the high temperature waters normally contain 1000–2000 mg/l. However, in some coastal areas, seawater has penetrated into geothermal reservoirs where the permeability of the bedrock is high. In such systems the mineral concentration of water is much higher, approaching that of seawater in some cases. Because of reactions with the rock, the ion ratios in these fluids are quite different from those of seawater. The potassium and calcium concentrations, in particular, are much higher in

Figure 9.3 Distribution of high and low temperature areas in Iceland and their relation to the volcanic zones.

Table 9.2 Typical chemical composition of some low temperature geothermal waters (mg/l)

Well *Date*	*LN-12* *12 Oct 1993*	*HA-11* *13 Oct 1993*	*SK-12* *15 Oct 1993*	*UV-08* *26 May 1993*	*LA-03* *16 Oct 1993*	*PK-13* *10 Feb 1993*	*BA-01* *14 Jan 1993*	*H-2* *25 Mar 1988*
Temperature (°C)	94.4	63.5	73.4	76.2	96	74.7	116	71
pH/°C[a]	9.75/16	10.32/19	10.08/17	9.81/24	9.22/22	8.57/24	8.90/22	7.30/22
CO_2[b]	14.7	16.3	19.9	16.8	13	18.8	3.6	40.3
H_2S	0.09	0.038	0	0.17	0.21	0	0.48	0
O_2	0	0	0.06	0	0	0	0.003	–
SiO_2	97.5	88.9	94.8	65.8	98.4	59.8	130.7	69
Na	51.7	49.5	43.8	67	147.5	147	397	11 041
K	1.18	0.53	0.7	0.96	3.58	3.72	17.8	399
Ca	2.91	2.08	1.54	6.94	24.5	28	78.4	1 915
Mg	0.001	0.003	0.004	0	0.001	0.064	0.01	109.2
F	0.41	0.46	0.35	0.68	3.55	0.21	0.52	0.04
Cl	11.3	8.9	8.7	44.4	140	229	676	19 950
SO_4	38.6	12.8	8.95	52.4	142	51.1	122	1 534
TDS	182	183	185	268	578	546	1432	36 690

[a] Temperature at which pH measured.

[b] Total carbonate.

the saline geothermal fluids than in seawater, whereas the sulphate concentration is low and magnesium almost absent. The main examples of such systems are the Reykjanes and Svartsengi high temperature geothermal fields. These are both located on the Reykjanes peninsula (Figure 9.3). These fields are situated on the southwestern rift zone of Iceland, where the bedrock consists mainly of neovolcanic basaltic lava flows and hyaloclastite formations.

Some low temperature waters from the lowlands of southern Iceland also exhibit elevated chloride concentrations. This also is explained by seawater influence: the salinity is thought to be derived from 'fossil' seawater which percolated into the bedrock prior to the isostatic uplift at the end of last glaciation. Concentrations of chloride in groundwater can be used as an indicator of seawater influence. Chloride is conservative: nearly all other dissolved species react with the surrounding rocks, forming alteration minerals controlled by thermodynamic equilibria which characterize the temperature, down to temperatures of 50°C (Gíslason and Arnórsson, 1990).

9.3 HISTORY OF EXPLOITATION OF GEOTHERMAL RESOURCES

Geothermal energy plays a crucial role in Iceland's energy economy. The dominant use is for space heating: almost 90% of houses in the country use geothermal water for this purpose. The installed capacity for direct application is about 800 $\mathrm{MW_t}$. The first district heating system was the Reykjavík Municipal Heating Service which commenced operations in 1930. It is still the largest geothermal district heating service in the world, serving the homes of about 150 000 people. In total there are about 60 district heating services of varying size in Iceland. Of these, 17 serve more than 1000 inhabitants. Iceland also has about 100 swimming pools throughout the country, which consume about 5% of the total exploited applied geothermal energy. Greenhouses covering an area of about 170 000 $\mathrm{m^2}$ use geothermal heat, consuming some 4% of the total. Other industrial uses of geothermal energy and geothermal waters include the drying of diatomite, seaweed and fish, wool washing, salt production, carbon dioxide production and fish farming, particularly for rearing smolt. Electricity produced by geothermal energy accounts for some 45 $\mathrm{MW_e}$, or 4.3% of the bulk electricity produced, while the remainder is obtained from hydroelectric power (84.2%) and oil (11.5%; Figure 9.4a).

Figure 9.4b indicates the increase in the use of geothermal reserves with time, compared with other primary energy sources. As the geothermal resource has been mined more extensively, it has become increasingly necessary to address environmental issues. Pumping from wells has, in many cases, led to the regional lowering of the water table and the derogation of surface features such as springs, or to an alteration in the manifestation of such features, e.g. to steam emission. Overabstraction may also lead to land subsidence. This may be alleviated or overcome by reinjecting the extracted fluid back into the reservoir.

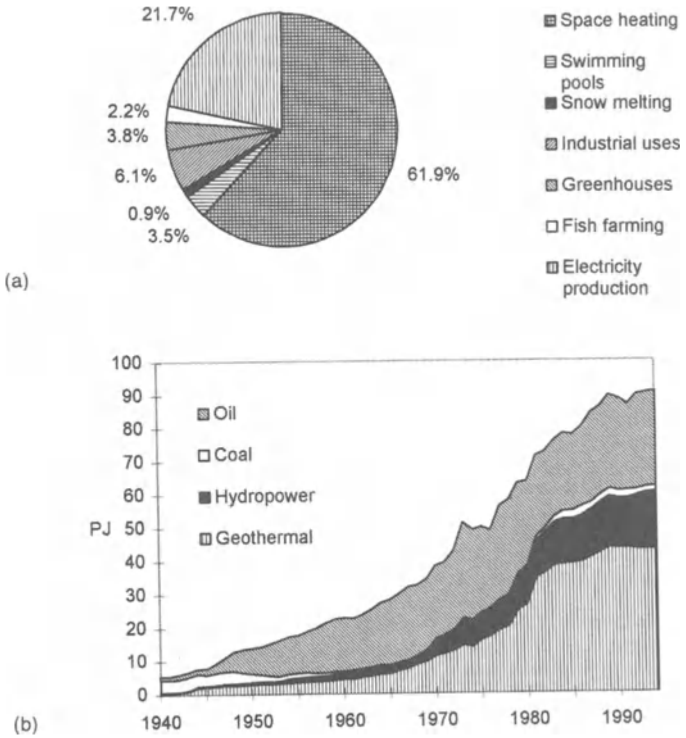

Figure 9.4 (a) Distribution of uses of geothermal energy and (b) primary energy supply in Iceland 1940–1994 in petajoules, classified by energy sources (excluding aircraft and ship refuelling outside Iceland). (Source: Ragnarsson, 1995.)

The high temperature geothermal fluids often contain minerals and gases which are discharged into the environment. The most notorious of these is H_2S which, when emitted from geothermal plants, has a noxious odour and can be toxic in moderate concentrations. In addition, CO_2 contributes to the greenhouse effect. Overall, however, the environmental impacts are insignificant in comparison with fossil fuel equivalents.

9.4 CASE STUDIES

9.4.1 Reykjavík Municipal District Heating Service

History of exploration

Four geothermal fields are exploited by the Reykjavík Municipal Heating Service (Hitaveita Reykjavíkur): Laugarnes, Elliðaár, Reykir and Nesjavellir (Figure 9.5). The first three fields are low temperature, but Nesjavellir is

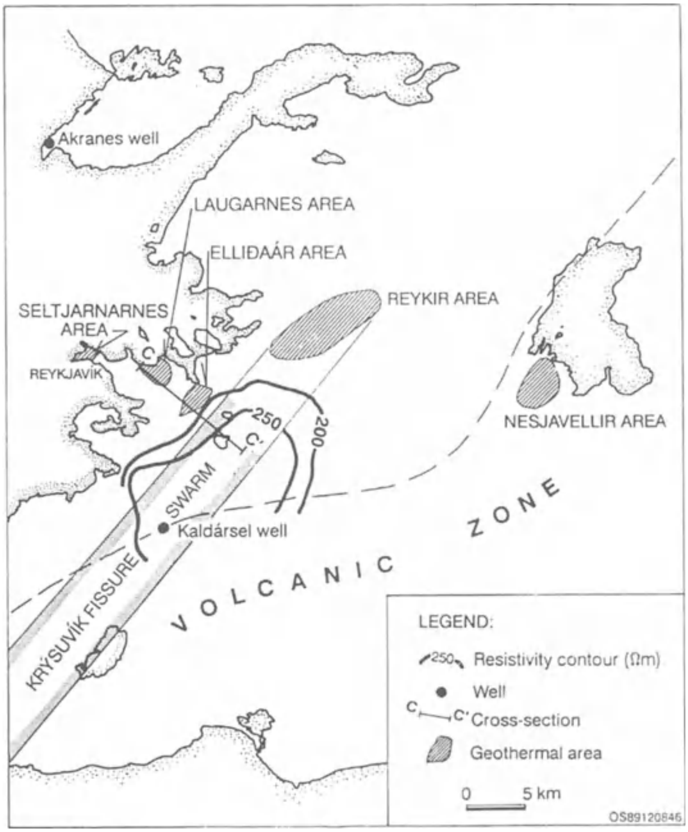

Figure 9.5 Location of geothermal areas exploited by Hitaveita Reykjavíkur and the Krýsuvík fissure swarm. (Revised from Tómasson, 1993.)

a high temperature area. In addition, the Seltjarnarnes field has been developed as a district heating system by the Seltjarnarnes municipality.

The exploitation of the geothermal water began in 1928–1930 in the Laugarnes area with the drilling of 14 small diameter wells near the Þvottalaugar hot springs (Thorsteinsson and Elíasson, 1970). The deepest well was 246 m deep and the well field delivered 15–20 l/s of artesian water at a temperature of 95°C, compared with 5–10 l/s previously from the natural springs. This water was used for the heating of 70 dwellings and a newly built swimming hall.

Exploration drilling started in the Reykir area in 1933 (Figure 9.5). Prior to drilling activities the area consisted of a major spring area with a total flow of 120 l/s (Thorsteinsson, 1975) and temperatures of 70–83°C. In 1943 the water from this area was piped to Reykjavík, and by the end of that year 200 l/s of water at 86°C was available for heating houses in Reykjavík. By 1944–1945 the annual consumption of geothermal water was already about 5 million metric tonnes. Drilling at Reykir continued until 1955, by which time some 70 wells, up to 628 m deep, had been drilled, with a total flow of 360 l/s at a temperature of 80°C.

In 1958 further drilling in the Laugarnes area commenced with a new type of rig (rotary drilling), which was able to construct both wider and deeper wells than previously. Between 1958 and 1963, 22 wells were completed in the Laugarnes area, with depths ranging from 650 to 2198 m, at a diameter of 220 mm. The water was pumped from these wells by submersible turbine pumps, whereas the water previously abstracted in Laugarnes and Reykir had been by free artesian flow from the wells. The maximum yield was thus increased to 330 l/s at a temperature of 127°C.

Drilling began in the Elliðaár area in 1967. Here there were only minor surface manifestations before drilling, typically relatively cold springs or ponds with maximum temperatures of 25°C. In the period 1967–1969 ten wells were drilled in this area, between 861 and 1613 m deep with a diameter of 220 mm. The maximum pumped yield from these wells in 1969 was about 165 l/s of water with a temperature of 101°C. Since 1969, more wells have been drilled in the Elliðaár and Laugarnes areas and the total number of wells in these two areas is now 41, with a maximum depth of 3085 m. In 1970 the Reykir geothermal system was redeveloped by the deep rotary drilling of large diameter wells. Between 1970 and 1977, 37 wells were drilled, to depths of 800 to 2042 m (at a diameter of 220–310 mm), with a total drilled length of 61.4 km. The maximum pumped yield from these wells was 1800 l/s at 86°C.

Production from the Nesjavellir high temperature field did not begin until 1990 (Gunnarsson *et al.*, 1992). The Nesjavellir geothermal plant was established because the low temperature fields described above were nearing full exploitation. Additionally, the energy yield of the low temperature fields was perceived to be gradually declining because of increasing drawdown with time and because of cooling. The energy production from Nesjavellir in 1993 accounted for 24% of the total energy production of the company Hitaveita Reykjavíkur (Figure 9.6).

The amount of water used by Hitaveita Reykjavíkur steadily increased until, in 1988, the consumption reached 60 million tonnes per annum. This amount remained stable until 1993 (Figure 9.6), when water consumption fell a little below 60 million tonnes due to good weather conditions. Another factor affecting the maximum consumption is that the energy required to heat each cubic metre of house space has gradually fallen due to better domestic insulation of houses and more efficient water flow control systems. The total population served by Hitaveita Reykjavíkur is about 150 000.

Geology and hydrology

Figure 9.5 shows the location of the fields described above, together with that of the Seltjarnarnes area. The three areas Seltjarnarnes, Laugarnes and

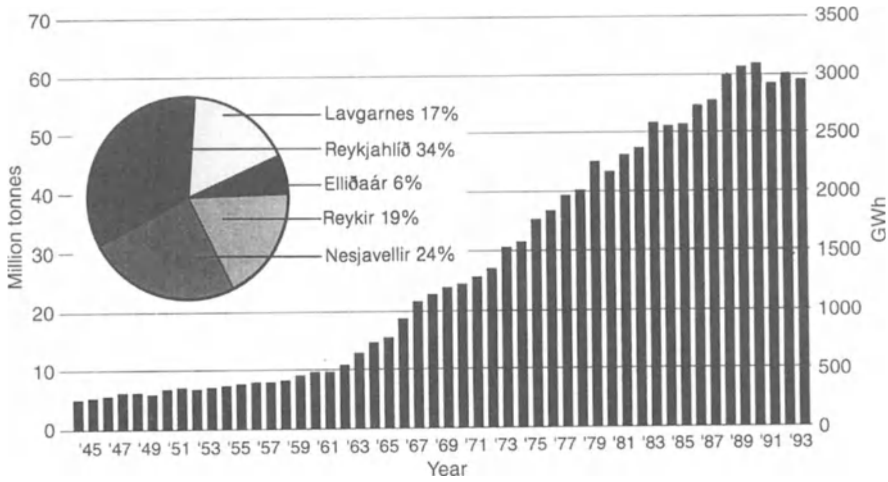

Figure 9.6 Yearly production of water by Hitaveita Reykjavíkur from 1944 to 1993, illustrating the subdivision of energy production between geothermal areas in 1993. (After *Year Book 1993 – Hitaveita Reykjavíkur*.)

Elliðaár lie close together and are collectively known as the Reykjavík geothermal areas. These areas do, however, appear to be separated by hydrogeological barriers: production from one area does not affect the groundwater level in the two others. In addition, the temperatures, isotopic compositions and geochemistry of the waters differ between the three areas. Shallow wells (less than 300 m deep) which lie between the three areas exhibit much lower geothermal gradients than those encountered within the geothermal areas proper. The three fields therefore appear to represent distinct thermal anomalies (Tómasson *et al.*, 1975).

The Reykjavík geothermal areas and the Reykir area are located in Upper Pleistocene rocks. In Figure 9.5 the location of the Krýsuvík fissure swarm is indicated, which extends beyond the volcanic zone towards the Reykir area. Resistivity measurements indicate that cold groundwater penetrates down to a depth of 750–1000 m in this swarm. Several wells have been drilled into the Krýsuvík fissure swarms ranging from 200 to 986 m in depth (Tómasson and Franzson, 1992).

The Elliðaár system lies only a few kilometres north of the Krýsuvík fissure swarm. Here, a cold groundwater layer about 10 m thick overlies the geothermal system. This layer increases in thickness towards the Krýsuvík fissure swarm where it reaches 750–1000 m depth.

Figure 9.7 shows a simplified cross-section through the Laugarnes and Elliðaár areas into the Krýsuvík fissure swarm. The rocks have been simply subdivided into three groups; the Upper Basalt, Hyaloclastite and Lower Basalt groups. The temperature of the Laugarnes geothermal system varies from 120°C at a depth of 300 m to 160°C at 2800 m. In the

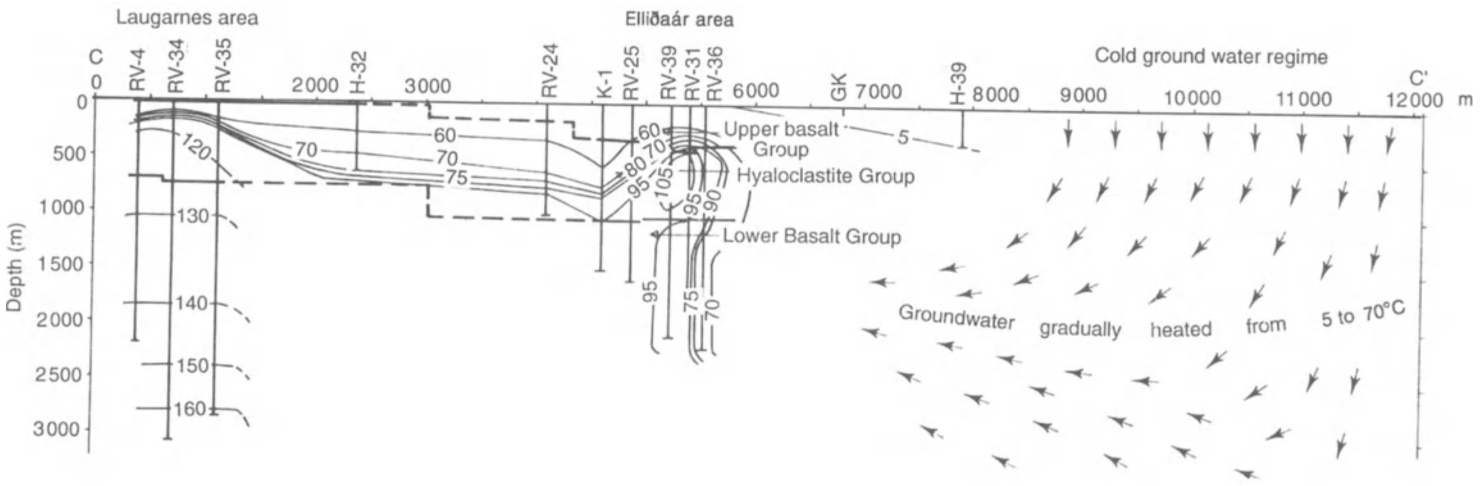

Figure 9.7 Cross-section C–C′ through the Laugarnes and Elliðaár areas into the Krýsuvík fissure swarm (see Figure 9.5 for location), contours of temperature in °C. (Source: Tómasson, 1993.)

Elliðaár area a reverse temperature gradient occurs, with a hot tongue of water approaching from the northeast with a maximum temperature of 109°C, as indicated in Figure 9.7. Below the hot tongue, temperatures range between 72 and 85°C. It is believed that the water below the hot tongue is of local origin, i.e. derived from the Krýsuvík fissure swarm to the south of the area (Tómasson, 1993). Indeed the northern end of the Krýsuvík fissure swarm is thought to extend into the Reykir low temperature area.

Fluid chemistry

The geothermal water used by Hitaveita Reykjavíkur generally has a typical low temperature water chemistry, as described above. However, the three exploited fields have some individual chemical characteristics, especially regarding chloride content. Table 9.3 shows representative chemical analyses of water from these areas, as well as one analysis of groundwater which is heated by the Nesjavellir high temperature fluid, and one analysis from the Seltjarnarnes area, in a coastal location at low elevation. The influence of seawater on the hydrochemistry of the geothermal waters is most notable in the Seltjarnarnes area. Under low elevation, coastal conditions, geothermal reservoirs are very sensitive to the inflow of either cold groundwater or seawater induced by pumping.

The low temperature water is used directly in the heating systems of houses in Reykjavík, but as the saline water of Seltjarnarnes is too corrosive for direct utilization, each house in the heating system of the Seltjarnarnes district is now equipped with a heat exchanger.

Table 9.3 Representative analyses from geothermal waters of the Reykjavík geothermal fields

	Area				
	Seltjarnarnes	*Laugarnes*	*Elliðaár*	*Reykir*	*Nesjavellir*
Date	3 Apr 1990	31 Jan 1990	16 Jan 1990	14 Feb 1990	7 Feb 1991
Temperature (°C)	117.7	130.1	86.3	92.4	83
pH/°C[a]	8.30/22.3	9.45/22.9	9.53/22.6	9.61/22.0	7.80/24.1
CO_2	11.1	17.5	26.3	21.9	36.5
H_2S	0.09	0.3	0	0.2	0.3
SiO_2	122.4	150.2	67.6	97.6	20.9
Na	654	70.3	46.2	46.6	9.4
K	17.5	3.5	1	0.8	1.1
Ca	568	3.68	2.23	1.91	8.56
Mg	1.13	0	0.01	0.01	4.99
F	0.67	–	0.18	0.75	–
Cl	1810	55.6	25.1	15.4	8
SO_4	323	28.7	13.3	18.2	12.1

[a] Temperature at which pH measured.

High temperature fluids are highly corrosive because of their low pH, high concentration of gases, and high temperature and concentration of total dissolved solids (which can also lead to scaling problems). Therefore, the Nesjavellir high temperature fluid is used for heating cold groundwater for space heating. Severe scaling problems can arise if the heated groundwater is mixed with the low temperature geothermal waters. When the groundwater, with its relatively high magnesium concentration, mixes with the geothermal water, with its high silica concentration, in conditions of rising pH induced by degassing, magnesium silicate incrustations are easily formed (Kristmannsdóttir *et al.*, 1989; Sverrisdóttir *et al.*, 1992). Therefore, the heated groundwater is mostly used separately from the other waters but, in case of minor mixing in the system, the pH of the heated water is buffered at 8.8–9.0.

Development of the reservoir

There has been considerable cooling in the Elliðaár field since production began in 1968, at an average rate of about 5°C per year for the water pumped from the area. This cooling rate is different from one well to another: the maximum cooling was 36°C from 1969 to 1990 in one well (Tómasson, 1993). As the geothermal water is pumped out, it is replaced by cold water lying above and to the east of it.

Pumping from the geothermal system causes a drawdown in the adjacent cold water systems. Currently, the degree of drawdown in the Elliðaár area, which ultimately depends on the quantity of abstracted water, is rather stable with time but, in the Reykir area, the drawdown is increasing significantly (Figure 9.8). One interpretation of this is that the Reykir area is a ‘closed’ system while Elliðaár has a more ‘open’ character.

Production from the Nesjavellir field, which started in 1990, has partly replaced production from the Reykir, Laugarnes and Elliðaár areas. This has led to a rise in the water table of these areas in places which will, in turn, increase the capacity of the low temperature areas to yield in the middle of the winter and in cold weather.

9.4.2 Svartsengi high temperature field

Regional geological setting and hydrogeology

The Svartsengi high temperature field is situated on the western part of the Reykjanes peninsula in southwest Iceland (Figures 9.1, 9.9). The Reykjanes peninsula is effectively the landward extension of the Reykjanes Ridge. The main tectonic structures are shown in Figure 9.9. The rifting is expressed at the surface as distinct NE–SW trending fissure swarms arranged *en echelon* along an E–W trending volcanic zone. Microseismic evidence suggests that the crustal boundary below about 2 km depth is an E–W trending zone

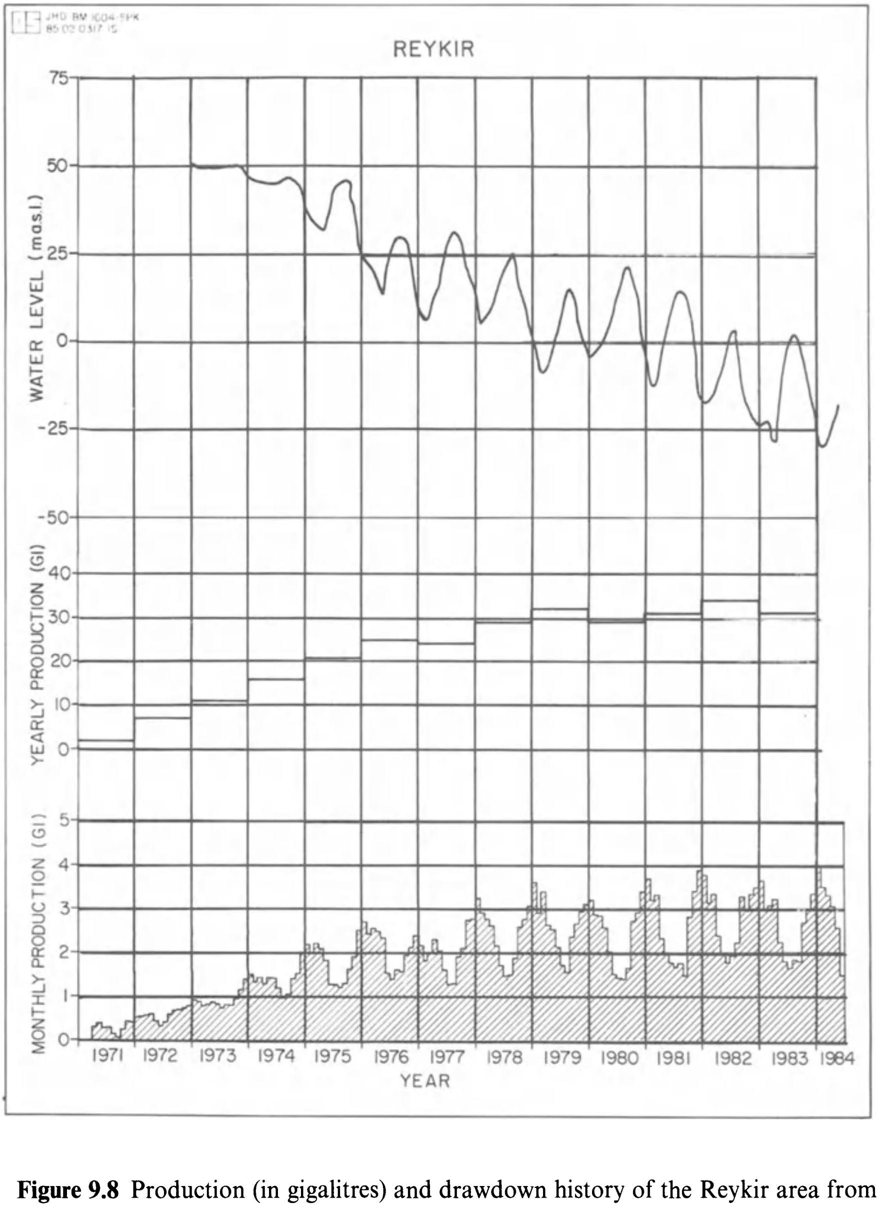

Figure 9.8 Production (in gigalitres) and drawdown history of the Reykir area from 1970 to 1984. (Source: Sigurðsson *et al.*, 1985.)

about 2 km wide. Surface volcanic features are of two main types:

- subaerial lava formations erupted during the last 12 000 years;
- hyaloclastite formations erupted mostly during the last glacial period (approximately 12 000–115 000 years ago).

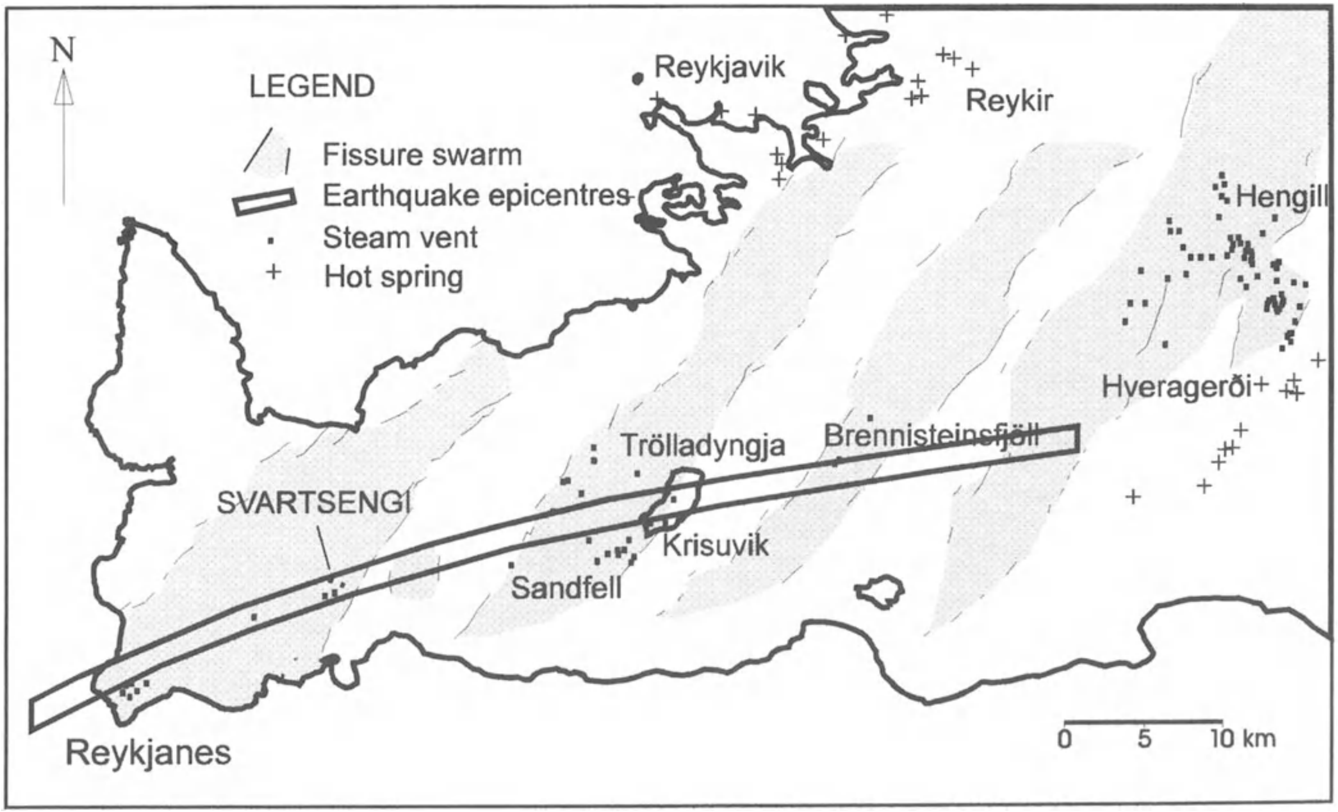

Figure 9.9 A tectonic outline of the Reykjanes peninsula, illustrating the location of the Reykjanes and Svartsengi high temperature fields.

Studies have shown that, during the last 5000 years, major volcanic episodes have occurred at about 1000 year intervals. The last such episode occurred in the 13th century.

There are three main types of groundwater system on the western Reykjanes peninsula.

- The uppermost system is a thin lens of fresh groundwater (Sigurðsson, 1986). The thickness of this freshwater lens varies from a few metres to a maximum of about 50 m. The water table lies approximately 1 m above sea level, reflecting the extreme permeability of both the postglacial lava sequence and the fissure swarms.
- The second groundwater system, underlying the fresh water lens is seawater dominated. Its temperature varies with depth, being less than 10°C down to depths where the permeability decreases, below which the temperature increases according to the prevailing geothermal gradient (>100°C/km).
- The third type comprises the high temperature systems. These generally lie at the intersection of the NE–SW fissure swarms and the underlying microseismic zone (Figure 9.9).

In addition there may exist a continuous, interconnected, high temperature reservoir extending from Svartsengi westwards to the Reykjanes high temperature field, along the E–W microseismic zone (Figure 9.3).

Surface geology

A simplified surface geological map of the Svartsengi area is shown in Figure 9.10. The oldest formations at the surface are hyaloclastites, the hills Svartsengisfell and Þorbjarnarfell being most prominent in the area. These were most probably formed during the last glacial period (12 000–115 000 years ago). Banked up against these hyaloclastites are postglacial lavas. The largest part of the Svartsengi field is covered by lavas dating back to the 13th century.

The dominant tectonic trend is NE–SW, being clearly visible in the hyaloclastite formations. Another more northerly trend is seen around the southern part of the Svartsengi field and vague indications of NNW–SSE tectonic lineaments may be observed on aerial photographs in the pass between Svartsengisfell and þorbjarnarfell. Tectonic lineaments are almost absent in the postglacial lavas, owing to their young age. Volcanic fissures trend similarly NE–SW, but shift to a N–S direction around Svartsengi.

Figure 9.11 illustrates surface alteration in the Svartsengi field. Alteration mineralization can be divided into two groups:

- an intense alteration with calcite and clay formation;
- a slight alteration where sporadic opaline deposition occurs.

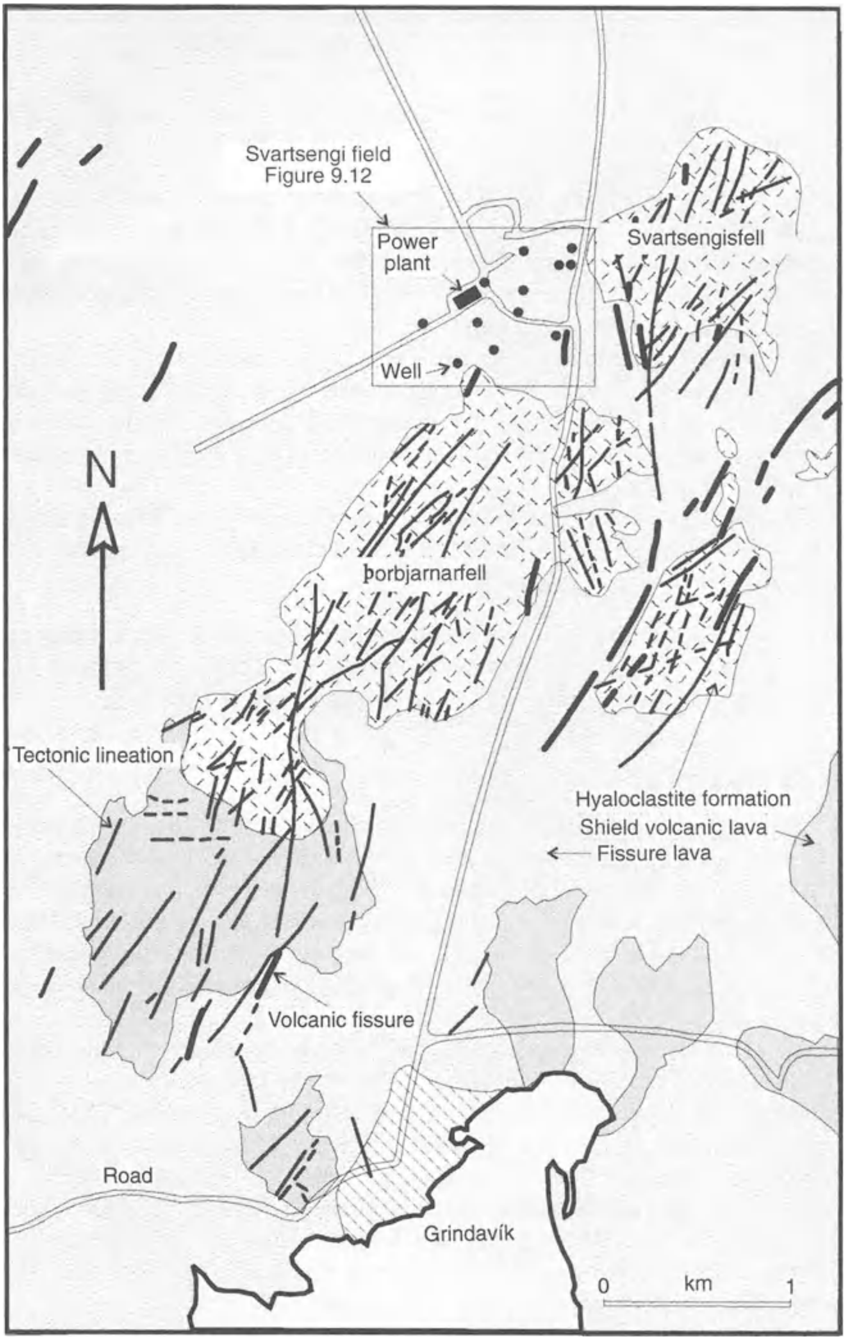

Figure 9.10 The main geological and tectonic features of the Svartsengi field.

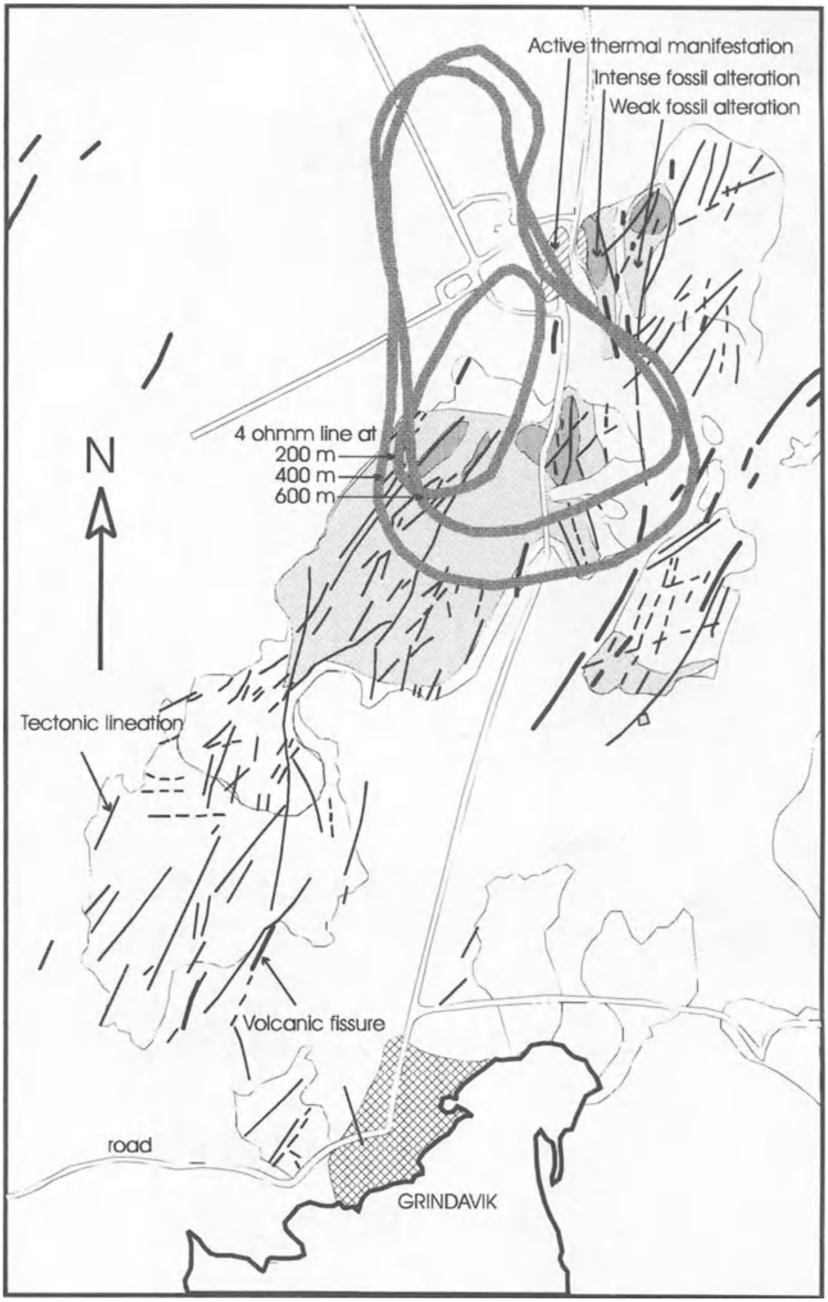

Figure 9.11 Surface alteration and resistivity anomalies in the Svartsengi geothermal field.

Table 9.4 Design and production characteristics of geothermal wells in the Svartsengi high temperature field

Well number	*Year drilled*	*Depth (m)*	*Production casing (m)*	*Temperature maximum (°C)*	*Wellhead pressure (bar)*	*Water flow (kg/s) (5.5 bar)*	*Steam flow (kg/s) (5.5 bar)*	*Remarks*
1	1971	262	–	–	–	–	–	Cold water
2	1972	239	198	–	–	–	–	Cemented
3	1972	402	143	–	–	–	–	Cemented
4	1974	1713	394	–	–	–	–	Damaged casing, not utilized
5	1974	1519	395	–	–	–	–	Cemented
6	1978	1737	612	–	–	–	–	–
Deepening	1982	2000	–	–	–	–	–	Damaged
7	1979	1438	600	240	15	38.3	8.6	Production well
8	1980	1604	622	240	15	36.5	7.9	Production well
9	1980	994	590	240	16	32	7	Production well
10	1980	425	232	231	24	–	25	Production well
11	1980	1141	582	240	16	36.2	7.9	Production well
12	1982	1488	607	234	12.5	25.3	4.8	Production well
14	1994	612	195	229	–	–	–	Production well
15	1992	140.6	97.4	190	–	–	–	Observation well

The former type is clearly associated with faults and fractures. It is questionable whether the latter type is due to the high temperature field or to a geothermal episode associated with hyaloclastite formations. Currently, active manifestations of the field are only seen in the northwestern area. This was hardly noticeable prior to exploitation of the field but has increased markedly in recent years, due to lowering of the water table concurrently increasing steam pressure and venting.

The electrical resistivity of the subsurface is very low, owing to the high salinity of fluids below the freshwater lens. As shown in Figure 9.11, the 4 Ω m isosurface trends NE–SW at 200 m depth, while at 400 m and 600 m the trend is just west of north (Georgsson, 1984).

Subsurface geology

To date, 15 wells have been drilled in the Svartsengi field. The data reported here are based on the first 12 of these. Their design and production characteristics are detailed in Table 9.4, and their locations are shown in Figure 9.12. The geological data are mainly derived from drill cutting

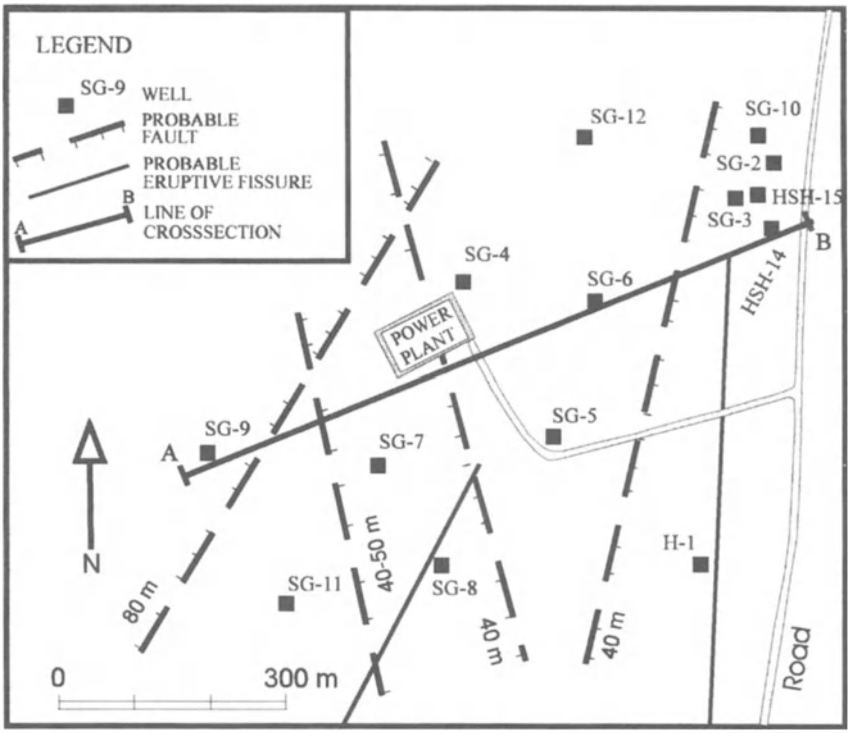

Figure 9.12 Locations of wells at the Svartsengi field, and their relation to faults and dykes. (Source: Franzson, 1995.)

samples taken at 2 m intervals during drilling. Correlation with geophysical logs confirms the geological interpretation.

Figure 9.13 shows the main geological features of the volcanic sequence in the reservoir. The succession consists of lava sequences erupted during interglacials, and hyaloclastites formed as eruptions underneath the glacial ice sheets. The geological data suggest that the main faults underlying the superficial lavas have two directions, NE–SW and NNW–SSE. The throw of these are about 40–50 m up to a maximum of about 80 m (Figure 9.12). Intrusive rocks begin to appear in the geothermal wells below about 600–700 m depth (Figure 9.13). They generally represent less than 10–30% of the succession until some 1000–1100 m depth, where they approach 100%. It is probable that their proportion diminishes to less than 30% below 1400 m depth. Their particular prominence at about 1000–1400 m depth, together with their doleritic petrography, suggests that they are subhorizontal sills.

Hydrothermal alteration

The hydrothermal alteration in the field has been studied in some detail by a number of workers (e.g. Ragnarsdóttir *et al.*, 1984; Lonker *et al.*, 1993; Franzson, 1995). The main minerals found in the field are calcite, aragonite, dolomite, magnesite, chalcedony, quartz, analcime, wairakite, anhydrite, albite, prehnite, epidote, pyrite, smectite, mixed layer clays, corrensite, chlorite and illite. A detailed mineralogical study by Lonker *et al.* (1993) also detected the presence of garnet, oligoclase, K-feldspar, titanite, haematite, anatase, chalcopyrite and halite. A study of hydrothermal alteration may yield considerable information on the geothermal system, including factors such as water–rock interaction and evolution of the geothermal system with time.

The temperature dependence of many alteration reactions is particularly useful in assessing reservoir temperatures: for example, the alteration zones shown in the cross-section of Figure 9.13 give an indication of the probable thermal distribution in the reservoir. The smectite–zeolite zone extends down to about 400 m and is succeeded by the mixed layer clay zone, then a chlorite zone and, lastly, the chlorite–epidote zone. These zones represent temperatures of approximately 200, 220, 230 and 250°C respectively. An epidote–amphibole zone which would indicate reservoir temperatures of over 270°C, has not yet been identified.

The measured temperature distribution (Figure 9.13) correlates fairly well with the alteration temperature estimates, except perhaps in that temperatures in the chlorite–epidote zone may be slightly lower than expected. Indeed, homogenization temperatures T_{h} measured in calcite, quartz and anhydrites in well 12 show that the present temperatures are 20–60°C lower than T_{h}, while higher values occur below 1000 m depth. Melting values (T_{m}) of fluid inclusions, where values near to fresh water

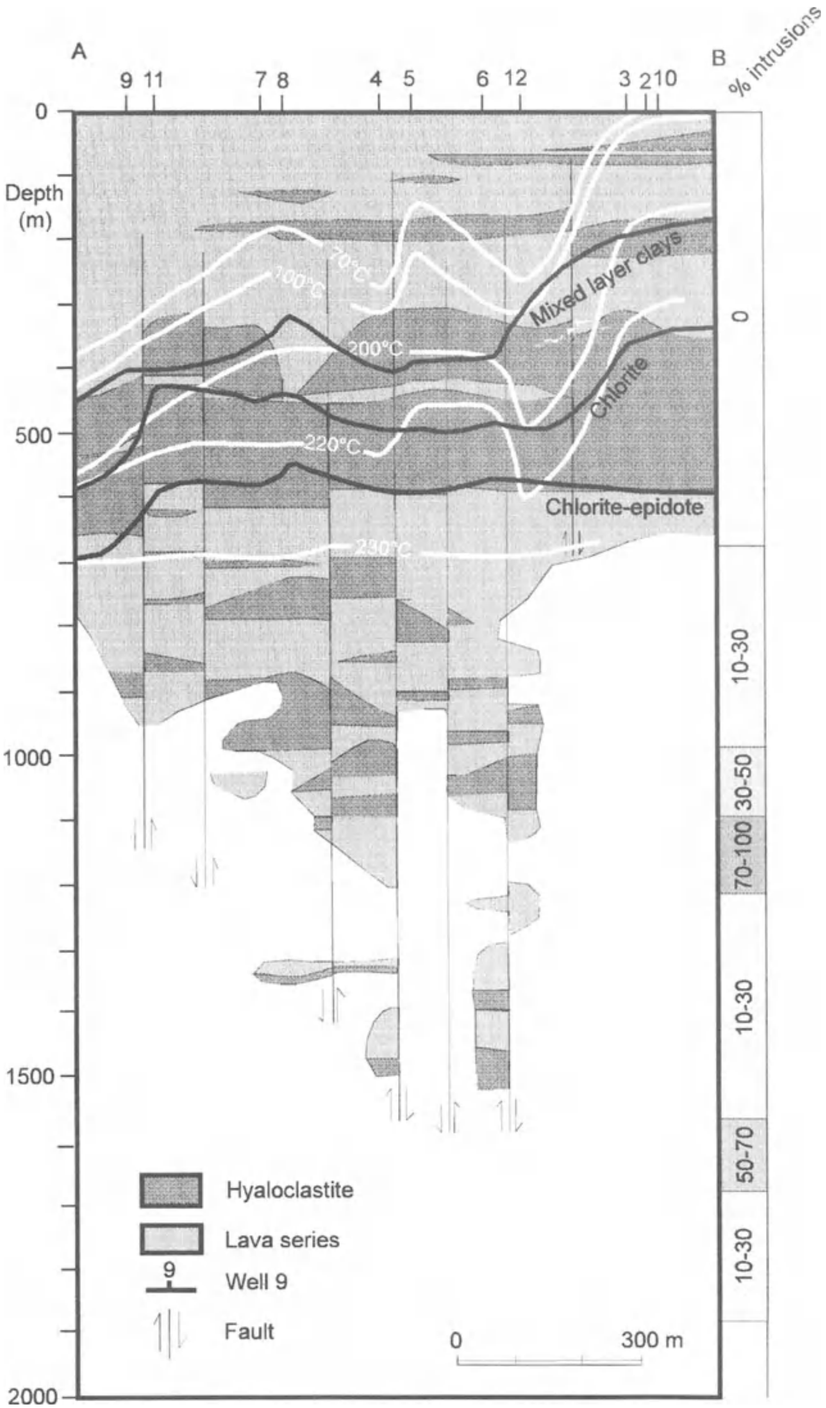

Figure 9.13 Geological cross-section, temperature distribution and alteration zones of Svartsengi field, along cross-section A–B (see Figure 9.12).

are observed, indicate that the fluids may once have been less saline than at present (Franzson, 1995).

The measured temperatures are less than 100°C down to approximately 300 m depth, while some 220°C is reached at 500 m depth (Bjórnsson and Steingrímsson, 1993). The reservoir temperature is typically 230–240°C. A shallow steam cap is found in the northeastern part of the field, partly induced by lowering of the water table through exploitation.

Aquifers

The reservoir permeability is high in Svartsengi, as indicated by the rather homogeneous temperature of 230–240°C. A close study of lithology and feed points in the wells has established the presence of a geological control on the water-yielding horizons in the reservoir, as indicated in Figure 9.14. Aquifer horizons are bimodally distributed, one maximum being found

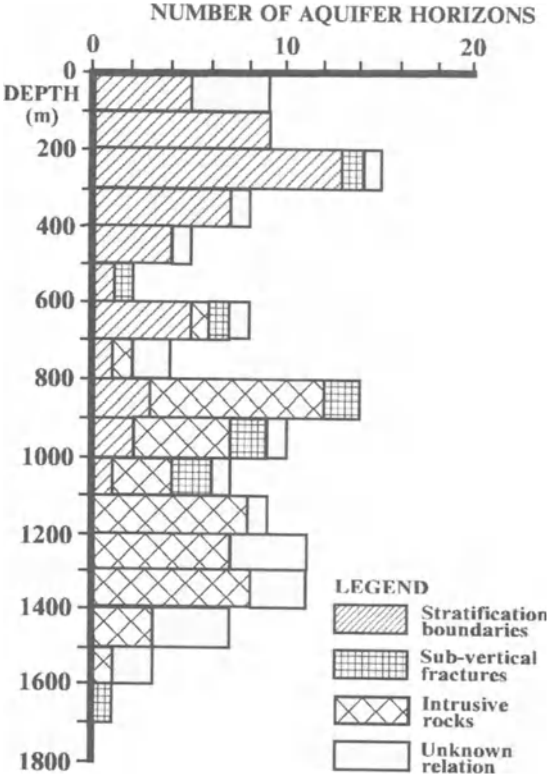

Figure 9.14 Correlation of aquifer horizons with geologic features at Svartsengi. (Source: Franzson, 1995.)

above 400 m depth and the second below about 800 m. The non-aquifer zone of 400–600 m coincides with an assumed cap-rock where the highest temperature gradient is measured (Figure 9.13). Aquifer horizons encountered above the cap-rock are mostly related to stratigraphic boundaries between accumulative units (lavas and hyaloclastites), whereas aquifer horizons in the reservoir itself are dominantly associated with intrusives and, to a lesser extent, tectonic fractures. The main upflow in the system is probably related to a N–S trending fault just east of wells 7 and 8 (Figure 9.12).

Chemistry

The geothermal fluid of the Svartsengi area is a high temperature brine. The fluid is a mixture of seawater and fresh water in a proportion of 2:3, although a degree of water–rock interaction in the geothermal reservoir has caused the fluid chemistry to deviate from a simple mixing line. For example, the concentration of SiO_2 is 50 times higher in the brine than would be expected from simple mixing, indicating the predominantly lithological derivation of silicon, due to its high solubility at temperatures up to 240°C (Bjarnason, 1988). On the contrary, magnesium concentrations are about 1000 times less than simple mixing would predict, presumably due to the precipitation of low solubility magnesium silicates from solution. Representative analyses of the deep geothermal fluid are given in Table 9.1.

Utilization

Exploration of the Svartsengi area commenced in the early 1970s and the power plant started operating in 1977. The main purpose of the Suðurnes Regional Heating enterprise, which Svartsengi feeds, is to supply water for district heating to the communities in the western part of the Reykjanes peninsula (Figure 9.15). The plant produces a total of 125 MW_t for heating in the four townships of the area, the NATO airbase and the Keflavík International airport. It also produces electricity at a rate of about 16 MW_e.

Because of its high temperature and salinity, the geothermal fluid at Svartsengi has to be used indirectly. The mixture of hot water and steam from the wells is used both for the production of electricity by turbines and for municipal heating systems by heating fresh groundwater in heat exchangers. Following heat extraction, the geothermal water is discharged into a pond close to the plant. The waste water is extremely enriched in silica and is used for balneological purposes. It has acquired the nickname 'The Blue Lagoon' and has proved a popular tourist attraction.

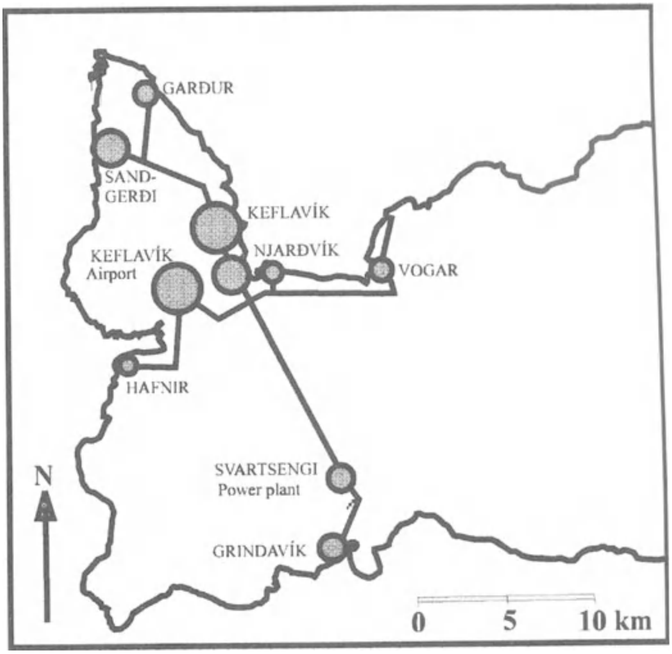

Figure 9.15 Distribution system for the Svartsengi geothermal power station.

A flow diagram of Power Plant II in Figure 9.16 shows the main components of the system. The brine flows from the wells at 240°C and passes through the high pressure separator. The high pressure steam passes on to a turbine electric generator, while the brine is either discarded to the silencers and thence to the Blue Lagoon or is diverted to the low pressure separator. The steam produced in the separator is mixed with incoming cold groundwater in the preheater/degasser before being pumped through two plate heat exchangers and into the distribution system. The cold groundwater is abstracted from the fresh groundwater lens and is pumped from an open fissure near Svartsengi into a storage tank. When entering the plant it passes through the condensers of the ORMAT binary power units and then enters the preheater/degasser unit, as mentioned above.

A total of eight binary units are operated producing some $10\,MW_e$. Additionally, $6 + 1 + 1\,MW_e$ steam turbines are operational, making a total electric production of $16\,MW_e$.

The temperature of the exported hot water is about 100°C and this is piped northwards to storage tanks at Fitjar. There, the water is mixed with return water from the NATO base, decreasing the temperature to about 80°C. This mixed water is then pumped to the other communities on the peninsula (Figure 9.15). A separate pipeline with water at 80°C supplies the township of Grindavík, south of Svartsengi.

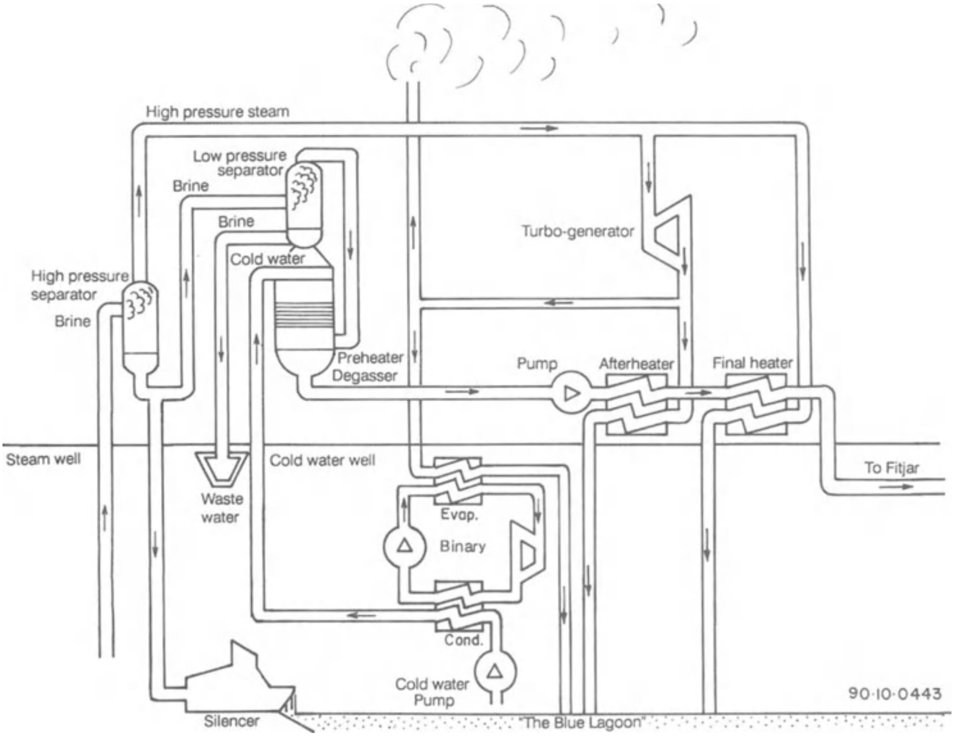

Figure 9.16 Schematic flow diagram of the Svartsengi geothermal Power Plant II.

Negative effects – scaling, drawdown and subsidence

Some of the wells have to be reamed out regularly due to calcium carbonate scaling, but no insurmountable scaling problems have occurred during utilization (Kristmannsdóttir, 1989). Magnesium silicate scaling has occurred in the heated fresh water system, and this problem is kept under continuous observation. The fluid abstraction rate from the reservoir has increased from about 26 kg/s in 1976 to 279 kg/s in 1991. This has resulted in a steady drawdown in the reservoir to about 150 m in 1985 and to about 200 m in 1991. A marked drawdown has also been monitored in the Eldvörp field at a distance of some 6 km from the Svartsengi field, suggesting an effective hydraulic connection along the microseismic belt. The drawdown has led to the formation of a steam cap, most pronounced in the northeast part of the field where the shallow wells have been drilled. The mass removal of fluid from the reservoir has also led to land subsidence within a 5 km radius of Svartsengi (Björnsson and Steingrímsson, 1993), the maximum subsidence reaching some 150 mm. Reservoir modelling indicates that continued fluid removal from the reservoir will, in future, cause the pressure to fall below the critical operation pressure of the power plant. To counter this, it may become necessary to (1) increase the reinjection rate of fluid to about 200 kg/s, at a distance of some 2 km from the reservoir, (2) increase production from the steam cap and (3) improve the efficiency of thermal utilization of the abstracted fluid (Vatnaskil Consulting Engineers, 1989).

ACKNOWLEDGMENTS

The Reykjavík Municipal Heating Service (Hitaveita Reykjavíkur) and Suðurnes Regional Heating are thanked for the permission to publish the data.

10

The spas of England

David Banks

> *Then in life's goblet freely press the leaves that give it bitterness: nor prize the healing waters less for in thy darkness and distress new light and strength they give.*
>
> *Ah! What avail the largest gifts of heaven when drooping health and spirits go amiss, how tasteless then whatever can be given, health is the vital principle of bliss and exercise of health*
>
> *Benedicte fontes domino*
>
> Inscription. Royal Baths, Harrogate

10.1 INTRODUCTION

Bad news... spas are no longer popular in England. A few have managed to continue to pull tourists in, notably Bath, Harrogate, Buxton and Matlock, but they rely rather on their rich history and architecture than on the properties of their waters. There is discussion about the possibility of opening public or private bathing establishments at one or two localities, but we will have to wait some years to see the fruit of these proposals. Britain is possibly unique among European nations in having let its rich heritage of spa waters fall into disrepair. This decline commenced in the second half of the 19th century, but the final straw came in the 1950s and 1960s when the Health Service veered away from spa therapy in favour of the application of medical drugs in more controlled forms.

But it wasn't always like this. There was a time when it was difficult to take the pony and trap for an afternoon's spin without plunging into one or another patent spa, some of them in the most unlikely sounding places, such as Croydon, South London. It would be a mammoth task to document all the ex-spas of England; in this chapter I have chosen a few that have a particularly interesting history and relatively good documentation, with the aim of illustrating the diverse provenances of spa waters, even in a rather geologically sedate country such as England. Some famous spas have been

Mineral and Thermal Groundwater Resources
M. Albu, D. Banks and H. Nash.
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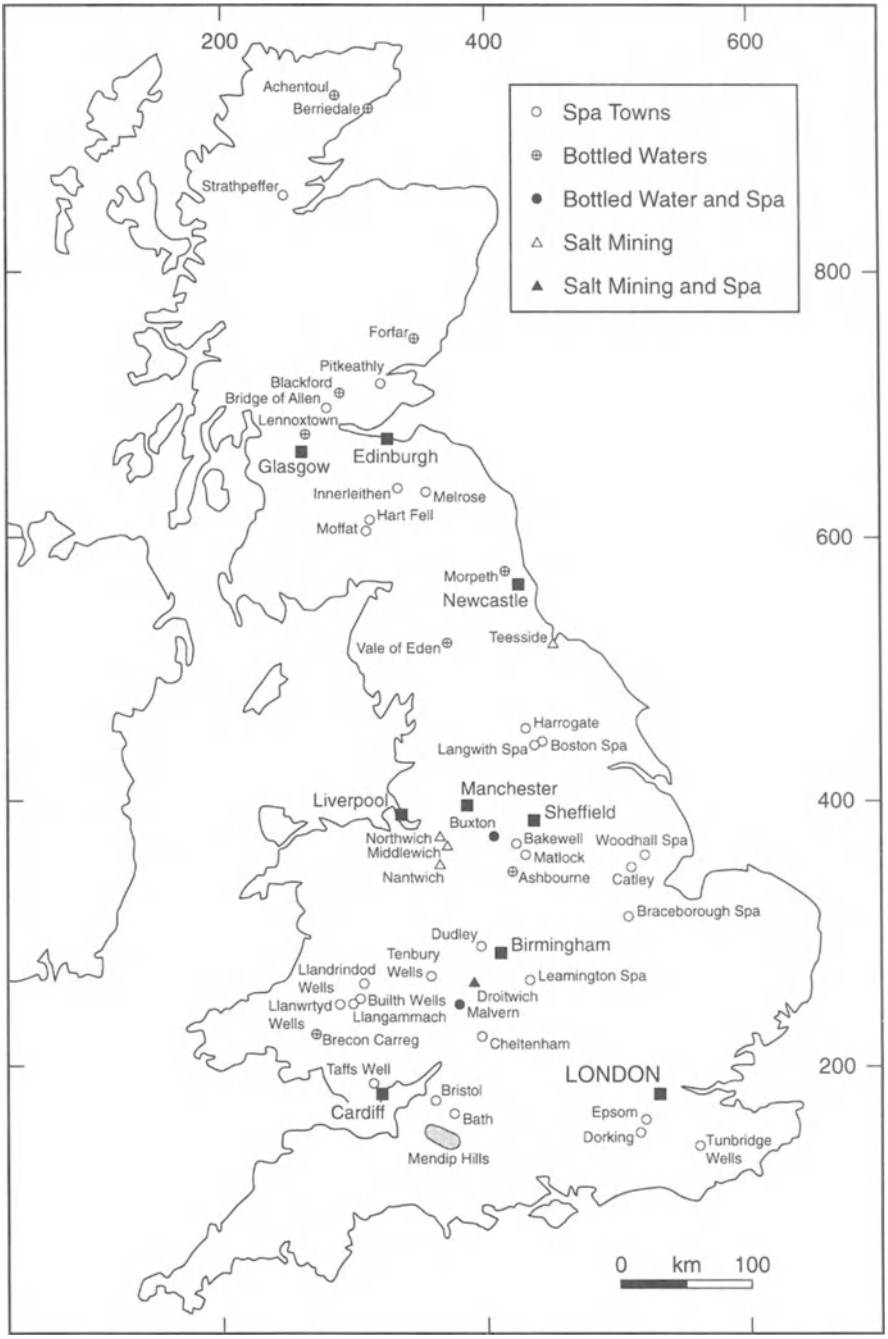

Figure 10.1 Map of Great Britain, showing locations of named spas.

omitted for lack of space: I merely mention such well heeled (or should I say well healed?) locations as Cheltenham Spa (Richardson, 1930a), Bishopton (near Stratford on Avon; Richardson, 1928), Tunbridge Wells (Whitaker, 1908; Pentecost, 1993), Saltwells at Dudley (Richardson, 1930b), Boston and Langwith Spas (Edwards *et al.*, 1950) and Tenbury Wells and leave the reader to explore these on what would undoubtedly make a very pleasant holiday tour, particularly if some spa towns of Scotland (Robins, 1990) and Wales (Edmunds *et al.*, 1969) could be included, such as Llandrindod, Llanwrtyd, Llangammarch and Builth Wells (Wales) and Strathpeffer (Scotland; Figure 10.1).

10.2 THE SPAS OF LONDON AND SURREY

The early development of London was controlled by the availability of water: most of the town and surrounding hamlets (e.g. Camberwell, Clapham, Kensington, Paddington and Islington) were erected on the flood plain or terrace gravels of the Thames (Figure 10.2). Significant development of the intervening areas, underlain by low permeability Eocene London Clay, only took place with the advent of water companies and a large scale piped water supply (Woodward and Bromehead, 1922).

The town was initially supplied by wells in the gravels and by waters from the spring lines at the base of the gravel terraces against the underlying London Clay (e.g. Holywell, Clerkenwell and Clement's Well; Buchan, 1938). In 1236 water was supplied to the city in conduits from wells and springs outside the populated area; from Tyburn (present day Oxford Street), and later from Paddington, Hackney and Aldgate. Other renowned wells and springs were located at Hyde Park, Sadler's Well, St Chad's Well, Bagnigge Well and Shepherds Well in Hampstead. Further exploration for pure water resources looked farther out from the city, until in 1725 the first deep well was sunk near Kilburn to obtain artesian water from the Lower London Tertiary Sands found at 300 ft (91 m) depth beneath the protective and confining layer of London Clay (Woodward and Bromehead, 1922). In the early 19th century these wells were extended even deeper by borings to reach the underlying main Cretaceous Chalk aquifer.

Nevertheless, shallower wells and springs continued to be favoured for medicinal purposes. Among the ex-spas of the area which Whitaker (1912) lists are the following;

- the renowned 'Purging Springs of Dulwich' were, according to Mr Whitaker, more accurately located in the borough of Lewisham. Their history is somewhat confused, but they may have been in use as early as *c.* 1640. The spring 'purges quickly – not sinking, but raising the spirits.... It is found to be diuretic'. Another account of the waters of Dulwich tells of a well sunk in 1739 by a Mr Cox to 60 ft (18 m) depth in pyritic clay.

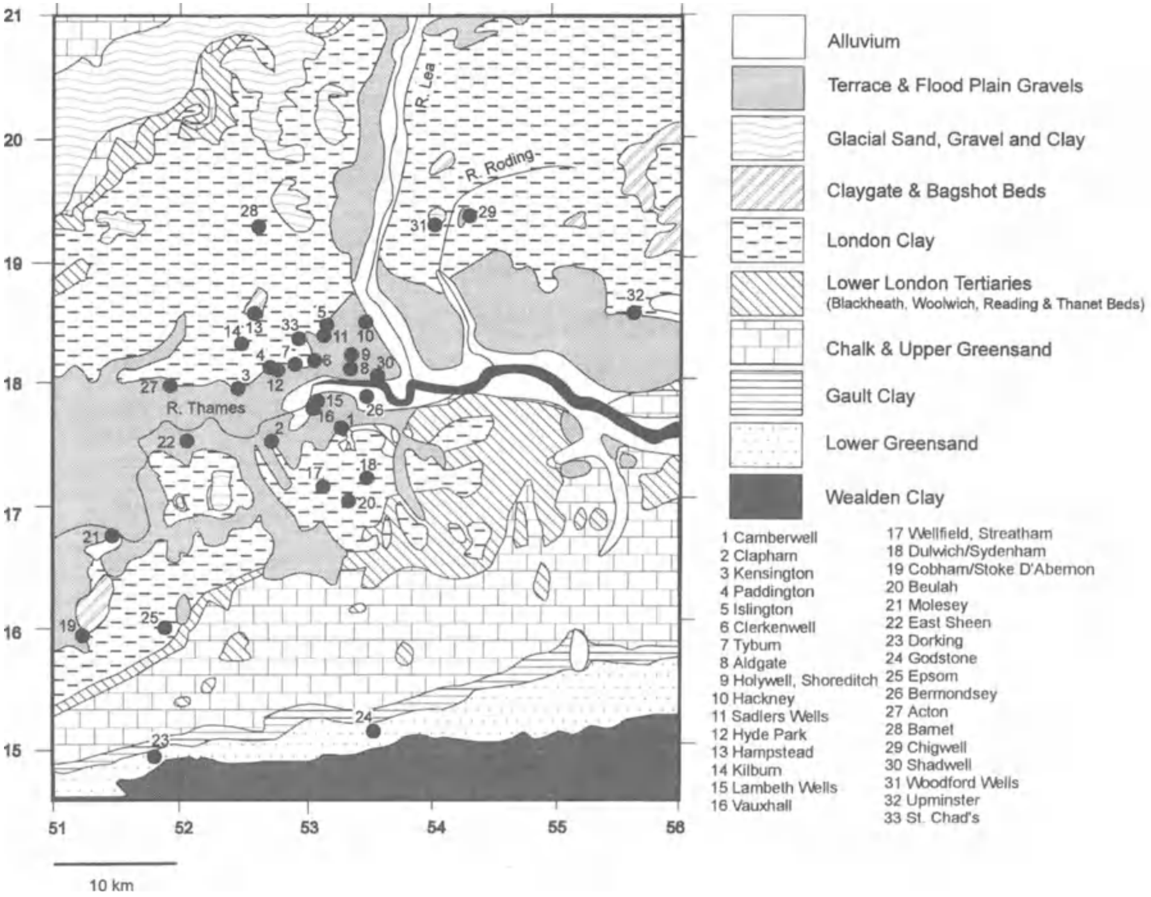

Figure 10.2 Simplified geological map of the London area, showing locations of named spas.

This well filled slowly with water and was used for medicinal purposes. Its use declined after around 1780.

- The borough of Lambeth contained several purging water sources, which were in use from 1696. Among these can be mentioned the Lambeth Wells, two springs in Coney Walk and Lambeth Walk respectively. These were put out of business in the mid-1700s by the nearby St George's Spa. St George's was probably derived from pyritic clay and had been known since 1695 for its aperient quality. The Vauxhall Well was yet another spring in the borough, famous for treating eye disorders.
- In Streatham, near Wellfield House, springs from London Clay strata were discovered during ploughing in 1660. The properties (yes, you've guessed it – purgative and emetic) were inadvertently discovered by agricultural weeders working in the field. Three wells were eventually opened on the site, and were reportedly effective in treating intestinal worms. One satisfied customer 'got rid of four worms, the least 5 ft [1.5 m] long and one $8\frac{1}{4}$ ft [2.5 m]. There were giants in those days', he concluded. The waters were analysed and the potent ingredient was demonstrated to be $Mg^{2+}SO_4^{2-}$ (magnesium sulphate).
- There were iron springs at Cobham, the pleasantly named Beulah Spa at Norwood (still in use as a hydropathic establishment in 1909 according to Woodward), and minor wells at Molesey and East Sheen. At Meriden, Dorking iron- and magnesium-containing springs from the Hythe Beds, a division of the Lower Cretaceous Lower Greensand, were used both for bathing and internal treatment.
- People went to Godstone for gout cures and Witley for sore eyes and ulcers. Bermondsey Spa was also operational in South London (Woodward, 1909).
- Stoke D'Abernon boasted the vicious Jessop's Well. This was only 10 ft (3 m) deep. One hapless man who, having been commissioned to clean the well, stood 'bare legg'd' in the water for 3 hours and was 'purged so severely for a week that he said that he would not venture, on any account, thus to clean the well again'. Upon analysis, the water was, rather strangely, found to be dominated by calcium nitrate. The nitrate would possibly tend to indicate either mis-analysis or anthropogenic contamination.
- An artesian well at Camberwell, was sunk in 1906 and used for the treatment of rheumatism. This presumably penetrated as deep as the Lower London Tertiary Sands or Chalk.
- The jewel in the crown of Surrey's waters might be thought to be Epsom, because of the world renown of its derived mineral, Epsom salts (or epsomite, $Mg^{2+}SO_4^{2-}.7H_2O$). The Epsom water had, however, rather inauspicious beginnings as a muddy puddle or, according to Whitaker, as a small water-filled hole in the ground, discovered in 1618 by a Mr Henry Wicker. Its unusual properties were indicated by the fact that cattle would not drink from it, and the water was first used as an external medicinal treatment. The water's purgative qualities were again discovered

by a bunch of hapless labourers in 1630. The original spring lost its reputation in the early 1700s, due to the opening of two new wells on the site in around 1708. Things were never quite the same again and Whitaker reports that the new water had 'no virtue'.

The more astute and sensitive reader will note that many of these wells were famous for their purgative and emetic properties. Whitaker (1912) commonly mentions that the shallower sources, typically low-yielding wells or small ponds, were in 'pyritic clay'. This usually refers to the rather low permeability Eocene London Clay, with its significant pyrite (FeS_2 or fool's gold) content which, on weathering, releases acid and sulphate:

$$\underset{\text{pyrite}}{2FeS_2} + \underset{\text{oxygen}}{7O_2} + \underset{\text{water}}{2H_2O} \rightleftharpoons \underset{\text{iron}}{2Fe^{2+}} + \underset{\text{sulphate}}{4SO_4^{2-}} + \underset{\text{acid}}{4H^+_{(aq)}}$$

Sulphate, in conjunction with magnesium, has the powerful purgative effect mentioned in connection with most of these springs. The magnesium is likely to be derived from ion exchange reactions, possibly of Fe^{2+} for Mg^{2+} in silicate minerals. London Clay mineral water sources included Beulah, Streatham, Sydenham, Epsom and Kilburn (Woodward and Bromehead, 1922).

Another favourable geological situation for mineral springs was the spring line at the base of the sandy Bagshot Beds, overlying the London Clay. The ironstone-rich horizons in the base of the Bagshot Beds often led to a chalybeate mineral water, as was found at Well Walk in Hampstead.

Whitaker (1912) bemoaned the demise of many of London's springs, which he ascribed to two factors:

- The overabstraction of deep artesian wells in the underlying Cretaceous Chalk, a major aquifer used for public water supply. The 'artesian well' at Camberwell (see above) may have been one of these. This pumping is known to have lowered the water table and dried up several marginal springs near the edge of the Chalk outcrop, although it is unlikely to have affected stratigraphically higher springs in the London Clay or Bagshot Beds. The Chalk aquifer is still recovering from this overabstraction, which is discussed in more detail by e.g. Nield (1986). The drying up of springs in connection with underdrainage by newly constructed railway tunnels is also mentioned by Whitaker.
- Contamination from urban activity; cesspits, sewage farms and cemeteries. Whitaker even describes the unpleasant example of an 'accident' involving a diarrhoeal well-digger as the source of an epidemic. He looks forward to the day when all sewage would be dealt with via a public sewer system.

It should perhaps be mentioned that spas were also found farther north in London, including the following which were well known during the period 1700–1800 (Woodward, 1909): London Spa at Clerkenwell; Islington Spa and Kilburn Wells.

Woodward also mentions mineral water sources at Acton, Barnet, Chigwell, St Pancras, Shadwell, Woodford and Upminster, while Dewey and Bromehead (1921) add Aubrey House (Holland Park) and St Govor's Well (Kensington Gardens) to the list.

10.3 THE 'WYCHES' OF MERCIA AND CHESHIRE

The Upper Permian sequences of northeastern England are famous for their content of evaporite deposits. These evaporites, in their ideal form, contain classic sequences of increasing solubility in an upward direction, as the minerals were successively precipitated from an ever shrinking and evapoconcentrated lagoon, i.e.

- carnallite ($[K^+, Mg^{2+}]Cl^-$);
- sylvite (K^+Cl^-);
- halite (Na^+Cl^-); ↑ increasing solubility
- anhydrite ($Ca^{2+}SO_4^{2-}$);
- dolomite ($[Ca^{2+}, Mg^{2+}]CO_3^{2-}$).

The classic sequences are related to the so-called Permian Zechstein Sea, stretching across the current North Sea to northern Europe, and are probably best observed at mines east of the Pennines in Teesside and at 1100 m depth at Boulby.

During the Triassic, within the Mercia Mudstone sequence, evaporites are also found in northwestern and central England, within the Worcester and Cheshire Basins. These deposits contain sulphates and halite and are thought by many to be derived from a playa lake environment.

Historically, mining of Triassic halite deposits took place at Droitwich in Worcestershire, where salt-bearing mudstone is found at shallow subcrop under a thin cover of Quaternary sands and gravels. Natural brine springs occur along the River Salwarpe. Archaeological evidence (Hereford and Worcester County Council, Archaeology Section) suggests that the deposits were worked in pre-Roman times using sunken tanks, each holding up to 14 000 l of brine (equivalent to 4 tonnes of salt). The Romans continued to work the springs, up until AD 150, during which time the fort town was known as *Salinae*. Later, the Anglo-Saxons worked the brine springs using furnaces and large lead boiling pans, and the town became known as *Saltwic*. In the 7th and 8th centuries the springs and brine wells belonged to the Kings of Mercia, who gave their nobles the right to evaporate brine to produce salt. The current name is possibly a later bastardization of Saxon and Norman elements; the *wich* or *wic* meaning a 'special place' (particularly used for saline springs) and the *Droit* being French for 'right'. The name thus means a 'legal right to extract salt'. Possibly the earliest documented record of salt mining at Droitwich comes from AD 816. Thereafter, during mediaeval times, the salt was in fact 'mined' by extracting brines from depths of some 45 to 70 m below ground level (b.g.l.). The importance of the brines for the economy of the town is indicated by the custom of well-dressing the brine wells up until the 16th century. The industry was a government monopoly until the late 17th century (Richardson, 1930b), when this right was effectively challenged by a Mr Staynor. Records exist of brine workings in the 17th to 19th centuries, when the brine is recorded as overflowing at the surface from depths of only 24 m b.g.l., although by 1884 it appears that abstraction had lowered brine levels to such a degree that brine had to be pumped actively from considerably deeper levels (60–70 m b.g.l.). In the nearby village of Stoke Prior, brines were pumped from as deep as 240–305 m b.g.l. (Mitchell *et al.*, 1961). Several brine works were in production in Droitwich, but the last closed in 1923. Since then the brines have only been pumped for spa and bathing purposes. The first therapeutic establishment was opened in 1832, when cholera patients were reportedly cured by bathing. Public baths were opened in 1836. The brines were also thought to be effective against gout, rheumatism and sciatica. The waters, in addition to their saline content (about 25% w/w sodium chloride at Tower Hill borehole; Mitchell *et al.*, 1961), reportedly contain 'one seventh of the amount' of radium which is found in King's Well at Bath (Richardson, 1930b). The centuries of pumping have caused great underground solution cavities and channels of river-like dimensions, in turn leading to local subsidence. Many Droitwich houses are consequently built on rafted foundations. An added complication followed when the town acquired a public mains water supply and many local groundwater wells were abandoned. This led to a rise in the water table and an overflowing of brines at or near the surface, resulting in serious corrosion of wrought iron, concrete and marble structures. Today, Droitwich brine is used in its undiluted form at the Brine Baths (the old public baths of 1836, reopened in 1985), operated by a private company offering hydrotherapeutic treatment. The spa water is also diluted by a factor of about ten, to seawater concentration, to supply the Droitwich Lido, a public baths.

Farther north, near the towns of Northwich, Middlewich, Nantwich, Whitchurch and Winsford, in Cheshire, salt has been worked since Roman times, the most ancient centre of mining activity being Nantwich (Figure 10.1). After 1856, Nantwich was supplanted by Northwich and Winsford as the centre of activity (Poole and Whiteman, 1966). The saliferous beds within the Mercia Mudstone have been mined by several methods:

- conventional mining;
- pumping of natural (wild) brines;
- solution mining (i.e. injection of water to dissolve the salt, followed by pumping).

The main target for mining is typically halite, which is used for production of chlorine gas, sodium hydroxide and sodium carbonate, in addition to its uses as table salt and road salt. The main deposit, known as the Northwich Halite, is up to 218 m thick and is currently worked in the Northwich/Winsford region. It contains traces of gypsum and dolomite 'impurities'. Another deposit, the Wilkesley Halite, about 335 m stratigraphically higher than the Northwich Halite, has historically been mined in the Middlewich, Nantwich and Sandbach areas.

The Northwich Halite occurs as southeasterly dipping beds, in a sequence of Mercia Mudstone deposited in the graben structure of the Cheshire Basin (Figure 10.3). Wild brines occur on the upper salt surface in subcrop in areas of active groundwater flow. As this groundwater flow dissolves bedrock, slow and relatively uniform subsidence of the surface occurs. The wild brines naturally discharge along groundwater flow pathways to main river valleys. It was in the bottom of such valleys (e.g. the River Weaver) that the ancient natural brine springs, which gave the towns their names, occurred. The 'Old Biot' spring near Nantwich produced salt up until 1818 (Poole and Whiteman, 1966). Most of these springs have since dried up due to the effects of pumped brine extractions. The *in situ* salt was discovered near Northwich in 1670, and underground mining was instigated to exploit it. These first mines were prone to flooding and dramatic subsidence collapse. These were followed by more sophisticated underground workings, such as the Meadowbank Mine, near Winsford, which commenced in 1884 and, at the time of Earp and Taylor's report (1986), was still active. The earliest miners knew only the so-called 'Top Bed' within the Northwich Halite, but in 1781 a stratigraphically lower 'Bottom Bed' was discovered. Mining by means of pumping wild brines in the Winsford and Northwich areas has led to uncontrolled dissolution of 'brineways' or underground channels in the salt. This in turn led to progressive and typically differential subsidence problems, often in linear geometries reflecting subsidence along collapsed brineways. Subsidence also caused fracturing of the overlying Mercia Mudstone, allowing ingress of water and a worsened situation. Nevertheless, in 1981 there were still two wild brine companies in operation (Earp and Taylor, 1986). Most production, however, has gone over to the controlled solution mining, first pioneered by ICI in the area, involving the development of artificial pressure-tight solution cavities in the salt. An alternative technique, used in the USA, is to develop artificial, but controlled, solution channels by hydraulic fracturing between two boreholes.

10.4 OTHER MERCIAN SPAS

10.4.1 Malvern

Great commercial success, continuing to the present day, was had by the springs of the Malvern Hills. These, too, form an up-faulted inlier of Precambrian and Lower Palaeozoic rocks (Figures 10.4, 10.5). The core of

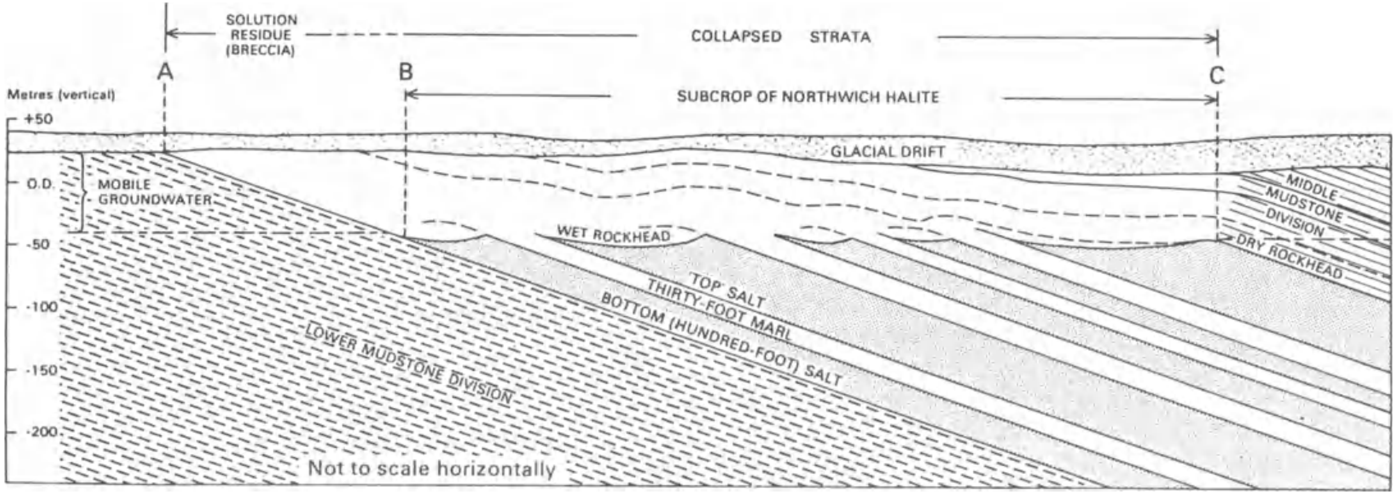

Figure 10.3 Geological section through the Northwich Halite deposits of the Cheshire Basin. (After Earp and Taylor, 1986. Copyright British Geological Survey, reproduced with permission.)

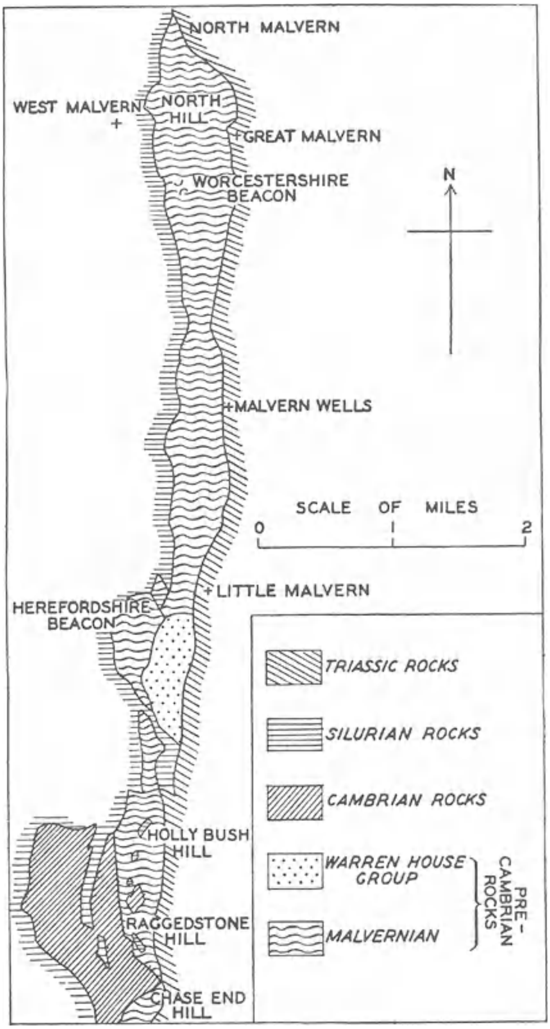

Figure 10.4 Simplified geological map of the Malvern Massif. (Source: Earp and Hains, 1971. Copyright British Geological Survey, reproduced with permission.)

the Malvern Hills is formed by Archaean granites, gneisses, diorites and schists, together with Uriconian volcanics (Figure 10.5). These were overlain, around the margins of the massif, by Silurian metasediments on the west and by the Triassic Mercia Mudstone of the Worcester Basin on the east. The occurrence of mineral water springs has controlled the development of several villages and towns around the hills: the Eye Well and the Holy Well at Malvern Wells, St Ann's Well and the Chalybeate Spa at Great Malvern, and Walms Well.

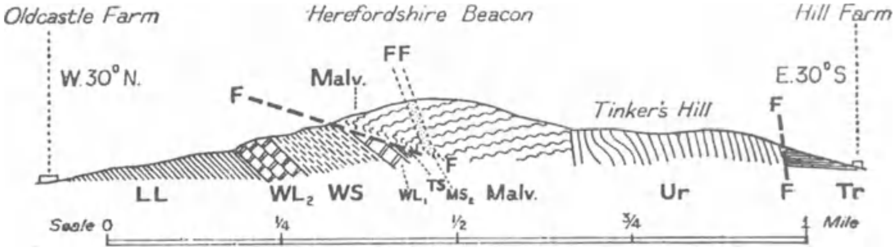

Figure 10.5 Simplified geological cross-section of the Malvern Massif (1 mile = 1.6 km). Tr = Triassic, LL = Lower Ludlow Shales, WL_2 = Wenlock Limestone, WS = Wenlock Shale, WL_1 = Woolhope Limestone, TS = Woolhope Shale, MS_2 = upper part of May Hill Sandstone, Ur = Uriconian, Malv = Malvernian, F = faults. (From Earp and Hains, 1971. Copyright British Geological Survey, reproduced with permission.)

The springs are of variable salinity according to their structural and stratigraphic position. The higher level springs, such as St Ann's and Holy Well, emerging from Precambrian bedrock, are soft and have low salinity. Lower level springs, thrown out against the fault boundary of Precambrian bedrock with Silurian or Triassic sediments, are more saline (Richardson, 1930b).

The springs were first mentioned in 1622 as a cure for eye diseases. Later, Walms Well was also reported to be effective against skin conditions. By the late 18th century, Malvern Wells had become a popular spa town, but was surpassed by Great Malvern in the early 19th century. The commercialization of 'The Water Cure' expanded dramatically in 1842, when Drs Wilson and Gully established the suitably teutonic-sounding 'Gräfenberg House' and opened it as a hydro. The good doctors then appear to have entered into some rivalry, Wilson building the 'Hydropathic Establishment' and Gully founding the 'Tudor' and 'Holyrood' houses for females and males respectively, connected by a 'Bridge of Sighs'. In its heyday, patrons of Malvern included Macaulay, Darwin and Lytton, but since 1870 the spas have been in decline. The exploitation of bottled mineral waters has continued, however. Jacob Schweppe's company started bottling Malvern water in 1850 from the Holy Well, marketing it under the name of Malvern Soda and, later, Malvern Seltzer. By 1890 Schweppes had purchased a bottling plant in Colwall village and piped in water from the western Primeswell spring. In the bottled water boom of the 1990s, Malvern Water has become established as a firm favourite, being enjoyed by the Royal family and the somewhat less civilized denizens of 10 Downing Street and the Houses of Parliament alike (Green and Green, 1985).

10.4.2 Leamington Spa

Leamington Spa, in Warwickshire, is also related to Triassic rocks. The springs emerge in the vicinity of the valley of the River Leam from the junction of the permeable Sherwood (formerly, Lower Keuper) Sandstone with the Passage Beds of the overlying Mercia Mudstone (Richardson, 1928). The origin of the salinity (Table 10.1) is rather unclear, but is probably at least partially derived from the leaching of gypsum from within the Mercia Mudstone into the underlying Sherwood Sandstone (Old *et al.*, 1987). This confined saline groundwater emerges from the window of the Sherwood Sandstone outcrop in the valley of the Leam, where it may mix with fresher unconfined sandstone groundwaters before discharging to the river. A schematic geological cross-section is illustrated in Figure 10.6.

The mineral waters have been known since the Middle Ages: the Original Spring (or Camden's Well) issued from a fissure in the crown of an anticlinal flexure. They were not substantially exploited, however, until the 18th century. The Original (or William Abbott's) Well was sunk beside a brookside spring in 1786. The heyday of Leamington was during the first half of the 19th century, during which time the population rose from 315 to 15 723 and the New Town was built. After 1848 the fashion of taking the waters began to decline and Leamington entered something of a recession.

In 1925, three sources were in operation:

• Original Spring (Camden's Well)	Rich in Mg^{2+}–SO_4^{2-}
• New Well (Royal Pump Room)	Mainly Na^+–Cl^-, with some Mg^{2+}–SO_4^{2-} and Mg^{2+}–Cl^-
• Alexandra Fountain	Fe, Na^+, Mg^{2+}

The wells are typically *c.* 60–70 ft (18–21 m) deep and penetrate into the upper horizons of the Sherwood Sandstone through a cover of river alluvium and gravel. Most are rich in iron and sulphate, as can be seen from the analyses in Table 10.1. By 1987 only the New Well was in use as a supply to the Royal Pump Room and Baths (Old *et al.*, 1987). In 1990 the Baths, where hydrotherapy had been practised on the National Health Service since the 1950s, were closed. Currently, the only public access to the spa waters is via a drinking water tap. Plans are, however, underway to redevelop the hydrotherapy baths within the private sector.

10.5 SPAS OF THE CARBONIFEROUS LIMESTONE OF THE WHITE PEAK

10.5.1 Occurrence of the spas

The Peak District, located largely in the counties of Derbyshire and South Yorkshire, forms the southern end of the Pennine Hills. Structurally, the area is a dome-shaped antiform, with Lower Carboniferous limestones (the 'White Peak') at the core and the dramatic scarps and valleys of the alternating gritstones, sandstones and black shales of the Namurian Millstone

Table 10.1 The analytical composition of some mineral waters from the English Midlands

Parameter (mg/l)	*New Well (Pump Room), Leamington Spa (analysis of 1923 after Richardson, 1928)*	*Aylesford Well, Leamington Spa (analysis of 1923 after Richardson, 1928)*	*Leamington Spa (analysis of 1967 after Edmunds et al., 1969)*	*Saltwells, Dudley (analysis of c.1884 after Edmunds et al., 1969)*	*Droitwich (analysis of 1958 after Edmunds et al., 1969)*
Ca^{2+}	1040	674	877	1502	1368
Mg^{2+}	288	146	287	119	132
Na^+	5020	2460	4447	4118	120 690
K^+	16	–	n.d.	8	n.d.
HCO_3^-	130	165	166	729	26
SO_4^{2-}	2700	2410	2276	21	4 491
Cl^-	8370	3530	7460	8917	185 550
Fe	10.5	1.8	1	74[a]	n.d.[b]
SiO_2	2	–	3	38	n.d.

[a] Combined Al and Fe oxides.
[b] n.d. = not determined.

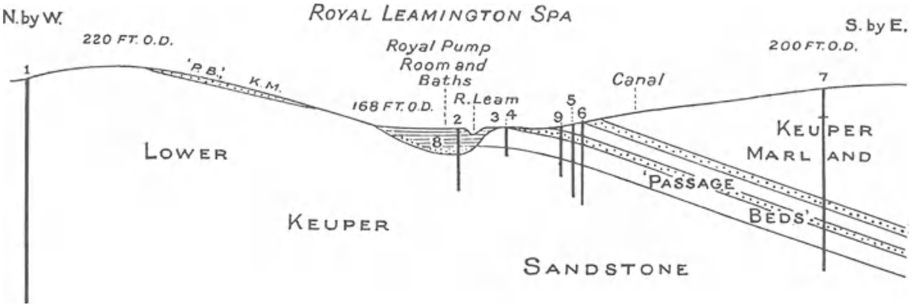

Figure 10.6 Schematic cross-section through Leamington Spa (1 mile = 1.6 km, 1 ft = 0.3 m). (1) Leamington brewery well and borehole (fresh water); (2) 'New Well'; (3) 'Original Spring'; (4) 'Original (Abbott's) Well'; (5) Read's (Hudson's) Well; (6) Smart's (Imperial Fount) Well'; (7) Leamington Steam Laundry borehole (salt water); (8) River Leam gravel and alluvium; (9) 'Alexandra Fountain (Wise's, Curtis's) Well'. (From Richardson, 1928. Copyright British Geological Survey, reproduced with permission.)

Grit on the flanks. The White Peak has a karst-like topography and hydrogeology, and is well drained, but with powerful calcareous springs emerging to feed the main streams and rivers. The water, despite its purported curative properties, extolled by so many spas, is generally deficient in iodine (typically only *c.* 2 μg/l; Edmunds *et al.*, 1989). This, together with the iodine-deficient nature of local soils, formerly led to a prevalence of goitre (or 'Derbyshire neck') amongst local inhabitants (Edmunds, 1971).

The Lower Carboniferous Limestone contains contemporaneous volcanic vents and is interbedded with thick basaltic lavas and ash beds related to Hercynian orogenic activity. Later hydrothermal activity, of controversial age (but possibly as late as Jurassic; Rodgers, 1977), led to the emplacement of rich mineral veins along fracture zones in the limestone. These subvertical veins or 'rakes' were initially worked for lead, in the form of galena (PbS), but have more recently been worked for fluorspar (CaF_2). Accessory minerals include sphalerite (ZnS), barytes or barite ($BaSO_4$), calcite ($CaCO_3$), pyrite (FeS_2), cerussite ($PbCO_3$) and smithsonite ($ZnCO_3$).

The limestones exhibit karstic features, but the surfaces of the lava flows have weathered to clays and act as low permeability aquitards, often throwing out groundwater in springlines. The lavas also acted as barriers to hydrothermal fluids and the rakes often end abruptly at lava horizons, possibly leading to their local name of 'toadstones', from the German *todt Stein* meaning 'dead stone'. Other plausible derivations of the word include reference to the mottled 'toad's-back' appearance of the lava, and even the dubious etymological derivation from local dialect 't'owd stone', as in the expression 'Oh no! It's that old (t'owd) stone again!'.

The hydrogeology of the limestones is even more dominated by the 'anthropogenic karst' formed by the network of mine passages and drainage

Table 10.2 Composition of waters from lead mine soughs of the White Peak of Derbyshire, compared with 'normal' groundwater (Priestcliffe, Chelmorton) for the Carboniferous Limestone of the White Peak (data from Edmunds *et al.*, 1989, samples taken June 1986). Saturation indices (SI) with respect to various mineral phases, calculated using the speciation code MINTEQ, are shown

	Meerbrook Sough	*Hillcarr Sough*	*Mandale Sough*	*Magpie Sough*	*Waterloo Inn Sough*	*Priestcliffe*	*Chelmorton*
Temperature (°C)	14.5	8.6	9.3	9.7	7.6	8.2	7.6
pH	7.2	7.2	7.1	7.2	7.0	7.0	7.0
Ca^{2+} (mg/l)	86	88	98	98	98	112	95
Mg^{2+} (mg/l)	19.4	13.5	5.9	8.0	1.4	2.2	1.3
Na^{+} (mg/l)	14	12	10	8	4	5	4
K^{+} (mg/l)	0.9	1.5	0.6	0.8	0.3	0.8	0.3
HCO_3^- (mg/l)	262	261	257	261	222	260	232
SO_4^{2-} (mg/l)	57	36	27	33	30	37	29
Cl^- (mg/l)	26	20	23	19	12	13	9
F^- (mg/l)	0.68	0.75	0.61	0.64	0.32	0.86	0.20
NO_3^- (mg/l)	9.7	16.4	14.2	14.2	18.6	20.8	12.4
Fe (μg/l)	<0.5	10.2	<0.5	<0.5	0.8	2.5	2.0
Al (μg/l)	4	16	9	5	<3	<3	5
Mn (μg/l)	0.3	8.2	<0.2	<0.2	<0.2	<0.2	0.2

Cu (μg/l)	0.9	0.6	0.4	0.4	0.5	0.3	0.4
Pb (μg/l)	17	<6	16	<6	<6	8	6
Zn (μg/l)	338	297	85	74	7	50	4
Cd (μg/l)	1.6	<0.5	0.8	0.8	<0.5	<0.5	<0.5
Ba (μg/l)	70	280	327	336	229	190	254
Si (mg/l)	2.9	3.0	2.3	2.4	1.3	2.1	1.2
Aragonite ($CaCO_3$) SI	−0.26	−0.35	−0.39	−0.29	−0.58	−0.46	−0.58
Barite ($BaSO_4$) SI	+0.19	+0.72	+0.65	+0.74	+0.59	+0.56	+0.62
Boehmite (AlO(OH)) SI	−0.23	−0.042	−0.24	−0.46	–	–	−0.63
Calcite ($CaCO_3$) SI	−0.089	−0.15	−0.20	−0.087	−0.38	−0.25	−0.37
Cerussite ($PbCO_3$) SI	−1.12	<−1.49	−1.09	<−1.51	<−1.51	−1.39	−1.51
Diaspore (AlO(OH)) SI	+1.57	+1.81	+1.60	+1.38	–	–	+1.24
Dolomite ($CaMg(CO_3)_2$) SI	−0.67	−1.06	−1.54	−1.19	−2.56	−2.17	−2.56
Fluorite (CaF_2) SI	−0.79	−0.58	−0.71	−0.68	−1.23	−0.34	−1.65
Gibbsite ($Al(OH)_3$) SI	−0.28	−0.007	−0.22	−0.45	–	–	−0.58
Otavite ($CdCO_3$) SI	−0.19	<−0.73	−0.61	−0.52	<−0.95	<−0.90	<−0.93
Strontianite ($SrCO_3$) SI	−1.87	−2.38	−2.40	−1.99	−2.76	−2.60	−2.78
$CuCO_3$ SI	−5.18	−5.38	−5.55	−5.55	−5.48	−5.68	−5.57
Tenorite (CuO) SI	−2.79	−3.16	−3.40	−3.30	−3.42	−3.67	−3.53
$ZnCO_3 \cdot H_2O$ Si	−1.06	−1.15	−1.77	−1.74	−3.00	−2.10	−3.22

adits which honeycomb the hills (Edmunds, 1971). Workings exceed 100 m depth and mines were typically dewatered either by deep pumping shafts or by shallowly draining adits or 'soughs', leading out of the hillside into the river valleys. Strangely, some of these soughs and pumping shafts are now used for public water supply (e.g. the Meerbrook Sough and Ladyflatts Shaft near Matlock). One might query the suitability of lead-mine drainage for public consumption, but the quality is surprisingly good. Possible explanations for this may include the following.

- Kinetic factors – the relatively slow rate of dissolution and oxidation of sulphide minerals compared with the rapid flux of limestone groundwater through the mine conduits.
- The solubility of heavy metals being suppressed by the high alkalinity of the water and the solubility of fluorides by the high calcium concentrations. Barium concentrations seem to be limited by barite solubility. Table 10.2 indicates that barite ($BaSO_4$) and calcite are the only two minerals (apart from the aluminium minerals) with respect to which the waters are saturated. Minerals such as fluorite and otavite approach saturation in some waters and, for zinc and lead, the respective carbonates yield saturation indices (SI) in the vicinity of -1. These values may be regarded as consistent with saturation of waters with respect to fluorite and heavy metal carbonates occurring in the immediate vicinity of the orebody (and thus limiting solubility), the water later being diluted by normal limestone groundwater during its passage along the sough.
- Surfaces of metal sulphides being coated with insoluble oxides or carbonates, preventing further oxidation.
- The fact that a hydraulic equilibrium situation has long been in place, with limited water table fluctuation and thus a limited flux of oxygen into the veins to promote sulphide oxidation.

Thermal springs or soughs are known at the locations listed below (after Edmunds, 1971), which have a tendency to be located around the fringes of the outcrop of the limestone dome, near the boundary with the overlying Millstone Grit (Figure 10.7). This is a logical location for such springs, representing the discharge point for long, deep flow pathways through the limestone dome. The exact locations of the springs are controlled by fault structures.

- Buxton: St Anne's Well (27.5–27.7°C);
- Matlock:
  - Fountain Bath (19.7°C);
  - New Bath Hotel (19.8°C);
  - East Bank of R. Derwent (17.4°C);
  - Meerbrook Sough (15.3°C);
  - Balls Eye Quarry borehole (13.6°C);

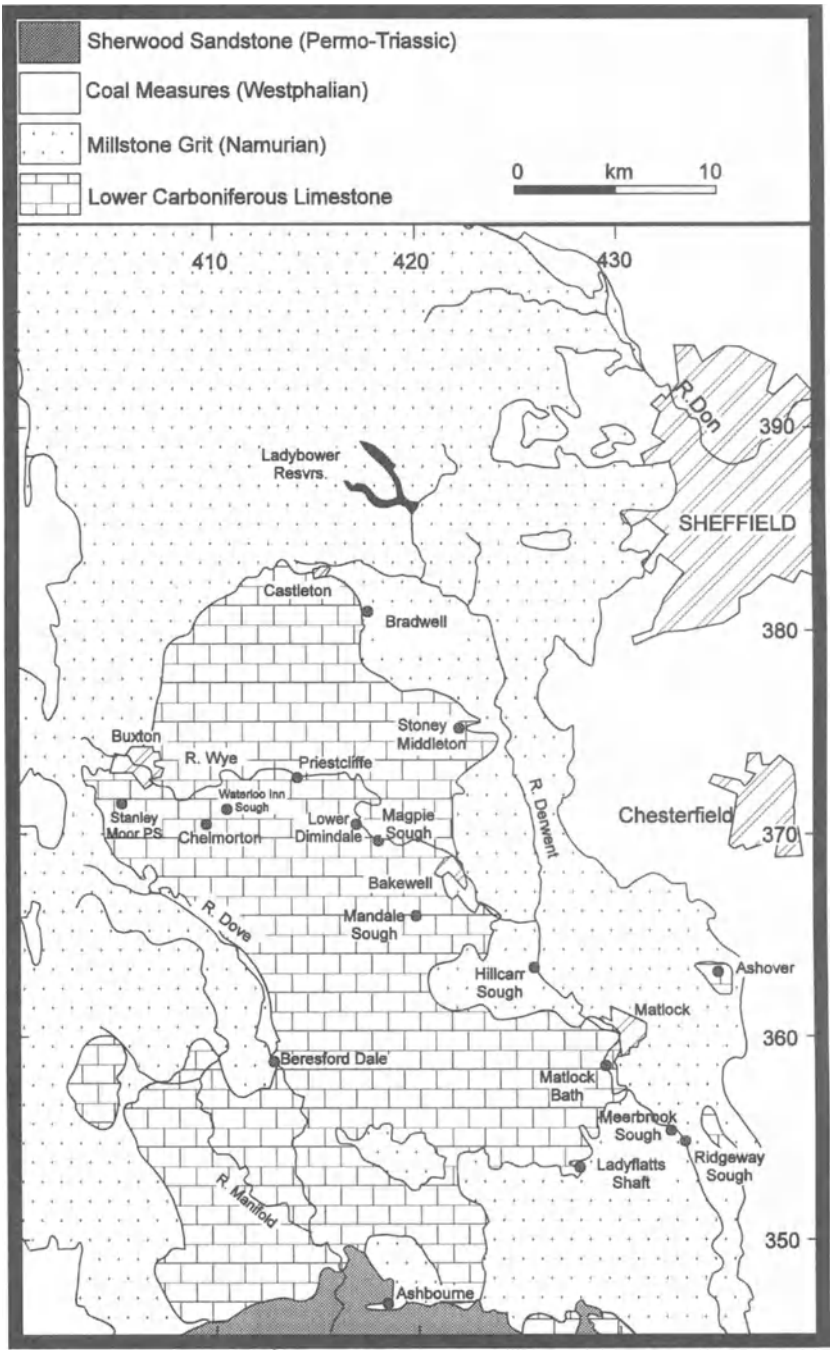

Figure 10.7 Simplified geological map of the Peak District.

- Stoney Middleton:
  - Stoney Middleton Spring (17.7°C);
  - Stoke Sough (11.6°C);
- Bakewell:
  - Recreation Ground (13.3°C);
  - British Legion (11.6°C);
- Bradwell: Bradwell Spring (12.4°C);
- Crich: Ridgeway Sough (14.1°C);
- Beresford Dale: spring (13.8°C);
- Lower Dimindale: spring (11.5°C).

The springs at Buxton were undoubtedly used by the Romans, and the waters of Stoney Middleton and Bradwell lie in the proximity of Roman settlements, indicating that they too may have a history spanning millennia.

Typical non-thermal waters tend to exhibit a temperature of about 6–9°C in this area. Edmunds (1971) noted a tentative positive correlation between temperature and discharge. He observed also that the sough waters had probably cooled considerably during their journey down the soughs from thermal sources in the mines.

The thermal waters are partly due to a significant thermal anomaly below the Peak District and partly due to flow mechanisms which allow rapid upward migration of deep, warm groundwater along transmissive fault zones. In fact, Downing *et al.* (1991) argue that the thermal anomaly is itself a product of upwelling of deep groundwaters rather than a primary heat source.

The tritium contents of the waters, as measured by Edmunds (1971) in 1968 and 1969, were mostly low. Buxton and Stoney Middleton exhibited <4 TU, indicating a water age of greater than about 20 years. Bradwell, Bakewell and Matlock gave between 4 and 10 TU, indicating either waters of age about 15–20 years or a substantially older water 'contaminated' with younger recharge. Balls Eye Quarry yielded 103.4 TU, indicating a substantial component of modern water. The results of more recent investigations are detailed by Evans *et al.* (1979), who report that Stoney Middleton Spring then yielded 10 TU, and St Anne's Well, Buxton, 4.5 TU. From these results it is concluded that, in all the thermal springs, some component of modern recharge is mixing with (presumably) considerably older, deep thermal water.

Many of the thermal waters are rather similar in gross chemical composition to typical Carboniferous Limestone groundwater (Table 10.3). In particular, Buxton thermal water, which lies in the rather unmineralized western part of the limestone, is a typical calcium bicarbonate water. Others, such as Matlock and particularly Bakewell, although still dominated by calcium as the cation, contain significant sulphate. This is probably leached from oxidation of pyrite during the water's passage through mineralized fractures or, alternatively, it may be derived from greater depths. Bradwell's water is atypical, being dominated by sodium chloride; Edmunds (1971) suggests this may be due to connate waters within the formation (Figure 10.8). A comparison between thermal and non-thermal waters reveals that, although the differences are relatively small, thermal waters are somewhat enriched in many parameters, presumably due to the greater solubility of most minerals at higher temperatures (Figure 10.9). The effect is most pronounced with Sr, Br, Mn, I and Mg. Strontium enrichment is particularly diagnostic for thermal waters. The waters lack any solubility control with regard to strontianite ($SrCO_3$) saturation; thus waters continue to dissolve strontium with increased contact time, despite being saturated with respect to, for example, calcite. The thermal waters tend to exhibit, on average, low concentrations of nitrate, although exceptions do occur. The low nitrate may be due to either chemical reduction or anion exchange at depth in the aquifer or to the lack of agricultural contamination at the time of recharge.

In addition to thermal springs, chalybeate springs issue from the stratigraphically higher, pyritic Millstone Grit at Buxton, Matlock Bank and Ashover (Stephens, 1929). Bottled waters are produced at Ashbourne and Buxton.

10.5.2 Buxton

The town was known to the Romans as *Aquae Arnemetiae* ('Waters of Arnemetia [a Celtic Goddess]' – possibly suggesting a pre-Roman history), but was only a village of local renown, paling in comparison with the internationally acclaimed *Aquae Sulis* (Bath). The town developed as a spa again in the Elizabethan era (late 16th century), but was known as a place of healing before this (Langham and Wells, 1986). The first document from the mediaeval period recording the spa is from 1460 and at about the same time another writer described Buxton as (Langham and Wells, 1986):

> Halywell (or Holy Well), the source of the water of (the River) Wye, in the County of Derby, about 100 miles from London, makes many miracles making the infirm healthy, and in winter it is warm, even as honeyed milk.

The combination of healing and saintly 'idols' made Buxton somewhat notorious among Protestant zealots. Indeed, during the Reformation period, Henry VIII, via his Chief Minister, Thomas Cromwell, ordered the destruction of images of St Anne here.

Buxton's most famous visitor was Mary Queen of Scots, Queen Elizabeth I's Catholic rival to the throne, who sought relief from her chronic arthritis in the period 1573–1583. During Mary's visits, Elizabeth had her kept under scrutiny for fear she might be hatching a plot, using Buxton as a nerve

Table 10.3 Comparison of chemical quality of thermal waters from the Carboniferous Limestone of Derbyshire with other limestone groundwaters (data after Edmunds, 1971)

	Buxton (thermal)[a]	*Matlock (New Bath Hotel)*[a]	*Matlock (Fountain Bath)*[a]	*Bakewell (Rec. Ground)*[a]	*Stoney Middleton (spring)*[a]	*Meerbrook Sough*[a]	*Bradwell*[a]	*Magpie Sough*[b]	*Stanley Moor P.S.*[c]
Date	*1 Nov 1967*	*21 Apr 1969*	*13 Jun 1968*	*25 Mar 1969*	*25 Oct 1967*	*14 Jun 1968*	*27 Mar 1969*	*26 Oct 1967*	*23 Oct 1967*
Discharge (l/s)	11	6	12	0.2	1.3	790	0.7	400	Pumped
pH	7.50	7.35	7.77	7.44	7.77	7.32	7.20	7.70	7.20
Ca^{2+} (mg/l)	58	105	103	186	92	75	162	104	82
Mg^{2+} (mg/l)	20	32	38	24	29	29	42	5.5	4.5
Na^{+} (mg/l)	24	30	29	19	61	9.8	240	6.5	4.0
K^{+} (mg/l)	1.2	0.9	0.8	0.9	1.5	0.9	5.2	0.8	0.4
Sr^{2+} (mg/l)	0.58	2.3	1.2	12.3	1.5	0.42	5.4	0.20	0.050
Li^{+} (μg/l)	30	45	19	130	67	17	220	20	17
Fe^{total} (μg/l)	<1	–	17	–	<1	27	–	1	<1
Cu (μg/l)	<2	12	3	15	<2	6	–	<2	2
Pb (μg/l)	<1	–	4	–	1	16	–	5	<1
Zn (μg/l)	<5	60	40	140	100	350	90	70	10
Mn (μg/l)	75	–	1	–	3	0.5	–	<0.5	12

HCO_3^- (mg/l)	252	271	280	199	256	280	217	279	234
SO_4^{2-} (mg/l)	12	150	192	384	100	54	326	32	14
Cl^- (mg/l)	39	57	52	23	110	22	420	13	9
F^- (mg/l)	0.19	1.27	0.9	1.6	1.45	0.7	1.80	0.62	0.34
Br^- (mg/l)	0.125	0.29	0.072	0.18	0.34	0.103	1.49	0.064	0.038
I^- (μg/l)	3.0	4.0	4.0	4.0	6.5	1.5	23	0.5	1.0
NO_3^- (mg/l)	<0.1	0.4	3.1	<0.1	14.2	9.7	0.2	9.3	4.9
NH_4–N (mg/l)	0.09	–	0.03	–	–	0.08	–	0.02	0.03
H_4SiO_4 (mg/l)	20.6	–	37.1	–	14.4	24.8	–	8.3	5.9
H_3BO_3 (μg/l)	90	230	170	230	260	140	800	90	30
SeO_4^{2-} (μg/l)	2	–	<1	–	<1	9	–	<1	2

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[a] Thermal water.

[b] Non-thermal mine sough (temperature = 9.4° C).

[c] Non-thermal limestone groundwater from pumping station (temperature = 9.1° C).

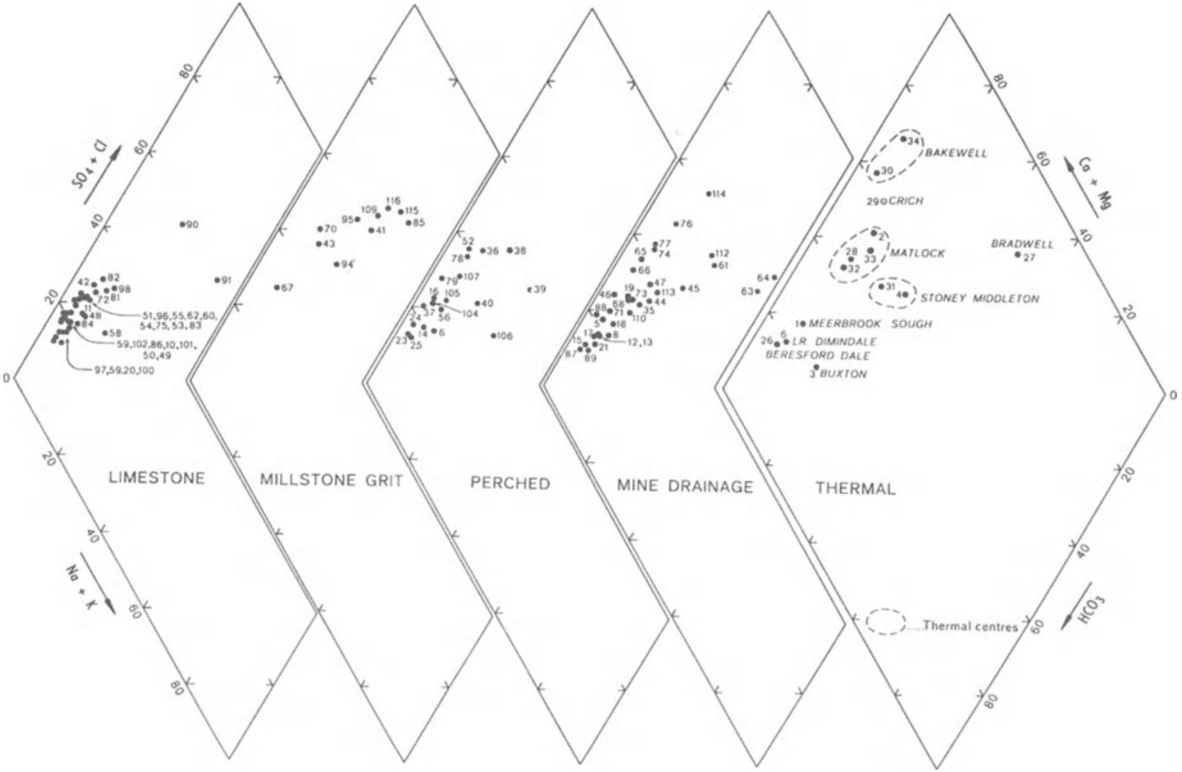


Figure 10.8 'Diamond' diagrams comparing the thermal waters of the Peak District with limestone waters from the main and perched aquifers, groundwaters from the overlying Millstone Grit and mine drainage waters from lead mines in the limestone. (After Edmunds, 1971. Copyright British Geological Survey, reproduced with permission.)

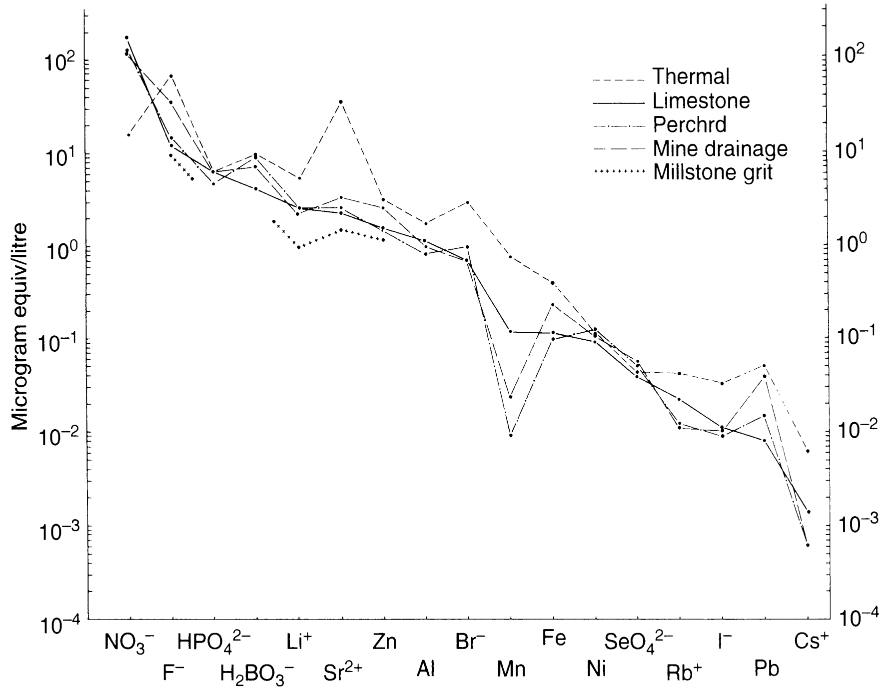


Figure 10.9 Comparison of median trace constituent content of thermal waters of the Peak District with limestone waters from the main and perched aquifers, groundwaters from the overlying Millstone Grit and mine drainage waters from lead mines in the limestone. (After Edmunds, 1971. Copyright British Geological Survey, reproduced with permission.)

centre for her operations. At around this time a medical practitioner, Dr John Jones, operated in Buxton. He described the properties of the water in perhaps a little too much detail (Langham and Wells, 1986):

> The Waters Helpe Women that by reason of overmuch moisture, or contrary temperature be unapt to conceave ... (and) ... al such as have their whisker too abundant and be overwatry ... weak men that be unfruitful ... Likewise for all that have Priapismus and that be perboyled in Venus Gulf. Profitable for such as have consumption of the lunges. Very good for the inflammation of the liver. Excellent for overmuch heat, and the stopping of the veins. Beneficial for such as vomit blood. Good for the continued desire to make water and unordinary desire to going to the stoole, doing nothing or very little with great payne. The haemmorroydes and pyles it soon mendeth. Against the overflowing of womens monthes, it much avayleth. Overmuch vomiting it cureth. It openeth the obstructions of the Milt and liver. For them that be short windeth, it much avayleth. The greene sickness perfectly it cureth and the Morphawe soon it expelleth.

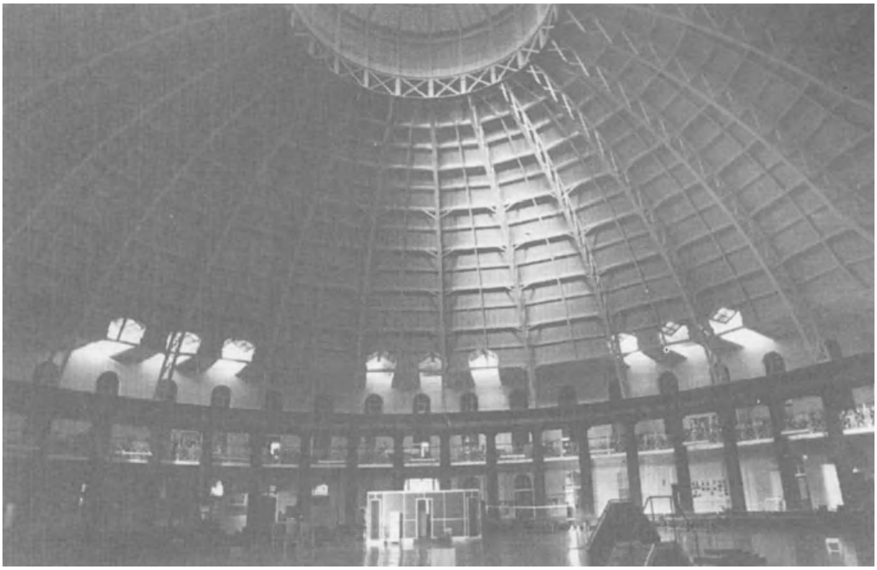


Figure 10.10 The inside of the dome of the Devonshire Royal Hospital, Buxton. (Copyright Richard Marpole, 21 Holmfield, Burbage, Buxton, Derbyshire SK17 9DF, UK; reproduced with permission.)

So who needed a National Health Service? It is noteworthy that, amongst this list of complaints, disorders involving regulation of fluid within the body and, possibly, blood pressure are prominent. This is not at all in disagreement with the more scientific investigations of O'Hare *et al.* (1991) and Heywood (1991; Chapter 2).

In 1572 the existence of a bathhouse large enough for some 30 persons was documented (Naylor, 1983), but was replaced in 1670 by a larger 'Great Hall'. In the 18th century, George III established a Buxton Bath Charity Hospital to aid the poor in seeking a water cure. There were strings attached, however (Devonshire Royal Hospital, 1990): the poor had to come from more than 7 miles away, arrive only between April and November, not stay longer than 5 weeks and not receive more than 6 shillings per week (in 1785). In 1858 the Charity acquired its own buildings (former stables), donated by the 6th Duke of Devonshire (the family who, in keeping with the perverseness of the English nobility, are connected with Chatsworth House in Derbyshire). However, the blockade of raw cotton from America during the Civil War had serious repercussions for the cotton trade of Lancashire, resulting in the Great Cotton Famine of 1862–1863. There was thus an acute need for places of convalescence for victims of the famine and the Charity campaigned vigorously for expansion. A response did not come until 1878, however, when the Duke and the Cotton Districts

Relief Fund financed the construction of a huge dome over the entire site. The hospital was, in 1934, officially recognized by George V and became the Devonshire Royal Hospital, Britain's only surviving large-scale hydropathic establishment, based on natural spa water, operated under the auspices of the National Health Service. The hospital is possibly the most impressive building in Buxton; its huge dome is completely open inside, with subways providing access to the hydrotherapy unit.

Both cold and thermal waters can be found in Buxton, but its thermal waters are some 10°C warmer than the hottest waters at Matlock Bath, placing it in a thermal league above the other Derbyshire spas. The Natural Baths were originally fed by several warm springs at a rate of some 7770 gallons per hour or 9.8 l/s (Stephens, 1929), while a number of others were known, bringing the total to at least nine. Manganese used to precipitate out in the thermal baths as a purple-brown mud, also containing barium, lead, cobalt, molybdenum and several other elements (Langham and Wells, 1986). The temperature of the waters is constant at around 27.7°C and bubbles of gas can be seen escaping from the water, found to be composed predominantly of N_2 with subsidiary CO_2. The waters are somewhat radioactive, containing 0.034 Bq/l radium and 77 Bq/l dissolved radon, with 2.78 μg/l uranium for good measure (Andrews, 1991).

The spa has influenced the town's development strongly, encouraging rich architecture and tourism. A well known opera house still flourishes in what would almost certainly otherwise be a modest Pennine market town! Most of the famous thermal springs were located in the grand Crescent of 1794, built by John Carr. Today, however, the tiled Hot Baths are converted to a shopping arcade and the Pump Room to a micrarium. St Anne's well is still accessible at a public pump adjacent to the Pump Room. The spring area feeding the so-called gentlemen's Natural Baths can still be observed in the basement of the right wing of the Crescent, in the town's tourist office. Water is currently piped from here, across town to Perrier's bottling plant where 'Buxton Mineral Water', one of the UK's most popular bottled waters, is produced. This spring also feeds the hydrotherapy unit of the Devonshire Royal Hospital and the town's public swimming pool.

Of the cold springs, the best known was probably a chalybeate spring behind the Crescent, but which is now lost. It appears to have arisen from a (probably pyritic) shale horizon at the junction of the Millstone Grit and the Carboniferous Limestone. The analysis from 1922 is given in Table 10.4 (Langham and Wells, 1986).

10.5.3 Matlock Bath

The second of the two major renowned spas of the White Peak is Matlock Bath, situated in the wooded steep gorge of the River Derwent as it crosses the edge of the limestone terrain. Low temperature thermal springs were

Table 10.4 Analysis from 1922 of the Chalybeate Spring at Buxton (derived from Langham and Wells, 1986)

Parameter	*Concentration (mg/l)*
Ca^{2+}	36.5
Mg^{2+}	8.1
Na^{+}	21.4
K^{+}	5.1
Fe^{II}	22.7
Mn^{II}	2.0
SO_4^{2-}	157.6
HCO_3^{-}	54.0
Cl^{-}	9.7
Si	1.7
Al	6.6

known to emerge in the gorge as early as the 17th century. Some claim that the springs were known to the Romans, who were certainly actively mining lead in the area, but this must remain conjecture (Naylor, 1983).

The earliest documented use of the springs was in 1698. One of the thermal springs (the 'Old Bath') from the hillside was harnessed by local clergy to supply a bath and was subsequently passed on to George Wragg. Wragg built a bathhouse and made provision for visitors (Naylor, 1983). However, according to the report of a visitor in the year 1732, cited by Flindall and Hayes (1976), the civilizing influence of the spa culture took some time to catch on:

> Here are no inhabitants, except for a few Groovers (miners) who dig lead oar, and whose Hutts are not higher than a good Hogstye ... I cannot omit observing to you the natural Innocence of these People ... I was up early in the Morning ... when came out of one of these Hutts a Woman, I may say, Naked, for I am sure she had no Shift on, at least but a Piece of one. I was surpriz'd at the Impudence of the Woman, and she as much surpriz'd to see me!

Our voyeuristic visitor also bemoaned the lack of any road passable by coach into Matlock. The turning point appeared to come later in the 1730s when the road was improved and a new bathhouse at the Old Bath erected by the new owners, Messrs Smith and Pennel. Later, another spring, the New Bath, was developed on the same springline in the hillside.

By 1800, hotel accommodation had increased further. Flindall and Hayes (1976) wryly observe that the 'Natural Innocence' of the people had now changed to a more familiar 'single-minded desire for visitors' money'. The tourist traffic increased after 1800, following the opening up of a number of

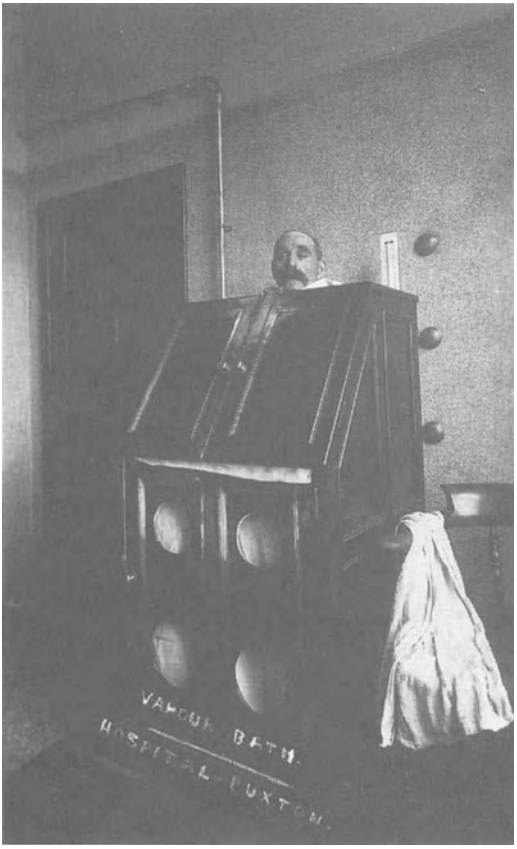


Figure 10.11 Old postcards from the collection of Mr Alan Bower, Wakefield, UK (Bower, 1985). (a) The ascending douche – 'Now sir, do sit still!'. A card sent from Matlock. (b) The vapour bath, Buxton Hospital. (Reproduced with the permission of Mr Bower and the Wye Valley Press.)

mines as 'show caves', and hydropathic establishments flourished. In 1878, Smith and Pennel's Old Bath was replaced by the Royal Hotel, later renamed the Royal Spa and Matlock Bath Hydro. At the height of its popularity, three main springs were utilized at Matlock Bath; at the New Bath Hotel (for the swimming pool, ornamental ponds and pump room), the Royal Hotel (for the hotel and official pump room) and the Thermal Swimming Baths (Stephens, 1929). Visitors included Queen Victoria, Byron, Ruskin and Turner (Naylor, 1983). Currently, the waters are only used to supply a public drinking fountain in the tourist office in the Pavilion and to feed a private swimming pool at the New Bath Hotel.

The locations of the original thermal springs in the gorge of the River Derwent are indicated by a large tufa deposit on the river's west bank in Matlock Bath. Stephens (1929) and Naylor (1983) remark that the springs issue from cracks in the upper surface of a lava bed, below a bed of pyritic blue marl in a zone 15–30 m above the level of the River Derwent.

Although the springs discussed above were largely natural, other thermal waters can be found at, and near, Matlock Bath which emerge from drainage adits (or soughs) associated with mine working. The Wragg Sough (otherwise known as the Bath Sough or Guildreye Sough), draining Nestus Mine (Figure 10.12), is one the most famous of these. It was about 440 m long, the first 180 m penetrating black Upper Lava, then 100 m of limestone and then 91 m of Lower Lava. After a further 64 m in limestone it encountered several thermal springs issuing out of limestone fissures associated with the Bacon Rake Fault (Flindall and Hayes, 1976; Rieuwerts, 1987), which the sough intercepted at 500 ft (*c.* 150 m) b.g.l. The springs ranged in temperature from 17 to 22°C, the most abundant being the warmest. The waters flowed down the sough, were diluted with cold water inflows, and then drained out of the sough into the River Derwent by the so-called Jubilee Footbridge. Later, interest in the thermal waters increased and at least one life was lost, that of John Cardon, a miner, in 1779 in explorations up the sough to locate the water source. In 1780 Dr Stephen Simpson purchased the hotel by the sough tail. He excavated a new adit, the Fountain Bath Sough, 40 ft (12 m) above the Wragg Sough past the cold water inflows. He then sank a shaft down to the Wragg Sough to tap the undiluted warm waters, having blocked off the Wragg Sough immediately downstream of the shaft. This work was completed by 1786, and the new adit discharged 200 gallons per minute (15 l/s) of water at 20°C into the 'Fountain Baths'. The obstruction of the drainage caused problems for the miners, however, and the Wragg Sough had to be unblocked. So, by 1791, wooden pipes were built from the thermal springs down the adit, preventing mixing with cold waters. The Fountain Baths have now been demolished, and the flow from the sough was diverted to supplement the town's drinking supply.

Another major sough, the Meerbrook Sough, drains water of a thermal character, at a rate of as much as 14–19 million gallons per day (740–1000 l/s),

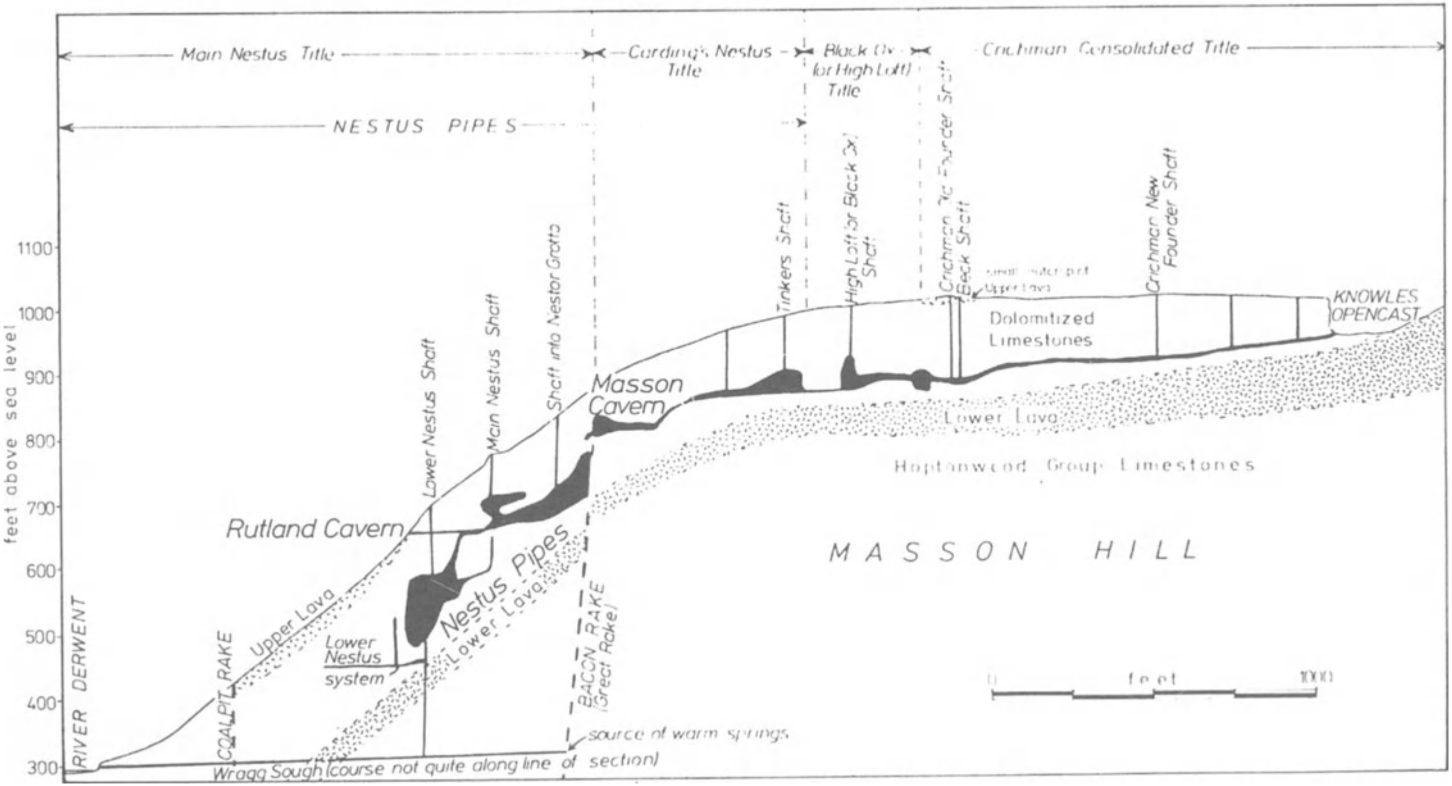


Figure 10.12 Simplified geological cross-section of the Nestus Mine, Matlock Bath (1 ft = 0.3048 m). (After Flindall and Hayes, 1976, with permission of Moorland Publishing Co.)

part of which is abstracted for public water supply by Severn Trent Water Company.

Geologically, the waters of Matlock Bath are of meteoric origin, having been subject to deep circulation at over 600 m (Smith *et al.*, 1967) and having risen rapidly up transmissive pathways in faults in the limestone such as the Bacon Rake. Matlock's thermal waters tend to have a relatively 'normal' limestone hydrochemistry, except for a slightly elevated sulphate content (Smith *et al.*, 1967). Like most limestone waters they have a high calcium bicarbonate content and the water has been used in Matlock's Petrifying Wells, where water was sprayed over objects which became coated in a precipitate of calcite.

10.5.4 Matlock Bank

The town of Matlock (as opposed to Matlock Bath) lies at the north end of the Derwent's limestone gorge. At Matlock, although the west bank of the river is underlain by limestone, the hills on the east side (Matlock Bank) are formed from Millstone Grit shales, capped by gritstones. Matlock is known for its hydropathic institutions (now fallen into disuse) based on springs issuing from the Millstone Grit. It can only be assumed that the idea of spa waters was encouraged by the success of Matlock Bath, a few kilometres farther south. The 'Hydros' of Matlock Bank were founded by John Smedley, who had found great relief for his ill health in the spa waters of Harrogate. Smedley opened his hydro in 1853, based on the springline at the gritstone/shale interface on the hillside. In 1859, Smedley's had 76 bedrooms, and in 1863 over 1000 patients were treated annually. In 1867 a further 94 bedrooms were added (Naylor, 1983). Others followed suit and at least seven hydros were in operation at the peak of Matlock Bank's success.

The National Health Act of 1948 sounded the death knell for the Matlock Bank hydros, as it did not encourage hydrotherapy based on spa waters as a valid treatment. The hydros have now been converted to local government offices and schools. However, the oldest spa feature of Matlock Bank, the Allen Hill Spaw, at the very foot of Matlock Bank, can still be seen. It carries the inscription, 'restored 1824' and is thought to be a mine sough driven into the shale. Its water is iron rich and ochre precipitating, the iron being presumably derived from pyrite oxidation in the black shales: a classic example of 'acid mine drainage' being regarded as a boon to society rather than a major pollution threat (e.g. Younger, 1995).

10.6 HARROGATE SPAS

Harrogate vies with Buxton and Leamington for the title of England's 'second' spa, after Bath. It lies astride a major NNE–SSW anticlinal

Table 10.5 The hydrochemical composition of Harrogate waters. Analyses dated (1931) are derived from British Spas Federation (1931); the final analysis, dated 16 July 1990, is derived from Leosson (1993)

Parameters (mg/l)	*Old Sulphur Well (1931)*	*Mild Sulphur Well (1931)*	*Starbeck Well (1931)*	*Chloride of Iron Well (1931)*	*Tewitt Well (1931)*	*Sulphur (Free) Well, Royal Pump Room 16 July 1990*
Ca^{2+}	428	254	48.1	326	55.2	423
Mg^{2+}	185	118	21.7	129	27.5	176
Na^{+}	5243	2789	831	2472	18.3	4880
K^{+}	73.5	47.0	10.2	39.0	2.2	60.5
Sr^{2+}	16.0	Trace	–	–	–	23.4
Li^{+}	1.0	Trace	Trace	Trace	Trace	2.69[a]
NH_4^{+}	3.0	3.8	2.0	1.2	0.3	–
Ba^{2+}	70.6	1.9	3.3	37.4	–	2.0
Fe	Trace	0.8	Trace	62.0	9.8	n.d. (0.20[a])
Mn	0.3	0.25	0.1	0.4	0.44	0.27
Si	–	–	–	–	–	5.3
Al	–	–	–	–	–	n.d. (0.95[a])
B	–	–	–	–	–	2.3
HCO_3^{-}	1220	1068	853	469	329	482
SO_4^{2-}	2.9	53.6	22.6	2.2	123	19.6
Cl^{-}	9090	4641	966	4544	23.9	9326
F^{-}	Trace	–	–	–	–	0.4
Br^{-}	28.0	15.0	–	10.0	–	–
I^{-}	0.06	–	–	0.03	–	–
Sulphides as S^{2-}	99.2	50.5	8.5	–	–	(23.0 H_2S)
NO_3^{-}	–	–	–	–	–	8.7
Radon (Bq/l)	20.3	0.44	11.8	3.6	2.4	–
Ra (ng/l)	0.081	0.0055	0.0132	–	Trace	–
pH	–	–	–	–	–	6.87
TDS (mg/l)	15852	8512	2458	7866	458	15438

[a] From a sample dated 19 Feb 1990.

n.d. = not determined. For 1931 data, bicarbonate is derived from original carbonate concentrations by multiplying by 2.03.

structure in the Carboniferous of West Yorkshire. The Harlow Hill Sandstone Member of the Carboniferous Limestone sequence crops out in the core of the anticline. The Namurian Millstone Grit sequence of sandstones, gritstones and carbonaceous, pyrite-rich shales forms the limbs of the anticline. The northwestern limb of the anticline coincides with the Harrogate Fault. The whole structure is covered with a veneer of drift, dominated by boulder clay (till).

The town is first mentioned in writing in 1200, where it is named 'Harelow'. The current name may be derived from the Danish 'Herrigate' (army street) due to it being on the looting and pillaging hotlist for marauding Scandinavians. The town only achieved fame after the discovery of the first spring, in 1571, by a Captain W. Slingsby. Slingsby, returning from a tour to Westphalia, was struck by the similarity between the waters found in his Tewitt Well (or English Spaw) and those he had observed in the German spas. The virtues of the Tewitt Well waters were praised by doctors as being good for headaches, migraines, ulcers and tumours, with the additional claim that they 'cheereth the spirit and reviveth the spirit, strengtheneth the stomacke, causeth a good and quicke appetite and furthereth digestion' (Leosson, 1993). Sometime shortly before 1626, the next spring, the Old Sulphur Well, was discovered, followed by the Old Spaw (or Sweet Spaw or St John's Well) around 1631. The importance of the springs increased during the 17th century and the town began to draw tourists of all sorts. The cross-section of society visiting the springs appears to have caused some friction, as noted by Michael Stanhope in 1632, who complained that they were being used by 'the vulgar sort (where) they wash their soares and clean their besmeared clouths (though unseen) where diverse after dippe their cups to drink'. Later, in 1733, the Alum Well in Bogs Field was found, while in 1770, 200 acres of land (81 ha), now known as the Stray, containing many spring seepages, were set aside as common land to preserve public access and as an early form of wellhead protection policy. This action required special provision in the Parliamentary Act of Enclosure for the surrounding forest of Knaresborough, and the Stray Act preserves the land as parkland today.

From the 17th century, mineral salts were produced from the springs and they came to be an industry important for the local economy. Indeed, the wells of a Mr Thackwray were said (Fox-Strangeways, 1908) to produce more than 15 tonnes per annum. They were claimed to relieve 'constipation, liver disorders, bilious complaints, gout and rheumatism'. Salts were even incorporated into Harrogate Soap. For some time Harrogate water was bottled and marketed as 'Harrogate Spring Water' or 'Aquaperia (Harrogate) Aperient Water'.

Springs continued to be discovered, including the Crescent Garden Spring in 1783, the Cheltenham (or Iron Chloride) Spring in 1819 (by drilling), the Montpellier Gardens Spring in 1822 and the Harlow Carr Spring in 1840.

The most popular springs were tended by intriguing 'waitresses' as documented in 1841 by the author of *Sketches of Harrogate by a Citizen of the World*, who had mastered the rare and subtle art of the double negative insult:

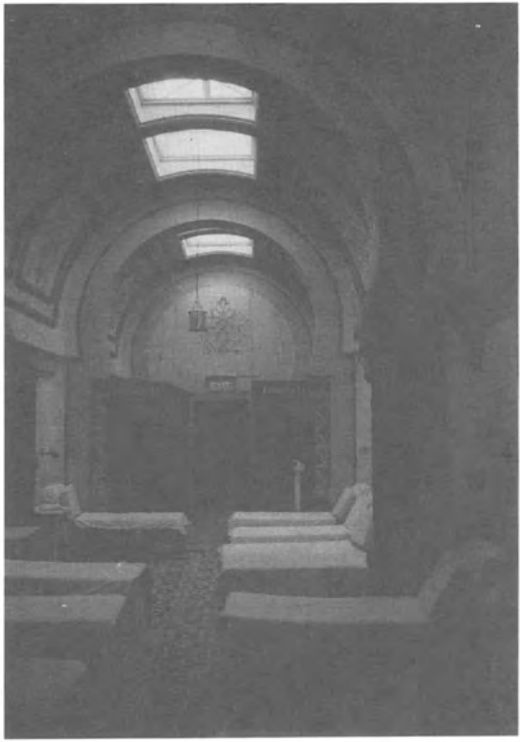
> At 7 o'clock (am) they flock down to the Old Sulphur Well, the waters of which are distributed by some 8 or 10 nymphs whose personal attractions are not calculated to make one insensible to the nauseous flavour of the draught they bestow. The lady paramount of the fount is an old dame, styled indifferently 'Old Betty' and 'the Queen of Harrogate' over whose head some 80 summers have passed without diminishing her activity of garrulity. She is a privileged person and disperses the waters and quips and quodlibets with equal liberality.

By 1908 some 80 springs were known. The Royal Baths in the centre of the lower town were opened by the Duke of Cambridge in 1897. Four or five wells existed below the Baths, but water from other wells and springs throughout the town were piped into the foyer of the Baths, to be distributed by tap-pullers at a 'bar' (Figure 10.13b shows a 'bar' in the Royal Pump Room). In addition to this drinking water facility, the Royal Baths held balneological facilities, treatment cubicles, consulting physicians, mudbaths and an adjacent Turkish Baths. The spa reached its height of popularity at the end of the 19th century. It had visitors as diverse as Queen Alexandra, Empress Marie Fedorovna of Russia, most of the British Government's Cabinet and Lords Byron and Tennyson. Charles Dickens was heard to comment wryly that Harrogate was 'the queerest place with the strangest people in it leading the oddest lives' (Blakeson, 1993)! Despite a decline in the spa's popularity in the interwar period of the 1920s and 1930s, due to general economic depression and shifts in medical opinion and leisure trends, a decision was taken by the Government to build a neo-Georgian balneotherapy annex to the baths. There are those who believe that the decision was taken with the wind of the coming World War II on the air, with a view to providing a treatment facility for war-injured. The annex was opened by the Minister for Health, Sir Kingsley Wood, in 1937, and within a few years the baths were being used by the Government for just that purpose. The Baths continued to be run by the National Health Service in the post-war period but, in the early 1960s, spa therapy was dropped as an 'approved' medicine, in favour of the new chemical drugs. Harrogate's fate was sealed, along with that of the other English spas, although mud bath facilities did persist up until 1987. Today, the annex is crumbling, although the original Royal Bath buildings are better maintained. The only bathing facilities left are the Turkish Baths, run by the Council, with their splendid (if somewhat kitsch) oriental interior of keyhole doorways and brightly coloured glazed tiles (Figure 10.13c). Sadly, however, the Turkish Baths use standard tap water, not genuine spa water. The only mineral water which can still be drunk at Harrogate is that of the

(a)

(b)

(c)



particularly potent Sulphur Wells, in the basement of the town museum in the Pump Room. Plans have been proposed to restore Harrogate's Royal Baths, however, by privatizing the Turkish Baths and opening a casino to give a certain continental spa atmosphere. An attempt to sell Harrogate waters as medicinal waters was dropped, due to the excessive costs associated with testing to comply with the 1967 Medicines Act and European legislation. At the time of writing, drilling is in progress at Harlow Hill, with the intention of finding a low mineralization, non-sulphide water for bottling as drinking water to rival the popular Buxton Water.

The aspect of Harrogate which has intrigued geologists is the wide variety of waters found in such a relatively small area, coupled with the fact that Harrogate is Britain's only major sulphide water spa. Total dissolved solids (TDS) range from 100 mg/l up to half that of seawater (Leosson, 1993). Fox-Strangeways (1908) categorized the waters as follows:

(I) Sulphur (H_2S) Waters:
  (a) Saline Sulphur:
    (i) Strong (High Cl^-, Na^+, H_2S), e.g. Old Sulphur Well;
    (ii) Mild (Moderate Cl^-, Na^+, H_2S), e.g. Crescent Saline Spring, Mild Sulphur Well;
  (b) Alkaline Sulphur (HCO_3^-, H_2S), e.g. Starbeck Spring, Harlow Carr Spring;
(II) Iron Waters:
  (a) Saline Iron (Cl^-, HCO_3^-, with some Fe, low H_2S), e.g. Kissingen Spring, Iron Chloride Well, Alum Well;
  (b) Pure Chalybeate or Non-Saline Iron (Mg^{2+}, Fe, HCO_3^-, low Cl^-), e.g. Tewitt Well, St John's Well.

There have historically been two schools of thought as to the origin of the waters. The locations of the waters tend to be focused on the outcrops of the Harlow Hill Sandstone and the Harrogate Roadstone (a limestone), in the vicinity of the Harrogate Fault. Fox-Strangeways observed that the salinity and sulphide content of the waters generally increased towards the core of the anticline, with the strong sulphur springs occurring near the core and the mild sulphur and saline chalybeate waters farther out on the limbs. He also noted that pumping one well usually did not affect other neighbouring wells. He believed, quite reasonably, that the various waters were related to different and progressively deeper strata outcropping successively towards the anticline's core. The waters were therefore recharged

Figure 10.13 (a) 'There's nothing like Harrogate Sulphur Water!' (A postcard from Blakeson, 1993; reproduced with permission of Harrogate Museum.) (b) Octagonal counter, Royal Pump Room, Harrogate, *c.* 1890. (Source: Blakeson, 1993; reproduced with permission of Harrogate Museum.) (c) The Turkish Baths at Harrogate. (Photo by David Banks, 1994.)

distally by meteoric water falling on the Pennine uplands to the west, the deeper waters having travelled further and having had longer residence times. Others, such as Edmunds *et al.* (1969) and Edmunds (1993) and Bottrell *et al.* (1996) have speculated whether the waters may be related to upwelling of Na–Cl saline waters (possibly formation brines) from a moderate depth, possibly along the Harrogate Fault, the variety of waters being related to varying proportions of mixing with fresher, shallower Ca/Mg–HCO_3 groundwaters. Relatively constant cation ratios tend to support the mixing model. Hudson (1938) noted the low temperature fluctuations of the most saline waters and took this to indicate a deep origin, in contrast to the iron waters which showed a marked seasonal variation in temperature. These two theories correspond to the 'aquifer' and 'injection' modes of mineral water respectively, according to Juodkazis *et al.* (Chapter 11). In fact, these two theories are not entirely contradictory, and the true picture is likely to contain elements of both models.

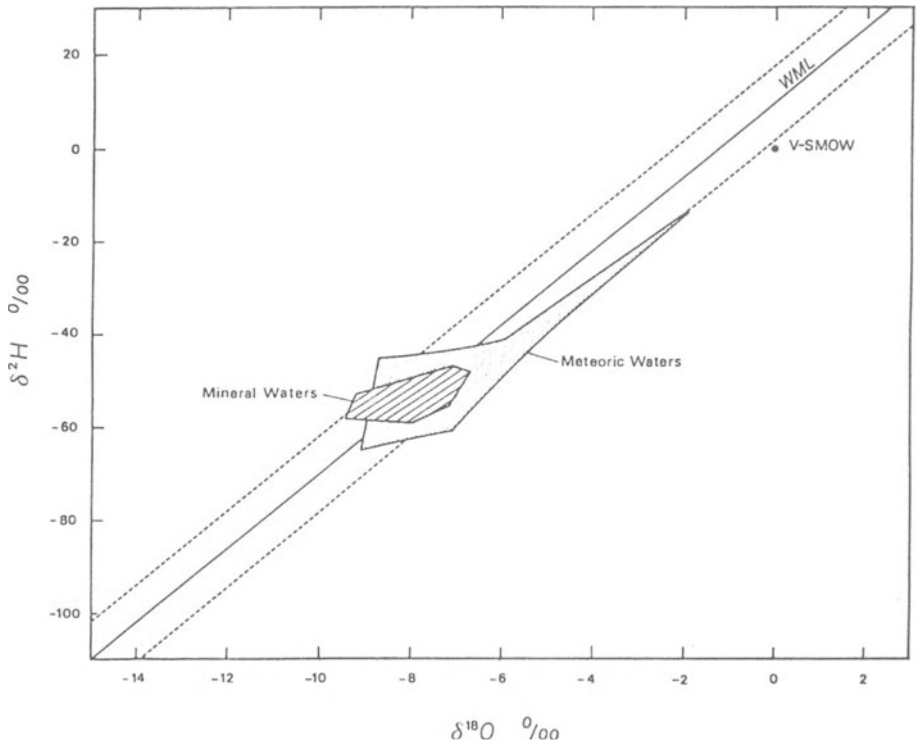


Figure 10.14 The use of δ^2H versus δ^{18}O plots to discern the palaeogeographic conditions of recharge of the Harrogate mineral waters. The isotopic data indicate the waters to have been recharged under climatic conditions similar to today. (After Leosson, 1993; reproduced with permission from Markus Leosson, University of Karlsrühe.)

The waters are not especially thermal. Some studies have noted that the most saline spring has a temperature of only 14°C, although Leosson (1993) determined temperatures as high as 18.9°C in waters from the Pump Room Sulphur Well. These low temperatures imply relatively shallow depths of circulation, dilution, or a very slow rate of rise from deeper strata (to allow time for cooling). Leosson (1993) studied the chemistry and stable isotope composition of the Pump Room Sulphur Wells and some 10 other nearby wells, and was able to categorize them as two distinct groups:

- 'Primary' waters: TDS $> 14\,000$ mg/l, mean $H_2S = 67.5$ mg/l;
  'Secondary' waters: TDS < 5700 mg/l, no detectable H_2S.

Leosson reports that hydrogen, carbon and oxygen isotope evidence suggests that all of the waters are derived from meteoric recharge, all waters plotting within 1% of the meteoric line on Figure 10.14. Evidence from sulphur isotopes (Bottrell *et al.*, 1996) is less straightforward, but strongly suggests that oxidation of disseminated pyrite in the Millstone Grit mudstones and shales is the source of sulphate in the secondary waters. The source of dissolved H_2S in primary waters is believed to be the microbial reduction of these sulphates at depth in the geological sequence. Immobilization of iron as iron sulphide is thought to be responsible for the low iron concentrations in the sulphide waters. In the near-well and in-well environment, further microbial oxidation and reduction occur to generate a complex equilibrium between sulphide and sulphate species in the final water.

10.7 BATH

Bath is probably the oldest and certainly the best known of the English spas. It was known from Celtic times as 'Sulis', but in the mid-1st century AD the Romans rechristened it *Aquae Sulis Minerva* after their goddess of wisdom, war and healing. After the departure of the Romans and the Saxon invasions, it fell into disrepair and came under the control of the Church, who rebuilt a lepers' bath at the Hetling Spring in 1138 (Heywood, 1991), until the dissolution of the monasteries in the reign of Henry VIII (Kellaway, 1991b). This setback did not permanently damage Bath's prosperity, and in the 17th and 18th centuries Bath achieved considerable national popularity. By the early 1800s, the spa was again in decline, but was reinvigorated in the 1880s by refurbishment of the springs. Its various historical, medical and geological features have already been described in detail in an excellent book edited by Kellaway (1991a); hence, only a relatively brief overview will be presented here.

The spa consists of three main springs (Figure 10.15):

- the King's Spring, (46–46.5°C) rising in the lead-lined Roman reservoir and feeding the famous Roman bath;

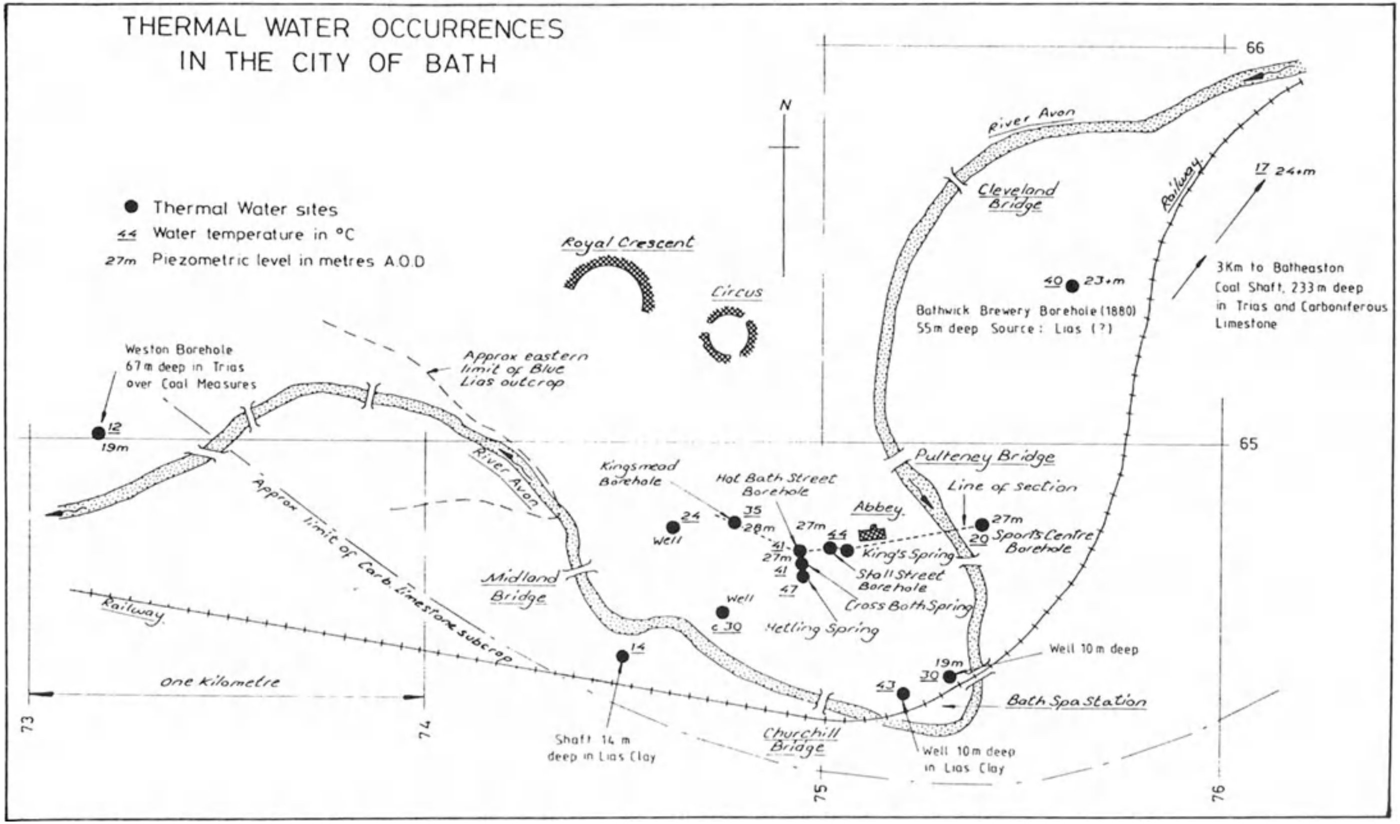


Figure 10.15 Thermal water occurrences in the City of Bath. (After Stanton, 1991. Copyright Wessex Water Authority, reproduced wit
permission.)

- the Hetling Spring (48°C);
- the Cross Bath Spring (41–42°C);

and several other minor ones. The total spring output is estimated as 15 l/s (Stanton, 1991). The springs are essentially upwellings along natural 'pipes' in fault zones in the underlying low permeability Lias clays, but humanity, from the Roman period onwards, has 'engineered' these springs in various ways, to some extent masking their natural character.

Geologically, Bath is underlain by Quaternary river deposits derived from the River Avon. Below this lies an aquitard consisting of Jurassic Lias clays and marly limestones and Triassic siltstone and marls. Under the eastern part of the city, this overlies a karstic Triassic Dolomitic Conglomerate. The Triassic strata are relatively undeformed and they unconformably overlie a succession of Carboniferous strata (Stanton, 1991; Figure 10.16).

At Bath the Carboniferous Limestone subcrops below the unconformity, the limestone forming the northern limb of the Radstock Syncline. To the south, in the core of the syncline, the subcropping strata are Namurian (Millstone Grit) and Westphalian (Coal Measures) sequences of shales, mudstones, siltstones and sandstones. The Carboniferous Limestone crops out in the southern limb of the syncline in the Mendip Hills, some 12 km south of Bath. It is generally accepted that the Mendip Hills form the main recharge area for the Bath thermal waters. The waters appear to travel through the limestone to the base of the syncline at a depth of some 2700 m where they are heated to temperatures of between 64° and 96°C by the prevailing geothermal gradient (Andrews, 1991; Burgess *et al.*, 1991; Figure 10.17). They then rise up the northern limb of the syncline, undergoing some cooling and chemical re-equilibrium, to the subcrop at Bath, recharging the Triassic Dolomitic Conglomerate aquifer. At this stage it is thought that some admixture with cool local recharge water occurs. The total transit time is estimated to be less than 10 000 years, maybe as little as 4000 years. The ultimate driving force for the entire system is the difference in head between the recharge zone in the Mendips and Bath itself. Up to a further 40 m of head may be caused by temperature-induced density differences assisting the water to rise up the northern limb of the anticline. Some workers, e.g. Burgess *et al.* (1991), have speculated whether the Mendips are the sole source of recharge, and have concluded that vertical 'seepage' through the Mesozoic cover and Coal Measures/Millstone Grit in the core of the syncline could account for a not inconsiderable portion of the recharge.

The impetus for the investigations which disclosed the exact nature of the springs at Bath was the discovery of a pathogenic amoeba *Naegleria fowleri*, causing meningoencephalitis, in the thermal spring sources in 1978 (Kilvington *et al.*, 1991). This led to the immediate closure of the Hetling and Cross Baths and of the Pump Room drinking fountain at the King's Bath. The

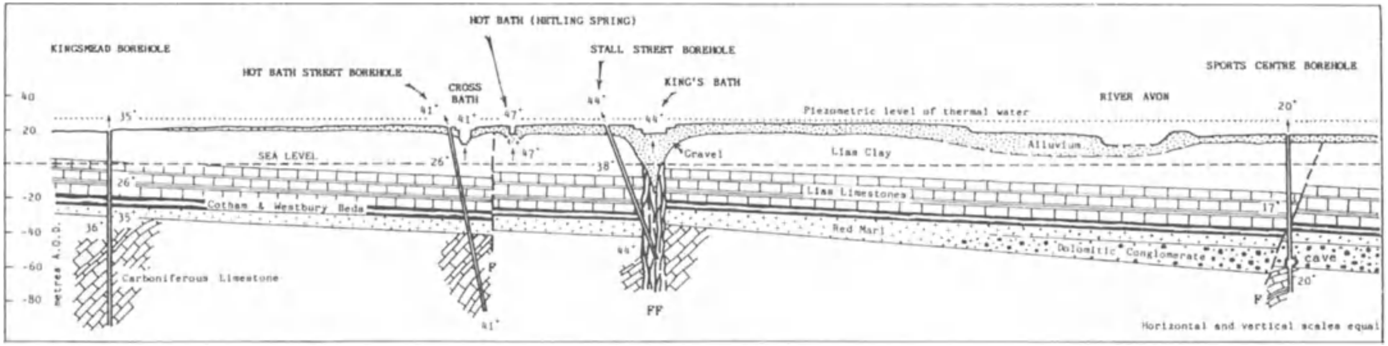


Figure 10.16 Schematic geological cross-section through the springs and boreholes at Bath, showing groundwater temperatures in degrees Celsius. (After Stanton, 1991. Copyright Wessex Water Authority, reproduced with permission.)

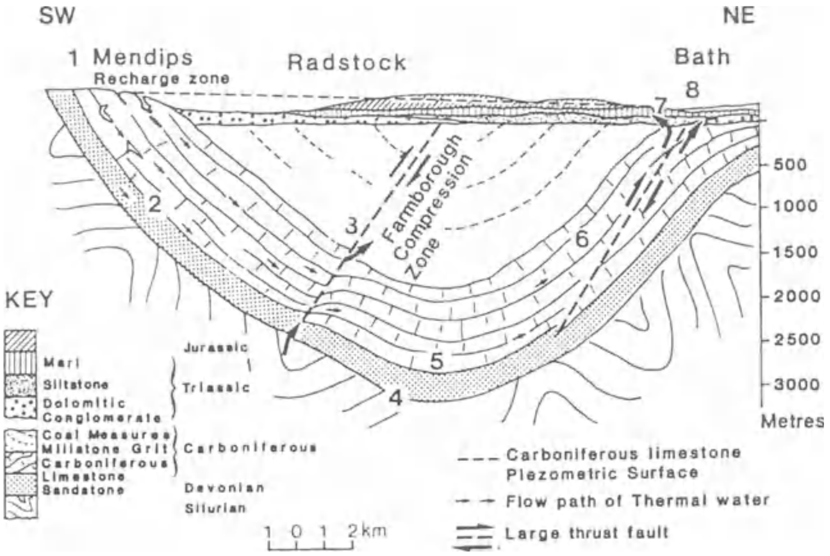


Figure 10.17 A conceptual model for the Bath thermal springs. (1) Recharge at the Mendip Hills to the Carboniferous Limestone; (2) down-gradient flow beyond the mature, phreatic, karstic system; (3, 4) possible communication between the Lower Palaeozoic rocks, the Carboniferous Limestone and the Upper Carboniferous strata at depth; (5) storage and chemical equilibration in the Carboniferous Limestone, with a temperature of at least 64°C (49°C minimum for the Hotwells, Bristol, flowpath); (6) relatively rapid upward flow in the Hercynian thrust fault system; (7) recharge of Triassic strata by thermal water at Bath; (8) discharge at the thermal springs (46.5°C at Bath). (After Burgess *et al.*, 1991. Copyright British Geological Survey, reproduced with permission.) Recent investigations indicate that the Coal Measures and Millstone Grit are much thicker, reaching a depth of about 3000 m in places, meaning that the Carboniferous Limestone also is deeper (Geoffrey Kellaway, personal communication, November 1995).

King's Bath had already been closed for structural repair. The subsequent investigations involved drilling boreholes into the spring pipes underlying the King's Spring and the Cross Bath Spring in search of microbiologically pure water (Kellaway, 1991c). It was discovered that the spring pipes, which lie along E–W to ESE–WSW fault zones, were typically of conical shape, penetrating the Lias clays. The pipes were filled with alluvial sand, silt and gravel and lenses of slumped Lias clay. The drillings were basically successful, encountering amoeba-free water at a temperature of 46.5°C and an artesian head of +30 m OD (compared to ground level of 17 m OD) at the King's Spring. This indicated that the microbes were essentially aerobic and were not present in groundwater at depth. Thus an inclined production borehole, the Stall Street borehole, was drilled to intercept the King's Spring pipe. The borehole was successfully terminated at 84 m depth, having encountered thermal waters in fractures in the Lias and Carboniferous strata. It now supplies the Pump Room drinking fountain with amoeba-free water. In 1988 a similar inclined borehole was drilled to supply pure thermal water to the Cross Bath.

Boreholes were also drilled at Kingsmead and at the Sports Centre. The Kingsmead borehole was successful, encountering water at 36°C in fractures in Triassic marls. The Sports Centre borehole found brackish water at only 21°C in the Dolomitic Conglomerate, too low a temperature for its intended use as a swimming pool supply.

These boreholes yielded much information on both the geology and hydrochemistry of Bath. It appeared that the virgin thermal waters are dominated by calcium and sulphate (Stanton, 1991) and are ultimately derived from the Carboniferous Limestone. Below Bath they ascend to the surface through fault-controlled pipes, but also migrate into the overlying Triassic strata, particularly the karstic Dolomitic Conglomerate, to form a recharge mound. As they migrate out from the centre the thermal waters cool and mix with the surrounding sodium chloride waters of the Trias, becoming increasingly brackish in composition. This is illustrated by analyses in Table 10.6.

Although by pumping the new boreholes the volume of thermal water can be increased, the heat output remains remarkably constant at about 55 000 Mcal/d (230 GJ/d; Stanton, 1991). This appears to be because there is a steady heat flux from the deep thermal groundwater. Manipulating the various sources can achieve higher temperatures in one spring, but eventually at the expense of thermal output from the other sources.

The output from Bath's springs appears to be remarkably constant, but nevertheless steps are being taken to safeguard the quantity and quality of the resource, as described by Kellaway (1991c):

- a long term program of test boring and monitoring of heat flux and yield;
- strict control on well and shaft sinking in the Bath area, as defined by the Avon Act (1979) legislation;
- evaluation of control measures in the Mendips recharge area to prevent adverse impacts of limestone quarrying and dewatering.

As a point of interest, another thermal spring (Hotwells, 24°C) emerges from the northern limb of the Carboniferous Limestone syncline further to the west, in the floor of the Avon Gorge in Bristol (Hawkins and Kellaway, 1991). This formed the basis for a thriving spa as recently as the 18th century and the water was bottled for export. Several other thermal spring and borehole waters are recorded in the same area of Bristol. The fact that Bath and Bristol are the only two known warm spring locations on the northern limb argues for some form of discrete preferential flow paths (discrete fissures), or even fault/fracture-controlled ascension pathways, although other possible controlling factors have been discussed by Kellaway (1991d).

Table 10.6 Chemical analyses from the Avon thermal water field, compiled from Edmunds *et al.* (1969), Hawkins and Kellaway (1991), Andrews (1991) and Edmunds and Miles (1991)

Parameter (mg/l unless otherwise specified)	*King's Spring*	*Hetling Spring*	*Stall Street borehole*	*Sports Centre borehole*	*Weston Maltings borehole*	*Hotwells, Bristol*
Ca^{2+}	382	385	390	296	110	205
Mg^{2+}	53	54	58	71	35	29
Na^+	183	179	228	486	420	96
K^+	17.4	16.8	18.1	23.0	22.8	n.d.
Sr^{2+}	5.9	5.5	6.3	7.4	10.5	–
Li^+	0.24	–	0.23	–	–	–
Ba^{2+}	0.024	0.024	0.030	0.010	<0.2	–
Fe	0.88	<0.01	1.0	0.88	0.17	10[a]
Mn	0.068	0.045	0.050	0.040	0.022	–
Si	20.6	19.3	19.5	6.5	4.7	8.4
Al	<0.05	–	<0.001	–	–	–
B	0.59	0.47	0.59	1.4	–	–
U (μg/l)	0.06	0.03	0.03	0.18	–	0.85
HCO_3^-	192	188	187	198	245	232
SO_4^{2-}	1032	1000	1030	898	795	405
Cl^-	287	284	335	820	235	76
F^-	2.08	2.00	2.0	2.3	3.1	–
Br^-	2.02	1.70	2.0	–	–	–
I^-	0.043	0.028	0.042	–	–	–
NO_3^-	<4.4	<4.4	<0.22	–	<2.2	–
^{222}Rn (Bq/l)	86	199	88	4.4	–	43
^{226}Ra (Bq/l)	0.38	0.40	0.44	0.04	–	0.04
$^4He^b$	1080	1000	1840	3525	–	410
TDS (mg/l)	2179	2136	2278	2811	1864	1071
pH	6.65	6.5	6.70	6.7	7.95[c]	–
Temperature (°C)	45.3	44.8	44.4	20.2	13.2	24.3

[a] Combined Fe and Al oxides = 10 mg/l. [b] Units are 10^{-8} cm^3 STP/cm^3 H_2O. [c] Laboratory determination (all other pH are field determined).
n.d. = not determined.

Much of the evidence for this conceptual model of the Bath spa is based on isotope hydrochemistry. The value $\delta^{13}C = -1.6‰$ implies that the Bath waters are in equilibrium with a marine limestone reservoir rock (i.e. the Carboniferous Limestone). ^{14}C data are problematic (Evans *et al.*, 1979) but tend to suggest a maximum age of some 19 200 years (Edmunds, 1986). A plot of $\delta^{18}O$ versus $\delta^{2}H$ implies that the waters are of meteoric origin (Chapter 3), and their similar position to current rainfall on the world meteoric water line implies that the recharge temperature was similar to the present day (Andrews, 1991). The ratios of the inert gases Ne, Ar, Kr and Xe also imply a recharge temperature of about 8.7°C, comparable to modern groundwaters (Edmunds, 1986). These findings in turn imply that the waters were recharged under non-glacial conditions, implying an age of either $>$100 000 years (considered unlikely on other grounds) or $<$10 000 years (the end of the last ice age). Andrews (1991) has performed much work on dissolved gases and radionuclides, which have been used to explore the origins of the waters. Several of his examples from Bath have been used in Chapter 3 to explain the application of these techniques.

Currently, the stage is set for something of a renaissance in the fortunes of Bath's waters. Plans have been put forward by a leading hotelier to bottle 'Bath Spa Water' and a private sector company is considering the option of redeveloping the Stall Street Baths as a full modern health and leisure spa.

11

Geothermal and mineral water resources of Lithuania

Vytautas Juodkazis, Povilas Suveizdis and Vita Rastenienė

11.1 GEOLOGICAL CONTEXT

Lithuania is a small but geologically varied country. With an area of 65 200 km^2 and a population of some 4 million, it is underlain by a relatively complete and undeformed sequence, from the Precambrian basement of the Baltic Shield up to the extensive glacial deposits of the Quaternary period. Lithuania is almost entirely dependent on groundwater for its drinking water supply; some 14 000 water supply wells abstract water from 20 aquifer horizons of varying age (Paukštys, 1993). There is growing concern regarding the deterioration of groundwater quality (Juodkazis and Klimas, 1991; Juodkazis, 1994). The regional dip of the strata is to the northwest, the sedimentary pile becoming thicker towards the basin of the Baltic Synclinorium. In the west, near the Baltic Sea, the sediments are thickest, with the basement at more than 2300 m depth. In the southeast of the country, on the margins of the Belorussian Anticlinorium, the crystalline Precambrian basement is found at only 250–300 m depth. Across the border in Belorussia, the depth of the basement is as little as 100 m (Klimas, 1993).

11.2 MINERAL WATERS OF LITHUANIA

11.2.1 Introduction

Lithuanian mineral water sources have been known since the 16th century. However, balneological spas using mineral water for treatment of diseases

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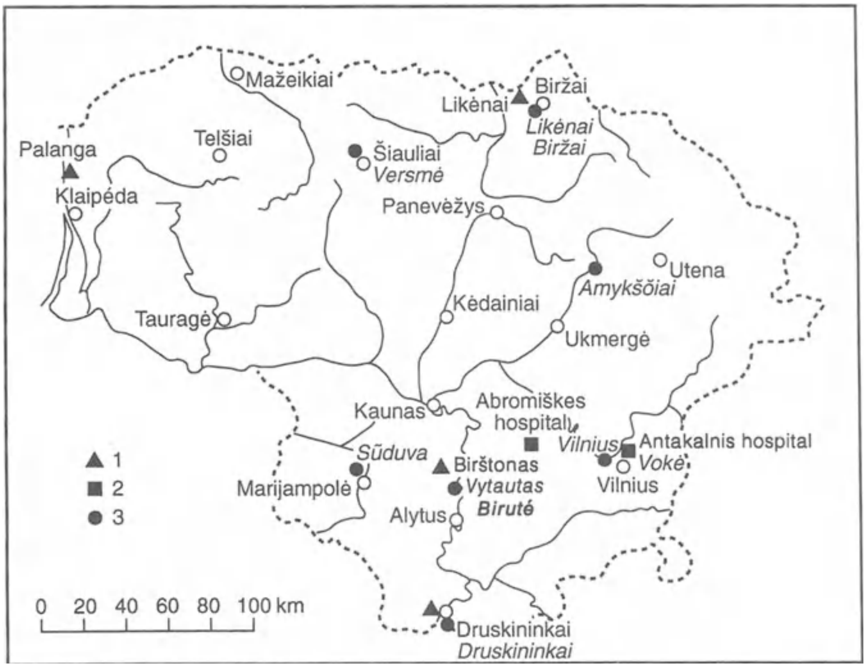


Figure 11.1 Mineral water use in Lithuania: (1) spas/resorts and (2) centres of medical rehabilitation where mineral water is used; (3) extraction of mineral water for industrial bottling.

were established much later: Druskininkai in 1837, Birštonas in 1846 and Likėnai in 1890. Almost 25 years ago, mineral water was successfully prospected in the sea resort of Palanga, where sanatoria are now in operation. Mineral water obtained from single boreholes is used in two medical treatment centres: Vilnius and Elektrėnai (Abromiškės). Moreover, boreholes used to supply bottled mineral water are established in Vilnius, Stakliškės, Biržai, Šiauliai and other sites (Figure 11.1).

Currently, mineral water of three types is being used in Lithuania: (1) water without specific 'esoteric' components, its curative features being determined by major anions and cations, (2) bromine-rich waters and (3) sulphide-rich waters (H_2S).

11.2.2 Chemical composition of the mineral waters

Non-component-specific mineral waters

Non-component-specific balneological mineral waters occur under the entire area of Lithuania at various depths. They differ, however, in mineralization and hydrogeochemical composition. According to mineralization, waters can be classified as of low (2–5 g/l) or high (15–35 g/l) mineralization, or as brines (>35 g/l). Chemical composition is typically of chloride (Cl^-–HCO_3^- or Cl^-–SO_4^{2-}) or sulphate (SO_4^{2-}–HCO_3^-) type. Sulphate-rich mineral waters are common in the northern and northwestern parts of Lithuania, where gypsiferous ($CaSO_4$-bearing) Permian and Devonian rocks occur.

The occurrence and formation of these mineral waters can be categorized as either (1) aquifer waters or (2) injectional waters. 'Aquifer' waters evolve by standard hydrogeochemical pathways; their mineralization progressively increases in zones of 'stagnant' (low flow) groundwater, or they may be related to specific strata or bodies of very soluble evaporite or halogen minerals. The 'injectional' water resources occur as localized hydrogeochemical anomalies formed by the vertical migration of highly mineralized groundwater from depth through tectonic fracture zones (Figure 11.2). When highly mineralized water reaches aquifers of slow but active groundwater flux, the latter's mineralization increases, their chemical composition

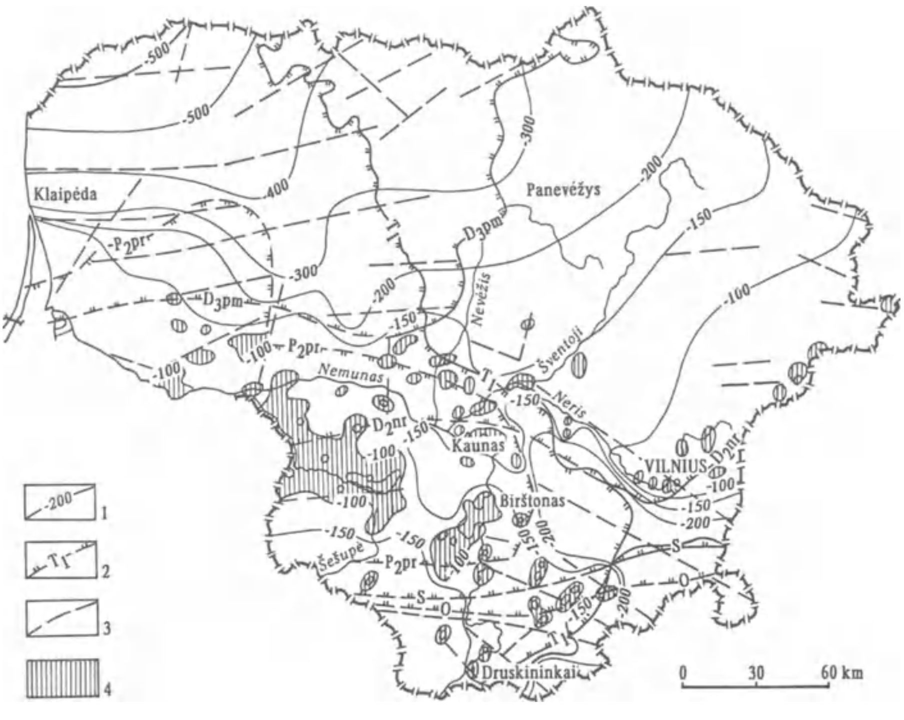


Figure 11.2 Local hydrogeochemical anomalies formed under conditions of mineral water upwelling from depth (according to Z. Šonta): (1) isohypse of occurrence depth (m) of groundwater containing over 350 mg/l of chloride, (2) limits of extent of regional aquicludes and their geological index, (3) tectonic fractures and (4) local hydrogeochemical anomalies of injectional type.

Table 11.1 Hydrochemical composition of natural mineral springs (Juodkazis and Mikalauskas, 1994)

Spring site and name	*Kurlov formula (mineralization M in g/l, ions in % equivalents)*	*Research year*	*References*
Druskininkai, high mineralization	$M_{9.2}\frac{Cl97HCO_3 2SO_4 1}{Na69Ca29Mg2}$	1835	Fonberg (1835)
Druskininkai, medium mineralization	$M_{5.5}\frac{Cl98HCO_3 1SO_4 1}{Na69Ca23Mg8}$	1835	Fonberg (1835)
Druskininkai, low mineralization	$M_{3.2}\frac{Cl98HCO_3 1SO_4 1}{Na63Ca23Mg14}$	1835	Fonberg (1835)
Druskininkai, 'Maršalka'	$M_{57.3}\frac{Cl93SO_4 5HCO_3 2}{Na70K2Ca17Mg11}$	1930	Safarevicz (1932)
Birštonas, central	$M_{7.9}\frac{Cl76SO_4 15HCO_3 9}{(Na+K)62Ca22Mg16}$	1935	Kaveckis (1949)
Birštonas, 'Vytauto'	$M_{7.6}\frac{Cl76SO_4 15HCO_3 9}{(Na+K)62Ca23Mg15}$	1935	Kaveckis (1949)
Birštonas, 'Birutės'	$M_{1.2}\frac{Cl47HCO_3 42SO_4 11}{(Na+K)40Ca40Mg20}$	1935	Kaveckis (1949)
Stakliškės, main	$M_{5.9}\frac{Cl79SO_4 16HCO_3 5}{Na69Ca30K1}$	1846	Kukulnik, unpublished archive data (1853)

is changed and, under favourable conditions, a mineral water field is formed. Often such fields occur near to rivers, because river valleys typically coincide with fracture lines. Valleys and other deep erosional incisions thus create favourable conditions for the occurrence, discharge and exploitation of mineral water resources.

Such sources, found in the valleys of the Nemunas and other rivers, tend to be characterized by sodium in their cation composition, although the total salt content varies somewhat (Table 11.1). The total mineralization of natural spring waters typically ranges from 1 to 5 g/l, but can be somewhat higher (Juodkazis, 1979; Juodkazis and Mikalauskas, 1994). The variety of mineralization is particularly well suited to the development of curative spas which require water types of differing salinities. However, due to the growth of spa resorts, it has become increasingly difficult to protect the resources from anthropogenic impact and contamination. Therefore, natural springs have been replaced by numerous boreholes to ensure a supply of deeper, sterile, uncontaminated mineral water. Now, natural springs of mineral water can only be found in obscure nooks of these spa areas and, unfortunately, such sites are usually uncared for and unimpressive. Happily some of them, e.g. Balbieriškis and Nemunaitis, have been declared natural hydrogeological monuments.

The mineral waters of the Druskininkai, Birštonas and Stakliškės fields are derived from Triassic, Cretaceous and Quaternary deposits respectively. They are injection type fields formed around zones of tectonic fractures. The mineral waters of Palanga and Likėnai are taken from Devonian strata and are typically of aquifer type. The mineralization of these waters is normally low to medium, with neutral pH (7–7.5; Table 11.2). For balneological purposes, injection type fields are particularly favourable as water of varying mineralization can be obtained by drilling to different depths and at various distances from the injection fracture zone (Juodkazis, 1979).

Bromide mineral water

Bromide mineral water, containing more than 25 mg/l of bromide, is formed under similar hydrogeological conditions to waters lacking specific 'esoteric' components. However, the mineralization of bromide waters is typically high, often exceeding 15 g/l. Thus in all Lithuanian spas, the zone of non-component-specific mineral water usually overlies a deeper zone of bromide mineral water (Table 11.3). In such waters, the bromide content ranges from 27 to 260 mg/l and depends on mineralization (Figure 11.3). Ionically, bromide waters are usually of sodium chloride type. The minimum depth to bromide type waters is typically 300–600 m.

Sulphide mineral water

The third balneological group consists of the sulphide mineral waters. According to quality requirements, the content of hydrogen sulphide (H_2S) should not exceed 10 mg/l. Such waters occur in the gypsiferous rocks of the Biržai and Pasvalys districts (Paukštys, 1995), although conditions for the formation of the waters are rather unfavourable, and typical H_2S contents are usually only 5–10 mg/l. The sulphide water is used only in the historic spa of Likėnai. First, at Likėnai, the water is used at the sanatorium, where it occurs in a karst pit 74 m in diameter and 3 m deep. This water is derived from the unconfined Tatula aquifer and the smell of hydrogen sulphide is distinctly unpleasant. Thus the spring and the 3–4 m wide brook flowing from it are named 'Smardonė' (or 'stinky'). Similar conditions prevail at the second source used at Likėnai, while the water from the third source is devoid of hydrogen sulphide (Table 11.4). The H_2S is formed from the bacterial reduction of sulphates. The sulphate content is also high in the gypsiferous karst waters (up to 1500 mg/l) in the Tatula aquifer. In order for sulphate to be reduced to hydrogen sulphide, the presence of organic matter is required. This enters the Tatula aquifer from the boggy landscapes around some parts of Likėnai. The chemical reaction can be written:

$$SO_4^{2-} + 2C + 2H_2O = H_2S + 2HCO_3^-$$

Table 11.2 Hydrochemical composition of non-component-specific mineral waters (Juodkazis and Mikalauskas, 1994)

Well name	*Aquifer index* / *Depth (m)*	*Mineralization and ion composition*	*Other components (mg/l) and indices*			
			Br	*Si*	*pH*	*T(°C)*
Druskininkai mineral water field						
Dzūkija	$\frac{Q}{51-61}$	$M_4 \frac{Cl90HCO_37SO_43}{(Na+K)64Ca25Mg11}$	3.3	8.1	7.8	11.7
Druskininkai	$\frac{K_2}{76-98}$	$M_{7.4} \frac{Cl92HCO_34SO_44}{(Na+K)59Ca27Mg14}$	17	7.8	7.4	11.3
M. Melnikaitė	$\frac{K_2+K_1}{182-197}$	$M_{8.4} \frac{Cl95HCO_33SO_42}{(Na+K)56Ca27Mg16}$	17	7.5	7	12
Rasa	$\frac{K_2+K_1}{182-195}$	$M_7 \frac{Cl92HCO_34SO_43}{(Na+K)60Ca24Mg15}$	13.2	6.9	7.4	12
Druskonis	$\frac{K_2cm+K_1}{194-224}$	$M_{14} \frac{Cl90SO_44HCO_36}{(Na+K)54Ca30Mg16}$	26.9	6.3	7.2	11.5
Aušra-1	$\frac{K_1}{198-218}$	$M_{11.5} \frac{Cl95SO_44}{(Na+K)54Ca30Mg15}$	18	n.d.	7.2	n.d.
Birštonas mineral water field						
Versmė	$\frac{Q}{16-18}$	$M_{7.7} \frac{Cl80SO_416HCO_33}{(Na+K)57Ca24Mg15}$	14.9	8.6	7.2	9.8
Vytautas	$\frac{Q}{47-57}$	$M_{7.5} \frac{Cl80SO_416HCO_34}{(Na+K)62Ca23Mg15}$	17.4	n.d.	7.1	n.d.
Vytautas	$\frac{K_2cm+K_1}{72-125}$	$M_{8.6} \frac{Cl82SO_415HCO_33}{(Na+K)60Ca27Mg12}$	17.9	5.8	7.4	8.9
Gražina	$\frac{K_2}{44-53}$	$M_{3.4} \frac{Cl76SO_417HCO_37}{(Na+K)65Ca21Mg14}$	5.9	10.2	7.5	10.8
Birutė	$\frac{K_2cm+K_1}{81-88}$	$M_{3.1} \frac{Cl81SO_411HCO_38}{(Na+K)57Ca26Mg17}$	4	8.2	7.7	9.8
Danutė	$\frac{K_2cm+K_1}{86-96}$	$M_{9.4} \frac{Cl81SO_416HCO_33}{(Na+K)61Ca21Mg17}$	18.2	7.6	7.9	9.8
Likėnai mineral water field						
Likėnai	$\frac{D_2pr+D_1km}{416-430}$	$M_{7.4} \frac{Cl62SO_437}{(Na+K)58Ca31Mg10}$	13.3	2.2	7.1	11.6
Palanga mineral water field						
Jūratė	$\frac{D_3kr+st}{306-375}$	$M_{3.2} \frac{SO_491Cl5HCO_34}{Ca54Mg34(Na+K)12}$	1.2	2.7	7	15
Kastytis	$\frac{D_3kr+ys}{317-439}$	$M_{3.2} \frac{SO_490Cl5HCO_35}{Ca55Mg36(Na+K)7}$	0.2	2.5	7.1	15

Table 11.2 Continued

Well name	*Aquifer index* / *Depth (m)*	*Mineralization and ion composition*	*Other components (mg/l) and indices*			
			Br	*Si*	*pH*	*T (°C)*
Stakliškės mineral water field						
Stakliškės-1	$\frac{\mathrm{P_2nk}}{297-355}$	$M_{9.32}\frac{Cl72SO_4 24HCO_3 4}{(Na+K)56Ca23Mg21}$	17.3	2.8	6.8	11.5
Stakliškės-2	$\frac{\mathrm{P_2nk}}{289-295}$	$M_{3.86}\frac{Cl46SO_4 41HCO_3 12}{(Na+K)62Ca22Mg15}$	4	2.8	7	11
Vilnius mineral water field						
Vilnius-3	$\frac{\epsilon_1}{354-362}$	$M_2\frac{Cl62HCO_3 24SO_4 14}{Na95Mg3Ca2}$	1.6	3.3	8	n.d.
Vilnius-2	$\frac{PR_3gd}{424-450}$	$M_{5.3}\frac{Cl74SO_4 20HCO_3 6}{(Na+K)79Ca14Mg6}$	10.1	3.1	7.7	n.d.

n.d. = no data available.

if elemental carbon is regarded as the electron donor, or

$$SO_4^{2-} + 2CH_2O = H_2S + 2HCO_3^-$$

if carbohydrate of some kind is regarded as the reducing agent.

It has been determined that the amount of organic carbon should be of the order of 40–80 mg/l for favourable conditions for biochemical sulphate reduction. Such conditions exist where bog deposits overlie the carbonate and gypsiferous Tatula rocks. If, as occurs in places, a thick moraine lies between the bogs and the Tatula aquifer, organic material is precluded from entering the aquifer and sulphates are not reduced (Figure 11.4).

Detailed investigations of the sulphide groundwater field of Likėnai, completed in 1980, have indicated that highly enriched hydrogen sulphide waters are not being formed at present. Hydrogen sulphide typically occurs in water in the range 0.1–2 mg/l in many recharge areas. Only in rather small peat-covered regions does it increase to 10–15 mg/l. Undoubtedly, these changes are at least partly due to human impact (Paukštys, 1995). For instance, H_2S in one borehole (32 m deep), drilled in 1960, ranged from 7 to 13 mg/l, whereas in 1976 the content was below 3 mg/l.

The temperature of mineral water in Lithuania governs its balneological suitability to a large extent. Mineral water of 37–40°C is particularly appreciated; being approximately blood temperature there is no necessity to heat or cool it for curative purposes. Sports swimming pools may utilize thermal waters up to about 25°C. Waters of such temperatures are present in the west of Lithuania, as will be discussed later, at depths of 900–1200 m. Such resources have hardly been exploited yet, however, and only cold mineral waters with temperatures of up to 19°C are utilized.

Table 11.3 Hydrochemical composition of bromide type balneological waters (Juodkazis and Mikalauskas, 1994)

Well name	*Aquifer index* / *Depth (m)*	*Kurlov formula (mineralization M in g/l, ions in %-equivalents)*	*Other components (mg/l) and indices*			
			Br	*Si*	*pH*	*T (°C)*
Druskininkai mineral water field						
Aušra-2	$\frac{\mathrm{K_1}}{198-218}$	$M_{19.2}\frac{Cl93SO_47}{(Na+K)56Ca30Mg14}$	39.5	n.d.	7.1	n.d.
Grožio šaltinis	$\frac{\mathrm{T_1}}{267-328}$	$M_{51.3}\frac{Cl95SO_45}{(Na+K)70Ca20Mg10}$	84	2.8	6.7	11
Sūrutis	$\frac{\mathrm{T_1}}{291-307}$	$M_{51.4}\frac{Cl95SO_45}{(Na+K)70Ca20Mg10}$	87	3.9	6.6	11.7
Birštonas mineral water field						
Vaidilutė	$\frac{\mathrm{T_1nm}}{272-304}$	$M_{26.9}\frac{Cl91SO_49}{(Na+K)47Mg35Ca17}$	58.2	2.3	7.1	12.8
Versmės sanatorija	$\frac{\mathrm{T_1nm}}{245-253}$	$M_{22.2}\frac{Cl89SO_411}{(Na+K)44Mg28Ca26}$	58.6	2.8	7	10.6
Rūta	$\frac{\mathrm{T_1nm}}{259-282}$	$M_{27.4}\frac{Cl91SO_48}{(Na+K)47Mg35Ca17}$	58.2	1.5	6.6	11.2
Birštonas	$\frac{\epsilon}{690-715}$	$M_{101.6}\frac{Cl97SO_43}{(Na+K)77Ca13Mg10}$	197.9	1.6	6.7	16
Likėnai mineral water field						
Aukštaitija	$\frac{\epsilon}{927-990}$	$M_{115}\frac{Cl98SO_42}{(Na+K)71Ca19Mg10}$	242.5	1.3	6.3	16.6
Palanga mineral water field						
Eglė	$\frac{\mathrm{D_3pl}}{459-468}$	$M_{12.3}\frac{Cl73SO_426}{(Na+K)61Ca24Mg13}$	32.2	2.8	7.7	16
Naglis	$\frac{\mathrm{D_3šv+D_2up}}{488-502}$	$M_{14.2}\frac{Cl83SO_416}{(Na+K)67Ca20Mg12}$	43.2	2.9	7.2	17
Palanga	$\frac{\mathrm{D_3šv+D_2up}}{495-565}$	$M_{18.5}\frac{Cl87SO_413}{(Na+K)67Ca19Mg14}$	48	n.d.	6.6	n.d.
Žilvinas	$\frac{\mathrm{D_3šv+D_2up}}{666-680}$	$M_{34.3}\frac{Cl91SO_48}{(Na+K)66Ca21Mg13}$	114.3	2.2	7	18.2

n.d. = no data available.

11.2.3 Groundwater fields

Druskininkai

At present, four spas are using mineral water for curative purposes in Lithuania. Druskininkai, the largest spa, has been active since 1837 and

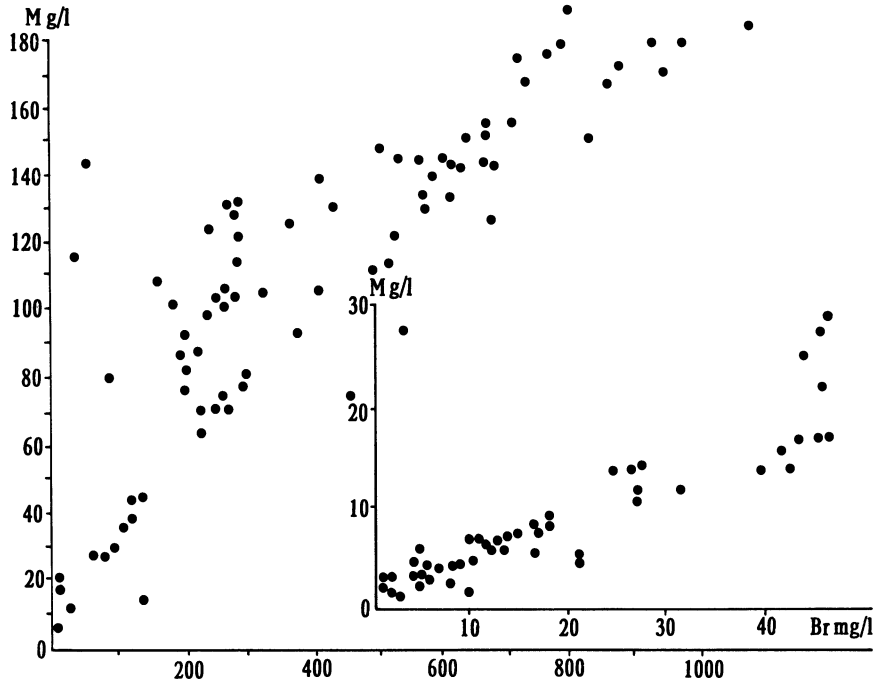


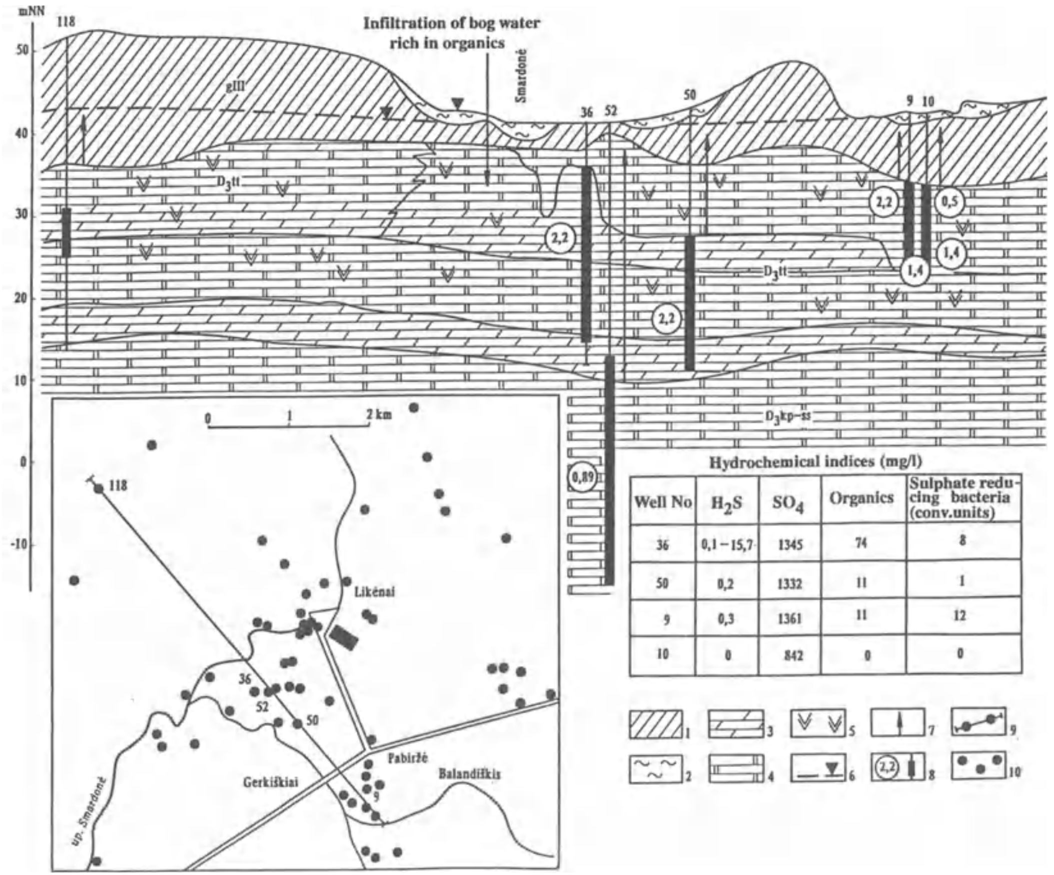
Figure 11.3 Dependence of bromide concentration in groundwater (Br) on total mineralization (M).

has a rich, long tradition. Historically, about 19 natural sources have been known in this area in the valley of the Nemunas River and at the mouth of the Ratnyčėlė Brook (Juodkazis, 1979; Juodkazis and Mikalauskas, 1994). Their mineralization varies considerably (Table 11.1).

The mineral water field of Druskininkai coincides with a tectonic fracture zone. A second fracture zone has been detected by geophysical methods, coinciding with an old valley, probably formed before the last glaciation. The second zone is believed to be hydrogeologically inactive. Therefore the

Table 11.4 Chemical composition of mineral water from the Likėnai spa sources/springs (according to A. Kondratas)

Source	*Water mineralization and ion composition, Kurlov formula*	*H_2S (mg/l)*	*pH*
1st Smardonė	$M_2 \frac{SO_4 85 HCO_3 14 Cl 1}{Ca 76 Na 15 Mg 9}$	1	7
2nd Smardonė	$M_{2.2} \frac{SO_4 83 HCO_3 16 Cl 1}{Ca 90 Mg 7 Na 3}$	1	7
3rd Smardonė	$M_{1.9} \frac{SO_4 86 HCO_3 14}{Ca 74 Na 17 Mg 9}$	–	7



Well No	H_2S	SO_4	Organics	Sulphate reducing bacteria (conv.units)
36	0,1–15,7	1345	74	8
50	0,2	1332	11	1
9	0,3	1361	11	12
10	0	842	0	0

Figure 11.4 Formation of sulphidic mineral water in the Likėnai field according to the data of G. Gurevičienė: (1) morainic loam, (2) peat, (3) marl, (4) dolomite, (5) gypsum, (6) unconfined groundwater level, (7) confined groundwater head, (8) tested aquifer interval (number shows mineralization in g/l), (9) hydrogeological cross-section, (10) prospecting and production wells.

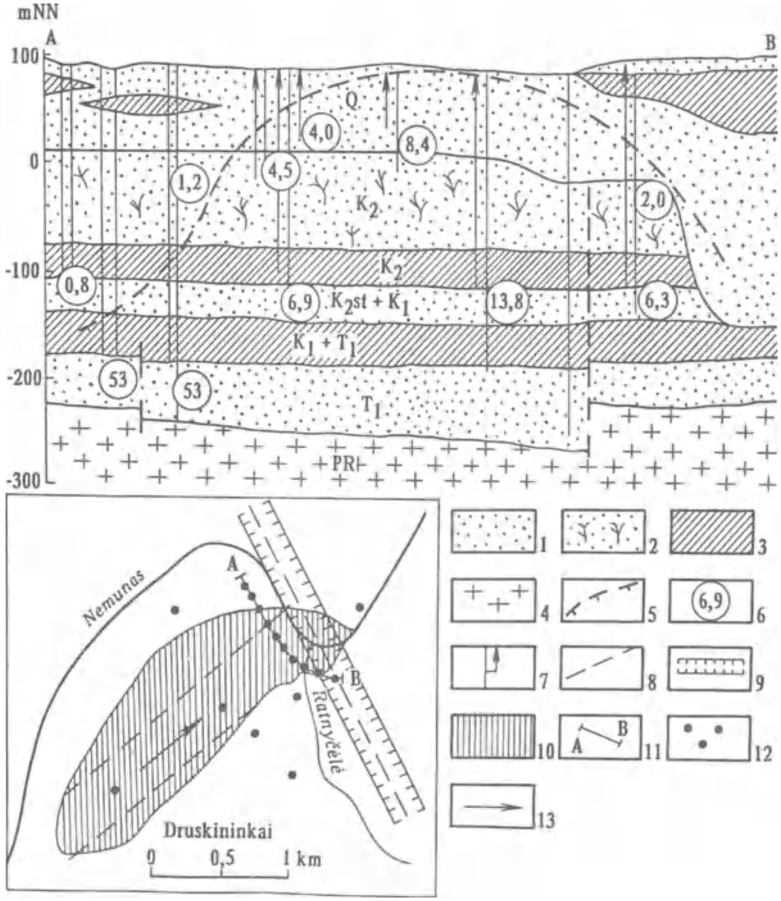


Figure 11.5 Druskininkai mineral water field (according to V. Juodkazis and Z. Šonta). (1) Fractured and (2) carbonate water-bearing rocks, (3) rocks of low permeability (aquitards), (4) crystalline basement rocks, (5) 1 g/l groundwater mineralization boundary, (6) groundwater mineralization (g/l) in different parts of the section, (7) borehole and piezometric level, (8) tectonic fractures, (9) erosional incision, (10) mineral water field, (11) geological section, (12) prospecting and production wells and (13) direction of groundwater flow.

elongated dome-shaped injectional field is surrounded on all sides by 'fresh' groundwater (Figure 11.5).

If boreholes are exploited incautiously, the chemistry of the mineral waters can be disturbed and the field damaged. In 1973 the Druskininkai field was explored in detail in order to devise a management plan for utilizing the resource. The available mineral water resources were found to satisfy the demands of the spa for the next two or three decades. Extraction of water of low mineralization can reach 110 m^3/d without significant damage to

Table 11.5 Mineral water resources; abstraction rates (m^3/d) and mineralization (g/l) in Druskininkai (D) and Birštonas (B)

	Non-component specific NaCl mineral water				*Bromide-rich NaCl mineral water*				*Total*	
Mineralization	2–5		5–15		15–35		>35		Total	
Location	D	B	D	B	D	B	D	B	D	B
Prospected resources (m^3/d)	112	45	2590	575	–	130	70	192	2772	943
Total extraction (m^3/d)	2	0.5	920	147.5	–	61	70	–	992	209
For sanatorium	–	–	915	110	–	61	70	–	985	171
For buvette	2	0.5	3	0.5	–	–	–	–	5	1
For bottling	–	–	2	37	–	–	–	–	2	37
Future demand	80	42	2500	358	–	240	450	–	3030	640

the field, whereas the demand is not projected to exceed 80 m^3/d. A similar situation exists with water of medium mineralization. Brines, however, are projected to become overexploited: the demand is forecast to reach 450 m^3/d, whereas an extraction rate of only 70 m^3/d is sustainable (Table 11.5). Therefore, in order to meet this need, brine resources should be prospected beyond the limits of the injectional field, farther from Druskininkai.

At present, about one-third of prospected resources are utilized, mainly for sanatorium baths. About 20 m^3/d are abstracted from 'Grožio šaltinis' (Beauty Spring), although only half of it is used, the rest being discharged to the Nemunas valley.

About 1–2 m^3/d of mineral water is abstracted for production of 'Druskininkai' bottled water (Figure 11.6). For this purpose, the water is transported from Druskininkai to Birštonas, where it is bottled and enriched with carbon dioxide.

Birštonas

According to its size and significance, Lithuania's second spa is Birštonas, established in 1846. For more than 100 years, up to 1950, only mineral water from natural springs was used. There were nine such springs on the right bank of the Nemunas River; a group of six springs named the Old Springs and Birutė Spring were situated on the second floodplain terrace. Vytautas Spring and Aldona Spring were on the floodplain itself (Figure 11.7). Vytautas Spring had the highest yield, some 150 m^3/d. The yields of the other springs ranged from 4 to 22 m^3/d. In 1960 a dam was constructed in connection with the Kaunas Hydroelectric Plant, and the Vytautas and Aldona Springs were flooded and other springs lost their significance. Therefore, they were 'liquidated' in 1961.

From 1959 the mineral water of Birštonas spa has been supplied from drilled wells. In 1978 hydrogeological prospecting works were completed in

LIETUVOS TSR MPM . ALAUS SUSIVIENIJIMAS „RAGUTIS" KAUNAS

Mineralinis vanduo

DRUSKININKAI

CHEMINĖ SUDĖTIS
(gramais litre):

ANIJONAI	
CHLORAS	2,7—3,2
SULFATAS	0,1—0,15
HIDROKARBONATAS	0,22—0,28
JODAS	0,003
BROMAS	0,003
KATIJONAI	
NATRIS IR KALIS	1,0—1,4
KALCIS	0,45—0,55
MAGNIS	0,15—0,18

Bendras ištirpusių druskų kiekis 4,8—5,8 g litre. Gali būti natūraliai iškritusių druskų nuosėdų. Vartojama esant skrandžio, žarnyno, kepenų ir tulžies lėtiniams susirgimams.
Butelius laikyti horizontalioje padėtyje vėsioje vietoje.

ХИМИЧЕСКИЙ СОСТАВ
(граммов в литре):

АНИОНЫ	
ХЛОР	2,7—3,2
СУЛЬФАТ	0,1—0,15
ГИДРОКАРБОНАТ	0,22—0,28
БРОМ	0,003
ЙОД	0,003
КАТИОНЫ	
НАТРИЙ И КАЛИЙ	1,0—1,4
КАЛЬЦИЙ	0,45—0,55
МАГНИЙ	0,15—0,18

Общая минерализация 4,8–5,8 г в литре.
Допускается осадок солей естественного выпадения.
Употребляется при хронических заболеваниях желудка, кишечника, печени и желчных путей.
Хранить в прохладном месте в горизонтальном положении.

Минеральная вода «Друскининкай»

ГОСТ 13273—73 СРОК ХРАНЕНИЯ 1 ГОД

МПП ЛИТОВСКОЙ ССР . ПИВОВАРЕННОЕ ОБЪЕДИНЕНИЕ «РАГУТИС», г. КАУНАС

LIET. TSR MPM KAUNO ALAUS KOMB. „RAGUTIS"

DRUSKININKAI

MINERALINIS VANDUO
CHEMINĖ SUDĖTIS
(gramais litre)

Anijonai	
Chloras	3,86
Sulfatas	0,75
Hidrokarbonatas	0,27
Katijonai	
Natris ir Kalis	1,91
Kalcis	0,58
Magnis	0,21

Bendras ištirpusių druskų kiekis 5,0 g. litre

VARTOJAMA

Esant skrandžio, žarnyno, kepenų ir tulžies lėtiniams susirgimams.
Gali būti natūraliai iškritusių druskų nuosėdų. Butelius laikyti paguldytus vėsioje vietoje.

МИНЕРАЛЬНАЯ ВОДА
ХИМИЧЕСКИЙ СОСТАВ:
(граммов в литре)

Анионы	
Хлор	3,86
Сульфат	0,75
Гидрокарбонат	0,27
Катионы	
Натрий и калий	1,91
Кальций	0,58
Магний	0,21

Общее количество растворенных солей 5,0 г в литре

УПОТРЕБЛЯЕТСЯ

при хронических заболеваниях желудка, кишечника, печени и желчных путей.
Допускается осадок солей естественного выпадения. Хранить в прохладном месте в горизонтальном положении.

ДРУСКИНИНКАЙ

МПП ЛИТ. ССР КАУНАССКИЙ ПИВ. К-Т „РАГУТИС"

Figure 11.6 Two mineral water labels from 'Druskininkai mineral water'. Analyses given read: (a) $Cl^- = 2.7–3.2\,g/l$, $SO_4^{2-} = 0.1–0.15\,g/l$, $HCO_3^- = 0.22–0.28\,g/l$, $I^- = 3\,mg/l$, $Br^- = 3\,mg/l$, $Na^+ + K^+ = 1.0–1.4\,g/l$, $Ca^{2+} = 0.45–0.55\,g/l$, $Mg^{2+} = 0.15–0.18\,g/l$, total mineralization = 4.8–5.8 g/l; (b) $Cl^- = 3.86\,g/l$, $SO_4^{2-} = 0.75\,g/l$, $HCO_3^- = 0.27\,g/l$, $Na^+ + K^+ = 1.91\,g/l$, $Ca^{2+} = 0.58\,g/l$, $Mg^{2+} = 0.21\,g/l$, total mineralization = 5.0 g/l.

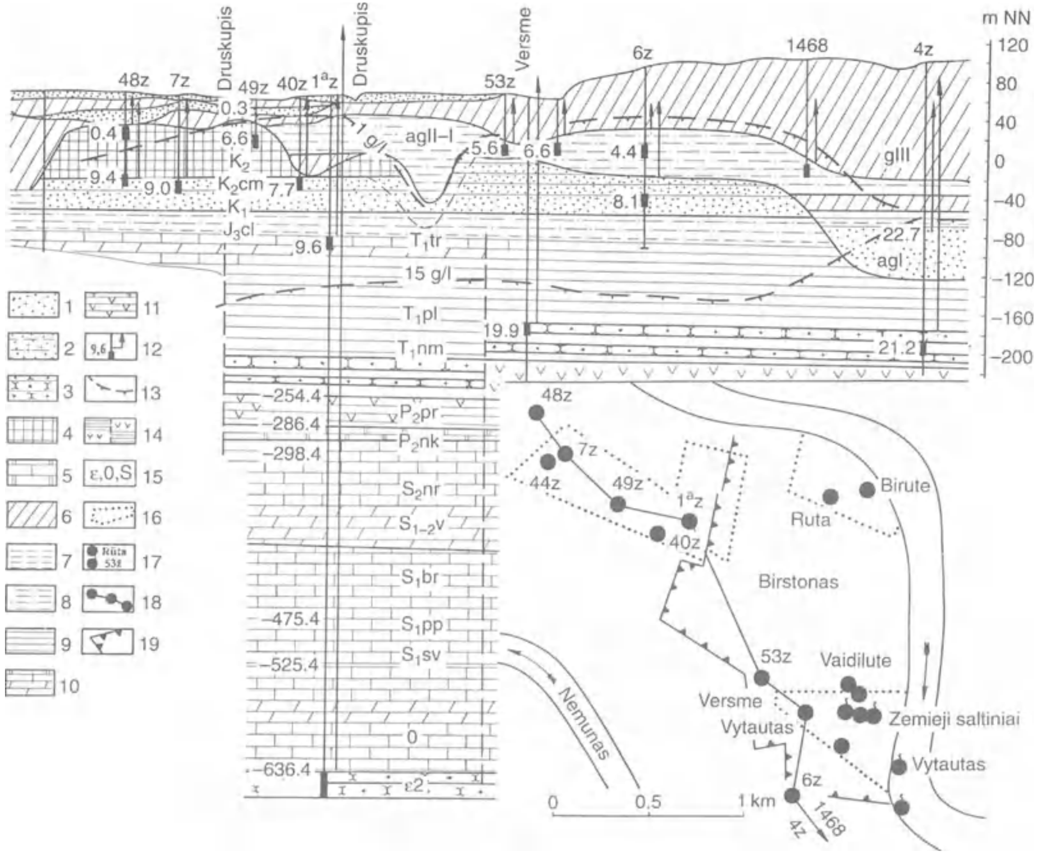


Figure 11.7 Birštonas mineral water field (according to the data of Z. Šonta). Water-bearing lithologies: (1) sand, (2) clayey sand, (3) sandstone, (4) chalk, (5) limestone and dolomite. Rocks of low permeability: (6) morainic loam, (7) silt/siltstone, (8) sandy clay, (9) clay, (10) clayey carbonate rocks, (11) gypsum. (12) Tested well and piezometric level (number shows water mineralization in g/l), (13) 1 g/l water mineralization boundary, (14) tectonic disturbances, (15) geological index, (16) areas of shallowest mineral water occurrence, (17) wells and springs, (18) hydrogeological section and (19) spa zone.

this area. The total mineral water resources were found to be almost 1000 m^3/d. At present, the daily use of mineral water at Birštonas spa is about 200 m^3/d. A part of this water is fed to the mineral water bottling shop producing 'Vytautas' and 'Birutė' drinking water (Figure 11.8). Vytautas water, of mineralization 5–7 g/l, is taken from the Vytautas Wells. Birutė water is produced from Vytautas water by a 1:1 dilution with fresh water (Banys *et al.*, 1978; Juodkazis and Mikalauskas, 1994).

Likėnai

The balneological spa of Likėnai was established in 1890. Until 1960 the waters of Smardonė Spring were used for curative purposes. These contained 3–6 mg/l of hydrogen sulphide. Later, a 32 m deep well was drilled, and its yield of calcium sulphate type water was as high as 2 l/s. About 20–35 m^3/d was used by the baths. The H_2S content of this water was initially 6.9–13.6 mg/l, but by 1976 this had reduced to 3.2 mg/l. In 1982 the well was abandoned due to the considerable decrease in H_2S content (caused by artificial drainage of the boggy recharge areas) and the worsening sanitary state of the aquifer. Since 1982, natural sulphide mineral waters have not been used at Likėnai spa.

At present, two boreholes supplying alternative water types are in use at Likėnai. One of them, named Likėnai Well, supplies 1 m^3/d of sulphate–chloride water of medium mineralization to the spa buvette and about 3–4 m^3/d for the bottling of 'Likėnai' mineral water in the Biržai bottling shop. The other borehole, Aukštaitija Well, supplies 8 m^3/d of brine to the sanatorium. Thus, the Likėnai spa now only uses about 12–13 m^3/d of mineral water. Its future demands are also estimated to be rather low, about 40–50 m^3/d, whereas the available mineral water resources are high (about 300 m^3/d; Juodkazis and Mikalauskas, 1994).

Some time ago, water from Likėnai Well was bottled and sold as 'Likėnai' mineral water. Now, water from the same aquifer is extracted via the well in Biržai. Water of Na–Cl type with a mineralization of 7 g/l is diluted by fresh water at a 1:1 ratio and sold as 'Biržai' mineral water (Figure 11.9).

Palanga

The seaside resort of Palanga is the youngest balneological spa in Lithuania. The first borehole, named Palanga Well, was drilled in 1959 at the end of Basanavičius Street, not far from the beach. Some time ago there was a buvette, where about 1 m^3/d of Na–Cl type water, with a high mineralization (18.5 g/l) and containing 48 mg/l bromide, was consumed. Moreover, 92 m^3/d of water was supplied to the Jūratė association sanatorium for curative purposes.

LIETUVOS TSR MPM · ALAUS SUSIVIENIJIMAS „RAGUTIS", KAUNAS

Mineralinis vanduo

VYTAUTAS

CHEMINĖ SUDĖTIS (gramais litre):

ANIJONAI

CHLORAS 3,5—4,2
SULFATAS 0,7—1,1
HIDROKARBONATAS 0,3—0,4
JODAS pėdsakai
BROMAS pėdsakai

KATIJONAI

NATRIS IR KALIS 2,1—3,0
KALCIS 0,5—0,6
MAGNIS 0,1—0,3
GELEŽIS pėdsakai

ХИМИЧЕСКИЙ СОСТАВ (граммов в литре):

АНИОНЫ

ХЛОР 3,5—4,2
СУЛЬФАТ 0,7—1,1
ГИДРОКАРБОНАТ 0,3—0,4
ЙОД следы
БРОМ следы

КАТИОНЫ

НАТРИЙ И КАЛИЙ 2,1—3,0
КАЛЬЦИЙ 0,5—0,6
МАГНИЙ 0,1—0,3
ЖЕЛЕЗО следы

РСТ Лит. ССР 162-74

срок хранения 1 год

Минеральная вода «Витаутас»

МПП ЛИТОВСКОЙ ССР . ПИВОВАРЕННОЕ ОБЪЕДИНЕНИЕ «РАГУТИС», г. КАУНАС

LIET. TSR MPM KAUNO ALAUS KOMB. „RAGUTIS"

Gali būti natūraliai iškritusių druskų nuosėdų. Butelius laikyti paguldytus vėsioje vietoje.

VARTOJAMA esant skrandžio, žarnyno, kepenų ir tulžies takų lėtiniams susirgimams, medžiagų apytakos sutrikimui. RTS 440—83

MINERALINIS VANDUO VYTAUTAS BIRŠTONO ŠALTINIO

CHEMINĖ SUDĖTIS:

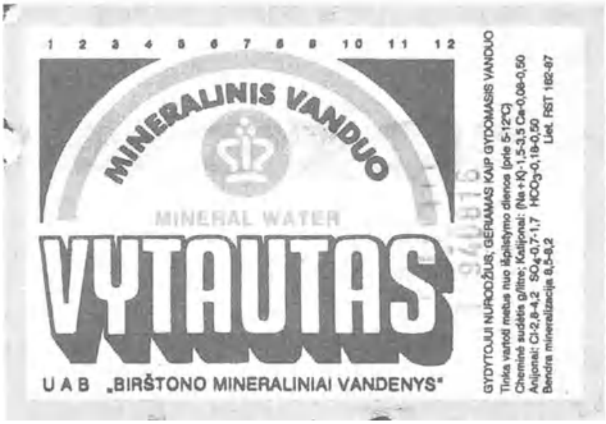
ХИМИЧЕСКИЙ СОСТАВ

МИНЕРАЛЬНАЯ ВОДА ВИТАУТАС БИРШТОНСКОГО ИСТОЧНИКА

Допускается осадок солей естественного выпадения. Хранить в прохладном месте в горизонтальном положении.

УПОТРЕБЛЯЕТСЯ при хронических заболеваниях желудка, кишечника, печени и желчных путей, при нарушении обмена веществ. РТУ 440—83

МПП ЛИТ. ССР КАУНАССКИЙ ПИВ. К-Т „РАГУТИС"



MINERALINIS VANDUO

MINERAL WATER

VYTAUTAS

UAB „BIRŠTONO MINERALINIAI VANDENYS"

GYDYTOJUI NURODŽIUS, GERIAMAS KAIP GYDOMASIS VANDUO

Tinka vartoti metus nuo išpilstymo dienos (prie 5-12°C)

Cheminė sudėtis g/litre; Katijonai: (Na+K)-1,5-3,5 Ca-0,08-0,50

Anijonai: Cl-2,8-4,2 SO_4-0,7-1,7 HCO_3-0,18-0,50

Bendra mineralizacija 6,5-8,2

Liet. RST 182-87

LIETUVOS TSR MPM

1 KAUNO ALAUS KOMB.•RAGUTIS•

CHEMINĖ SUDĖTIS:
(gramais litre)

2 ANIJONAI

Chloras	1,12
Sulfatas	0,29
Hidrokarbonatas	0,23

3 KATIJONAI

Natris ir kalis	0,47
Kalcis	0,14
Magnis	0,17

4 Bendras ištirpusių druskų kiekis 2,4 g litre.

Gali būti natūraliai iškritusių druskų nuosėdų. Butelius laikyti paguldytus vėsioje vietoje.

5 VARTOJAMAS kaip stalo ir gaivinantis vanduo.

RTS 440–63

6 MINERALINIS VANDUO

BIRUTĖ

МПП ЛИТОВСКОЙ ССР

КАУНАССКИЙ ПИВ. К-Т •РАГУТИС• 7

ХИМИЧЕСКИЙ СОСТАВ:
(граммов в литре)

АНИОНЫ 8

Хлор	1,12
Сульфат	0,29
Гидрокарбонат	0,23

КАТИОНЫ 9

Натрий и калий	0,47
Кальций	0,14
Магний	0.17

Общее количество растворенных солей 2,4 г в литре. 10

Допускается осадок солей естественного выпадения. Хранить в прохладном месте в горизонтальном положении.

УПОТРЕБЛЯЕТСЯ как столовая освежающая вода 11

РТУ 440–63

МИНЕРАЛЬНАЯ ВОДА 12

БИРУТЕ

UAB "BIRŠTONO MINERALINIAI VANDENYS"

19 24

BIRUTĖ

mineralinis vanduo • mineral water

Talpa 0,5dm^3
Bendra mineralizacija 2,8-5,7 g/dm^3
Tinka vartoti metus
nuo išpylimo dienos(prie 5-20^{0}C)
Gydytojui nurodžius,
geriamas kaip gydomasis vanduo.
Liet.RST 162-92

Anijonai:

Cl	mg/dm^3	1200-3400
SO$_4$	mg/dm^3	200-1100
HCO$_3$	mg/dm^3	100-500

Katijonai:

Na+K$^+$	mg/dm^3	200-1700
Ca$^+$	mg/dm^3	200-600
Mg$^+$	mg/dm^3	50-300

Figure 11.8 Mineral water labels from 'Vytautas' and 'Birutė' mineral waters. Analyses given read as follows.

Parameter (g/l)	*Vytautas (top)*	*Vytautas (middle)*	*Vytautas (bottom)*	*Birutė (top)*	*Birutė (bottom)*
Cl^-	3.5–4.2	3.9–4.3	2.8–4.2	1.12	1.2–3.4
SO_4^{2-}	0.7–1.1	0.7–1.1	0.7–1.7	0.29	0.2–1.1
HCO_3^-	0.3–0.4	0.31–0.34	0.18–0.5	0.23	0.1–0.5
I^- (mg/l)		6.2			
Br^- (mg/l)		6.9			
$Na^+ + K^+$	2.1–3.0	1.5–2.5	1.5–3.5	0.47	0.2–1.7
Ca^{2+}	0.5–0.6	0.63–0.69	0.08–0.5	0.14	0.2–0.6
Mg^{2+}	0.1–0.3	0.2–0.4		0.17	0.05–0.3
Li^+ (mg/l)		0.2			
Total mineralization	7.2–9.6	8.7	8.2–8.5	2.4	2.8–5.7

(a)

LIKĖNAI

MINERALINIS GERIAMAS GYDOMASIS STALO VANDUO
МИНЕРАЛЬНАЯ . ПИТЬЕВАЯ . ЛЕЧЕБНО-СТОЛОВАЯ ВОДА „ЛИКЕНАЙ"

CHEMINĖ SUDĖTIS G/LITRE:
Anijonai
Chloras — 2,4 — 2,7
Sulfatai — 1,8–2,0
Hidrokarbonatai —0,18–0,21
Katijonai
Natris ir kalis 1,2—1,4
Kalcis — 0,6 —0,7
Magnis —0,2—0, 3
Bendra mineraliz.–6,0–7,5
Vartojamas gydant lėtines skrandžio, kepenų, tulžies pūslės bei latakų ir žarnyno ligas.
Tinka vartoti metus nuo išpilstymo dienos, laikant butelius horizontalioje padėtyje, prie 5—12 °C
FCT Лит. CCP 162-78

ХИМИЧЕСКИЙ СОСТАВ В Г/Л:
Анионы
Хлор 2,4–2,7
Сульфат 1,8–2,0
Гидрокарбонат 0,18—0,21
Катионы
Натрий и калий 1,2–1,4
Кальций 0,6 —0,7
Магний 0,2—0, 3
Общая минерал. 6,0—7,5
Употребляется при лечении хронических болезней желудка, печени, желчеводящих путей и кишечника.
Срок хранения при температуре 5—12 °C в горизонтальном положении — один год со дня разлива

„LIKĖNŲ" ŠALTINIS
ИСТОЧНИК „ЛИКЕНАЙ"

Lietuvos TSR MPM Panevėžio alaus pramonės g/s „Kalnapilis".
МПП Литовской ССР Паневежское п/о пивпрома «Калнапилис»

1 2 3 4 5 6 7 8 9 10 11 12

(b)

BIRŽAI

MINERALINIS GERIAMAS GYDOMASIS VANDUO
МИНЕРАЛЬНАЯ ПИТЬЕВАЯ ЛЕЧЕБНАЯ ВОДА «БИРЖАЙ» ИСТОЧНИК БИРЖАЙ

CHEMINĖ SUDĖTIS G/DM³
ANIJONAI АНИОНЫ
CHLORAS — 1,1—1,45
ХЛОР
SULFATAS — 0,95—1,25
СУЛЬФАТ
HIDROKARBONATAS – 0,25—0,35
ГИДРОКАРБОНАТ

Vartojamas virškinimo ligoms gydyti, nesistemingai geriant — kaip gaivinantis gėrimas. Tinka vartoti 6 mėn. nuo išpilstymo dienos, laikant butelius prie 5-10°C

ТУ 18 ЛИТ. ССР 13-82

Kaina 10 kap. (be butelio)
Цена 10 коп. (без стоим. посуды)

ХИМИЧЕСКИЙ СОСТАВ В Г/DM³

KATIJONAI КАТИОНЫ
NATRIS IR KALIS — 0,6-0, 95
НАТРИЙ И КАЛИЙ
KALCIS — 0,35-0,6
КАЛЬЦИЙ

MAGNIS — 0,07-0,15
МАГНИЙ
Bendra mineraliz. — 3,3-5,0
Общая минерал.

Применяется при заболеваниях органов пищеварения, а при несистемическом употреблении в качестве столовой воды. Срок хранения при температуре 5-20° C — — 6 мес. со дня разлива.

BIRŽŲ ŠALTINIS

LTSR valst. agropramoninis k-tas Panevėžio alaus pramonės g/s „Kalnapilis"
Госагропром Литовской ССР Паневежское п/о пивовар. пром. «Калнапилис»

1 2 3 4 5 6 7 8 9 10 11 12

Figure 11.9 Mineral water labels from (a) 'Likėnai' and (b) 'Biržai' mineral waters. Analyses given read: (Likėnai) $Cl^- = 2.4–2.7\,g/l$, $SO_4^{2-} = 1.8–2.0\,g/l$, $HCO_3^- = 0.18–0.21\,g/l$, $Na^+ + K^+ = 1.2–1.4\,g/l$, $Ca^{2+} = 0.6–0.7\,g/l$, $Mg^{2+} = 0.2–0.3\,g/l$, total mineralization = 6.0–7.5 g/l; (Biržai) $Cl^- = 1.1–1.45\,g/l$, $SO_4^{2-} = 0.95–1.25\,g/l$, $HCO_3^- = 0.25–0.35\,g/l$, $Na^+ + K^+ = 0.6–0.95\,g/l$, $Ca^{2+} = 0.35–0.6\,g/l$, $Mg^{2+} = 0.07–0.15\,g/l$, total mineralization = 3.3–5.0 g/l.

The Jūratė Well was drilled in 1974, not far from the Palanga Well. It supplies calcium sulphate water of low mineralization. This water is being used in the buvette mentioned above (3 m^3/d). In 1974 detailed hydrogeological studies of Palanga's mineral water resources were carried out. New wells have been drilled and equipped in the northern part of Palanga, where sulphatic mineral waters, of similar composition to Jūratė, have been named 'Kastytis' waters. The daily yield of this water is about 12 m^3. In addition, the boreholes named Eglė and Naglis wells have a yield of 545 m^3/d. Also, extraction of Na–Cl water with high mineralization (33–35 g/l) is planned from a depth of 700 m using the Žilvinas borehole, with a daily yield of 518 m^3 (Juodkazis, 1979; Juodkazis and Mikalauskas, 1994). Thus the prospected water reserves of 1075 m^3/d at Palanga can satisfy projected demand for the next 25 years.

11.2.4 Bottled mineral water

In Lithuania bottling of mineral water has never been a central interest, either for manufacturers and salesmen or for hydrogeologists. Nevertheless mineral water has been continuously produced and purchased for refreshment and perceived prophylactic or curative purposes. During Soviet times, not only Lithuanian mineral water was on sale. Consumers could also buy 'Borzomi' from Georgia, 'Arzni' from Armenia, 'Yessentuki' and 'Narzan' from Russia (Chapter 12), 'Varska' from Estonia and several others.

Following the restoration of Lithuanian independence, exotic mineral waters flooded in from the West. The sales of such waters are modest, because of their high price and perhaps also because their properties are unknown to Lithuanians. Lithuanian water, which is much cheaper, can still be found and to attract the buyer, the bottle labels and even the shape of bottles have been redesigned. At present, ten varieties of mineral water are bottled in Lithuania, as shown in Table 11.6. Labels from two more of these, 'Vilnius' and 'Anykščiai', are shown in Figures 11.10 and 11.11 respectively.

Lithuanian mineral water is noted for its curative properties. This is confirmed by the durability and popularity of the Lithuanian spa resorts and their associated balneological practices. During production, bottled mineral water is subject to strict standards of hygiene. The waters themselves are of high quality and excellent taste and it is expected that Lithuanian mineral water will one day be drunk and appreciated in other countries.

11.2.5 Geochemical origin of Lithuanian mineral waters

The origin of Lithuanian mineral waters remains a partially unsolved problem. Why should such a variety of mineral water springs occur in an

Table 11.6 Bottled mineral water in Lithuania

Mineral water name	*Site*	*Aquifer index* / *Depth (m)*	*Kurlov formula (mineralization M in g/l, ions in %-equiv)*	*Abstraction (m^3/year)*	*Comments*
Vokė	Vilnius, A. Paneriai	$\frac{\epsilon}{354-362}$	$M_{2.0}\frac{Cl46SO_4 41HCO_3 12}{(Na+K)62Ca22Mg15}$	4000	Natural
Vilnius	Vilnius, A. Paneriai	$\frac{\mathrm{PR}_3}{424-450}$	$M_{5.3}\frac{Cl74SO_4 20HCO_3 6}{(Na+K)79Ca14Mg6}$	–	Temporarily not used
Vytautas	Birštonas	$\frac{\mathrm{Q}_{1-2}}{48-58}$	$M_{7.0}\frac{Cl81SO_4 15HCO_3 4}{(Na+K)63Ca22Mg15}$	4000	Natural
Birutė	Birštonas	$\frac{\mathrm{Q}_{1-2}}{48-58}$	$M_{3.5}\frac{Cl76SO_4 16HCO_3 8}{(Na+K)59Ca25Mg16}$		Vytautas diluted with fresh water
Likėnai	Biržai	$\frac{\mathrm{D}_1+\mathrm{D}_2}{370-430}$	$M_{7.4}\frac{Cl59SO_4 39HCO_3 2}{(Na+K)58Ca31Mg11}$	2000	Natural
Biržai	Biržai	$\frac{\mathrm{D}_1+\mathrm{D}_2}{370-430}$	$M_{4.4}\frac{Cl60SO_4 35HCO_3 5}{(Na+K)57Ca31Mg12}$		Likėnai diluted with fresh water
Druskininkai	Druskininkai	$\frac{\mathrm{K}_2}{78-114}$	$M_{7.5}\frac{Cl94SO_4 3HCO_3 3}{(Na+K)56Ca29Mg15}$	–	Temporarily not used
Sūduva	Antanava	$\frac{\mathrm{K}_2}{59-80}$	$M_{2.4}\frac{Cl81SO_4 7HCO_3 12}{(Na+K)56Mg22Ca22}$	2000	Natural
Versmė	Šiauliai	$\frac{\mathrm{D}_2+\mathrm{D}_3}{708-740}$	$M_{7.0}\frac{Cl58SO_4 41HCO_3 1}{(Na+K)51Ca38Mg11}$	2000	Natural
Anykščiai	Anykščiai	$\frac{\mathrm{D}_1+\mathrm{D}_2}{269-336}$	$M_{4.0-6.5}\frac{Cl66SO_4 26HCO_3 8}{(Na+K)44Mg35Ca21}$	500	Diluted with fresh water

Vilniaus valst. alaus ir nealk. gėrimų įmonė „Tauras"
CHEMINĖ SUDĖTIS mg /dc^3:
ANIJONAI: HCO_3^- 250–450
SO_4^{2-} 700–1000 CL^- 1900–2350
KATIJONAI: CA^{2+}–180–250 MG^{2+}–40–60
$(NA^+ + K^+)$ –1300–1600 Bendra
mineralizacija–4,5–5,5 g/dc^3

AUKŠTIEJI PANERIAI, GRĘŽINYS Nr2Z
Pagal gydytojų rekomendacijas vartojamas gydant lėtinius skrandžio, tulžies pūslės ir latakų bei žarnyno susirgimus. Nepastoviai vartojant – kaip stalo vanduo.
Tinka vartoti metus nuo išpilstymo dienos laikant butelius prie +5°C +20°C
Lietuvos Respublika
TS 252-04-11-90
0,33L

Vilnius
MINERALINIS GERIAMAS
GYDOMASIS–STALO VANDUO
Kaina
be butelio vertės 8 kap.

1 2 3 4 5 6 7 8 9 10 11 12

Figure 11.10 Mineral water label from 'Vilnius' mineral water. Analysis given reads: $Cl^- = 1.9–2.35$ g/l, $SO_4^{2-} = 0.7–1.0$ g/l, $HCO_3^- = 0.25–0.45$ g/l, $Na^+ + K^+ = 1.3–1.6$ g/l, $Ca^{2+} = 0.18–0.25$ g/l, $Mg^{2+} = 0.04–0.06$ g/l, total mineralization = 4.5–5.5 g/l.

area that is relatively tectonically stable? We have seen that mineral waters can be divided into two types, 'aquifer' waters and 'injectional' waters.

Aquifer waters appear to be waters that have formed by normal processes of hydrochemical evolution, carried to highly mineralized endpoints by slow

VALSTYBINĖ ĮMONĖ
Anykščių Vynas

Mineralizacija 4–6,5g/dm^3
Laikymo temperatūra 5-20°C
Garantinis laikas - 6men.
RST 162-92
Katijonai
$(Na+Ka)^+$ 1,1 - 1,6
Ca^{2+} 0,2 - 0,4
Mg^{2+} 0,6 - 1,1
Anijonai
Cl^- 1,8 - 2,5
SO_4^{2-} 0,6 - 1,0
HCO_3^- 0,22 - 0,44
0,5dm^3

ANYKŠČIAI
Gydomasis geriamas mineralinis vanduo

I II III IV V VI VII VIII IX X XI XII 93 94 95 96

Figure 11.11 Mineral water label from 'Anykščiai' mineral water. Analysis reads: $Cl^- = 1.8–2.5$ g/l, $SO_4^{2-} = 0.6–1.0$ g/l, $HCO_3^- = 0.22–0.44$ g/l, $Na^+ + K^+ = 1.1–1.6$ g/l, $Ca^{2+} = 0.2–0.4$ g/l, $Mg^{2+} = 0.6–1.1$ g/l, total mineralization = 4.0–6.5 g/l.

throughflow, long residence time and, in some deep aquifers in the western Lithuanian geothermal basin, by elevated temperatures. The long residence times are partially a result of Lithuania's low topography. In addition to hydrogeochemical evolution, connate waters (i.e. fossil seawaters and formation waters) may play a role. In the karst area of Lithuania, the presence of soluble evaporite minerals leads to high mineralization even in waters of relatively rapid throughflow.

Injectional waters are deep, hydrochemically evolved waters (possibly with a component of connate/formation waters) and rise along tectonic fractures to higher and more accessible aquifer levels. In some cases, the ultimate source of mineralization may be near to, or within, the Precambrian crystalline basement (Paukštys, 1993).

The basement consists dominantly of Archaean and Lower–Middle Proterozoic gneisses, intruded by granite and granitoid bodies. The top surface of the basement is altered to a kaolinite–chlorite crust up to 10 m thick, although at the Birštonas Health Resort up to 40 m is found (Paukštys, 1993). The recharge area for the crystalline basement rocks and, to some extent, the overlying sedimentary aquifers, is the Belorussian Anticlinorium. There are few aquitardes overlying the basement in this area (Klimas, 1993). In the centre of the anticlinorium, groundwaters in the basement are thus relatively fresh, of Na– or Ca–HCO_3 type, with total dissolved solids (TDS) rarely exceeding 0.5 g/l. Farther northwest, away from the recharge area, the salinity of the crystalline basement groundwaters increases, becoming more dominated by sodium and chloride. The deep Vilnius well (to over 500 m) yielded water with the composition shown in Table 11.7. The trend increases towards the deepest part of the Baltic Synclinorium in western Lithuania, where Paukštys (1993) cites the groundwater composition shown in Table 11.8 as typical.

Some anomalous zones of saline water also occur nearer the centre of the Belorussian Anticlinorium and Klimas (1993) has suggested that this might be due to local salinity-driven head differences inducing saline water to flow southeast, against the prevailing expected regional trend. He has suggested that the Druskininkai spa may be a manifestation of such a southeasterly saline reverse flow zone.

Table 11.7 Chemical composition of groundwater from a well in the crystalline basement at Vilnius (after Paukštys 1993)

Cations	*Anions*	*Minor elements*
$Na^+ + K^+ = 5.44$ g/l	$Cl^- = 10.7$ g/l	$Br^- = 5$ mg/l
$Ca^{2+} = 1.3$ g/l	$SO_4^{2-} = 2.7$ g/l	Mn = 8.4 mg/l
$Mg^{2+} = 0.73$ g/l	$HCO_3^- = 0.2$ g/l	Fe = 6 mg/l
	Total mineralization = 21 g/l	

Table 11.8 Chemical composition of crystalline basement groundwater in western Lithuania (after Paukštys 1993)

Cations	*Anions*	*Minor elements*	
Na^+ = 30–40 g/l	Cl^- = 100–200 g/l	Sr^{2+} = 300–400 mg/l	Br^- = 700–1200 mg/l
K^+ = 0.7–0.9 g/l	SO_4^{2-} = 0.03–0.4 g/l	Li^+ = 9–10 mg/l	I^- = 2–4 mg/l
Ca^{2+} = 20–30 g/l	HCO_3^- = 10–30 g/l	Rb^+ = 2.4–2.8 mg/l	NH_4^+ = 20–100 mg/l
Mg^{2+} = 3–4 g/l	–	Zn^{2+} = 3–32 mg/l	Fe = 100–500 mg/l
Total mineralization = 140–200 g/l			

11.3 GEOTHERMAL ENERGY

11.3.1 Introduction

In contrast to the mineral waters, the most promising geothermal reserves are found in the thickest part of the sedimentary sequence, near the Baltic Sea coast in West Lithuania (Astafyev and Muromceva, 1973; Juodkazis, 1979). The West Lithuanian geothermal anomaly (WLGA) encompasses several significant towns including the port city of Klaipėda, the holiday resort of Palanga, Kretinga, Plungė, Gargždai, Nida, Šilutė and Šilalė. The geothermal resources are characterized by three parameters.

- The geothermal gradient, or the increment of rock temperature per 100 m; this may exceed 4°C per 100 m.
- Heat flow; this may reach 108 mW/m^2.
- Resources; this is the amount of available energy in kcal/m^2. In Lithuania it has been common to express this in tonnes CF units per square metre. CF is a 'conventional fuel unit' which, when burnt, releases some 7000 kcal/kg.

Geothermal water can be extracted from three aquifer complexes:

- the Upper and Middle Devonian complex;
- the Middle and Lower Devonian complex;
- the Cambrian.

These are separated by low permeability aquitards and are regarded as hydraulically independent aquifer units.

In addition, the underlying low permeability basement has potential for hot dry rock energy extraction.

The recommended practice for exploitation is a closed geothermal circulation system (GCS) involving reinjection of used thermal water into the rock. Aquifer properties may be suitable for exploitation of geothermal waters in their natural state, but sometimes stimulation, e.g. by hydraulic fracturing (Dyadkin, 1992), is necessary to allow the recommended target abstraction of 30–50 l/s to be achieved.

11.3.2 History of geothermal exploration

The first indications of elevated temperatures at depth in the sedimentary pile came in 1948 and 1953, when boreholes were drilled at Vilnius and Stoniškiai respectively (Kondratas, 1969). Later, oil prospecting boreholes and laboratory studies of heat flow in core samples allowed the WLGA of the Baltic Basin to be identified. The zone of seasonal temperature variation was shown to be around 20 m, below which a stable geothermal gradient prevailed, varying geographically from 1 to 5°C per 100 m (Figure 11.12).

The potential exploitation of the Baltic geothermal anomaly (including Lithuania and parts of Kaliningrad and Latvia) was assessed by Latvian scientists, including Drs Freimanis, Grikevič and Skrupškele. The first applied studies of the WLGA commenced in 1986. In 1988 Prof. J. Dyadkin of the St Petersburg Mining Institute demonstrated that the available resources were sufficient to supply some seven towns and cities in West Lithuania. By 1990, detailed projections had been made for the town of

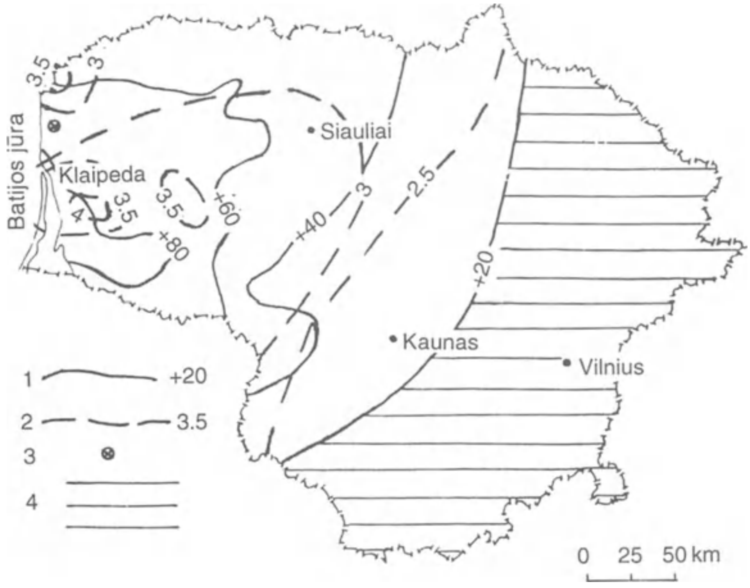


Figure 11.12 Distribution of geothermal gradient in sedimentary cover in the Baltic Synclinorium and roof temperature of the deepest Cambrian hydrogeothermal complex. (1) Isotherms of Cambrian complex roof temperature in degrees Celsius, (2) isolines of geothermal gradient in °C/100 m, (3) the Vydmantai site and (4) areas where groundwater temperature in the Cambrian hydrogeothermal complex is less than 20°C. (After Suveizdis and Rastenienė, 1993. Copyright Geological Society of Lithuania, reproduced with permission.)

Palanga, using hot dry rock energy. In 1991 the GEOTERMA enterprise was established for implementation of the geothermal programme and, at present, detailed planning of seven potential geothermal plants has been carried out by the Institute of Geology in Lithuania.

11.3.3 Resource evaluation

The St Petersburg Mining Institute considered three methods for assessing the quantity of geothermal resources (Vainblat and Shuvalov, 1982; Boguslavskij, 1984; Dyadkin, 1985), illustrated in Figure 11.13.

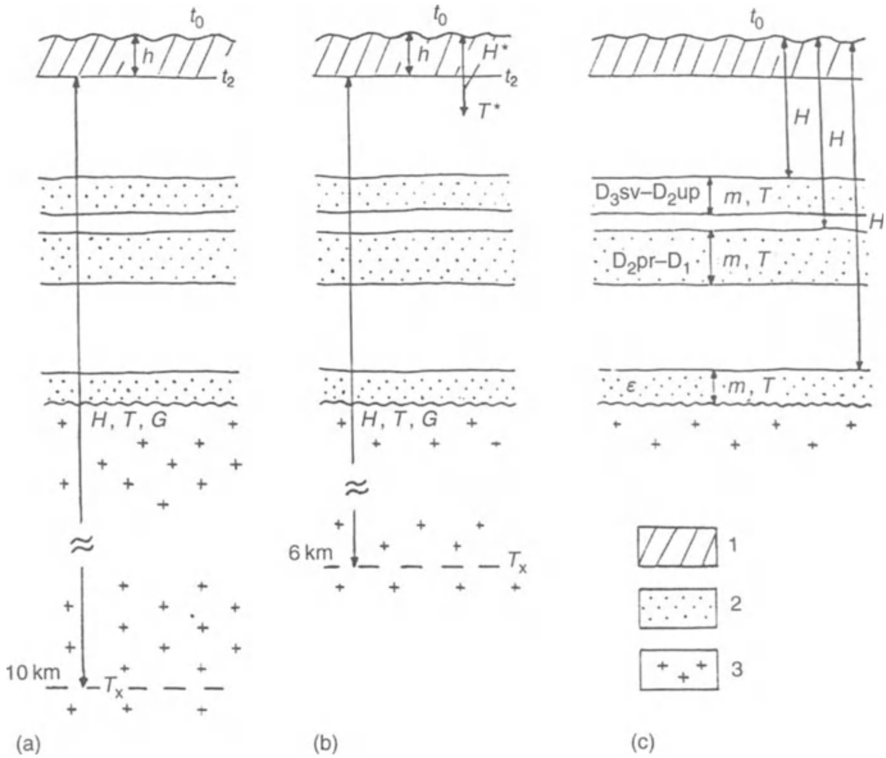


Figure 11.13 Schematic diagram to illustrate modes of calculation of geothermal resources of (a) P_2 category, (b) P_1 category and (c) C_3 category. (1) Zone of seasonally fluctuating temperature, (2) hydrogeothermal complexes, (3) petrogeothermal massif, i.e. crystalline basement. Symbols are as given in the text: additionally, t_z = temperature at upper limit of zone of stable temperature, T_x = temperature at prognostic depth, G = geothermal gradient. (After Suveizdis and Rastenienė, 1993. Copyright Geological Society of Lithuania, reproduced with permission.)

Prognostic (P_2) category

The P_2 category of resources is calculated for a depth of 10 km. They are the theoretical energy resources from the block of rock down to that depth. They reflect both the regional long term resources of an area and regional geothermal anomalies. The controlling factor for the resource is the differential between the resource temperature and the temperature of the return heat carrier (ideally water at the prevailing surface temperature).

$$q_{P_2} = KC_v(H - h)(T - t_0)$$

where q_{P_2} = the density of the geothermal energy for the P_2 category [tCF/m^2]; K = the conversion coefficient for thermal energy into conventional fuel units = 0.042×10^{-9} tCF/J; C_v = the volumetric heat capacity of the rocks [J/(m^3 °C)]; H = the prognostic depth [m] = 10 000 m for P_2; h = depth from the land surface to the zone of stable temperature [m]; T = the mean temperature in the zone of utilization [°C] and t_0 = the mean annual temperature of the environment and heat carrier (i.e. temperature of returned groundwater) [°C].

Prognostic (P_1) resources

P_1 resources represent a more realistic estimate of resources potentially available in the top 6 km of strata (i.e. the depth realistically achievable with boreholes). They incorporate heat obtained by the consumer and returned to the aquifer and also a coefficient of heat extraction:

$$q_{P_1} = K\xi_t C_v(H - H^*)(T - t_0)$$

$$H^* = \frac{T^* - t_z}{G} + h$$

$$\xi_t = \frac{T - 1/2(t_g + t_0)}{T - t_0}$$

where q_{P_1} = the density of the geothermal energy for P_1 category [tCF/m^2]; ξ_t = the temperature coefficient (<1) to correct for heat extraction in the exchanger; H^* = the upper limit of utilization of geothermal energy [m], controlled by T^*, the (lower) temperature limit for utilizable groundwater; G = the geothermal gradient; t_g = the temperature of the heat carrier (groundwater) as it enters the heat exchangers [°C] and t_z = the temperature at the top of the zone of stable temperature (corresponding to depth h) [°C].

For sedimentary sequences of a finite thickness m, less than 6 km deep, containing hydrothermal groundwater, calculation of P_1 is based only on the exploitable thickness of the hydrothermal complex:

$$q_{P_1} = K\xi_k\xi_t C_v m(T - t_0)$$

where ξ_k = the coefficient of conductive heat transport from the rocks to the hydrogeothermal complex (i.e. it represents the rate of replenishment of hydrogeothermal water from the regional geothermal gradient).

Prospective (C_3) resources

These are the resources which it is hydrogeologically possible to develop, taking account of a hydraulic flow coefficient ξ_f to estimate the proportion of flux extractable by a given well configuration:

$$q_{C_3} = q_{P_1} \cdot \xi_f$$

where

$$\xi_f = 0.5 + 0.1 \frac{L_0}{L'}$$

L_0 = the distance between geothermal wells of the same purpose (either abstraction or reinjection wells) [m] and L' = the distance between abstraction wells and injection wells [m].

11.3.4 Geothermal aquifer complexes

The three aquifer complexes (Upper–Middle Devonian, Middle–Lower Devonian and Cambrian) are regarded as hydraulically and geothermally separate units, possibly with limited connections via deep fracture zones (Figures 11.14–11.16).

Upper–Middle Devonian complex

This complex consists of two hydraulically continuous stratigraphic units, the Šventoji and Upninkai formations, consisting of sands, weakly cemented sandstones, silts, clays and occasionally dolomitic marl. Sandy horizons, 1–25 m thick, typically alternate with clayey horizons of a similar thickness. In the western part of Lithuania, the Šventoji Formation is more clayey and less hydraulically conductive than the Upninkai. Both formations become more clayey westwards, towards the deepest and more distal parts of the original sedimentary basin (Narbutas, 1981). The total thickness of the complex varies from 131 m in the Stoniškiai-1 borehole to 222 m in Purmaliai-1. In east Lithuania the unit subcrops immediately beneath Quaternary deposits, but it dips to the southwest attaining depths of more than −600 m OD. In the south of the country it wedges out.

The aquifer horizons typically comprise 25–60% of the entire Šventoji–Upninkai complex. Porosities range from 16 to 25%, although samples from the Reneva-25, Gargždai-40 and Plungė-41 boreholes exhibit favourable characteristics: porosities of 17–30% and permeabilities of 435–2895 mD (4×10^{-6} to 2×10^{-5} m/s).

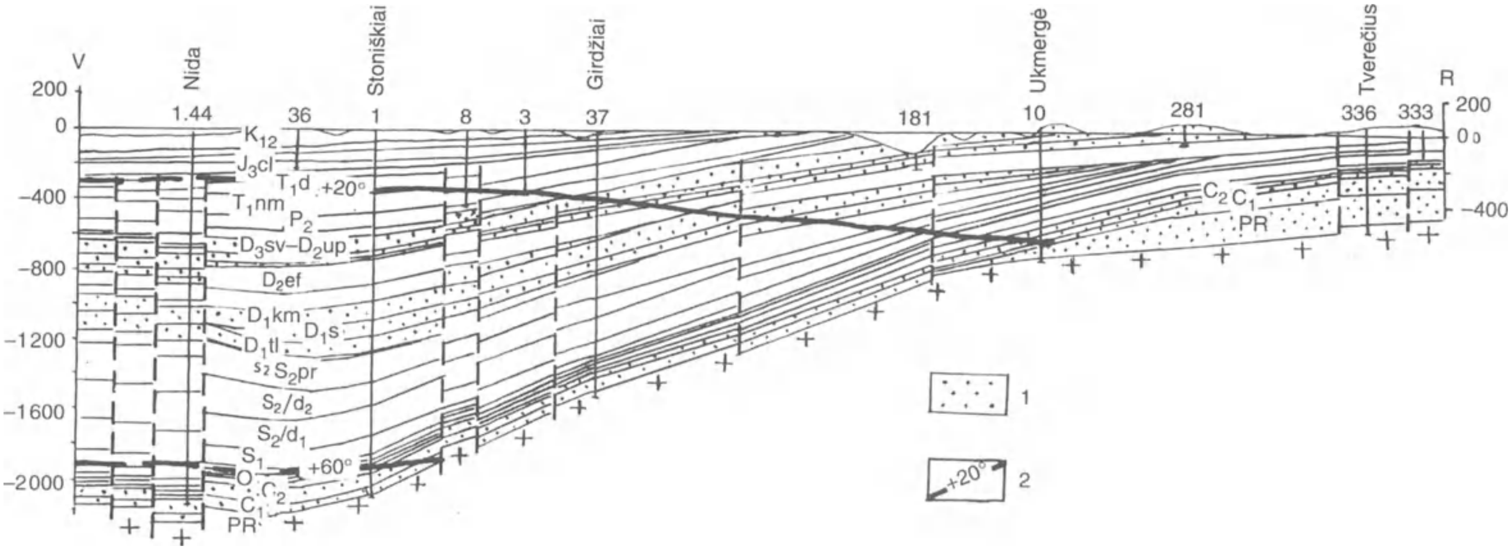


Figure 11.14 Geological cross-section from Nida to Tverečius. (1) Hydrogeothermal complexes and (2) geoisotherm. For line of section, see Figure 11.15. (After Suveizdis and Rastenienė, 1993. Copyright Geological Society of Lithuania, reproduced with permission.)

Figure 11.15 Location map for named boreholes, also showing the line of geological section in Figure 11.14. (Modified after Suveizdis and Rastenienė, 1993.)

The Šventoji–Upninkai complex is confined by the overlying dolomitic marls and clays of the Pliavina Formation and underlain by the marls and clays of the Narva Formation.

The part of the Šventoji–Upninkai hydrogeothermal complex exceeding 20°C is located in the southwest of Lithuania. The highest temperatures recorded are in the Gorainiai borehole, ranging from 35.5°C at the top of the unit to 37°C at the base. The piezometric level in much of this region is artesian, reaching 0.6–8.1 m above ground level in the vicinity of Palanga. When the Stoniškiai borehole was drilled to the complex at a depth of 645–680 m, an artesian fountain of water reached a height of 14 m at a rate of 864 m^3/d.

The water from the complex is typically gaseous and of the calcium chloride type. Total dissolved solids range from 5–15 g/l in the upper part of the complex to 15–35 g/l in the lower part.

In terms of thermal resources, an area of more than 10 000 km^2 possesses a prognostic P_1 resource density of 0.2–0.3 CFt/m^2. Only some 3240 km^2 has a P_1 resource density of >0.3 CFt/m^2.

Middle–Lower Devonian complex

This complex consists of several discrete stratigraphic horizons, as detailed below.

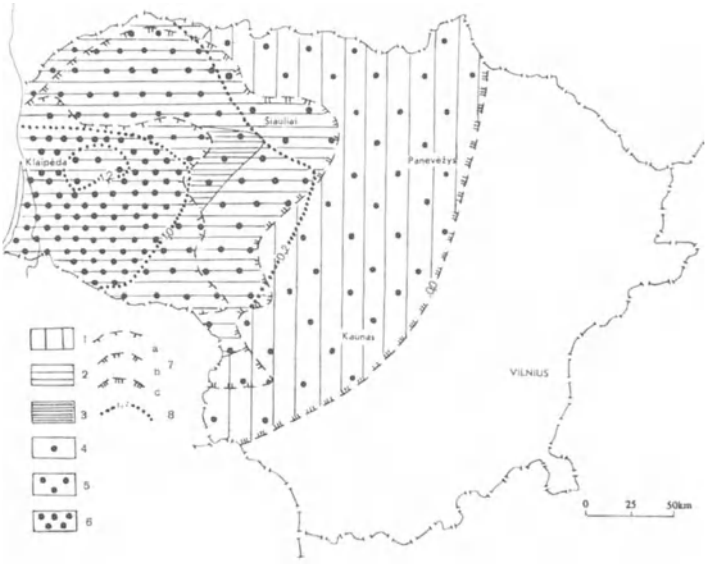


Figure 11.16 Summary map of geothermal resources in the hydrogeothermal complexes of the sedimentary cover. (1–3) Thickness of complexes in metres: (1) <100 m, (2) 100–300 m, (3) >300 m; (4–6) resource density in tCF/m^2: (4) <0.2, (5) 0.2–1.0, (6) 1.0–1.2; (7) 20°C isotherm for (a) Middle/Upper Devonian, (b) Lower/Middle Devonian and (c) Cambrian hydrogeothermal complexes; (8) isolines of resources density in tCF/m^2. (After Suveizdis and Rastenienė, 1993. Copyright Geological Society of Lithuania, reproduced with permission.)

Parnu Sandstones	(20–40 m thick)
Kemeri Series	Viešvilė Clays (about 35 m)
	Šešuvis Sandstones (about 100 m)
Gargždai Series	Stoniškiai Strata (sandy, up to 200 m)
	Tilžė Strata (more clayey, up to 200 m)

The strata are typically more clayey, marly and distal in character in west Lithuania than the corresponding deposits in the east of the country. The depositional environment of the rocks is typically continental. The Parnu Beds typically consist of gypsiferous sandstone interbedded with siltstone, clay and dolomitic marl. The Kemeri Series consists of laminated, fine-grained sandstone with silt and clay, while the Gargždai Series is composed of clayey silts, clays, sandstone and coarse-grained silts.

The total thickness of the complex in western Lithuania can thus exceed 400 m, but is more typically in the range 200–300 m. The complex has undergone extensive fracturing, and uplift has led to denudation in some areas. This is illustrated by the thickness of the complex 'wedging' out towards the south. In central Lithuania, the complex can occur at depths as shallow as 200 m, but in west Lithuania it is up to 900 m deep.

The aquifer properties of the strata have been investigated by formation testing during oil exploration. The Kemeri sandstones possess some of the best hydraulic properties of the complex; individual sand strata can reach 14 m in thickness, with a total sand content of 70–80%. Porosities vary between 15 and 25%, while permeabilities are typically several hundred, or even thousands, of millidarcys, reaching 12 000 mD (1×10^{-4} m/s) at Tauragė. Yield characteristics are exemplified by a yield of 807 m^3/d for a drawdown in head of about 10 m (1 atmosphere) in Vilkyčiai-3 borehole. The effective hydraulic thickness of the Kemeri Series varies between 140 m at Laužai and Meškinė, down to less than 60 m at Žalgiriai and Tryškiai.

The Gargždai Series exhibits poorer aquifer properties. Sandstone beds are typically only 2–7 m thick, and the total sand content does not exceed 30%. Permeabilities can reach several hundred millidarcys (767 mD or 6.5×10^{-6} m/s in Sakučiai area), but are often much lower.

The geothermal province of the Middle–Lower Devonian is defined as being bounded by the 20°C temperature isotherm at the top of the complex. This province stretches in west Lithuania almost from the Latvian border in the north to the Kaliningrad border in the south. The highest temperatures recorded are 46.5°C and 57°C, at the top and base of the complex respectively, in the Gorainiai borehole.

Piezometrically and hydrochemically, the Parnu–Kemeri part of the complex appears distinct from the Gargždai Series. Mineralization increases with depth, ranging from 6.6 to 85 g/l in the Parnu–Kemeri strata and from 10.8 to 110 g/l in the Gargždai strata. Again, the water is typically dominated by sodium and chloride, but with a Na/Cl equivalent ratio of <1, probably indicating enrichment of calcium at the expense of sodium by ion exchange. Chloride accounts for 58–98% of the anion equivalents, while the cation content is dominated by sodium (55–83%). The calcium content ranges from 7 to 35% of the cations, while magnesium is 2–15%. The waters are rich in bromide (up to 576 mg/l at Mikoliškiai-1) and often contain minor quantities of iodide, boron, manganese, copper, zinc, molybdenum and cobalt.

In terms of geothermal resources, three subfields can be defined in the province, as described in Table 11.9. The total P_1 resources of the complex are calculated to be 12.0 Gt CF, while the C_3 resources are approximately half this figure.

Cambrian hydrogeothermal complex

This complex has mainly been investigated by means of oil prospecting boreholes. It comprises:

- the Upper/Middle Cambrian Deimena Series, which consists of quartz sandstones with occasional silt or silty clay interbeds;

Table 11.9 Projected geothermal resources based on data from Laugaliai-3 well. Upper table (a) shows P_1 and P_2 resources for the entire petrogeothermal massif. The lower table (b) shows the P_1 and C_3 resources based on wells in the three major hydrogeothermal aquifer units (with t_0 ~5°C)

(a)

	Consumers' regime	*H (m)*	*h (m)*	*G (°C/100 m)*	t_0 *(°C)*	*q (tCF/m²)*
P_2 category	–	10 000	25	3	5	155.3
P_1 category	90°/40°C	6 000	25	3	40	4.8
P_1 category	70°/20°C	6 000	25	3	20	6.7

(b)

Complex	*Depth interval (m)*	*Thickness (m)*	*T (°C)*	t_g *(°C)*	ξ_k	ξ_t	ξ_f	*q (tCF/m²)*	
								P_1	C_3
Upper–Mid Devonian	646–827	181	26.75	24.4	1.2	0.55	0.6	0.281	0.169
Mid–Lower Devonian	948–1312	354	36.1	32.6	1.2	0.56	0.6	0.789	0.473
Cambrian	2091–2231	140	77	69.7	1.2	0.55	0.6	0.716	0.429

- the Kybartai Series, which contains a higher proportion of silts, with lenses of fine-grained sandstone;
- parts of the Gegė and Virbalis strata of the Middle Cambrian, which consists of repeated sequences of fine and medium grained sandstone, interbedded with siltstone and argillite beds.

The rocks tend to become more sandy and proximal in character towards the east. The depth of occurrence ranges from 600 m in the east to 2100 m in the west. The strata are tectonically disturbed by both normal and reverse faulting, the latter leading to the repetition of the succession in some boreholes.

The effective thickness of the hydrogeothermal complex varies from only 13 m (Likėnai-396) to 67.5 m (Kybartai-2). The measured permeability ranges from 3.5 mD up to 380 mD (3×10^{-8} to 4×10^{-6} m/s), with one exceptional case of 1100 mD (1×10^{-5} m/s) in the Ablinga-4 borehole. The generally high permeabilities are reflected in the yields from the complex; one free-flowing borehole, Graužai-105, overflowed at 765 m^3/d.

The Cambrian complex is the most extensive of the three geothermal complexes, as defined by the 20°C isoline, reaching as far west as Kaunas and Panevėžys and extending north and south into Latvia and Kaliningrad. Maximum temperatures (typically >80°C) have been recorded in the Baltic coastal region (borehole Vabalai-1 recorded temperatures of at least 92–95°C at the top of the complex) and the southern part of the Telšiai fracture.

Generally the waters in the complex are highly saline, typically with a total mineralization of more than 100 g/l, with a maximum of 203 g/l in borehole Žalgiriai-1. Water mineralization typically increases westward with increasing depth. As with the Lower to Middle Devonian complex, the water is of sodium chloride type, but the sodium content (in equivalents) is less than the chloride. In a few sub-areas, calcium is the prevalent cation, the water being of calcium chloride type. Chloride is always the dominant anion, comprising 95% of the anion equivalents. Bromide concentrations are high, ranging up to 1138 mg/l in Purmaliai-1, and typically 700–800 mg/l.

The resources of the Cambrian complex can be subdivided into three subfields of increasing resource density in the eastern, central and western areas. The P_1 and C_3 resources are described in Table 11.10. The total P_1 resources are some 12.2 Gt CF, while the C_3 resources are slightly more than half this figure at 7.5 Gt CF.

11.3.5 Hot dry rock potential

The crystalline basement rocks have considerable potential as hot dry rock geothermal (or in Lithuanian terminology, petrogeothermal) resources. Calculations of the resources are based on two sets of possible

Table 11.10 Summary of geothermal resources of the various hydrogeothermal complexes (see also Figure 11.16)

P_1 *resources*			C_3 *resources*		
Resource density (CFt/m²)	*Area (km²)*	*Quantity (Gt CF)*	*Resource density (CFt/m²)*	*Area (km²)*	*Quantity (Gt CF)*
Upper–Middle Devonian hydrogeothermal complex					
0.2–0.3	10 044	2.51	0.1–0.2	9 000	1.35
>0.3	3 240	1.13	>0.2	1 368	0.34
Middle–Lower Devonian hydrogeothermal complex					
0.2–0.6	15 732	6.29	0.2–0.4	8 676	2.60
0.6–1.0	5 904	4.72	0.4–0.6	6 120	3.06
>1.0	990	1.00	>0.6	666	0.4
Cambrian hydrogeothermal complex					
<0.2	19 548	1.95	<0.2	28 584	2.86
0.2–0.6	17 388	6.96	0.2–0.4	9 336	2.80
>0.6	5 508	3.31	>0.4	4 524	1.81
Total	42 444	26.9		42 444	16.4

consumption regimes:

1. water is extracted at 70°C and returned at 20°C;
2. water is extracted at 90°C and returned at 40°C.

The prognostic P_1 resources for these regimes are shown in Figure 11.17. Near the Baltic Coast around Klaipeda, the P_1 resource density is as high as 8 tCF/m² for regime 1. The total resources evaluated to a depth of 6 km are shown in Table 11.11.

The data in Table 11.11 include the hydrogeothermal resources of the sedimentary cover as described above. It should be noted that these form an insignificant part of the total resource to 6 km depth. Thus far, very few data have been collected to evaluate the hydraulic properties of the crystalline basement rocks, and an assessment of the true hot dry rock resources is still in its infancy.

11.3.6 The Vydmantai project

Currently, a major study is being undertaken at the town of Vydmantai, near Palanga. Here water is being abstracted at some 32 m³/h from a depth of 2000 m from an aquifer complex of Cambrian age and utilized in a GCS system. The abstraction temperature is 73.3°C, the water having a total mineralization of 164 g/l. The power extracted will be used for the trial heating of a greenhouse complex and is planned to be expanded in the near future.

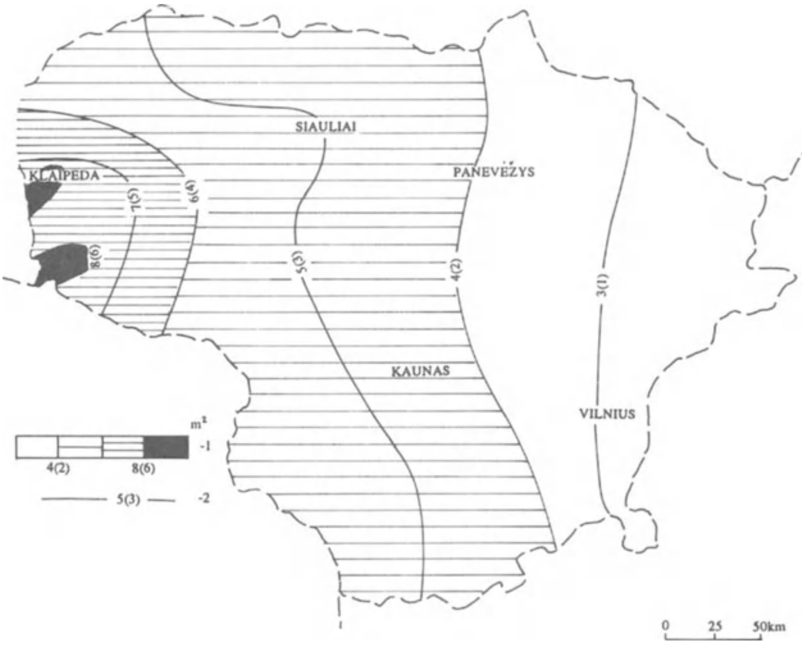


Figure 11.17 Map showing distribution of prognostic P_1 petrogeothermal resources. (1) Resources density in tCF/m^2 for two consumption regimes, 70°/20°C and 90°/40°C (latter in parentheses), (2) isolines of resources density in tCF/m^2 for the same two consumption regimes. (After Suveizdis and Rastenienė, 1993. Copyright Geological Society of Lithuania, reproduced with permission.)

11.3.7 The future

The Vydmantai project shows much potential for the use of geothermal energy from the aquifers of the Cambrian complex. The potential use of shallower Devonian waters of temperature about 60°C is to be assessed in the near future, as is the use of deeper crystalline basement at 3000–4000 m depth for hot dry rock energy at temperatures of 100–120°C.

There is a good potential for the development of geothermal power in Lithuania and neighbouring Baltic states. Under similar hydrogeological and economic conditions, geothermal plants are now operational in

Table 11.11 Total geothermal resources of the upper 6 km of the Lithuanian petrogeothermal province

	P_1 *total resource (Gt CF)*	C_3 *total resource (Gt CF)*
70°/20° regime	298.5	248.5
90°/40° regime	168.0	115.8

Neubrandenburg (Germany), Thistedt (Denmark), Lund (Sweden) and Pryrzyce (Poland) (BRGM, 1981; Jand, 1985; Eliasson *et al.*, 1987; Lund, 1988; Gorecki, 1990; Hodgson, 1991; Sultz *et al.*, 1992). In the not too distant future, tourists returning to their hotels in Palanga from an icy dip in the Baltic might be able to look forward to the luxury of geothermally heated apartments.

12

Natural mineral waters of Mineralnye Vody region of north Caucasus, CIS

John Ferry

12.1 INTRODUCTION

In the Russian classic *A Hero of Our Time* by Lermontov, published in 1840, much of the action takes place in the foothills of the Caucasus in the Mineralnye Vody (meaning Mineral Water) region. The romantic and tragic nature of the novel is reflected in the settings of lonely picturesque gorges and the fashionable mountain spa towns of Pyatigorsk and Kislovodsk. The belief in the region's healing mineral waters was already well established 150 years ago, and was a magnet for both wealthy and jaded Russians.

Mineralnye Vody is Russia's prime source of mineral water, and abstraction and bottling of waters in the region is widespread. In particular, the region is noted for its medicinal natural mineral waters. As well as Pyatigorsk and Kislovodsk, the region contains the spa towns of Yessentuki and Zheleznovodsk. Yessentuki was the base for the mysterious Gurdjieff and his followers in the second decade of the 20th century when Russia was undergoing the upheavals of the Revolution. Gurdjieff seems to have been drawn by the medicinal and mystical qualities of the waters. Yessentuki waters are still the most renowned medicinal waters in Russia. There are three different types of Yessentuki water. It is the most expensively priced bottled water due to the small production scope, limited resource and distance from the main markets. The other well known brands of mineral water produced in the Mineralnye Vody region and formerly distributed

Mineral and Thermal Groundwater Resources
M. Albu, D. Banks and H. Nash.
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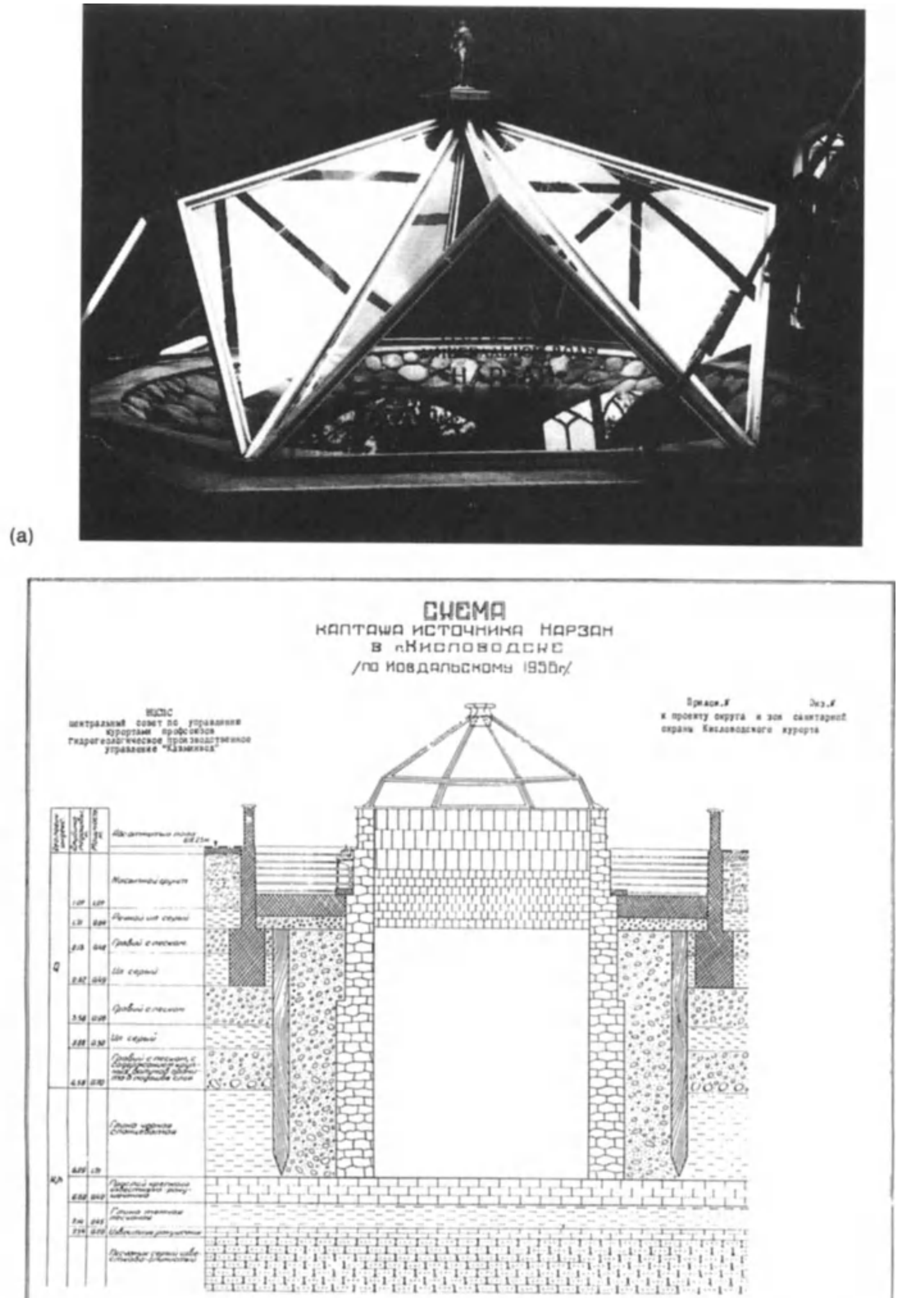


Figure 12.1 (a) Photograph and (b) section through the Narzan spring.

widely across the Soviet Union are Slaynovskaya, Smirnovskaya and Zeleznovodsk. Outside the Mineralnye Vody region, but still in the foothills of the northern Caucasus, there are mineral water plants at Maikop and Gorychiy Klych.

The mineral water which this case history focuses on is perhaps the most famous of the many different mineral waters of the region, Narzan. The information reported was gathered by the author as a part of a preliminary 'due diligence' environmental assessment of the Narzan bottling plant in June 1994. In Lermontov's novel, Narzan is called 'the Champion's Spring'. Originally, Narzan was the name of a series of natural mineral water springs in the Olkhovka River. The valley was known as 'the valley of the Narzan springs'. More than 200 years ago, the river was diverted around the main one of these spring sources and a large health resort park with spas and bath houses, fountains and tasting galleries was constructed around the source. The present day resort town of Kislovodsk grew around this large park. The original spring source has been developed with a glass dome cover (Figure 12.1) and is still the centrepiece of the present day tasting gallery in the resort park surrounded by taps and fountains gushing a variety of mineral waters of different tastes and composition derived from different depths of the underlying mineral water aquifers. Some of these waters are hot and more sulphurous tasting than the common Narzan water, and are regarded as a medicinal tonic rather than as table water. Tourists and local residents alike gather here to taste and fill their own containers with their chosen water.

The Narzan bottling plant was set up by Tsar Alexander II over 100 years ago, in 1895. Since then the mineral water resource underlying the town has been developed, and today Narzan mineral water is bottled in Kislovodsk from water supplied from a series of deep boreholes, both within the town and in the neighbouring countryside. The tasting gallery is in fact the old bottling hall from pre-revolutionary days.

12.2 GEOGRAPHY

Kislovodsk is the southernmost town of the Mineralnye Vody region. Kislovodsk is located at 42° 50′ 6″ E 44° 1′ 18″ N at an elevation of about 800 m, in a basin on the northern edge of the central Caucasus mountains, about 40 km from Mount Elbrus. The hills surrounding Kislovodsk are densely wooded for several kilometres before grading into open highland grassland. Elevations then rise steeply southwards towards Mount Elbrus, the highest peak of the Caucasus at 5600 m above sea level.

Two rivers, the Olkhovka and Pudhkumok which rise in the Caucasus, flow through the town to join the Kuona River which drains into the Caspian Sea in the east. These river valleys have cut deep gorges through the mountains. The gorges continue into the Kislovodsk Basin. When visited in summer 1995, little flow was observed in the rivers, although Lermontov talks of raging torrents.

Rainfall in Kislovodsk is 570 mm/year, rising to 700 mm/year in the surrounding hills.

12.3 GEOLOGY

The Caucasus mountains are in a zone of recent tectonic, volcanic and seismic activity. This activity is connected with their mode of formation: the collision of the Arabian and Indian plates with the Eurasian plate.

The main structural axis in the north of the Caucasus is an area of crumpling uplift typified by young volcanoes and volcanic outpourings on top of an older crystalline basement of granites and metamorphic rocks. Below this axis to the north, the crumpling dies out quickly and the Caucasus foothills have the structure of a gently dipping monocline where an increasingly thick sedimentary cover laid down predominantly by marginal seas overlies the crystalline basement. This area, which includes the Mineralnye Vody region, is known as the North Caucasian Foredeep. Parts of this foredeep area contain oil and gas. To the south of the axis, the crumpling extends for many hundreds of kilometres, accounting for the distinctive mountainous character of Georgia.

The age of the sedimentary cover at Kislovodsk ranges from Jurassic (200 Ma) through to Quaternary (1.6 Ma). As Kislovodsk is close to the southern edge of the foredeep, the sedimentary cover is relatively shallow, between 200 and 300 m thick, depending upon the undulating surface of the crystalline basement. The sediments in Kislovodsk and the catchment areas to the south comprise a sequence of clastic terrigenous rocks and karstic limestones, dolomites and marls with sandy and clay horizons.

The region has been subject to recent volcanism from the late Tertiary Period (2.5 Ma), through to the Holocene Epoch (0.01 Ma) along major N–S faults extending from the main E–W Caucasus axis. This tectonic and volcanic activity is essentially responsible for the mineralized groundwater of the region, including Narzan. Many small domes of carbon dioxide gas of magmatic origin emanating from these faults have been mapped in Mineralnye Vody region, including several under Kislovodsk itself. Intrusions are also often closely associated with the fractures. In the region of Pyatigorsk and Zheleznovodsk, there are a number of laccoliths composed of acid rocks, trachyliparites, of Neogene age. These have been emplaced as dome-like bodies pushing up the strata into which they are intruded. In some cases, the magma in the process of rising has dragged whole blocks of Cretaceous sediments into vertical positions. The valuable mineral waters of the region are associated with this young volcanicity.

12.4 HYDROGEOLOGY

12.4.1 Description of the aquifer flow system

The Kislovodsk mineral water area covers 100 km^2. A geological sketch map of the region and a schematic hydrogeological sketch map are shown in Figures 12.2 and 12.3. The groundwater catchment for Kislovodsk extends at least 10 km south and to an elevation of up to 2000 m, well into the Caucasus foothills. The aquifers are fed by snow, river, stream and rainwater infiltrating into the very permeable karstic Jurassic and Cretaceous limestones and dolomites. The base of the aquifer system is the low permeability crystalline basement which contains negligible groundwater resources.

Groundwater flow in this karstic terrain is fast and Kislovodsk natural mineral water is estimated by local Russian hydrogeologists to be between 0.5 and 2 years old.

For most of the Narzan catchment area, the water table is more than 100 m below ground level (b.g.l.), but in the Kislovodsk Basin the deeply incised river beds cut into the water table, and river bed springs and shallow depths to groundwater are encountered. The mineral waters in Kislovodsk are, however, distributed throughout the aquifer system, not just in the near-surface layers.

There are three main aquifers underlying Kislovodsk separated by relatively thin clay and marl horizons. Groundwater in the two deeper aquifers is confined and has potentiometric heads acquired from the higher elevation of water tables in the recharge zone. Groundwater from these horizons will tend to rise and flow upwards to ground level along lines of weakness caused by the N–S faults.

The deepest aquifer unit is immediately above the crystalline basement at a depth of 170 m under the main spring source, but ranging up to 300 m elsewhere in the Kislovodsk area. This deep layer is composed of old, very weathered continental rocks with a relatively low permeability. Groundwater in this unit is the most mineralized at 6000–7000 mg/l with an artesian head of 20 m above ground level (a.g.l.). This water is of elevated temperature.

The second unit occurs between 150 and 70 m b.g.l. in very porous karstic marine carbonates. Highly mineralized water from the deeper layer mixes with less mineralized younger water in this layer to give waters with mineral content of 2500–4000 mg/l and a head of 10–12 m a.g.l. Water from this unit is supplied to the Narzan bottling plant.

The top unit from 70 m b.g.l. to ground level is a sandy carbonate with much decreased mineralization due to mixing with fresher waters. Groundwater in this unit is semi-confined to unconfined. The main spring source belongs to this unit.

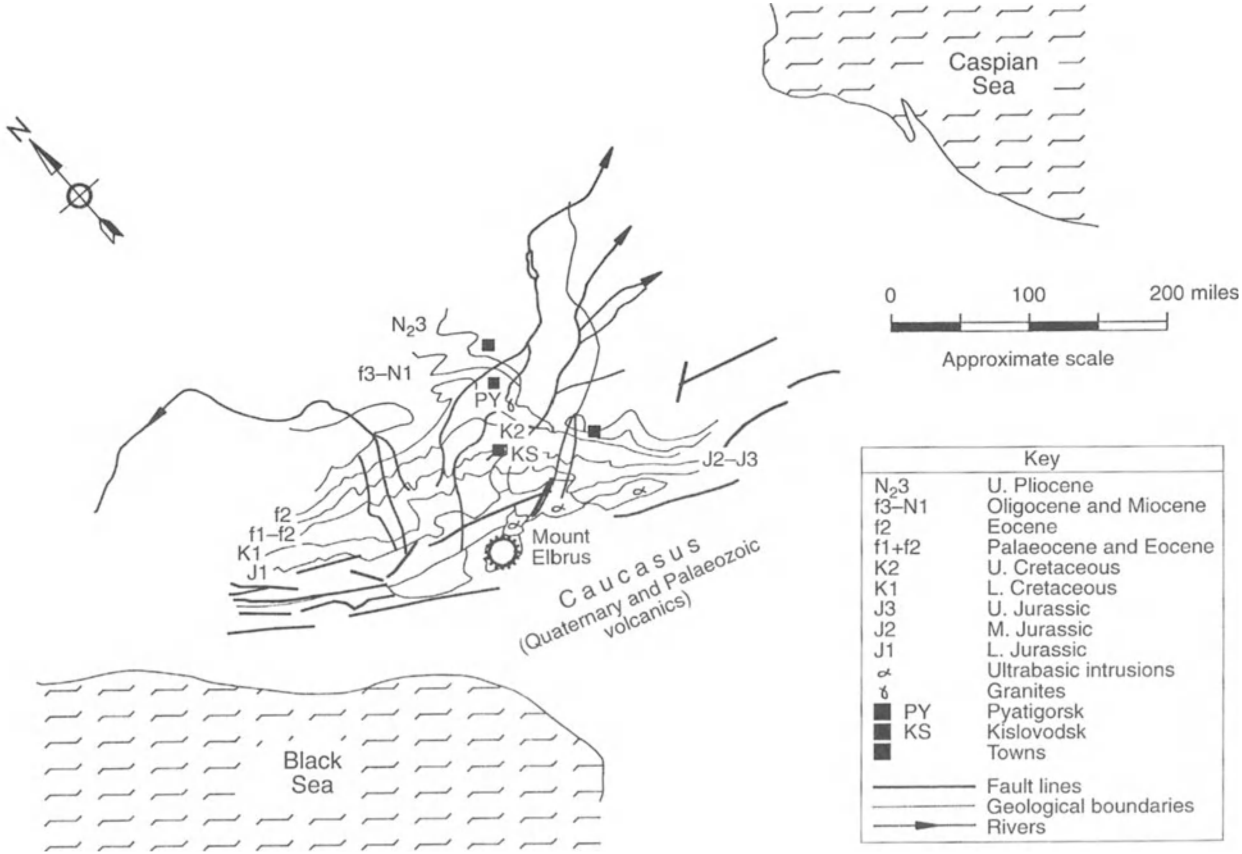


Figure 12.2 Geological sketch map of the Kislovodsk mineral water area (1 mile = 1.6 km).

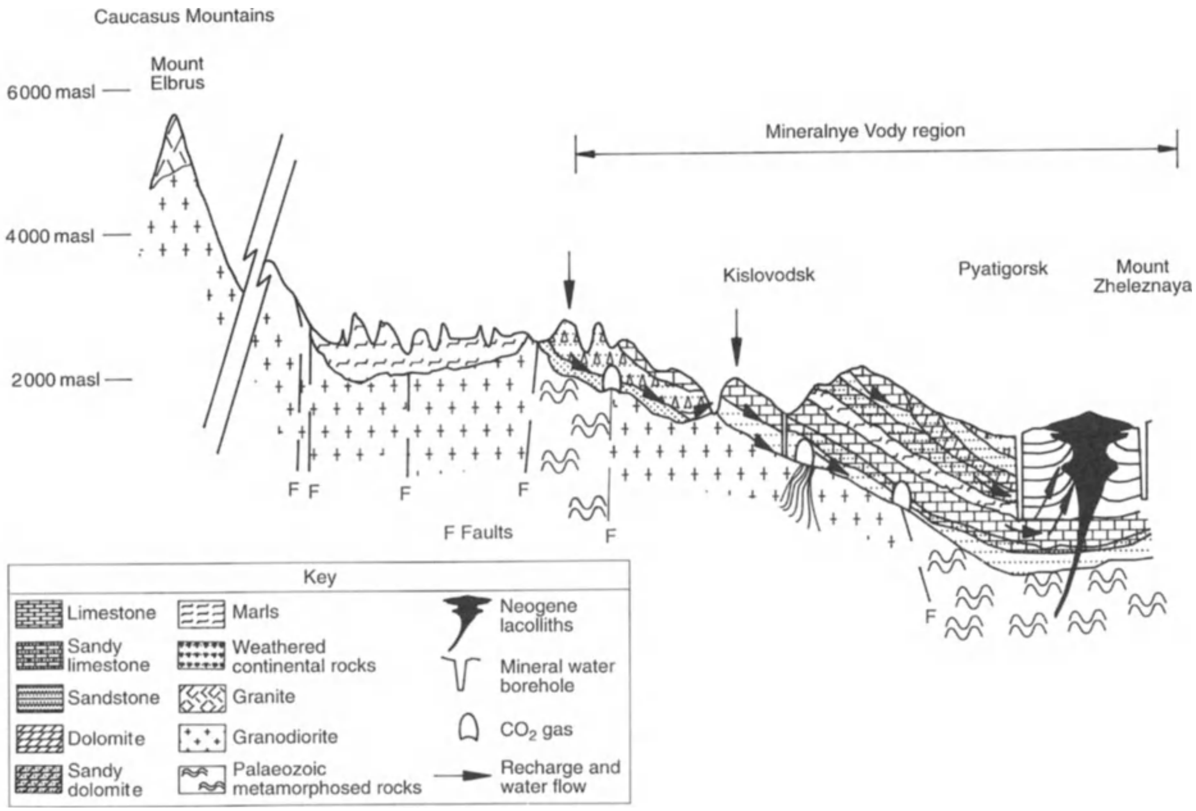


Figure 12.3 Hydrogeological sketch map of the Kislovodsk mineral water area.

12.4.2 Mineralization mechanisms

The key feature of mineralization of the groundwater to produce the various mineral waters is the occurrence of small localized domes of carbon dioxide gas in the aquifers above the crystalline basement. These are elliptical in plan and of magmatic origin, emanating from the tectonic faults. The fresh groundwater of meteoric origin flowing through these carbon dioxide domes is charged with carbon dioxide which promotes dissolution of aquifer rocks and mineralization of the circulating groundwater.

Several of these carbon dioxide domes are present under Kislovodsk and in nearby fault-defined valleys. The carbon dioxide is most prevalent in the deep continental aquifer, leading to the high degree of mineralization in this unit which is aided by the weathered nature of these rocks.

The main dissolved ionic components of the mineral waters: calcium, magnesium, bicarbonate and sulphate can be accounted for by dissolution of dolomite and limestone rocks and gypsum minerals within the carbon dioxide-rich groundwaters. The origin of at least some of Narzan water's many trace components, including mercury, fluorine, arsenic, bromine, iodine, strontium, silver and iron, may be from associated constituents of the volcanic gas.

All the valuable mineral waters of the Mineralnye Vody region are associated with the young tectonics and volcanism and its gaseous products. Downgradient of Kislovodsk, the aquifers are deeper and thicker, and folding, fracturing and igneous intrusions give rise to a wide variety of mineral waters, many with elevated temperatures.

Groundwater which does not encounter the relatively restricted carbon dioxide deposits, faults and igneous intrusions remains fresh with relatively low mineralization.

12.4.3 Development and use of the Kislovodsk natural mineral water resource

Over the years the Kislovodsk mineral water resource has been much explored and developed by state hydrogeologists. Over 200 boreholes have been drilled to various depths around the Kislovodsk region. The carbon dioxide domes and water quality distribution have been closely mapped and a number of secondary mineral water resources in nearby valleys and in the mountains have been identified. Detailed geological and hydrogeological maps, sections and descriptions have been prepared. Historical records of abstraction, water level fluctuations, meteorology and water quality are maintained by state hydrogeologists.

The Narzan resource, used for drinking, bottling, bathing and washing within the resort and bottling plant, is estimated to have a safe yield of about $2500\,m^3/d$. This safe yield was tested in 1989/1990 when, due to high turnover of visitors to the resort, in excess of $2500\,m^3/d$ was required. Mineral water had to be piped in to supplement the local resource from both nearby and distant mineral springs. This activity inevitably changes the exact nature of the mineral water used, and hence the medicinal qualities from that of the original Narzan river bed springs. However, knowledge of the resource is such that the operators were able to maintain a similar quality of water supply.

To preserve the resource, it is forbidden to use fresh groundwater from upgradient of the town, or to use groundwater from shallow alluvial deposits in the valleys. The potable domestic and commercial supply for the town and surrounding areas is supplied from a distant snow melt reservoir in the Caucasus. Effluent from town mineral water usage (2000 m^3/d) is discharged into the river bed adjacent to source 5 (see below).

12.5 NARZAN BOTTLED WATER SOURCE

Narzan is the largest bottling plant in Russia; the only larger one in the former Soviet Union is in Georgia, but production has suffered in recent years due to the conflict in Georgia. The principal production difference between Narzan plant and others in the region is that the water is transported from source to factory by pipeline rather than by trucks and water bowser, as is commonly the case.

All water is bottled in 0.5 l glass bottles of different colour shades. There are three bottling lines with a capacity to bottle 130 million bottles per annum, although currently only one line is functioning, producing only 40 million bottles per annum. Only the regular, relatively low mineralized (by Russian standards) carbonated mineral water is bottled, not the hotter so-called sulphurous waters.

12.5.1 Source description

The main supply of mineral water to the Narzan bottling plant is via a 300 mm pipeline from borehole 5, which is located approximately 1.5 km from the factory. Details of this borehole are given below and in Figure 12.4.

Total depth	147.55 m	
Date drilled	1953	
Elevation	810 m a.s.l.	
Construction	0–4 m b.g.l.	Steel casing, cemented, 355 mm diameter
	0–62 m b.g.l.	Steel casing, cemented, 305 mm diameter
	0–40 m b.g.l.	Steel casing, cemented, 152 mm diameter
	0–75 m b.g.l.	Ni/Cr casing sleeve, 104 mm diameter, 10 mm thick
	75–147.5 m b.g.l.	Open hole 98 mm diameter
Geology	0–4 m b.g.l.	Quaternary sands and gravels
	4–45 m b.g.l.	Sandy limestone with clay bands
	45–144 m b.g.l.	Limestone and dolomite with marl
	144–147.5 m b.g.l.	Sandy limestone

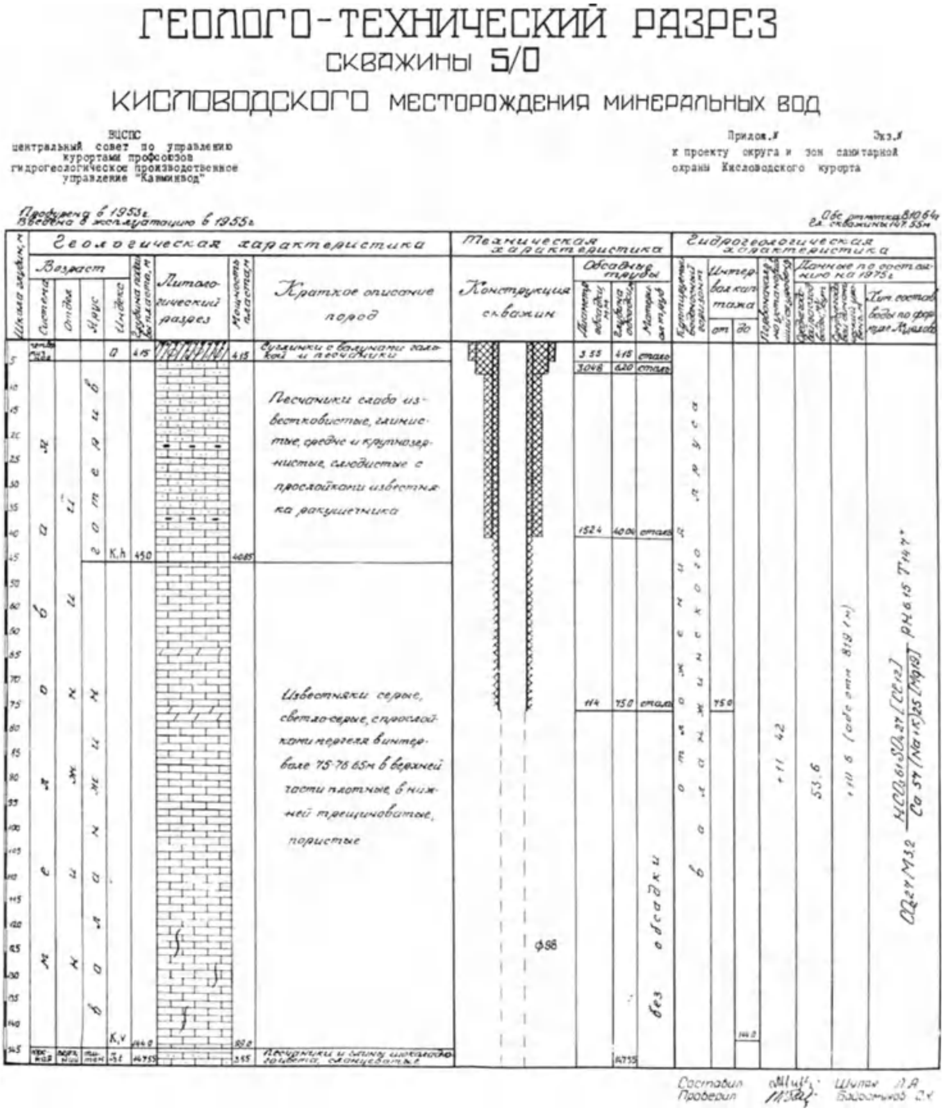


Figure 12.4 Completion details for the borehole supplying the Narzan bottling plant.

Piezometric head	816.68 m a.s.l.	(1994)
Pump details	Not ascertained on site	

Note: Ni/Cr steel casing protects against the aggressive corrosivity capability of the mineral waters.

The borehole is located in the town centre, about 50 m from a busy road and several hundred metres from a river valley. There are two other boreholes on this site, each tapping a different aquifer and each with a different mineral water composition. Adjacent to the source is one of the many marble drinking galleries to be found in the town. The borehole chambers are very clean, well sealed with good working instrumentation for head measurements and discharge control and with well positioned sampling taps.

The source, borehole 5, can supply up to 500 m^3/d. Currently, it is supplying the bottling plant with 50–80 m^3/d, although it is licensed to supply 250 m^3/d, or approximately 10% of the total Narzan (Kislovodsk) mineral water resource.

12.6 RESOURCE MANAGEMENT

12.6.1 GOST Standards

The bottled mineral water industry is controlled by the State Standards of Soviet Union (now adopted by the CIS), i.e.:

- GOST Standard 13273-88 'Drinking medicinal and medicinal-table mineral waters. Specifications', 1988;
- GOST Standard 23268.0-78 'Drinking medicinal, medicinal-table and natural-table mineral waters. Acceptance and sampling regulations', 1984.

These Standards can be regarded as generally equivalent to EC Directives 80/777 96/70/EC, and National Regulations which control natural mineral water in European Community countries. In addition to specifying natural mineral water types and compositions, they lay down monitoring programmes and methods for analysis of a wide range of parameters, and identify and place limit values on significant components, including phenols and organic compounds.

12.6.2 Regulatory bodies

The Narzan resource and sources are controlled by a complex state structure. Licences to exploit the resource are granted by the Kislovodsk branch of the Caucasus Mineral Water Resort Resources Exploitation Regime Unit, which seems to come under the Russian Council for the Direction of Resorts. Licensing quotas, however, are arranged via a national Governmental Committee which has the power to override local authorities. Close links are maintained with the Ministry of Geology to assist in the identification and exploitation of the underground resource, and the production of maps.

The structure is, according to the local unit Director, undergoing change, as are many institutions in Russia, with the existing state assets and duties to be reallocated between Government, municipalities and trading units. This restructuring has extended to the privatization of the bottling factory which is currently in negotiations with Western bottling companies and distributors.

12.6.3 Aquifer protection

High quality aquifer protection maps at 1:100 000 and 1:25 000 scales have been drawn up. Three zones of protection are indicated on these maps with varying degrees of protection implemented by land use, development and building controls. Development permissions are given by the Caucasus Mineral Water Resort Resources Unit overseen by a regional Committee for Environment Protection and the Government Committee for Nature.

There are few industries in Kislovodsk and these relate mostly to the tourist industry, e.g. a ceramics factory. The catchment is remarkably free of urbanization or other polluting land use, which is a powerful reflection of strict catchment control to protect the purity of the mineral water resource. As an example of the strict control, grazing by cattle belonging to nomads on the catchment upgradient is strictly controlled. In this respect, the location of Narzan on the edge of the Caucasus proper and on the historic border of Russia is beneficial to source protection. As the area has long been a sensitive military control area, there is no permanent population, which renders source and planning protection easier.

12.7 NARZAN WATER QUALITY

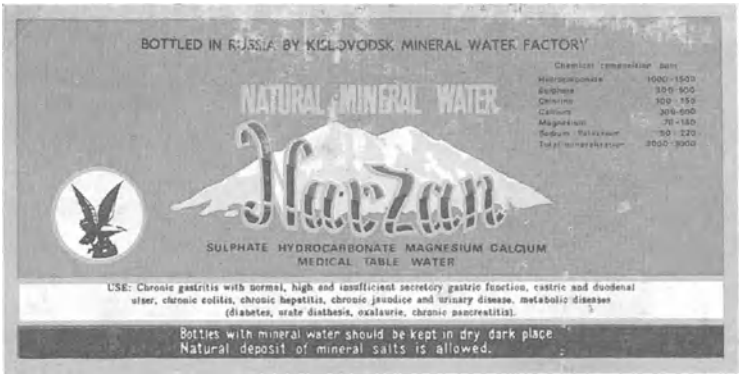
The chemical and physical monitoring regime for Narzan mineral water is given below. This is in accordance with the GOST Standards which lay down mineral water composition, acceptance and sampling regulations.

- Daily: chemical indicators (chloride, permanganate oxidation, hydrogen-carbonate, ammonia, nitrate, nitrite and bacteriology).
- Monthly: full major ions.
- Biannual: full analysis.

Routine analyses are carried out by the bottling factory laboratories and by the Pyatigorsk Scientific Research Unit, the main testing laboratory for the Mineralnye Vody region. A full analysis is carried out by the Balneological Institute.

Narzan bottled water is currently promoted as a sulphate–hydrocarbonate–magnesium–calcium water but also contains sodium and chloride major ions. The composition on the bottle labels is reported in parts per million (ppm), roughly equivalent to mg/l, and as concentration ranges rather than absolute concentrations (Figure 12.5). Table 12.1 shows the chemical composition of the water. Figures in brackets show the variation in those sample analyses examined (1980–1983). Other analyses were not available from the archive at time of the author's visit. Those examined fall within the range expressed on the label.

The variability of the concentration of major ions in the mineral water is greater than that allowed under EC 80-777 Directive on Natural Mineral



USE: Chronic gastritis with normal, high and insufficient secretory gastric function, castric and duodenal ulser, chronic colitis, chronic hepatitis, chronic jaundice and urinary disease, metabolic diseases (diabetes, urate diathesis, oxalaurie, chronic pancreatitis).

Bottles with mineral water should be kept in dry dark place. Natural deposit of mineral salts is allowed.

Figure 12.5 Narzan water label.

Waters. It is noted, however, that the equivalent Russian GOST Standards formalize the variation in mineral water composition. These standards cite Kislovodsk mineral water as a recognized type of carbon dioxide mineral water and subdivide it into four geographical names, three of which are Narzan: borehole 5/0-6UC with no prefix (this is the bottled Narzan water), borehole 7, 5/0 entitled 'dolomitic Narzan' and a 'sulphate Narzan' from borehole 8. Each of these named types has a different set of concentration ranges but all have very high carbon dioxide contents varying from 1800 to 2700 mg/l. The different types of waters reflect the different depths and locations of the respective sources.

It is noted that the GOST concentration range for the Narzan water from borehole 5 differs from the ranges shown on the bottle labels for the cations, Mg, Na + K and Ca. The labels have extended the concentration ranges.

The pH of borehole 5 water is 6.24 and temperature is a relatively constant 13–14°C. Trace amounts of Mn, Hg, Sr, F, As, I, Br and Fe are listed on the analyses examined. Short-lived pulses of ammonia have been reported in the samples, of an origin and concentration not known to the author.

It is not the purpose of this description to discuss the medicinal qualities of the Narzan mineral water and the Mineralnye Vody waters in general.

Table 12.1 Composition of Narzan bottled water

	Bottle labels (mg/l)	*Analysed values (mg/l)*
$Na_2O + K_2O$	220	167.2–211.7
Ca	300–500	323.2–410.4
Mg	70–140	83.5–97.3
Cl^-	100–150	95.8–146.5
SO_4^{2-}	300–500	378.2–456.8
HCO_3^-	1000–1500	1065–1393
TDS	1850–3010	2067–2689

However, note must be made of the claims made for the water. The Narzan label announces that Narzan is a sulphate hydrocarbonate magnesium table water, but then goes on to list other uses as 'chronic gastritis with normal and high secretory gastric function, gastric and duodenal ulcer, chronic colitis, chronic hepatitis, chronic jaundice and urinary disease, metabolic diseases (diabetes, urate diathesis, oxalaurie) and chronic pancreatitis'. These claims reflect worldwide claims regarding the medicinal value of mineral waters.

The author passes on a plea from the Mineralnye Vody hydrogeologists and balneologists to enter into scientific exchange on hydrogeological and balneological issues. There is a huge body of knowledge in the region which can only benefit the West medicinally and technically. Sample issues are the contribution of carbon dioxide gas 'impurities' to trace element mineral content of water, and the corresponding medicinal value of these trace elements. Should anyone be interested in pursuing co-operation, please contact the author.

13

Geological, hydrochemical, regulatory and economic aspects of natural packaged water production: Nordland County, Norway

Arve Misund and Patrice de Caritat

13.1 INTRODUCTION

Nordland County is a region remote from English industrial smokestacks and with an 'ultra clean Arctic' image. Studies of acid rain have demonstrated pH values above 5 in precipitation, which is typical for areas with little or no industrial pollution (Figure 13.1). This is in stark contrast to southern Norway, which is affected by airborne pollution from central and western Europe, and northeast Norway, which is exposed to acid rainfall from the nickel smelters on the Kola peninsula. The perceived clean conditions were an important factor when the Geological Survey of Norway (NGU), together with Nordland County Council and six municipalities, initiated a 1-year monitoring programme of seven water sources in Nordland County (Figure 13.2). The main object of this investigation was to find water sources or springs with a water quality suitable for bottling and export. Three of the sources are near-coastal high mountain lakes, remote from human activity; two springs emerge from Quaternary deposits while the remaining two are Palaeozoic limestone karst springs. The fieldwork and water sampling were carried out from November 1992 to February 1994, and included

- water sampling on a monthly basis;

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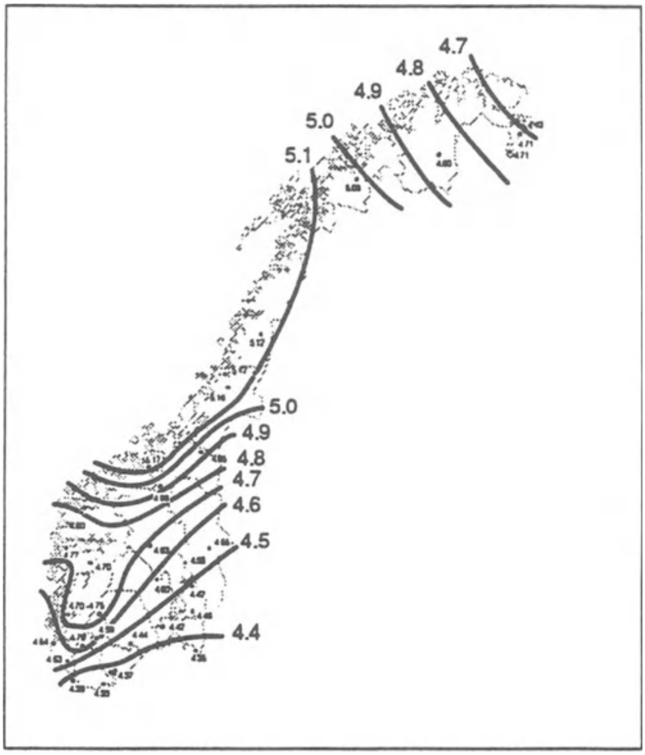


Figure 13.1 Map of Norway showing the mean value for pH in precipitation in 1991.

- field investigations;
- continuous monitoring of water discharge and temperature.

At the Kattdalen karst spring, electrical conductivity was also monitored continuously. The sampling procedure was in accordance with the Norwegian legislation on the sale of bottled water (Sosialdepartementet, 1977). The Centre for Business Development Ltd in Bodø was responsible for market analysis and development.

During the spring of 1993 it became clear that the three sources from the coastal high mountain lake areas could not be recognized as 'natural mineral water', due to the lack of natural protection (which might have been present had they been groundwater sources). Because of this, the sampling programme was stopped for Vestre Nøkkvann and Storvannet in August 1993, and Isvannet in December 1993. These mountain lakes can still be packaged as general water, although treatment would be necessary to accord with the EC Drinking Water Directive (80/778/EEC). Due to the European Economic Zone (EØS) trade agreement between the EU and

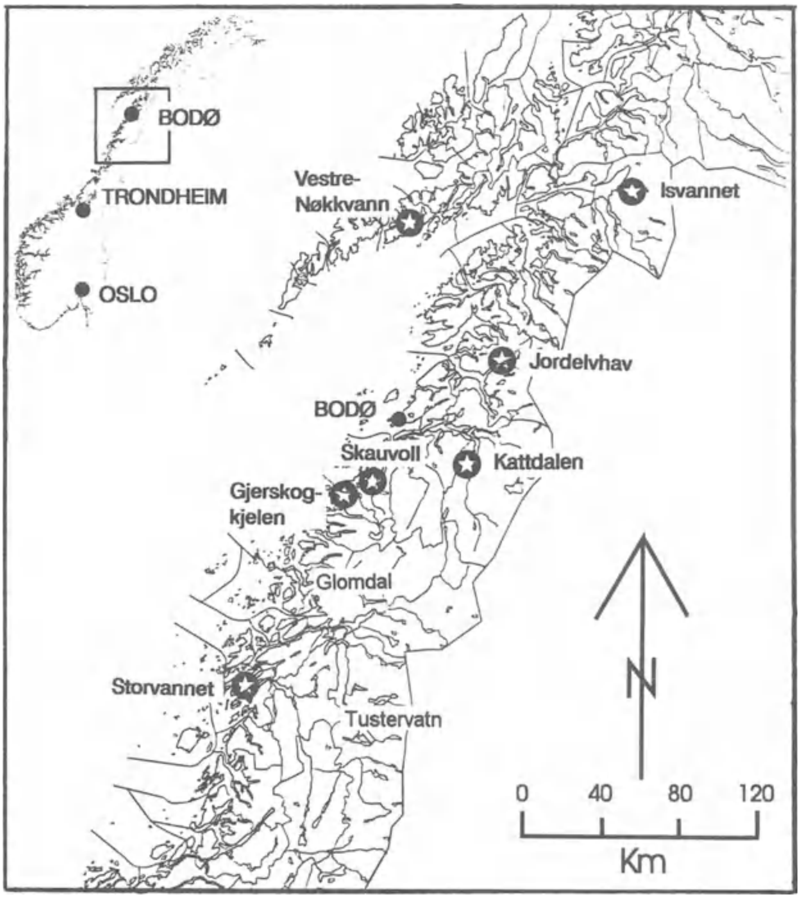


Figure 13.2 Location of the sites of the water monitoring programme in Nordland County.

Norway, this Directive has been part of the Norwegian legislation since 1 January 1995. To make this type of pure lake water appear more 'exotic', it is considered feasible to add CO_2, as is currently done with the natural Norwegian mineral water 'Farris'.

Full site investigations were not completed for the mountain lakes, but for the four springs, site investigations were continued during the summer of 1993.

13.2 METHODOLOGY

Due to the prospect of future commercialization, spring water sampling was undertaken without filtration or acidification of samples. The Norwegian health control authority bases health standards for bottled water on the total mineral and bacteriological content of marketed raw water. In fact, the water from the two Quaternary springs (Jordelvhav and Gjerskogkjelen) and the two karst springs (Kattdalen and Skauvoll) contains very low amounts of suspended solids, as shown by the turbidity measurements (varying between 0.03 and 0.4 FTU) and the UV transmission results (varying between 82 and 99%).

Electrical conductivity, pH and alkalinity were measured in the laboratory on untreated 500 ml aliquots. The spring waters were analysed in the field for pH, conductivity, temperature and oxygen with a Water Quality Logger 3800 from Grant/YSI. Water samples were analysed for 29 elements by inductively coupled plasma emission spectroscopy (ICP-ES). Seven anions were analysed by ion chromatography (HPIC) using a DIONEX 2010i (Ødegård and Andreassen, 1987). In addition, Pb and Cr concentrations were determined by atomic adsorption, as was Hg (with the use of a hydride system). Total organic carbon (TOC) was determined by an Astro model 1850. Microbiological analyses were performed at the local laboratory in Nordland to determine the revivable total colony count of *E. coli* and other coliforms in 250 ml at 37°C and 44.5°C, and to determine the total revivable colony count per millilitre of water at 20–22°C in 72 h on an agar–agar mixture.

13.3 GEOLOGY AND HYDROGEOLOGY

The time-series water quality data from this study show a strong negative correlation between water discharge and the concentrations of Ca^{2+} and Mg^{2+} in the spring water, reflecting the interplay between water residence time and mineral–water interaction and dilution. For the karst spring at Kattdalen, the Ca^{2+} concentration fluctuates between 48 and 55 mg/l which, in Norway, is generally regarded as a high value (Figure 13.3). Table 13.1 shows the summarized results of water quality monitoring.

All the investigated sources have flat water, with no natural CO_2 effervescence. Figure 13.4 shows time-series data for conductivity, pH, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^- and SO_4^{2-} at Jordelvhav. In Figure 13.5, Ca^{2+} and Na^+ are presented in the same diagram to distinguish between waters whose hydrogeochemistry is mainly dominated by water–rock interaction (Ca^{2+}) and those that are mainly dominated by seawater spray and precipitation (Na^+). The same distinction can be identified by looking at HCO_3^- and Cl^-. During major autumn and winter storms, sea spray has been observed as much as 150 km from the sea, and at altitudes of about 300 m above sea level (a.s.l.) (I. Lindahl, NGU, personal communication). During the winter season, sea salts accumulate in the snow cover, and are released during the snowmelt in the spring. Figure 13.6 shows the average precipitation at Tustervatn monitoring station, Nordland, for 1993, illustrating that the peak inputs for Na^+

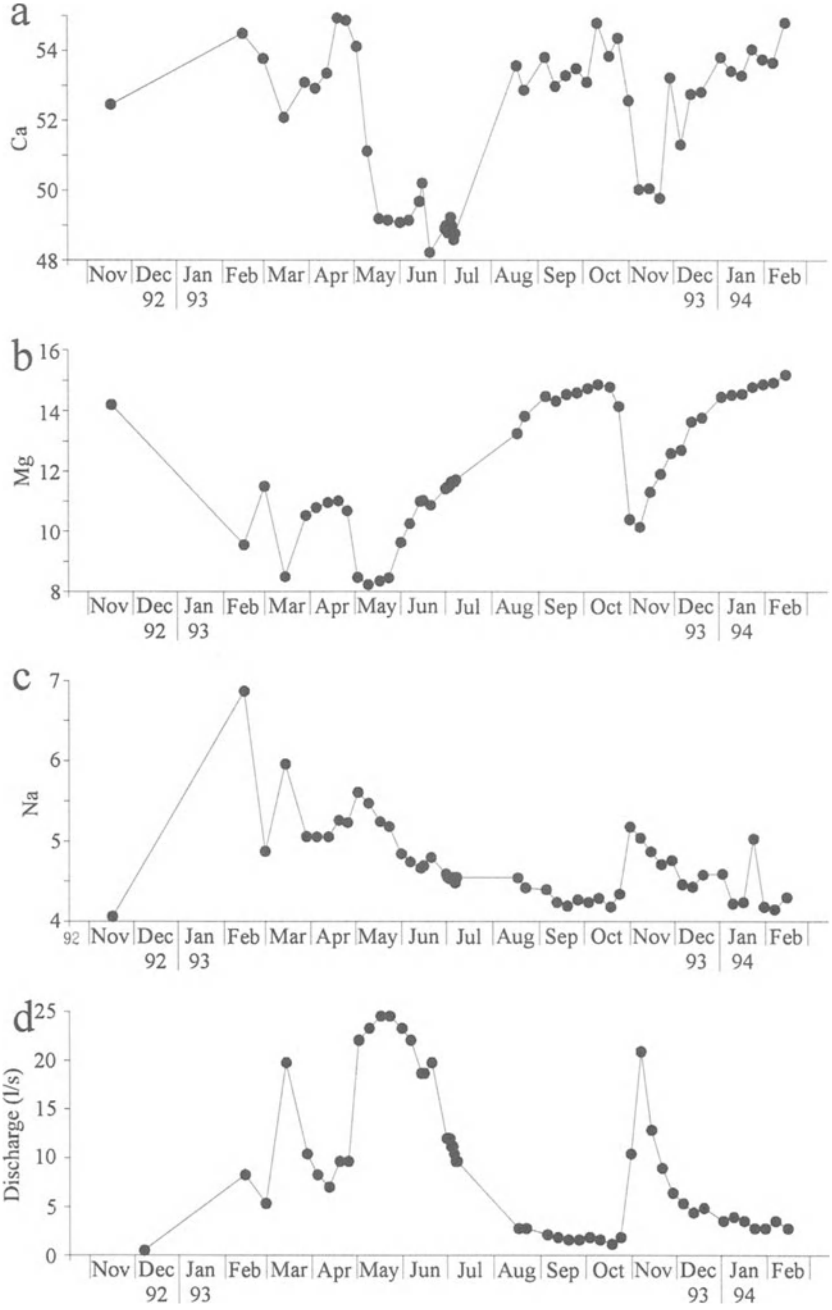


Figure 13.3 Time series for (a) calcium, (b) magnesium, (c) sodium concentrations (mg/l) and (d) discharge from Kattdalen spring, Norway (November 1992 to February 1994).

Table 13.1 Major ionic components at the monitored sources in Nordland County, sampled between 15 February 1993 and 15 February 1994

	Jordelvhav		*Kattdalen*		*Skauvoll*		*Gjerskogkjelen*		*Isvannet*		*Vestre-Nøkkvann*		*Storvannet*	
	Min	*Max*	*Min*	*Max*	*Min*	*Max*	*Min*	*Max*	*Min*	*Max*	*Min*	*Max*	*Min*	*Max*
Type	Q		K		K		Q		L		L		L	
Discharge	6.7	40	1	24	>10		1	30	–	–	–	–	–	–
Conductivity	38.3	99.2	315	386	94.8	159	79.9	104.0	15.3	23.2	35.7	61.4	43.5	63.5
pH	7.5	7.8	7.7	8.4	7.7	8.1	6.9	7.6	6.4	6.9	5.6	6.4	5.4	5.8
Alkalinity	0.3	0.6	2.6	3.1	0.5	1.2	0.3	0.5	0.06	0.08	0.01	0.03	0	0.02
Ca^{2+}	3.5	10.7	48.8	54.8	11.6	23.9	7.7	11.4	1.2	1.7	1.0	1.2	0.9	1.8
Mg^{2+}	1.1	3.5	8.3	15.2	0.2	1.7	1.1	1.4	0.2	0.4	0.5	1.1	0.7	1.0
Na^+	1.7	4.6	4.1	6.9	4.9	11.4	5.0	5.9	0.9	1.5	4.3	8.6	5.5	8.5
K^+	<0.2	0.6	<0.2	1.9	<0.2	1.1	<0.2	1.8	<0.2	0.7	<0.2	<0.2	<0.2	<0.2
HCO_3^-	16.5	37.8	160	191	30.5	75.6	17.7	31.7	3.7	4.9	0.6	1.8	0	1.2
Cl^-	2.1	17.4	6.8	20.9	7.1	26.9	9.1	16.8	1.3	3.3	6.2	15.9	8.2	16.8
SO_4^{2-}	1.2	2.5	7.8	50.5	3.0	4.7	3.5	5.4	1.3	1.5	2.2	3.3	2.4	3.5
NO_3^-	0.1	0.5	0.1	0.4	0.1	0.5	0.2	0.5	0.2	0.4	0.1	1.9	0.5	0.6
Bacteria	5	155	1	64	5	355	0	24	6	50	4	910	15	135
Colour	0.5	15	0.5	4	0.5	3	0.5	1	0.5	1	4	5	0.5	2

All values in mg/l, except discharge in l/s, conductivity in μS/cm, alkalinity in mmol/l, bacteria in total colony count per ml at 20°C and colour in mg Pt/l. Q = Quaternary spring, K = Karst spring, L = Lake. For the first four sites n (no. of samples) = 14, for the last three $n = 8$.

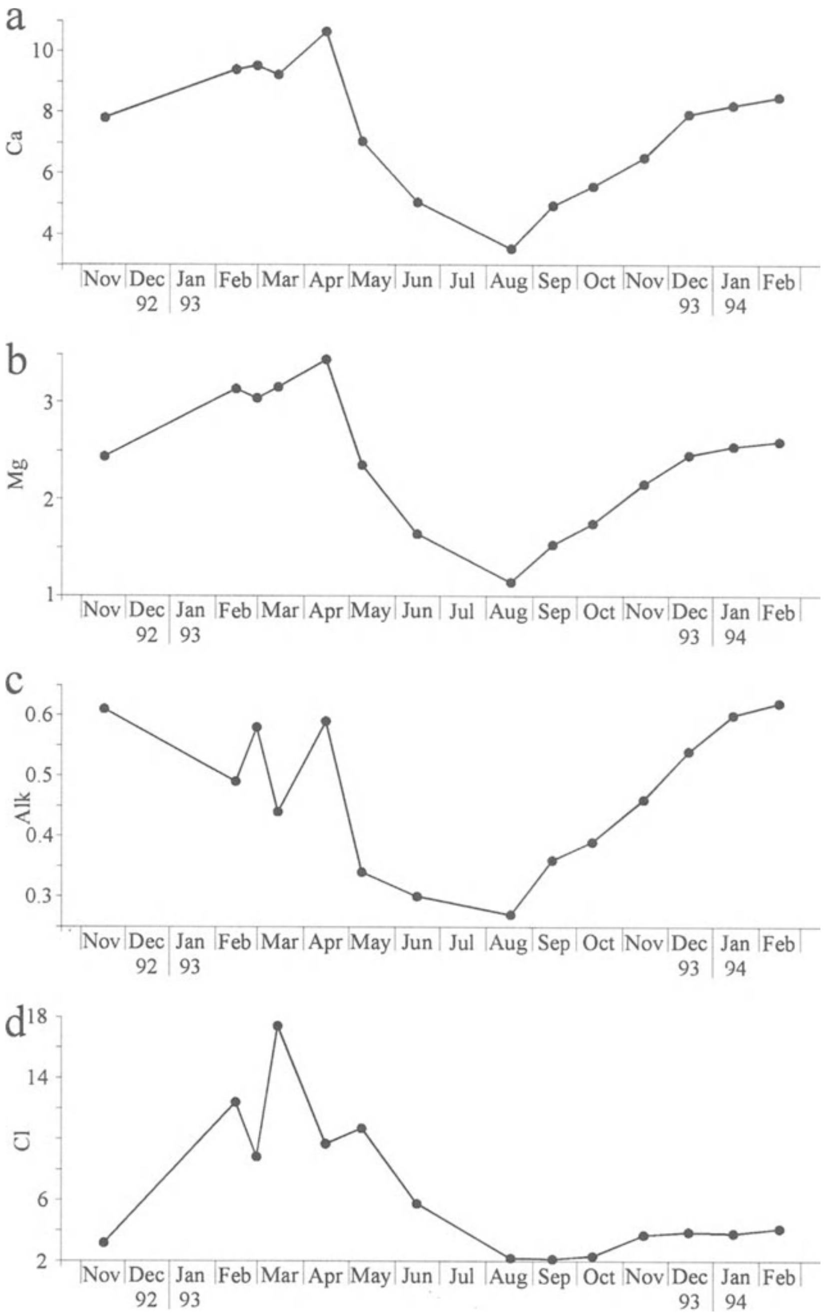


Figure 13.4 Time series for (a) calcium (mg/l), (b) magnesium concentrations (mg/l), (c) alkalinity (meq/l) and (d) chloride concentrations (mg/l) for Jordelvhav spring, Norway (November 1992 to February 1994).

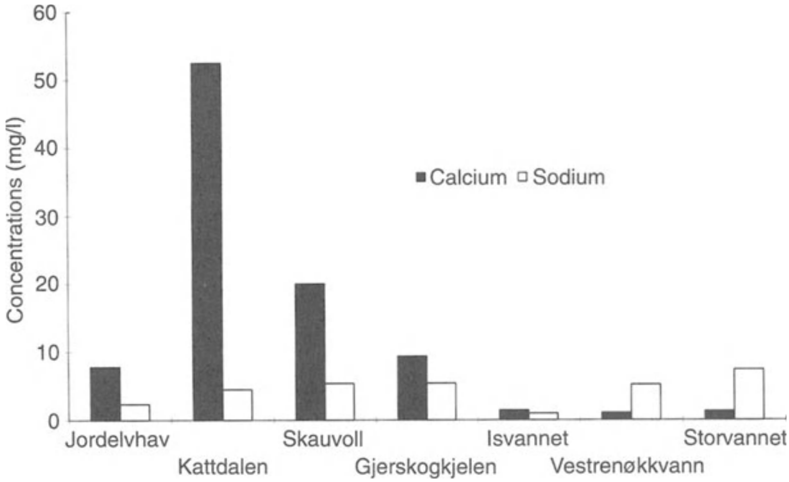


Figure 13.5 Bar diagram for comparison between Ca and Na concentrations for the seven investigated locations.

and Cl^- are during the autumn and winter storms (Statens Forurensningstilsyn, 1994).

The bacteriological quality is excellent at all sites, including the high mountain lakes. Only on one occasion were *E. coli* or coliform bacteria observed, although for some sources the total colony count exceeded 100/ml. For most of these cases, a high total colony count merely shows the presence of natural soil bacteria.

In Arctic Norway, in contrast to most temperate lands, groundwater recharge (and thus groundwater levels and discharge) often reaches a minimum in winter due to the frozen ground and the accumulation of precipitation as snow cover (Kirkhusmo, 1986; Haldorsen *et al.*, 1992). This investigation shows that, for Kattdalen and the other springs, the discharge throughout the year varies, reflecting natural, seasonal fluctuations.

13.3.1 Jordelvhav spring

The spring emerges from a southeast-facing mountainside, approximately 90 m a.s.l., on the northern side of Leirfjord (Figure 13.7). The spring is located on a high mountain face reaching up to 1100 m a.s.l. The catchment area is approximately 2 km^2, with an annual precipitation of 1300 mm. The bedrock in this area has a rather complex origin, with metamorphosed sedimentary and volcanic rocks and gneisses of Precambrian and/or Cambro-Silurian age. At the spring the bedrock is dominated by mica schist and mica gneiss. At approximately 90 m a.s.l. a calcite/dolomite marble lens, about 50 m long and 15 m high, crops out prominently from

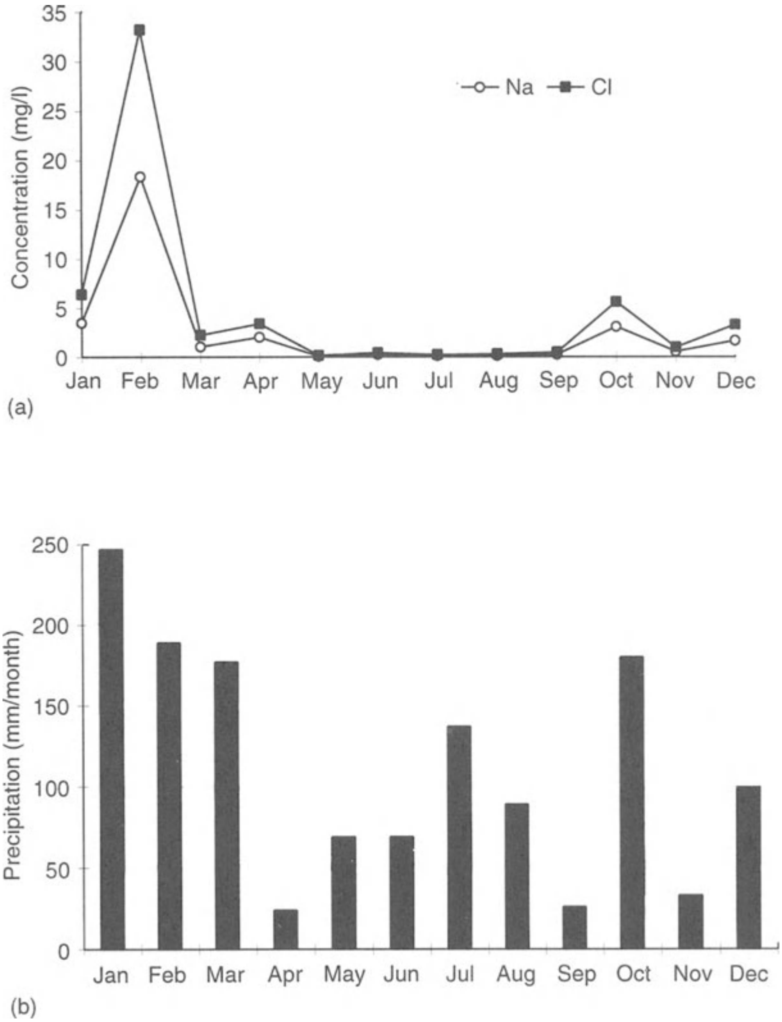


Figure 13.6 (a) NaCl content in precipitation and (b) precipitation in millimetres for 1993 at Tustervatnan, Nordland County. State Pollution Control Authority monitoring station.

the mountainside. The spring is derived from the contact zone between the mica schist and the marble, emerging through Quaternary sand deposits to a pond. During the 1993 summer season, the discharge reached 40 l/s, while the lowest flow of 7 l/s was in February 1994.

The analytical results show that the Jordelvhav spring water is of calcium–bicarbonate type (Figure 13.8), with a relatively low mineral content (conductivity 70 μS/cm), and a pH value of about 7.6. While the pH was relatively

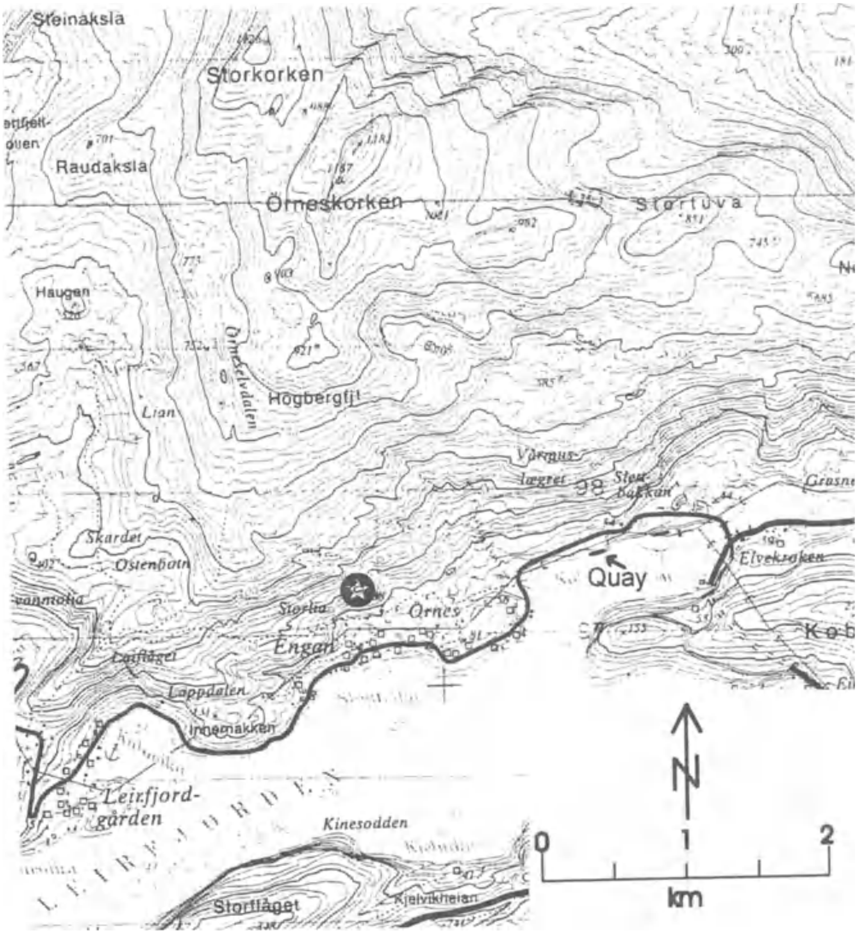


Figure 13.7 Topographical map of the area around Jordelvhav spring.

stable during the testing period, conductivity varied between 38 μS/cm (August 1993) and 99 μS/cm (March/April 1993), mainly due to changes in Ca^{2+} and Cl^-. The Cl^- content is related to sea spray and heavy winter storms/rainfall. All the analytical results show that Jordelvhav spring has an excellent bacteriological quality. On only one occasion did the total colony count exceed 100/ml.

For a number of reasons, this spring has a promising future as a source of bottled natural mineral water:

- beautiful location;
- no problems with cattle fouling (remote mountain area with steep slopes, with only a narrow shoulder separating the steep mountainside from the spring);

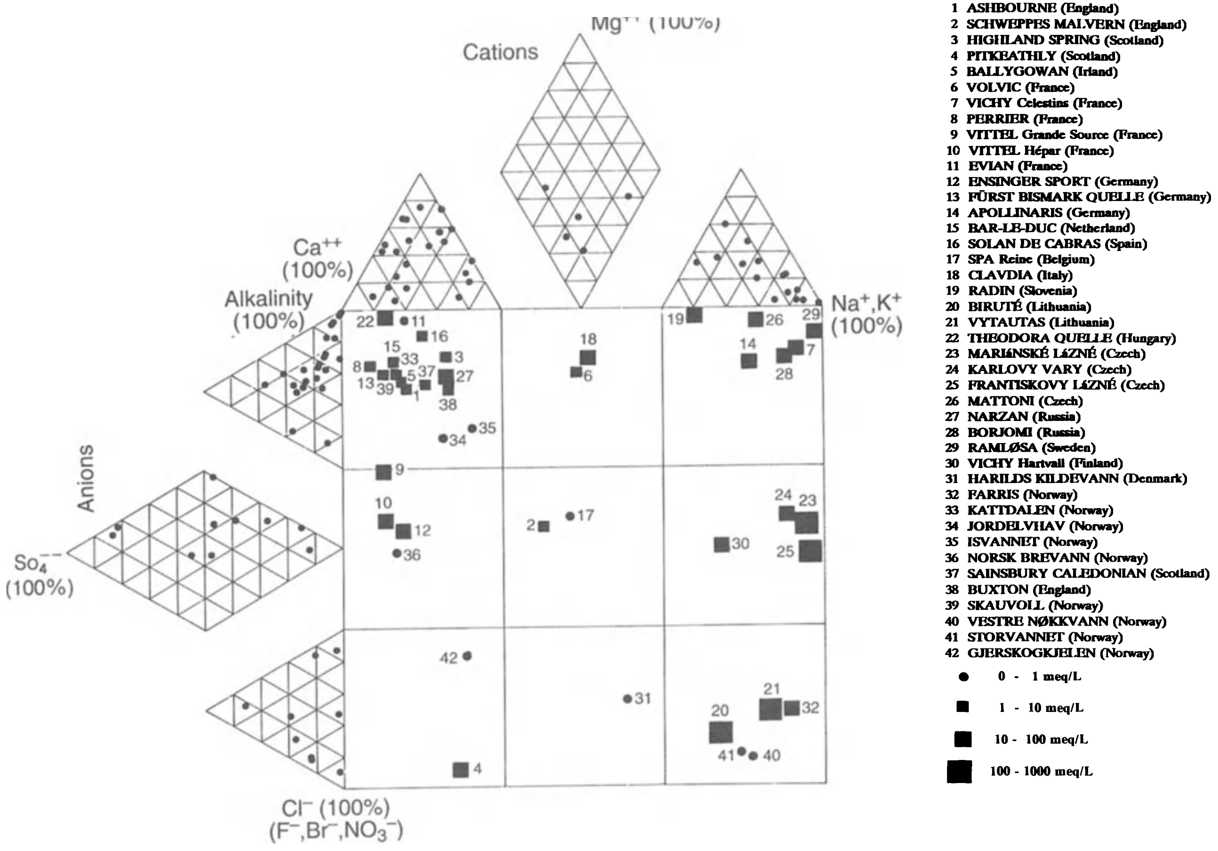


Figure 13.8 Expanded Durov diagram showing cations (as percentages) along the top and anions along the side (from Misund *et al.*, 1995). Total mineral content [(cations + anions)/2] is indicated by the symbol size. Data for the more famous mineral water types are from Green and Green (1985). The Nordland waters described in this study are nos. 33, 34, 35, 39, 40, 41 and 42. See text for further explanation.

- the production and bottling facility could be located at sea level, 90 m below the spring, allowing gravity feeding of the plant;
- the spring pond is entirely groundwater fed, with no inflows of surface water;
- the catchment area is easy to protect.

13.3.2 Kattdalen spring

The spring is situated at the present valley floor, approximately 50 m a.s.l., on the western side of the 440 m deep Saltdalen valley (Figure 13.9) at latitude 67°N. The bedrock in this area consists again of metamorphosed sedimentary and volcanic rocks and gneisses (of Precambrian and/or Cambro-Silurian age). Most of the catchment area (0.32 km^2, with an annual precipitation of 1300 mm) is autogenic with respect to marble. Part of the surface catchment is extremely steep (61°) and partially devoid of vegetation due to frequent avalanches and rock falls. The whole region is dominated by karst features, including sinkholes, caves and springs; indeed, three other springs emerge within a distance of 30 m from the studied

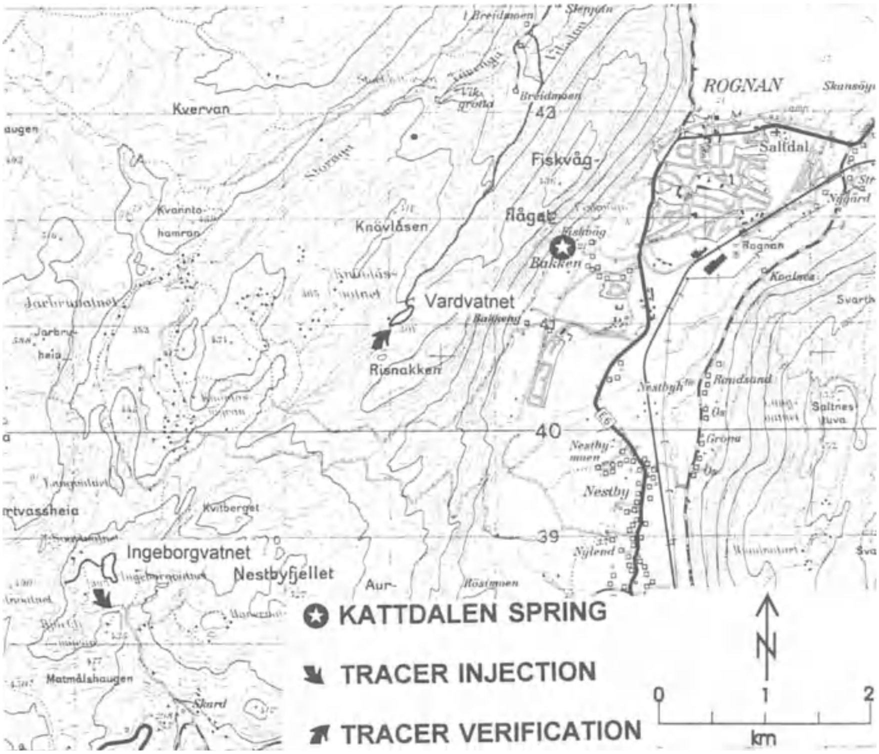


Figure 13.9 Topographical map of the area around Kattdalen spring.

karst spring. The bedding planes in the marble strike in a NE–SW direction and control the development of the karst system.

The mountain range overshadowing the spring also extends in the direction of strike, while beyond lies the valley of Lake Vardevatnet (301 m a.s.l.). It is considered possible that the Kattdalen spring water may ultimately be derived from this lake. An argument against this hypothesis, though, is that a hydraulically connected cave or fissure system must extend through the entire mountain range. A closer investigation of the sloping outcrop behind the Kattdalen spring shows that the calcite marble contains some mica schist horizons, indicating the possible presence of zones of weakness that can give rise to the development of karst features. Lauritzen *et al.* (1985) found this to be the case in the Glomdal area, where a cave follows the contact between karstified marble and impermeable mica schist. Preliminary results from a tracer experiment conducted in June 1994 suggest that there is a connection between an inflow in a sinkhole (close to Lake Ingeborgvannet) and Lake Vardevatnet (Figure 13.9). This study did not give any indication of a further connection to Kattdalen.

The analytical results show that the Kattdalen spring is a calcium–bicarbonate type of water (Figure 13.8). Important seasonal variations in discharge and pH, caused mainly by snowmelt during spring and rainfall during autumn, profoundly influence most other parameters. Interestingly the temperature displays only a slight seasonal variation, being almost constant at 4.8–4.9°C (the approximate annual mean temperature of the area), even during the snowmelt floods of spring. The water has a relatively high mineral content (conductivity 350 μS/cm) with a pH of about 8. Both the pH and conductivity were quite stable during the test period. The conductivity varies between 315 μS/cm (May 1993) and 386 μS/cm (February 1994), mainly due to changes in SO_4^{2-}, Ca^{2+} and Mg^{2+}. There are very strong positive correlations between SO_4^{2-} and Mg^{2+}, between Na^+ and Cl^-, as well as between conductivity and Mg^{2+}, SO_4^{2-} and alkalinity. A very strong negative correlation exists between conductivity and discharge. From Figure 13.3 it is obvious that the fluctuations in SO_4^{2-} are not related to sea salts. Cl^- values are much lower than those of SO_4^{2-} values, in contrast to seawater composition (where Cl^- exceeds SO_4^{2-} by a factor of ten). The elements found in solution in the Kattdalen spring water may have their ultimate source in (1) the marble aquifer rock (Ca^{2+}, Mg^{2+}, HCO_3^- and Sr^{2+}), (2) the soil/Quaternary cover and mica schist zones in the bedrock (Si and SO_4^{2-} in part), or (3) the seawater-influenced precipitation (Na^+, Cl^-, Mg^{2+} and SO_4^{2-} in part). All the analytical results show that the spring exhibits good water quality. No *E. coli* bacteria were observed, and the total colony count did not exceed 64/ml during the testing period.

The low discharge (1 l/s) recorded from the Kattdalen spring in winter 1993 is not necessarily a problem for the operation of a bottling plant, provided that water can also be tapped from other nearby springs. The time-series chemistry data for the Kattdalen spring, together with genetic implications of the various ions, are discussed in detail in Misund *et al.* (1994).

13.3.3 Skauvoll spring

The spring emerges from a north-facing mountainside, approximately 5 km south of the local municipality centre (Figure 13.10). The bedrock in this

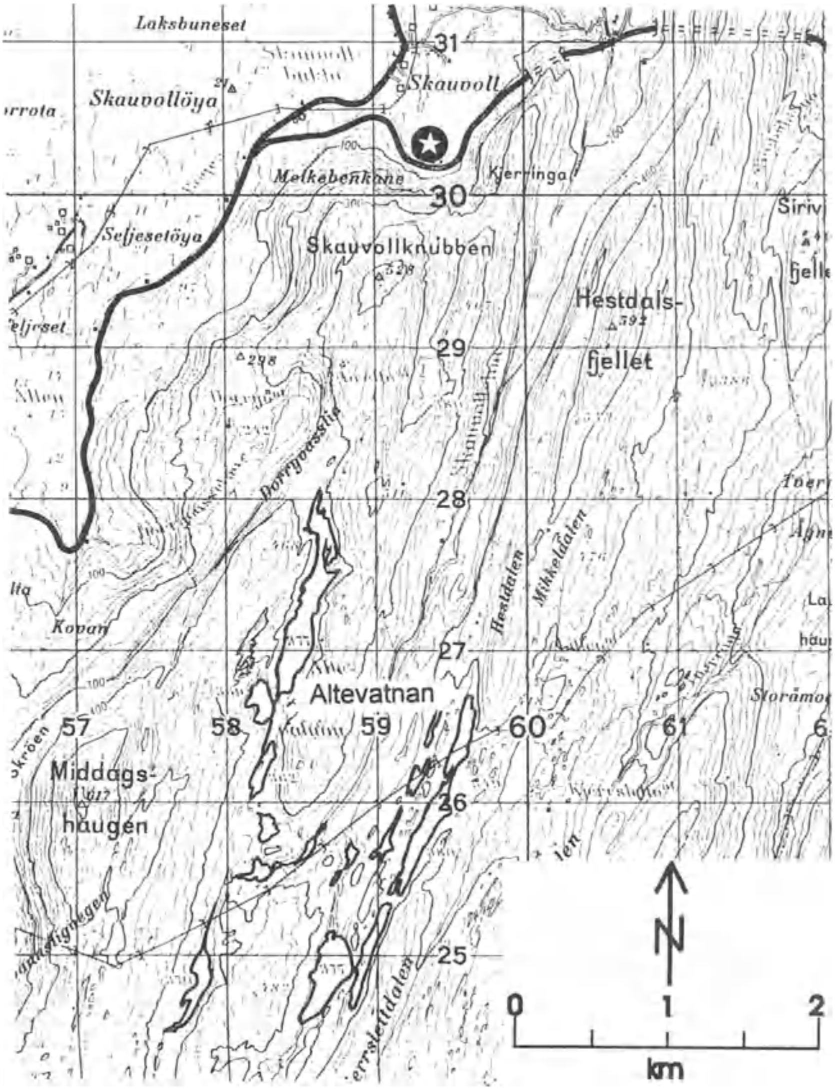


Figure 13.10 Topographical map of the area around Skauvoll spring.

area consists of metasediments, metavolcanics and gneisses of Precambrian and/or Cambro-Silurian age. At the spring the bedrock is dominated by calcite marble and dolomite marble surrounded by mica schist and mica gneiss. The spring area (15 m a.s.l.) is located at the lower part of a boulder-dominated talus of Quaternary age. At least three springs have been observed in this talus, differing in both yield and chemical composition. The survey has concentrated on the main spring in the centre of the talus. The catchment area is approximately 6 km^2, with the inflow in the area of Lake Altevatnan at 377 m a.s.l., approximately 3 km from the spring outlet. Annual precipitation is estimated as 2000 mm. Tracer experiments have indicated a travel time of approximately 3 days from sinkholes in the area of Altevatnan to the spring outlet (S.-E. Lauritzen, University of Bergen, personal communication). The spring has a high discharge, but the location is not particularly suitable for the commercial production of mineral water, due to the presence of a new road only 50 m upstream of the spring outlet.

The analytical results show that the Skauvoll spring is of calcium–bicarbonate type of water (Figure 13.8), relatively poor in mineral content (conductivity 140 μS/cm), with a pH value of about 8. While the pH was relatively stable during the test period, conductivity varied between 95 μS/cm (March and May 1993) and 160 μS/cm (April and August 1993), mainly due to changes in Ca^{2+}. High values for Cl^- in February 1993 were related to sea spray and rainfall during heavy winter storms. All the analytical results indicate that Skauvoll spring has good water quality. Only on one occasion were *E. coli* bacteria observed, and only on three occasions did the total colony count exceed 100/ml.

13.3.4 Gjerskogkjelen spring

The spring emerges from a north-facing mountainside, approximately 1.5 km from the seashore (Figure 13.11). The bedrock (yet again) consists of a complex series of metasediments, metavolcanics and gneisses of Precambrian and/or Cambro-Silurian age. At the spring the bedrock is dominated by mica schist and mica gneiss. The catchment area is approximately 6 km^2, with an annual precipitation of approximately 2000 mm. The spring is located at the foot of a steep mountain, where a large Quaternary talus abuts a finer grained Quaternary marine deposit. Superimposed on the talus is an old river channel, indicated by well rounded stones at the foot of the talus. This old river channel is considered to act as a collecting 'drain' for a large area. In front of the old river channel the marine deposits are covered by peat, which impedes any deeper outflow from the talus, forcing the water to emerge in a pond of about 9 m^2 at 45 m a.s.l. This pond then flows into a bog at 25 m a.s.l.

The analytical results show that the Gjerskogkjelen spring water is a mixture of calcium-bicarbonate and sodium–chloride water types (Figure 13.8).

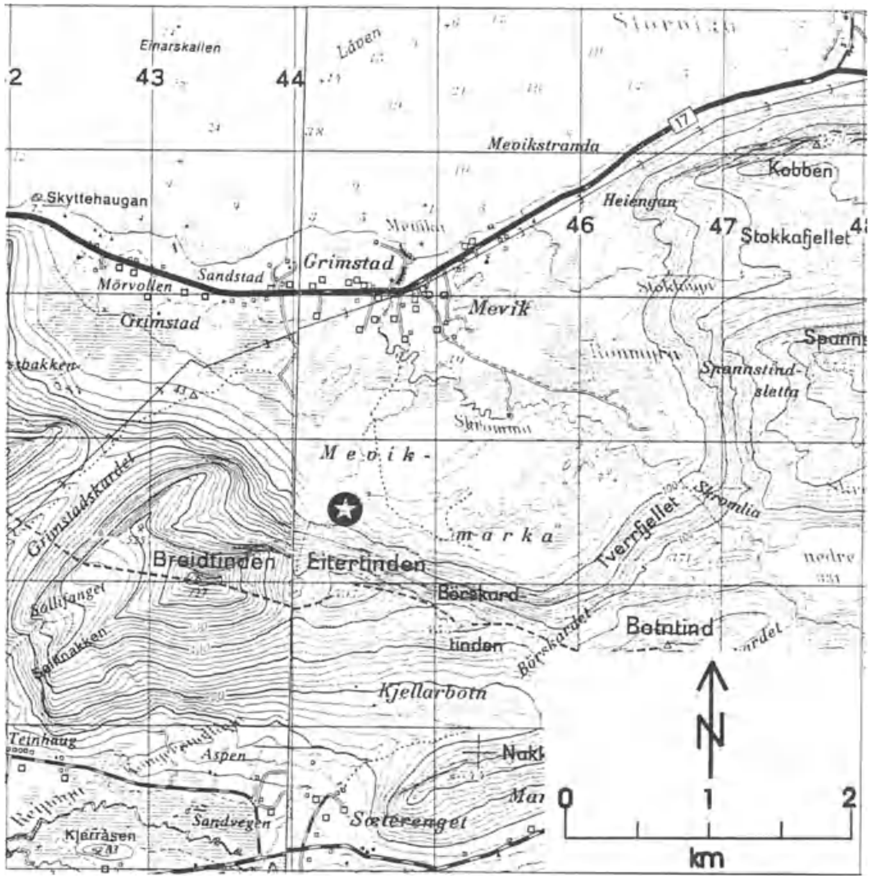


Figure 13.11 Topographical map of the area around Gjerskogkjelen spring.

The contribution of sodium chloride is due to the location only 1.5 km from the seashore. The water is relatively poor in mineral content (conductivity 90 μS/cm), with a pH value of about 7.3. Both pH and conductivity were relatively stable during the test period. Conductivity varied between 80 μS/cm (June 1993) and 104 μS/cm (February 1994), mainly due to changes in Ca^{2+} and Cl^-, while pH varied between 6.9 (May/June 1993, due to snowmelt) and 7.6 (November 1992 and February 1994). High values of Cl^- are related to sea spray and rainfall due to heavy winter storms. All the analytical results indicate that the spring has good water quality. No *E. coli* bacteria were observed, and the total colony count did not exceed 24/ml during the test period.

The low discharge in winter (possibly as low as 1 l/s) can be a limiting factor, but Gjerskogkjelen spring has a number of advantages for the production of natural mineral water:

- no conflict with cattle fouling (steep slopes, and narrow shoulder between the steep slope and the spring);
- good protection from pollution sources due to the considerable thickness of Quaternary deposits surrounding the spring discharge.

13.4 SPRING WATER, MINERAL WATER OR PACKAGED WATER?

Up to 1995 there was only one Directive concerning bottled water in Norway. After the ratification of the EØS trade agreement between the European Union and Norway, Norwegian legislation adopted the relevant EC Directive. Throughout Norway, much political pressure has recently been exerted to improve standards of drinking water generally (Ellingsen and Banks, 1993). Norwegians are not a natural market for bottled water, as they generally consider themselves to have an abundance of good quality water 'on tap' at their homes. In recent years, bottled water has slowly become more popular as a fashionable drink and Norwegians have also recognized the export potential of 'pure, Nordic' bottled water to the pollution-ridden lands of continental Europe and the UK.

In the interest of protecting the consumer, the EC has produced a Mineral Water Directive (80/777/EEC, modified in 1996 by Directive 96/70/EC, which relates mainly to the treatment allowed). In this Directive 'Natural mineral water' is defined as

> microbiologically wholesome water, originating in an underground water table or deposits and emerging from a spring tapped at one or more natural or bored exits.... [Natural mineral water can, in addition,] ... be clearly distinguished from ordinary drinking water:
>
> (a) by its nature, which is characterised by its mineral content, trace elements or other constituents and, where appropriate, by certain effects;
> (b) by its 'original' state,
>
> both characteristics having been preserved intact because of the underground origin of such water, which has been protected from all risk of pollution. The composition, temperature and other essential characteristics of natural mineral water must remain stable at source within the limits of natural fluctuation; in particular, they must not be affected by possible variations in the rate of flow.

In the Norwegian version of the Directive, 'in the rate of flow' is substituted with the rather meaningless term 'due to movement in the ground'; thus, there is no explicit demand for stable chemistry relative to rates of flow. Investigations of Jordelvhav, Kattdalen, Skauvoll and Gjerskogkjelen springs show that important seasonal variations in flow and conductivity do occur, with concomitant fluctuations in water chemistry, mainly due to

Table 13.2 A high mineralization bottled water from continental Europe compared with the Norwegian Norwater from Imsdalen (see Figure 13.14a, b) – = not specified

Parameter	*Concentration (mg/l)*	
	Ensinger Sport	*Norwater*
Li^+	0.6	–
Na^+	29.5	1
K^+	7.7	–
Ca^{2+}	501.0	12
Mg^{2+}	155.6	–
F^-	0.4	–
Cl^-	28.3	–
NO_3^-	1.8	0
SO_4^{2-}	1550.0	4
HCO_3^-	393.4	37
pH	–	6.7–7.3

snowmelt in spring and increased precipitation in autumn. For most Norwegian springs, such variations are normal (Haldorsen *et al.*, 1992); it is thus an open question whether these springs can be approved as natural mineral waters, or if they are indeed affected by 'movement in the ground'. Wells with a constant yield or 'rate of flow' can also show seasonal variations in their chemical composition (Storrø, 1995) and thus the meaning of the expression 'natural variation' will be crucial for the verification of any source as natural mineral water.

In the Mineral Water Directive there are very few explicit standards given for a mineral water's chemical composition, despite the fact that some constituents may far exceed the standards given in the Drinking Water Directive (80/778/EEC). One example is the German mineral water Ensinger Sport (Figure 13.13), which contains 155 mg/l Mg (Table 13.2), while Norway and the EU define 20 mg/l and 50 mg/l respectively as their MACs (maximum admissible concentrations), based on the possible laxative effects. The quality of the bottled mineral water is in fact only controlled by the specification that 'the natural mineral water may not contain any organoleptic defects' and by parameters regarding bacterial content, e.g. among other specifications, no *E. coli*, coliforms, pathogenic organisms or faecal streptococci. The bacterial standards are designed to ensure that 'the revival total colony count of a natural mineral water may only be that resulting from the normal increase in the bacteria content which it had at source'. These criteria are intended to ensure that the source is not anthropogenically contaminated with bacteria and that bacteria are not introduced during the bottling procedure. As regards 'natural' bacterial content, at source, this should not exceed 20/ml, but this has to be considered as a guide figure and not as a maximum permitted concentration. Traditionally, this has not been a problem in Europe, where mineral water has been pumped from up to several hundred metres depth, where there is relatively little bacterial activity. LeClerc (1992) writes that bottles of effervescent or sparkling mineral waters are normally free of microorganisms, whereas flat mineral water contains 10^3 to 10^5 revivable microorganisms per millilitre. This microbial content of flat waters reflects normal growth of the microorganisms present at source, as specified by the Council Directive.

13.5 HYDROGEOCHEMISTRY

The composition of groundwater reflects both the mineralogical composition of the aquifer and the geographical location. Groundwaters from carbonate-rich aquifers (e.g. Kattdalen and Jordelvhav, nos. 33, 34 in Figure 13.8) are typically dominated by calcium and bicarbonate ions. Investigations of surface water in Nordland also show that areas underlain by carbonate rocks have good overall drinking water quality with a high alkalinity (Nilsen, 1990). The near-coastal environment can be noted in the generally mineral poor, but sodium chloride dominated nature of most Norwegian surface water sources (nos. 40 and 41 in Figure 13.8). Waters from aquifers overlain by, or which interfinger with, marine clays may also have a high sodium chloride content (e.g. Farris, no. 32 in Figure 13.8). Additionally, the composition will be affected by kinetic factors, such as the residence time in the formation during which mineral–rock interaction can take place. Many Norwegian groundwaters and surface waters tend to be rather mineral poor, due to

- the prevailing high topographical gradients and fast throughflow times; and
- the rather inert, silica-rich nature of much of the bedrock.

The waters from the Skauvoll (limestone aquifer) and Gjerskogkjelen (mica schist) springs have a rather curious character (nos. 39 and 42 in Figure 13.8). The cation content is dominated by calcium, but the anion content, though typically dominated by bicarbonate, can be dominated by chloride during some periods. The chloride content significantly outweighs the sodium content. Chloride is usually regarded as a conservative parameter, being derived from marine salts and having no significant lithological origin in most shallow groundwaters (Banks *et al.*, 1993), but here it appears that one of two processes occurs in these springs. Either (1) the excess chloride is being derived from mineral–water interactions or (2) sodium is being removed by some form of ion exchange reaction for calcium.

The waters investigated in Nordland have, generally speaking, low mineral contents (Figure 13.12). This is not necessarily a disadvantage; different parts of the world have their own favourite taste (Figure 13.13). While, in

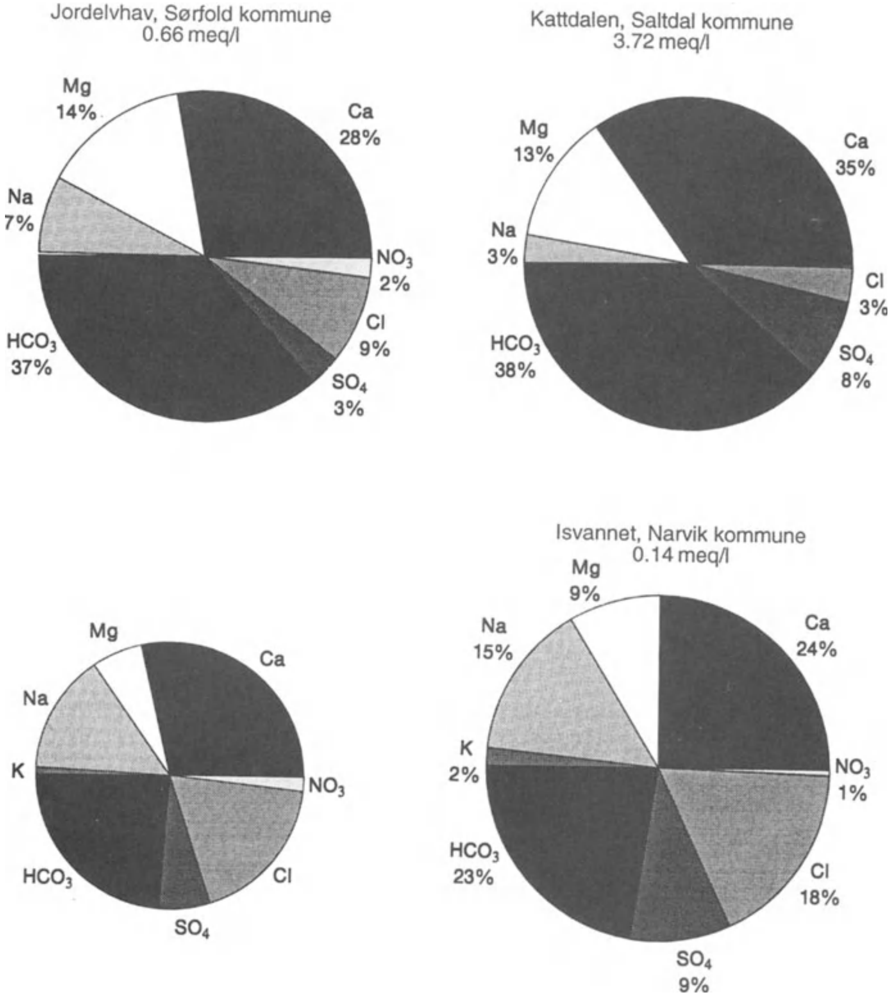


Figure 13.12 Pie diagrams showing the chemical composition of the seven locations investigated in Nordland.

Lithuania, people drink fizzy salt water, the Japanese prefer water with a low to very low mineral content, such as that we have found in Nordland. Indeed, Norwegians also consume low mineralization waters, as evidenced by the sales of 'Norwater' from Imsdalen in Østerdalen, farther south in Norway (Figure 13.14a; Figures 1.4 and 1.6). By adding CO_2, even the very mineral-poor water from the surface water sources in Nordland can acquire a more exclusive character, finding its own niche in the bottled water market.

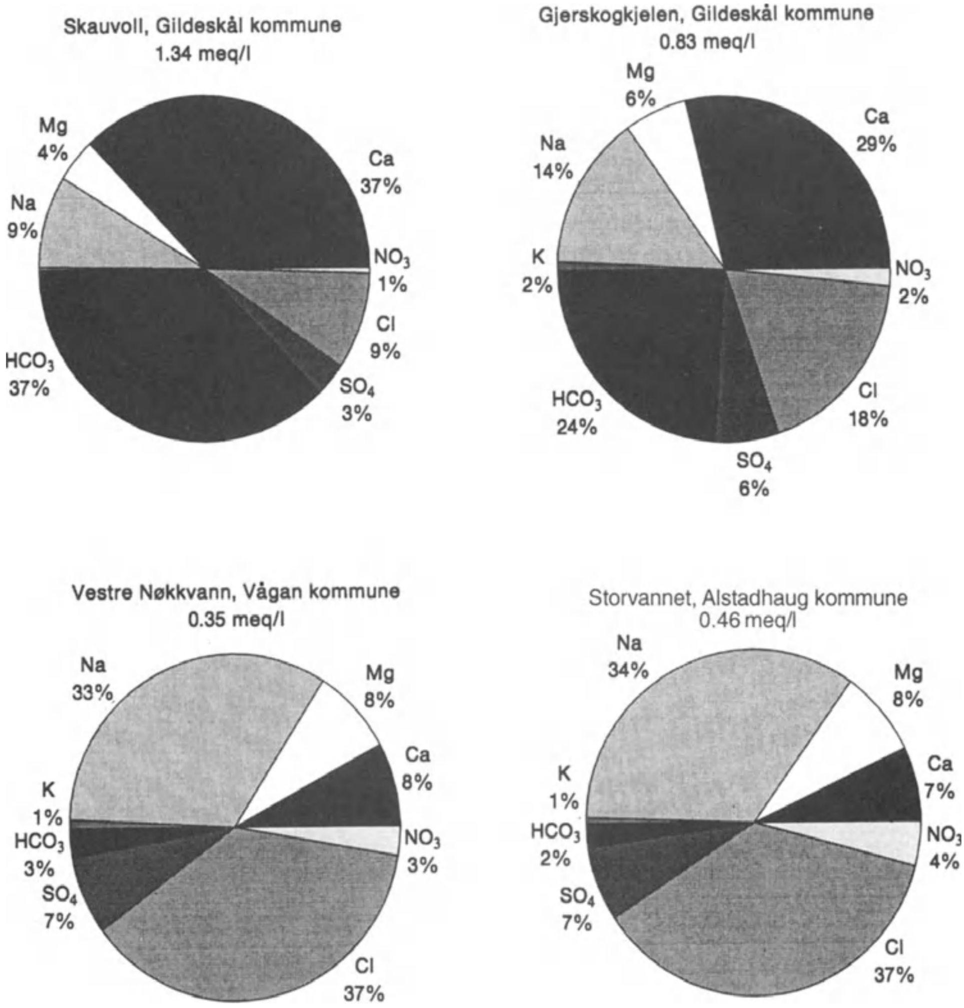


Figure 13.12 Continued.

13.6 LOGISTICAL CONSIDERATIONS

The investigation has, of course, involved considerations of the possibilities for export of water from Nordland. Deserved or not, Norway has an image as an unpolluted and undisturbed country in the far north. In particular, Nordland is one of the most unpolluted regions in Norway and several types of bottled water might find their way onto the market:

- packaged surface water from high altitude lakes;
- groundwater from the springs described above;
- natural waters extracted from the deposits in front of several hundred-year-old glaciers.

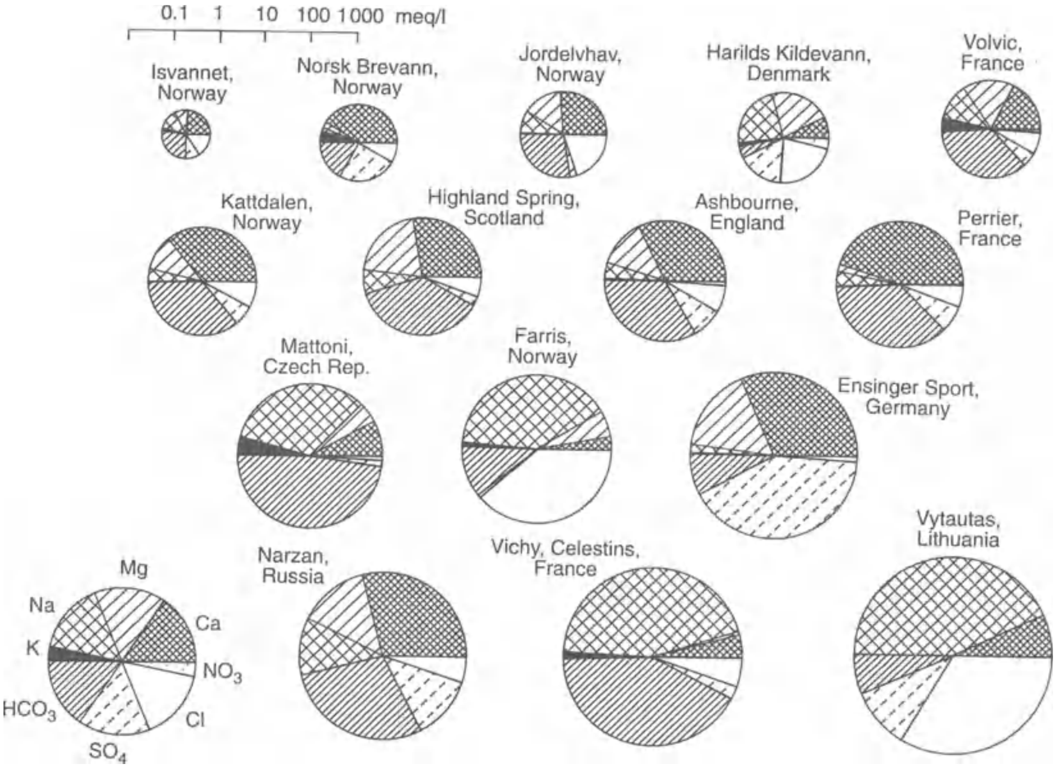


Figure 13.13 Pie diagrams showing the chemical composition of a range of mineral waters. Diameter is related to mineral content [(cations + anions)/2] according to the logarithmic scale in the top left. The key is situated to the lower left. (From Misund and Banks, 1994, with permission of Geological Society Publishing House.)

To be economically viable, any source has to have a capacity of 150 million bottles per year, or a yield of 5–10 l/s. Because of the large potential volume, it is important that the product can be transported at as low a cost as possible. To make this possible, the water source should be close to an adequate transport facility. In north Norway this usually means a quay (preferably an already existing one) that can take container ships of the size of 10–25 000 dwt. The water will ideally be transported by pipeline under gravity to a bottling factory at the quay. To keep the total cost as low as possible, it is important that there is no internal transport between the factory and the ship. Thus the following conditions should be met for any water source in Nordland to be viable:

- the export has to be to an international market; the home market in Scandinavia is too small to achieve profitability;
- the volume has to be at least 50–100 million litres per year;
- the source should be close to a quay;
- it is regarded as necessary to obtain a sales agreement for a minimum period of 5 years before establishing a factory.

13.7 EXPORT POSSIBILITIES

In Germany consumption of bottled water increased by 11.4% between 1989 and 1990 to 5.5 billion litres; in the UK it increased by 56% to 360 million litres. In Western Europe as a whole the consumption increased by 11.2% to 22.2 billion litres. Germany, France and Italy alone account for 75% of the European consumption of bottled water. These three nations and, in particular, Germany, thus represent a key export market.

In Germany, waters are categorized into the groundwater types, 'Naturlisches Mineralwasser' (Figure 13.14b) and 'Quellewasser', and the surface water types, 'Abgefulltes Trinkwasser' (without CO_2) and 'Tafelwasser' (with CO_2). Mineral water is recognized in the market as the premier quality product (which also commands the highest price), while flat surface water is at the bottom end of the price range. The consumers' choice of container also varies between the different countries: in Germany the market is dominated by glass bottles of carbonated water, while the English seem to prefer PET bottles and still water.

For Norwegian surface waters, marketing the water too strongly on the basis of its origin is not legal (e.g. ultraclean environment, sub-Arctic, etc.). The strongest permissible phrasing would be something like 'clean water from Norway'. It is thus possible to conclude that Norwegian surface water would be very difficult to market in a country such as Germany. One alternative possibility would be to carbonate it mildly and market it as 'Tafelwasser' with low mineral content.

Any water product should ideally be introduced as a supplementary product for an already well established distributor. The price should be

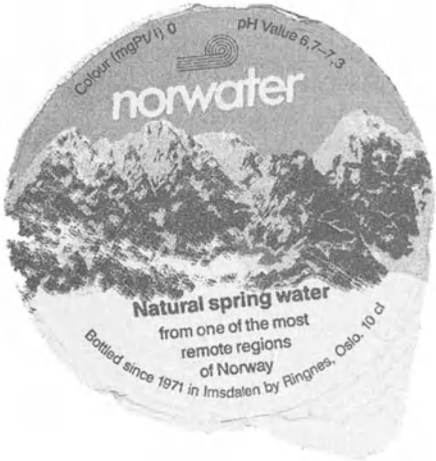
Na⁺ (sodium) = 1 mg/l
Ca²⁺ (calcium) = 12
SO_4^{2-} (sulfate) = 4
HCO_3^- (bicarbonate) = 37
NO_3^- (nitrate) = 0
pH = 6.9–7.1

1.5 l

norwater®

Spring water from Imsdalen - Norway. Not carbonated
Kildevand fra Imsdalen - Norge. Uden kulsyre
Kallvatten från Imsdalen - Norge. Utan kolsyra

Bottled since 1971
in Imsdalen by:
Tappet siden 1971
i Imsdalen av:
RINGNES A/S,
OSLO NORWAY



Colour (mgPt/l) 0
pH Value 6,7–7,3

norwater

Natural spring water
from one of the most
remote regions
of Norway

Bottled since 1971 in Imsdalen by Ringnes, Oslo. 10 cl

MINERAL-HEILQUELLEN
ENSINGEN

0,7 l

Ensinger

SPORT

Natürliches Mineralwasser mit Kohlensäure
versetzt, aus der Ensinger Mineralquelle.

Auszug aus der amtlich anerkannten Analyse des Inst. Prof. H. Gockel, Stuttgart vom 02.06.89. Bestätigt durch Kontrollanalyse vom 15.04.91.

Kationen:		mg/l	Anionen:		mg/l
Lithium	Li^+	0,6	Fluorid	F^-	0,4
Natrium	Na^+	29.5	Chlorid	Cl^-	28.3
Kalium	K^+	7,7	Nitrat	NO_3^-	1,8
Calcium	Ca^{2+}	501,0	Sulfat	SO_4^-	1550,0
Magnesium	Mg^{2+}	155.6	Hydr. Carb.	HCO_3^-	393,4

4 002343 001504

Mit dem wertvollen
Magnesiumgehalt

28.07.96 09
Mindestens haltbar bis:

Ensinger Mineral-Heilquellen GmbH · 7143 Vaihingen/Ensingen around 4.5 NOK/litre (about £0.45 sterling or 0.55 ECU), slightly above the average price, which may be justifiable on the basis of perceived Norwegian 'purity'. This means that the producer has to deliver to the distributor in, say, Germany at a price of 3.0 NOK (2 NOK being accounted for by the cost of the PET bottle and transport). Advertising costs are projected to be around NOK 1 million per year for a duration of 2–3 years.

13.8 DISCUSSION AND CONCLUSIONS

The monitoring programme in Nordland has demonstrated that all the analysed springs meet the standards set by the EC Drinking Water Directive. Taking into consideration water quality, location and flow rate, Jordelvhav spring stands out as the most promising candidate for commercial production of bottled water. Kattdalen spring is very well investigated (e.g. Misund *et al.*, 1994), but has a low flow rate in winter and is not as favourably located from a logistical point of view.

The EC Mineral Water Directive emphasizes that 'The composition, temperature and other essential characteristics of natural mineral water must remain stable at source within the limits of natural fluctuation; in particular, they must not be affected by possible variations in the rate of flow.' This Directive is mainly concerned with bacterial pollution.

For the Kattdalen spring, the fluctuation in discharge throughout the year varies from 1 l/s to 25 l/s, reflecting natural seasonal variations. A seasonal variation of the chemical parameters is also observed and whether these variations are within the limits of the definition of the term 'stable' in the Mineral Water Directive is an open question. These variations are, in any event, affected by 'the rate of flow'.

Generally speaking, the waters that have been monitored in Nordland County have very low total mineral contents. This is not necessarily a disadvantage; different water types suit different cultures. While East Europeans are used to drinking semi-seawater, low salinity waters, such as those from Nordland, are preferred by the Japanese. Kattdalen and Jordelvhav spring waters are classified as calcium–bicarbonate waters with a low mineral content, and many Scandinavians may find them preferable to the more mineral-rich Norwegian water, Farris. For a sodium–chloride type of water with a lower mineral content than Farris, possible candidates are the Vestre Nøkkvann water or the Storvannet water (nos. 40 and 41 in Figure 13.8).

Figure 13.14 (a) Norwater, a very low mineralization water from a source in Imsdalen, Østerdalen, Norway, and sold in bottles and cartons (see Table 13.2). (b) Ensinger Sport mineral water from Ensingen in Germany (155 mg/l Mg^{2+}; see Table 13.2).

The three sources from coastal high mountain lakes cannot be recognized as natural mineral waters; thus the need for extensive documentation of raw water quality is limited. Water from these lakes can be commercialized as ‘packaged water’ or ‘general water’. Indeed, the EC Drinking Water Directive allows the packaging and marketing of water ‘from any source, including water which is known to be bacteriologically unsafe in its raw state and which has a significant proportion of waste water in its make-up, as long as it can satisfy the chemical and bacteriological standards after treatment’ (Finlayson, 1992).

ACKNOWLEDGMENTS

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14

The mineral and thermal waters of the Krušné Hory rift valley, Czech Republic

Zbyněk Hrkal

14.1 INTRODUCTION

Despite the small area of its territory (90 000 km^2), the Czech Republic can be, in a certain sense, considered a nation of abundant hydrogeological resources. More than 100 mineral water springs are exploited and several thousand others are registered. In particular, the extremely diverse geology of the Bohemian Massif is reflected in the huge variety of its different types of mineral groundwaters. For example, cold acidic springs occur in very close proximity to thermal or radioactive mineral waters, high in H_2S and arsenic. The 'balneal triangle' of west Bohemia has acquired a worldwide reputation due to the famous spas of Karlovy Vary, Mariánské Lázně and Františkovy Lázně (Figure 14.1).

Geologically, the western part of the Bohemian Massif consists of a crystalline complex of Proterozoic and Palaeozoic rocks dominated by phyllites, schists, gneisses and migmatites. These are intruded by several phases of Variscan granites (the 'older' and 'younger' granites). The emplacement of the younger granites was associated with pneumatolysis (the alteration of host rocks by gaseous substances other than water, such as hydrogen fluoride or boron fluoride). This pneumatolysis gave rise to abundant greisens (pneumatolysed rocks containing fluorine-rich micas, topaz and/or tourmaline) associated with pneumatolytic–hydrothermal Sn–W–Mo–Li deposits and other mineralization.

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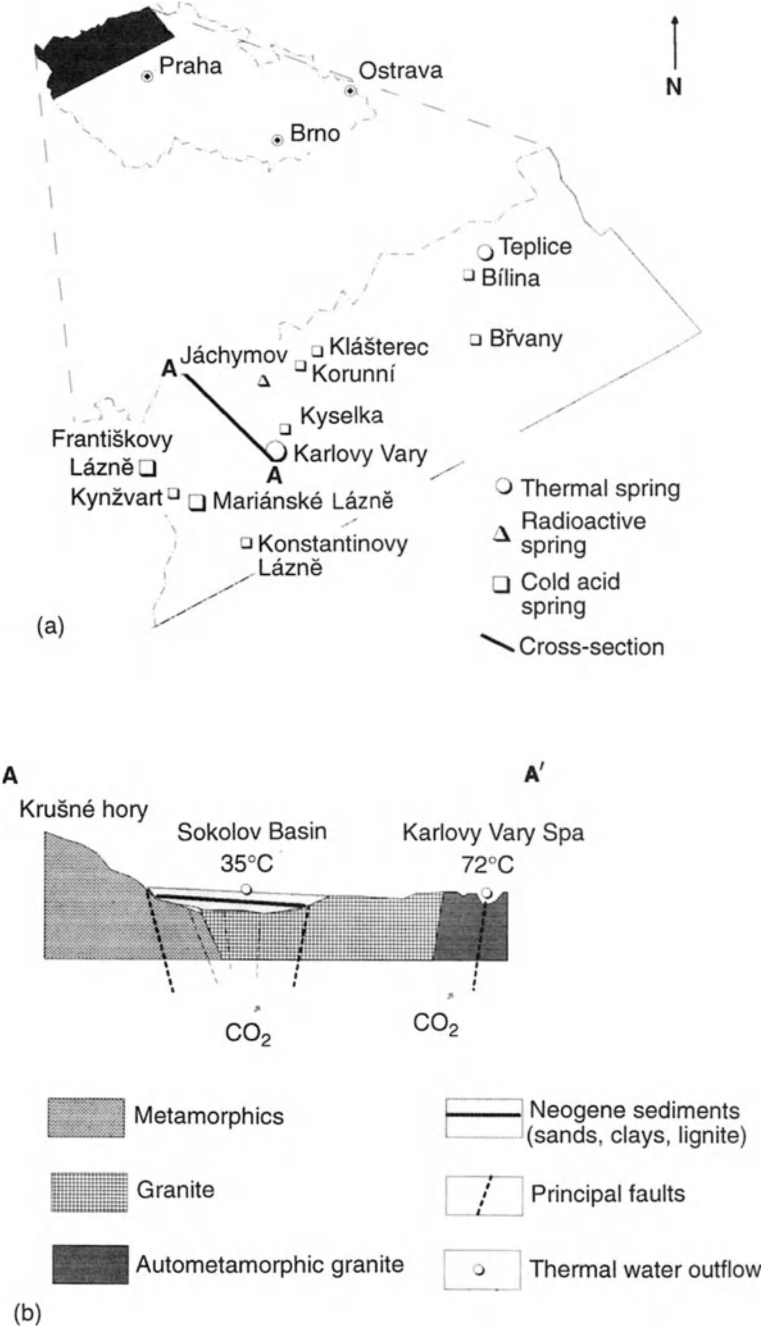
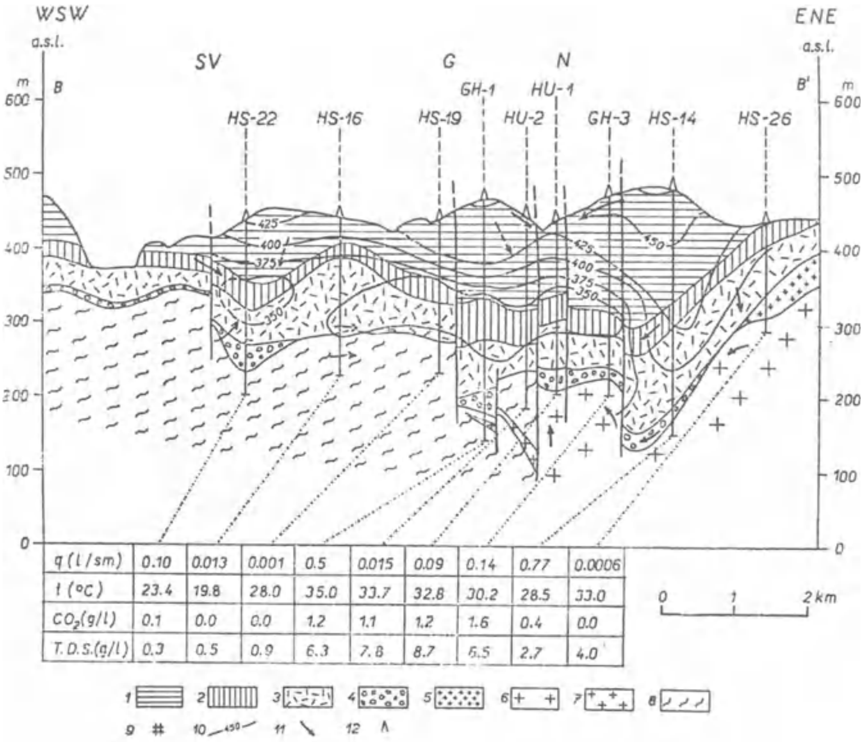


Figure 14.1 (a) The balneal triangle of western Bohemia and (b) a schematic section A–A′ across the Sokolov Basin.



q (l/sm)	0.10	0.013	0.001	0.5	0.015	0.09	0.14	0.77	0.0006
t (°C)	23.4	19.8	28.0	35.0	33.7	32.8	30.2	28.5	33.0
CO_2(g/l)	0.1	0.0	0.0	1.2	1.1	1.2	1.6	0.4	0.0
T.D.S.(g/l)	0.3	0.5	0.9	6.3	7.8	8.7	6.5	2.7	4.0

Figure 14.2 More detailed WSW–ENE section along the Sokolov Coal Basin. (1) Cypris claystone, (2) Main Seam formation, (3) volcanogenic series with Josef Seam at base, (4) Staré Sedlo basal clastics, (5) primary kaolin, (6) normal granite, (7) leucocratic granite to aplite, (8) metamorphics, (9) Marie Majerová mine, (10) groundwater equipotentials (heads in metres a.s.l.), (11) direction of groundwater flow, (12) boreholes. Borehole pumping test data for the basal aquifer; q = borehole specific capacity, t = temperature of pumped water at surface, CO_2 and TDS are carbon dioxide and total dissolved solids in water, respectively. (After Jetel, 1970. Copyright Czech Geological Society (UUG), reproduced with permission.)

Once the major Variscan orogenic movements ended, the whole mountain range was uplifted along a master fault and later broken into several large blocks. Morphologically, the most pronounced feature is represented by the huge, fault-bounded Krušné hory or North Bohemian rift valley. This is infilled with Tertiary sediments consisting mostly of clayey deposits and the infamous sulphur-rich lignites or brown coals (Tyrácek *et al.*, 1990), whose exploitation and combustion have been blamed for significant air, water and soil pollution in the border area of the Czech Republic, Poland and the former DDR (Hrkal, 1992). Major movements along longitudinal and transverse faults, trending NE–SW and NW–SE respectively, occurred contemporaneously with the formation and development of Tertiary basins.

However, the maximum fault displacement in the rift valley, of up to several hundred metres, largely took place towards the end of the Pliocene. A more detailed section through the rift valley is shown in Figure 14.2.

The origin of the thermal and mineral waters is intimately related to the geologically recent volcanism of the area. The Tertiary period was characterized by volcanic activity, including the development of the large basalt stratovolcano of the Doupovské hory Mountains, straddling the rift valley, and some smaller effusions scattered throughout western Bohemia. Volcanic activity declined during the Quaternary, although one of the most recent volcanic episodes in Central Europe, active in the Pleistocene, can be found at Komorní hůrka Hill, just 3 km southwest of Františkovy Lázně.

The distribution and location of mineral springs in the area are mostly controlled by structural phenomena, particularly by faults related to the rift zone of the Krušné hory Mountains. The rift zones are typically infilled by Tertiary sediments consisting of lignite, clays, silts and sands. These sediments also play a role in controlling the location of mineral and thermal water springs: they may to some extent act as reservoirs for groundwater, where mixing with juvenile CO_2, ascending from underlying bedrock takes place, as at Soos and Frantiskovy Lazne, and they may also exert a confining influence. Most of the mineral water springs in west Bohemia can be described as cold acidic waters, with juvenile dissolved fluids, such as CO_2. This CO_2 is considered to be derived from postvolcanic activity, i.e. released from a magmatic chamber. Several thermal springs are found in the central part of the Krušné hory rift zone and are believed to be related to the elevated geothermal heat flow of the area (Figure 14.3). All these thermal springs lie on the so-called 'Bohemian thermal line' running from Karlovy Vary

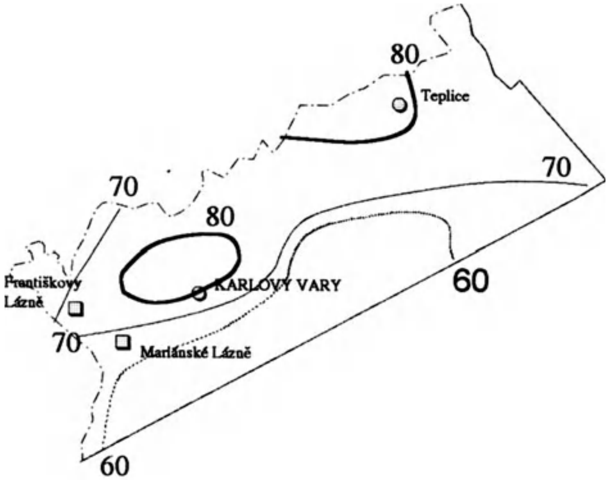


Figure 14.3 Geothermal heat flow in western Bohemia (mW/m^2).

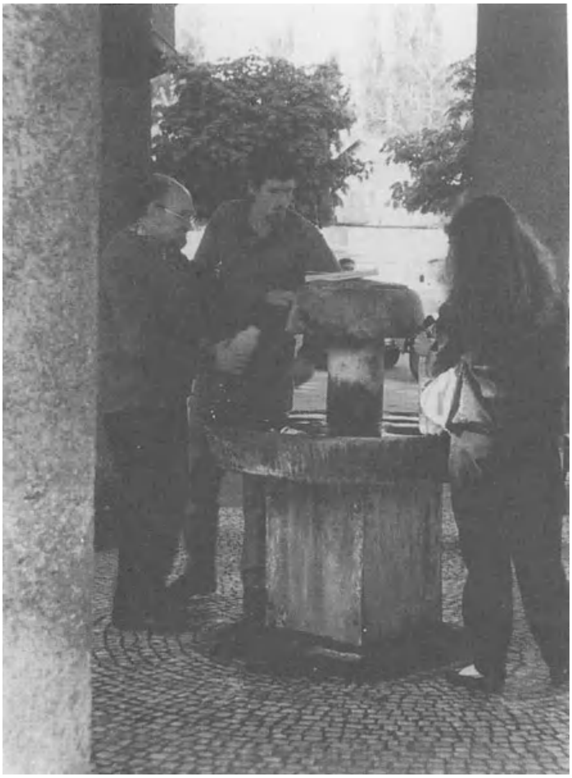


Figure 14.4 Hydrogeologists from the Czech Geological Survey vie with locals to obtain containers full of mineral water at Poděbrady, east of Prague. (Photo by David Banks.)

(73°C) to Jáchymov (28°C) and Teplice (49°C). Most of the waters have a high mineralization, which is probably related to the elevated CO_2 content and temperature of most waters, as well as to the residence times in the aquifer system.

The mineral waters of western Bohemia represent the best known, but by no means the only, mineral and thermal water resources of the Czech Republic (Figure 14.4). Readers are referred to the excellent maps produced by Franko *et al.* (1985) for a full survey of Czech and Slovak mineral waters, together with analyses of which a selection is given here (Table 14.1).

14.2 KARLOVY VARY

Utilization of the local thermal springs at Karlovy Vary (the German 'Carlsbad'), which are supersaturated with CO_2, for curative purposes started

Table 14.1 Composition of mineral waters at western Bohemian spas (compiled from Franko *et al.*, 1985)

Town	*Karlovy Vary*	*Karlovy Vary*	*Františkovy Lázně*	*Hájek*	*Teplice*	*Jáchymov*	*Lázně Kynžvart*	*Prameny*	*Konstantinovy Lázně*
Source	*Mlýnský*	*Mattoni*	*Glauber III*	*Císařský*	*Pravřídlo*	*Bore HG-1*	*Richard*	*Betonová Jímka*	*Bore BV-11*
Type	Catchpit	Bottled water	Borehole	Catchpit	Catchpit bore	Borehole	Catchpit	Well	Borehole
Yield (l/s)	0.05	–	0.9	0.7	11.4	9.1	0.2–0.6	0.3	2.0
pH	6.9	–	6.2	7.5	6.8	8.1	5.7	4.9	5.3
Temperature (°C)	52.1	–	12.5	15.0	39.0	34.2	8.0	6.8	13.3
Gas content: Total (ml/l)	486.6	–	1211.5	903.2	–	–	–	–	–
Gas content: Non-acid (ml/l)	15.2	–	–	–	14.5	–	–	4.7	–
CO_2 content (mg/l)	–	3100	2301	1714	–	–	2715	2250	1730
Gas composition (Vol%)[a]	d	–	d	d	–	–	–	s	d
CO_2	96.8	–	99.7	99.0	–	–	–	98.2	99.72
N_2	2.45	–	–	0.9	–	–	–	0.7	–
Non-acid gases (%)[a]	d	–	d	d	d	–	–	d	–
N_2	78.5	–	91.0	80.0	95.0	–	–	95.7	–
O_2	20.0	–	6.7	11.5	3.0	–	–	1.36	–
Ar	1.13	–	2.1	2.2	2.0	–	–	2.6	–

TDS (g/l)	6.5	1.58	10.1	5.6	1.0	0.7	0.2	0.4	0.9
Si (mg/l)	25.3	23.7	30.2	46.9	32.6	29.5	11.4	–	27.2
Cations (mg/l)									
Na^+	1713.0	274.8	3221.0	1575.0	231.8	144.7	7.98	8.5	101.0
K^+	98.0	58.4	63.5	37.1	11.9	11.1	2.06	1.5	12.8
Mg^{2+}	37.3	20.75	41.3	24.3	9.5	4.4	8.22	23.1	37.1
Ca^{2+}	135.9	59.38	185.3	71.1	43.0	17.0	26.9	34.0	38.1
Fe^{2+}	–	–	15.0	40.1	–	–	–	38.0	40.8
Mn^{2+}	–	0.174	–	–	–	–	–	–	–
Anions (mg/l)									
Cl^-	607.7	11.2	1306.0	594.6	50.1	7.2	5.87	5.3	42.6
F^-	6.07	4.02	–	–	7.5	–	–	–	–
SO_4^{2-}	1639.0	24.5	3975.0	1769.0	125.4	15.2	29.1	27.6	11.5
HCO_3^-	2163.0	1060.0	1939.0	1469.3	560.0	390.5	105.0	288.6	593.1
Rn (Bq/l)						8880			

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[a] d = dissolved gas, s = spontaneously released gas.

Figure 14.5 Mattoni, a mineral water from Karlovy Vary. See Table 14.1 for composition.

several hundred years ago. Legend says that Karlovy Vary was founded by the Czech king Charles IV in 1358, who discovered the hot springs when hunting deer. The locality subsequently became famous worldwide, reaching its zenith in the 19th century with visits from such luminaries as Beethoven, Brahms, Bismarck, Liszt, Paganini, Peter the Great, Schiller and Tolstoy. The town is still a popular resort and tourist area, attracting foreign visitors due to its proximity to Germany and Austria. The spa area lies along the valley of the River Teplá (Figure 14.6), immediately south of its confluence with the Ohře, and is surrounded by easily accessible wooded hills.

The thermal springs are located in a granite massif at the intersection of several fault zones. The waters are thought to be derived from rainfall recharge on the hills to the northwest of the town. The waters are believed to circulate to a depth of some 2000 m, before ascending to the surface along the fault pathway, having mixed with deep juvenile CO_2, rising along the fault zones. The CO_2 comes out of solution during the ascent providing extra density-driven artesian head. The chemical compositions of the various springs are very similar, regardless of their temperature (maximum 73°C), indicating that they are all derived from ostensibly the same flow path. The waters of the Karlovy Vary spring system (e.g. Figure 14.5) are classed as CO_2-rich, sodium–sulphate–bicarbonate–chloride, with a total dissolved solid content varying between 6.0 and 6.6 g/l. A total of 29 springs are registered at the locality, but 95% of the whole utilized capacity (2500 l/min) comes from the major 'Vřídlo' spring. This is an attractive geyser, spouting to a height of up to 12 m, forming the centrepiece of the Karlovy Vary spa.

Figure 14.6 The River Teplá in Karlovy Vary; the steam is from a discharge point for thermal waters. (Photo by David Banks.)

The springs originally rose from the bed of the Teplá, but now the waters are tapped by means of boreholes and the river bed has been artificially sealed. The spring waters continue to drain into the Teplá, however, depositing lime-rich travertine on the river bed.

Lignite mining is forbidden from the Tertiary sediments of the rift valley in the immediate vicinity of Karlovy Vary, for fear of 'puncturing' Tertiary strata which may exert a confining effect on the rising thermal waters.

Pačes (1974) notes the high concentrations of sulphate and chloride in the waters compared with the Cl and S content of the granites of the area (about 0.03% Cl and 0.01–0.2% S). He does not rule out the possible origin of sulphate in the oxidation of sulphides at depth in the granite, nor the derivation of chloride from chlorine in biotite, apatite or fluid inclusions. He does, however, express doubt that the quantities present are sufficient and implies that the injection of hydrogen sulphide or hydrogen chloride, as well as carbon dioxide, at depth must be a possibility.

14.3 MARIÁNSKÉ LÁZNĚ

Utilization of the mineral water springs of Mariánské Lázně (the German 'Marienbad') commenced at the end of the 16th century, and the first bathing facilities were built in 1710. Analyses were undertaken by J.G. Zeuschner of Karlovy University, Prague, in 1766. Under the patronage of the abbot of the Teplá Monastery, K.K. Reitenberg, the spa developed and expanded. Mariánské Lázně was declared a spa in 1818, some springs being used for drinking water purposes and some for bathing and bottling. The geologist J.W. Goethe was a frequent visitor: he collected the minerals and rocks of the area and published a brief geological guide. He also dabbled in literature; as well as epics such as *Faust*, he wrote *Marienbader Elegie*, dedicated to Ulrika von Levetzow. A total of 46 springs are presently utilized with an overall yield of about 500 l/min. The town probably forms the centre of Czech spa culture and the various springs can be sampled at drinking fountains throughout the length of the town (Figure 14.7). At the more popular of these, serving ladies guard racks of personal drinking pots reserved for regular customers.

Geologically, the Mariánské Lázně area is underlain by various types of metamorphic and igneous rocks (Figure 14.8), which can be divided into three units (Pačes, 1974).

Figure 14.7 The pavilion and spring at Ferdinandův pramen (spring) in Mariánské Lázně. (Photo by David Banks.)

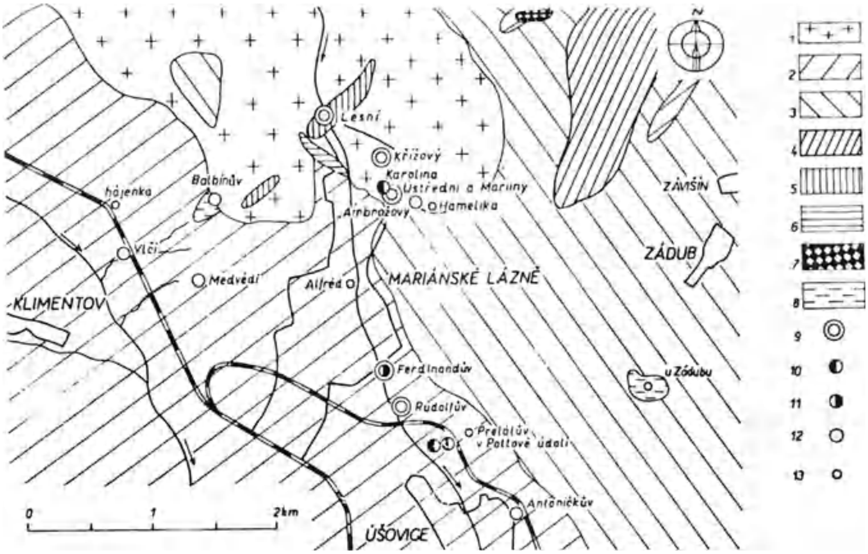

Figure 14.8 Geological map of the Mariánské Lázně area, showing locations of the main springs. (1) Granite, (2) gneiss, (3) amphibolite, (4) garnet pyroxene gneiss, (5) diorite, (6) quartzic breccia, (7) basalt and (8) peat. (After Kolářová and Myslil, 1979. Copyright Czech Geological Survey (UUG), reproduced with permission.)

- The sillimanite and biotite paragneisses, graphitic gneiss and quartzite forming the Tachov Plain, west of the town.
- The amphibolites, with gneisses, marbles and serpentinites, of the Mariánské Lázně complex forming the Slavkovský les Mountains and Tepelská plošina Upland to the east and northeast of the town. These are penetrated by a small Permian biotite granite body and two Tertiary basaltic dykes.
- The Bor biotite granite massif south of the town.

The town of Mariánské Lázně lies approximately at the junction of these units, on the trace of the Mariánské Lázně fault zone. This zone runs for 90 km, starting in southwestern Bohemia and ending in the Cheb Basin. It separates the Tachov Plain unit from the Slavkovský les/Tepelská plošina Upland, and is believed to form the main rising conduit for the mineral waters and associated gases.

Acidic, carbon dioxide-rich waters are generally derived from shallow depths and are relatively cool. It is thought that the hills surrounding the spa (the Slavkovský les Mountains and Tepelská plošina Upland) form the recharge area for the waters which, having descended to depths of 100–150 m (indicated by the water temperature of 7–10°C, about 1–2°C above mean annual air temperature; Pačes, 1974), rise along fault zones, where they undergo mixing with deep juvenile carbon dioxide rising along the

Table 14.2 Chemical composition of various springs at Mariánské Lázně; samples taken in period 1966–1974 (Kolářová and Myslil, 1979)

Spring	*Lesní*	*Křížový III*	*Ambrož*	*Ferdinand II*	*Rudolf 'starý'*	*Medvědí*	*Balbínův*	*Antoníčkův*	*Rudolf I + II*
Type, depth	Well, 7 m	Bore, 45 m	Well, 7 m	Bore, 20 m	Bore, 26 m	Well, 0.5 m	Bore, 6 m	Well, 1 m	Well, 3 m
Yield (l/s)	0.25	0.02	0.2	0.4	0.25	0.07	1.0	0.1	0.2
Temperature (°C)	10.0	7.0	10.2	10.2	7.5	7.1	7.8	7.8	6.5
TDS (g/l)	3.50	9.49	0.70	9.48	2.05	1.78	1.33	1.12	1.90
pH	5.95	6.11	5.82	6.35	5.77	5.5	5.5	5.7	5.76
CO_2 (mg/l)	2631	2896	2761	2165	2444	1928	2068	2464	1861
B (mg/l)	0.54	1.0	0.25	1.9	0.21	–	–	–	0.22
Si (mg/l)	42.6	35.6	16.5	49.16	40.4	25.2	35.1	28.8	32.6
Cations (mg/l)									
Li^+	1.8	5.0	0.1	3.52	0.37	0.89	0.41	0.14	0.30
Na^+	710.5	2588	69.2	2385	80.4	418.0	91.5	31.5	51.2
K^+	26.1	46.3	6.4	51.6	9.9	10.7	13.8	4.2	8.1
NH_4^+	0.1	0.26	1.2	0.86	0.15	0.0	0.0	0.17	0.17
Mg^{2+}	104.9	92.5	28.9	153.7	122.2	36.5	83.9	48.4	113.8
Ca^{2+}	105.4	148.0	54.3	241.2	232.7	45.1	106.2	171.5	244.7
Mn^{2+}	0.25	0.58	1.1	0.94	0.65	0.4	1.12	0.37	0.46

Fe^{2+}	22.2	28.4	22.4	27.9	16.0	13.0	30.2	13.4	13.6
Anions (mg/l)									
Cl^-	178.3	857.9	24.1	955.4	31.8	150.7	70.9	17.7	18.5
F^-	0.17	0.30	0.08	0.32	0.15	–	–	0.27	0.15
NO_3^-	0.0	0.0	0.0	–	–	0.6	<0.6	0.0	–
SO_4^{2-}	622.6	2945	96.7	2606	83.1	426.0	152.6	29.1	178.9
HPO_4^{2-}	0.38	0.74	1.3	0.07	0.41	1.03	0.75	0.16	0.47
HCO_3^-	1724	2770	391.8	3044	1468	677.2	774.9	803.2	1264
Trace (μg/l)									
Ba	40	40	14	40	113	–	–	60	135
Sr	600	850	140	1860	221	–	–	345	284
V	0.3	1.1	5.6	2.9	2.2	–	–	–	0.3
Ni	35.8	13.6	–	1.4	–	10.8	66.0	706	–
Zn	118	12.6	64.5	17.4	22	38.0	55.0	20.6	41
Cu	25.3	13.7	11.1	8.1	5.7	14.4	6.8	–	5.2
Al	50	4310	37.8	40	41	–	–	30	135
As	–	470	29.0	65	26	101.4	157	–	32
						Co = 7.8	Co = 17.8	Br^- = 110	
						Be = 0.87	Pb = 1.0	I^- = 90	
						Pb = 1.0			

Table 14.3 Dissolved gas content (mg/l) of selected mineral waters from Mariánské Lázně (after Pačes, 1974)

Spring	*Křížový III*	*Křížový IV*	*Antoníček*	*Rudolf 'starý'*	*Lesní*	*Ferdinand VI*	*Ferdinand I*
CO_2	2896	2474	2464	2444	2631	3440	2508
N_2	6.94	6.79	9.25	3.55	4.21	3.22	6.92
H_2S	0.096	0.008	0.0	–	0.0	–	0.0
O_2	–	–	–	0.0	–	0.0	–

Ferdinand IV also discharges a gas phase at a rate of 0.014 l/s, containing 99.35 vol% CO_2, 0.65% N_2 and 0.0% O_2.

same faults. The exsolution of carbon dioxide, as the waters near the surface, reduces the density of the water, aiding the rise still further. The dissolved mineralization of the waters is otherwise closely related to the composition of the rocks through which they ascend. The spring waters fall into one of three hydrogeochemical groups, corresponding to the dominant aquifer type:

- Mg^{2+}–HCO_3^- waters: ultrabasic rocks (e.g. serpentinite), occurring some 8 km north of the town;
- Ca^{2+}–HCO_3^- water: basic rocks (e.g. amphibolite), in the southern part of the town;
- Na^+–HCO_3^-, SO_4^{2-}, Cl^-: granites, in the northern part of the town.

Some chemical analyses are given in Table 14.2. The contents of dissolved solids vary considerably from 0.3 to 11.6 g/l, while the dissolved CO_2 ranges from 2.0 to more than 3.4 g/l (e.g. Table 4.3), depending on the mineralogy of the rocks through which the waters ascend. The total yield of the more than 140 acidic springs of the Mariánské Lázně region is relatively small, varying between 300 and 450 l/min, i.e. considerably lower than that of Karlovy Vary.

Stable isotope measurements of ^2H and ^{18}O confirm that the waters are of meteoric origin. The $\delta^{13}C$ readings are typically in the range 0 to −4‰ (Table 14.4), similar to those found at Karlovy Vary.

Table 14.4 Stable isotope measurements from water and gas from springs in the Mariánské Lázně area (after Pačes, 1974)

Spring	*Ferdinand I*	*Balbín spring*		*Podhorní myslivna (W. of Mariánské Lázně)*	*Nimrod*
Type of sample	Aqueous solution	Aqueous solution	Gas	Dry gas discharge	Dry gas discharge
δ^2H ‰SMOW	−66.4	–	–	–	–
$\delta^{18}O$ ‰SMOW	−10.5	–	–	–	–
$\delta^{13}C$ ‰PDB	–	−0.5	−3.9	−2.5	−2.5
$\delta^{34}S$ ‰CDT	+5.2	–	–	+2.3	–

14.4 FRANTIŠKOVY LÁZNĚ

This locality, formerly known by the German name of 'Franzenbad', represents one of the oldest Bohemian spas (Figure 14.9). The first reports of the cold sulphate–alkaline springs in the vicinity of today's Františkovy Lázně spa date from 1196. Later, bottling plants were built in 1600 and 1660. The spa itself was founded in 1783. At present 23 springs are utilized, having a total yield which fluctuates between 700 and 1000 l/min depending on the rate of atmospheric precipitation.

The springs occur in the Cheb sedimentary basin of Tertiary age (Figure 14.10), which is about 80 m thick in the vicinity of the spa. The Tertiary sediments, consisting of sands, clays and lignite, overlie granites and Palaeozoic phyllites. The spa lies approximately over the subcropping contact between the phyllites and granites. The waters, which are high in Na^+ and SO_4^{2-}, are thought to have originated in the weathered near-surface parts of a granite body and in the overlying basal Tertiary sediments. The carbon dioxide content of the water is likely to be derived from depth, probably from discontinuities along the contact of a granitic body with its phyllite mantle. Ascendant carbon dioxide rises along faults to form secondary accumulations in the Tertiary sedimentary sequence. The CO_2-charged spa waters then ascend to the surface through faults or discontinuities in the Tertiary sequence. Elevated Cl^- contents, characteristic of many of the mineral waters, are believed to have resulted from leaching processes and enrichment in a zone of deep catamorphic mineralization.

Figure 14.9 Františkovy Lázně. (Photo by David Banks.)

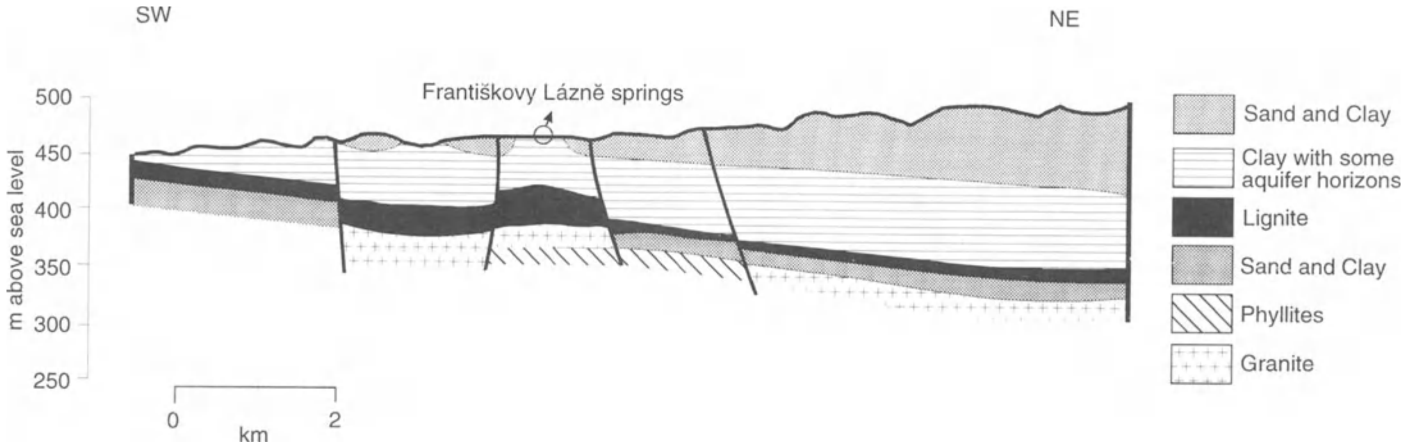

Figure 14.10 Schematic cross-section across the Cheb Coal Basin.

The maximum content of dissolved solids in the Františkovy Lázně area is found in the Glauber IV spring (23 g/l). The Kostelni spring claims a content of 0.5 mg/l dissolved arsenic. The amount of free CO_2 in the mineral water varies between 1.5 and 2.5 g/l. Exhalations of dry CO_2 are also used for therapeutic purposes at Františkovy Lázně.

14.5 HÁJEK–SOOS

The mineral–thermal mofette complex at Soos, near the village of Hájek, in the vicinity of Františkovy Lázně, is unique in largely retaining its natural state, never having been developed into a spa (Figures 14.11, 14.12). It is not totally unexploited, and the area has been worked for peat (for combustion), while mineral-impregnated sulpho-ferruginous peats have been exported to Karlovy Vary for therapeutic purposes, and a salt factory once extracted mineral salts from the springs (Brož, 1989). In addition, the locality is mined for kieselguhr, a siliceous diatomite, which is used as an

Figure 14.11 Mofettes at Soos. (Photo by David Banks.)

Figure 14.12 The Emperor Spring at Soos. (Photo by David Banks.)

adsorbent, a filter medium and an abrasive. The diatoms are believed to have flourished in a shallow lake impregnated with rising mineral waters.

The geology of the Soos area consists of some 10 m of peat and diatomite overlying about 40 m of Neogene sediments which in turn overlie granitic crystalline basement. The Neogene sediments act as a reservoir for groundwater, which mixes with impregnating juvenile fluids (e.g. CO_2) from the basement. The peat and diatomite act as a confining layer. Mineral waters and gases rise via discrete fractures or pipes in the confining layer to occur as springs or mofettes at the surface. The most significant mineral water spring is the Pramen Císařský (Emperor or Kaiser Spring), which overflows into an iron-stained ceramic vessel. It has a total dissolved solids content of up to 6.5 g/l (Brož, 1989) and 40 mg/l iron. The 'Vera' spring at Soos is perhaps notable on the grounds of its low mineralization, only about 0.18 g/l. Several exhalations of dry CO_2 through cone-shaped funnels give rise to impressive mofettic 'mud volcanoes'.

14.6 JÁCHYMOV

Radioactive thermal waters were discovered at Jáchymov during mining, which dates from the 16th century. However, utilization of the local radioactive water did not commence until 1908, following several years of testing their purported healing properties. Radioactive springs are found at the 12th level of the Svornost mine; these occur in mica schists forming the mantle of a granite body extending from the Karlovy Vary pluton. The radioactive thermal springs have a vadose origin and are dominated by sodium–bicarbonate hydrogeochemistry. The maximum content of dissolved solids is 0.72 g/l, the radon content has been cited as being as high as 13 000 Bq/l (Kačura *et al.*, 1968), while the mean temperature is 25–28°C.

15

The spa of Buziaş, Romania

Mircea U. Feru and Adrian Feru

15.1 POSITION AND BRIEF HISTORY

The spa town of Buziaş is situated in the southeastern part of the Romanian Plain, at the border between the plain and the hills of Banat, about 30 km southeast of Timişoara (Figure 16.1). Mineral waters are found in the upper terrace of the Timiş river along the Salcia Valley, which has a maximum width of 8 km. The waters here are similar in character to those of Spa (Belgium), Royat (France) and Bad Pyrmont (Germany).

The locality is first documented in a decree of 1321 by King Carol Robert of Anjou. In 1811 Professor Paul Kiteibel analysed the water from three shallow wells and revealed the high CO_2 content (more than 1000 mg/l) and the therapeutic value of the waters. His research formed the basis of the development of the locality, especially after 1819 when it was declared a balneological resort.

Under the leadership of Dr Lindenmayer, who was the physician here between 1830 and 1839, two dug wells named the St Joseph and St Michael springs were developed. The use of the mineral waters for internal treatment and the initiation of mineral water bottling in 1840 made the resort famous.

Treatment was diversified, with a hydrotherapy building being completed in 1858. In 1896 the railway was inaugurated between Timişoara and Buziaş and the ferruginous bath (Bath no. 2) modernized. Thus Buziaş became well known in Europe and in 1898 it was visited by Emperor Franz Josef.

Due to the ever increasing water requirements, in 1903 a borehole was drilled to a depth of 103 m. This produced an artesian flow of water at 6.6 l/s, with free CO_2, to a height of 40 m above the surface. Because of the richness in CO_2, the owner decided to set up a bottling plant for CO_2 that started operation in 1907.

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Because of the high water levels (meaning low pumping costs), and the therapeutic properties and pleasant taste of the water, the factory decided to establish a section for mineral water bottling in 1908. A shallow well called Phoenix Springs was drilled for this purpose, and gave its name to the bottling company. The daily production was 2000 1-litre bottles of mineral water and 600 kg of CO_2. To avoid the inconvenience of iron deposition, a filtering plant and reimpregnation station for enrichment of the bottled water with CO_2 were built. The mineral water was awarded the gold medal at the International Exhibition of Bratislava in 1908.

Exploitation of the therapeutic mineral waters and CO_2 increased after World War II and a modern bottling station was built. The annual production was about 30 million litres of mineral water for consumption and about 1 million kg of CO_2.

15.2 GEOLOGY AND OCCURRENCE OF GROUNDWATER

The region comprises metamorphic formations overlain by sedimentary deposits of Pliocene and Quaternary age (Figure 15.1).

The metamorphic formations are mainly gneiss and sericite–chlorite schists. They are exposed to the southeast of the resort, forming the hill of Silagiu which reaches an elevation of 325 m. The schists are intercepted by boreholes which are 75–80 m deep in the east of the resort, increasing to 137 m in the west (Figure 15.2). The network of faults and fissures allows groundwater flow.

The metamorphic rocks are overlain by Pliocene (Pontian) sedimentary deposits. These are made up of an irregular sequence of fine sands with gravel lenses, argillaceous sands, clays and sandy clays. The layers usually have a lenticular development. The Pliocene deposits are the main mineral water resource, comprising an aquifer complex with very variable hydrogeological characteristics. A small proportion of groundwater recharge is due to downward leakage from the overlying Quaternary deposits, but much of the recharge occurs by direct infiltration in the outcrop area, around the base of Silagiu hill.

The lower aquifer horizon, which lies directly above the crystalline basement, has an upward hydraulic gradient. In the area of the resort this is manifested as artesian flow, due to the very large amounts of free gas (CO_2) causing a natural lifting phenomenon. The discharge of pumped wells in this aquifer complex varies between 2 and 6 l/s for 4–13 m of drawdown, while the sources with artesian flow have discharges between 0.1 and 2.5 l/s.

The Quaternary sediments are sands, sandy clays and gravels 1.5–4.0 m thick, directly overlying the Pontian sands. The area of Silagiu hill and the terraces are covered by a thin, silty–sandy–clay deposit of diluvial origin.

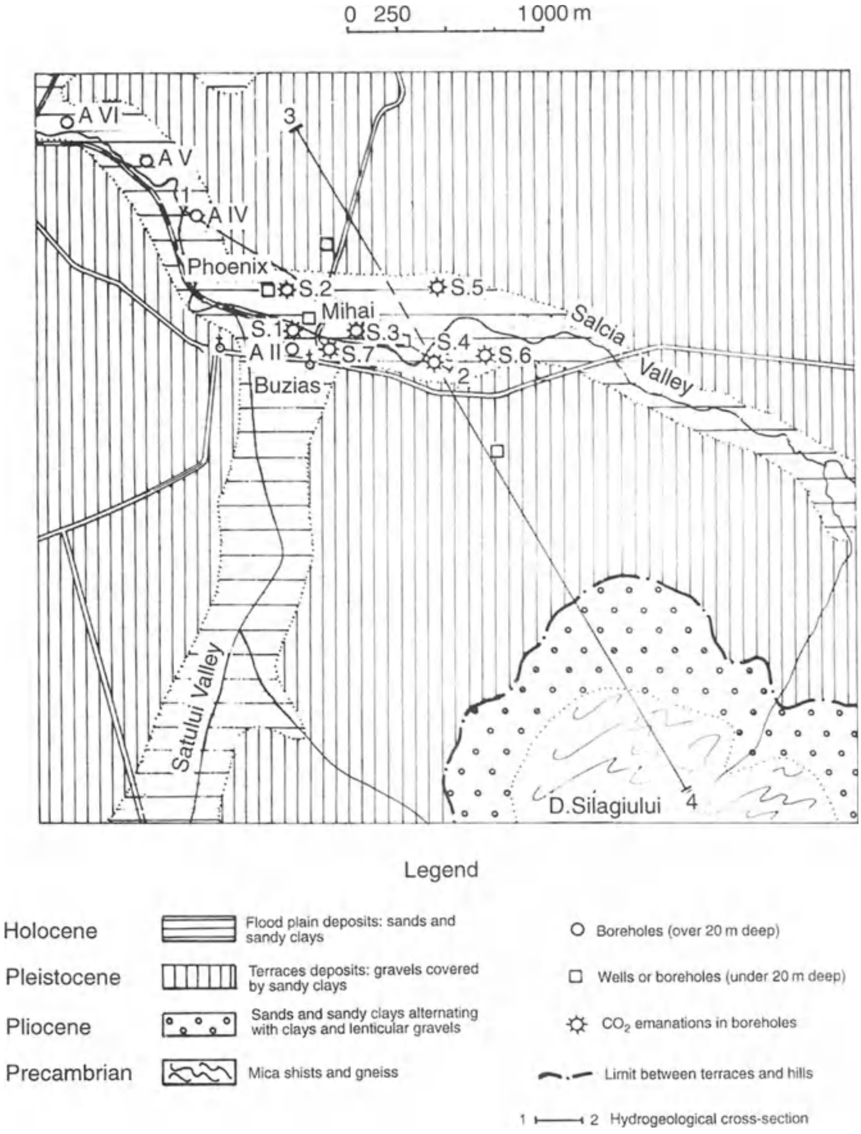

Figure 15.1 Geology of the area around Buziaş.

15.3 THE MINERAL WATER RESOURCE

15.3.1 Chemistry of the waters

The waters of Buziaş are dominantly bicarbonate and chloride with sodium, calcium and magnesium and carbon dioxide. Small but significant quantities of iron and in most cases bromide and iodide are also present.

Table 15.1 Chemical composition of groundwater from Buziaş area

Source	*TDS (mg/l)*	*CO_2 (mg/l)*	*Anions*					*Cations*					
			Cl^-	Br^-	I^-	NO_3^-	HCO_3^-	Na^+	K^+	NH_4^+	Ca^{2+}	Mg^{2+}	Fe^{2+}
Mineral carbogaseous waters:													
Well S1	4348.2	2101	882.9	2.0	0.5	0.5	2269.2	696.0	49.0	8.0	181.6	251.9	11.3
Well S2	4260.5	2000	833.3	0.5	0.5	Abs.	2183.8	586.3	57.0	8.0	296.6	201.4	15.5
Well S3	3192.9	1600	446.8	0.5	0.2	Abs.	1830.0	335.3	39.5	4.0	278.9	135.2	24.9
Well S4	2294.3	1867	280.1	Trace	0.2	Abs.	1342.0	186.5	19.5	2.0	233.3	106.5	25.2
Well AII	1009.2	1762	132.8	Abs.	Abs.	Abs.	590.7	124.8	8.1	1.0	91.0	49.0	9.8
Fresh water[a]	736–1931	26–353	11–334	Abs.	Abs.	Abs.	329–951	17–206	10–18	0.5–1.5	136–284	30–65	0.8–5.3
Fresh water[b]	845–1960	81–387	7–14	Abs.	Abs.	Abs.	597–1120	8–49	3–13	–	94–214	34–76	1.8–9.6
Brackish water[c]	–	–	8246.6	–	–	–	3934.5	6727.9	–	–	58.3	23.6	–

[a] Shallow water from Quaternary deposits.

[b] Underground water from Pliocene deposits in the surrounding area.

[c] Brackish water associated with oil fields from Pliocene deposits, located west of Buziaş.

Abs. = absent.

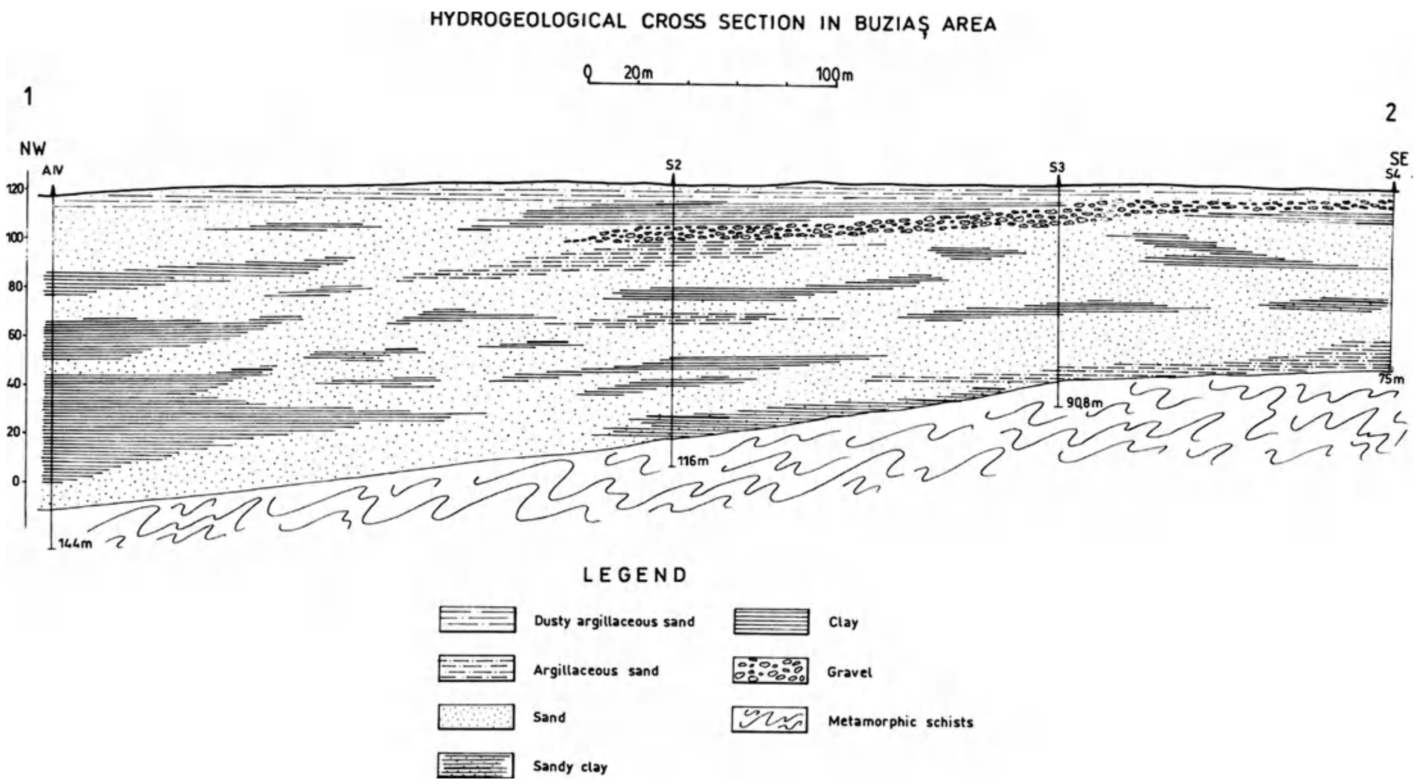

Figure 15.2 Geological cross-section 1–2 (Figure 15.1) through the alluvial deposits.

The chemical content differs clearly from the waters of the same aquifer complex in neighbouring areas, which are calcium–bicarbonate waters with no bromide or iodide (Table 15.1; Figure 15.3). Therefore, in the area of Buziaş, a sodium–chloride, bromide–iodide character is superimposed on a calcium–bicarbonate chemical background.

The mineralization decreases upwards, from 4.1–5.5 g/l for the lower artesian aquifer, situated directly above the crystalline schists, to 3.0–3.7 g/l

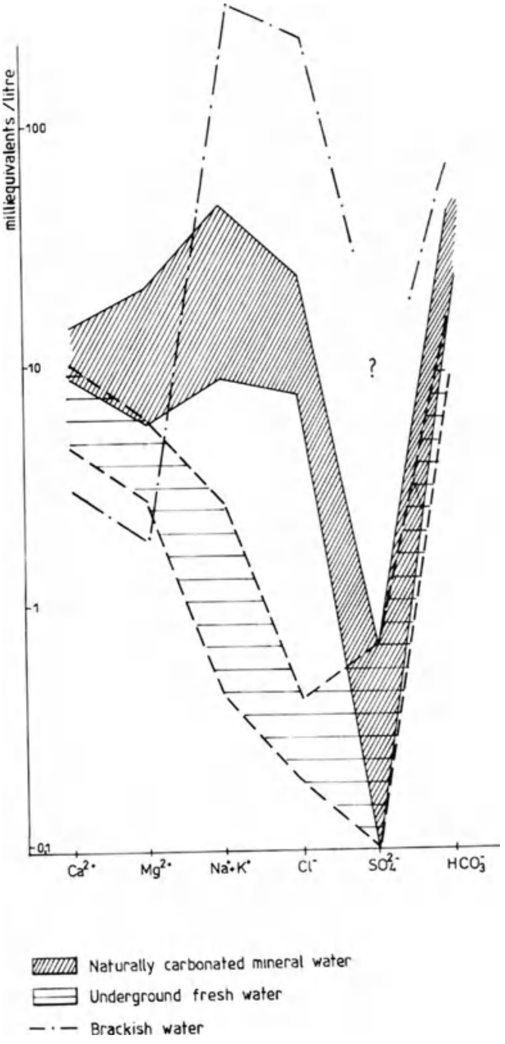

Figure 15.3 Chemical content of Buziaş water compared with that of adjacent areas.

for the middle confined horizons and to 1.0–2.7 g/l for the upper horizon with a free water table.

15.3.2 Free gases

The carbonated mineral waters are due to strong issues of mofettic carbon dioxide. The ascent of CO_2 to the surface is facilitated by a major regional fracture zone which runs approximately N–S passing through Lipova, Buziaş and Vrseţ (in Yugoslavia). Eruptions of Quaternary basalts at Lucareţ (to the north of Buziaş) and Gătaia (to the southwest) are on the same fracture zone.

Compared with adjacent areas, Buziaş benefits from favourable geological conditions in that the permeable Pliocene deposits are relatively thin and lie directly upon the crystalline schists, allowing a rapid upward flow of gas (Figure 15.4). Within the Pliocene deposits the discontinuous nature of the impermeable horizons allows the ascent of the CO_2 to the surface. Thus the aquifers at Buziaş comprise an open, non-thermal, carbogaseous system.

Chemical analyses show that the gases have the following composition (percent by volume):

CO_2	91.5–96.6
N_2	2.4–4.4
CH_4 and its relatives	0.86–0.15
Ar	0.00–0.03

Hydrogen sulphide, hydrogen and helium are absent.

The presence of CO_2, both dissolved in water and as free gas is a decisive factor in the occurrence of mineral water at Buziaş, determining the artesian character of the lower aquifer horizon in the Pontian deposits in the area of the resort.

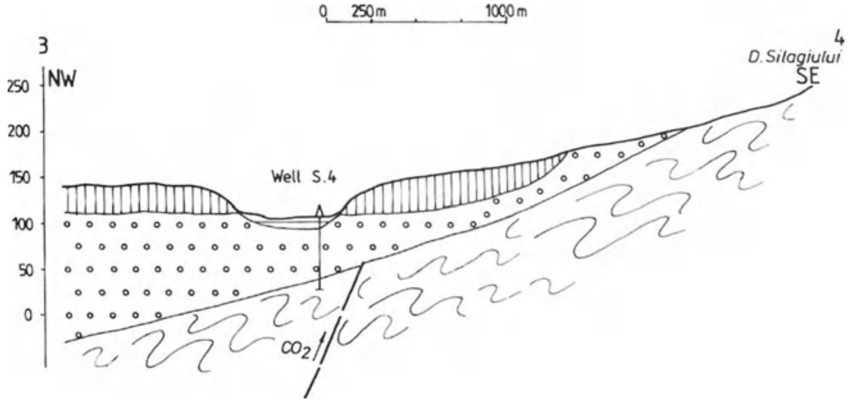

Figure 15.4 Geological cross-section 3–4 (Figure 15.1) showing the source of CO_2.

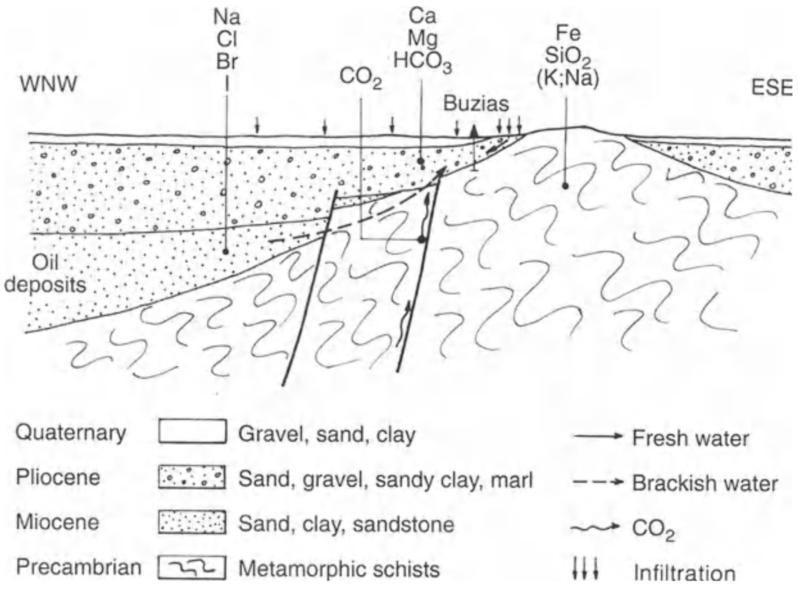

Figure 15.5 Schematic hydrogeological cross-section showing lithological control of the genesis of naturally carbonated waters and their migration, at Buziaş.

15.3.3 Genesis of mineral waters

The research carried out leads to the conclusion that the mineral waters of Buziaş are a mixture, with variable percentages, of low TDS calcium–bicarbonate waters from the permeable horizons of the Pliocene with more strongly mineralized waters containing chloride, bromide and iodide. We consider that this last type of water migrates from the west, from permeable Miocene deposits containing brackish waters associated with oil fields, through the intervening crystalline schists (Figure 15.5). The presence in very small amounts of methane and other hydrocarbons in the free and dissolved gases in the mineral waters of Buziaş, reinforces this hypothesis.

The carbogaseous character of the mineral waters is due to the existence of strong issues of mofettic carbon dioxide. The ascent of the CO_2 to the surface is facilitated by a major fracture along which two Quaternary basalt eruption centres are found, to the northeast and southwest of the town. Recently, mineral waters from Buziaş have been sampled for $^{13}C/^{12}C$ contents to establish whether the origin of CO_2 is a result of the heat-induced decomposition of carbonate rocks at depth or a mantle contribution.

The enrichment of carbogaseous mineral waters with HCO_3^-, Ca^{2+} and Mg^{2+} ions is achieved by the dissolution of carbonate minerals in the Pliocene deposits, in the presence of the carbon dioxide.

15.4 EXPLOITATION OF MINERAL WATERS

15.4.1 Exploitation

During the last two decades, 22 wells have been drilled for research and exploitation. Many of these were sealed by grouting in order to avoid the loss of carbon dioxide and to preserve the chemical characteristics of the mineral waters.

Currently the carbonated mineral water aquifer is exploited by five wells, four of which are used for balneary purposes and one for bottling. Besides these, three drilled wells are kept in reserve. The mineral water of Buziaş is exploited by controlled flow for the sources used for balneological treatment and by pumping for the well used for bottling. All the boreholes are equipped with PVC casing, as experience has proven that metal casings corrode within 2–4 years due to the aggressiveness of the carbon dioxide.

15.4.2 Wells exploited for balneological purposes

Four wells, S1 to S4 (Figure 15.6), are in use. They are all exploiting from the Pliocene (Pontian) aquifer.

Well S1 was drilled in 1962 and is 120 m deep. The thickness of Quaternary–Pliocene deposits was established as 93 m. The initial discharge was 4.4 l/s, by artesian flow. At this discharge the well was drawing much fine sand and there was a decrease of CO_2 with time. The discharge was therefore gradually reduced and the discharge authorized at present is 0.6 l/s.

Well S2 was drilled in 1962 down to 116 m. At first it had an artesian discharge of 3.5 l/s at 5 m above the ground. However, as this borehole also drew in fine sand, so the discharge was reduced to 1.5 l/s, at which rate fines were not drawn in. The content of dissolved CO_2 varies between 1800 and 2200 mg/l.

Well S3 was drilled in 1960 and is 90.8 m deep. At the beginning it had an artesian discharge of 3.8 l/s and an average content of 2240 mg/l of dissolved CO_2. The authorized exploitation discharge is 3.1 l/s.

Well S4 was drilled in 1965 down to 75 m, where the metamorphic rocks were intercepted. At present, the mean exploited discharge is 2 l/s and the average dissolved CO_2 content is 1800 mg/l.

The balneary resort has three more boreholes (wells S5, S6 and S7) which are kept in reserve. They were drilled in 1979–1980 and range from 79.3 to 96.2 m in depth. The optimum exploitation discharges established by hydrogeological tests, without sand ingress, are 1 l/s (well S6) and 2 l/s (wells S5 and S7). The CO_2 content at these wells is between 1386 and 2000 mg/l.

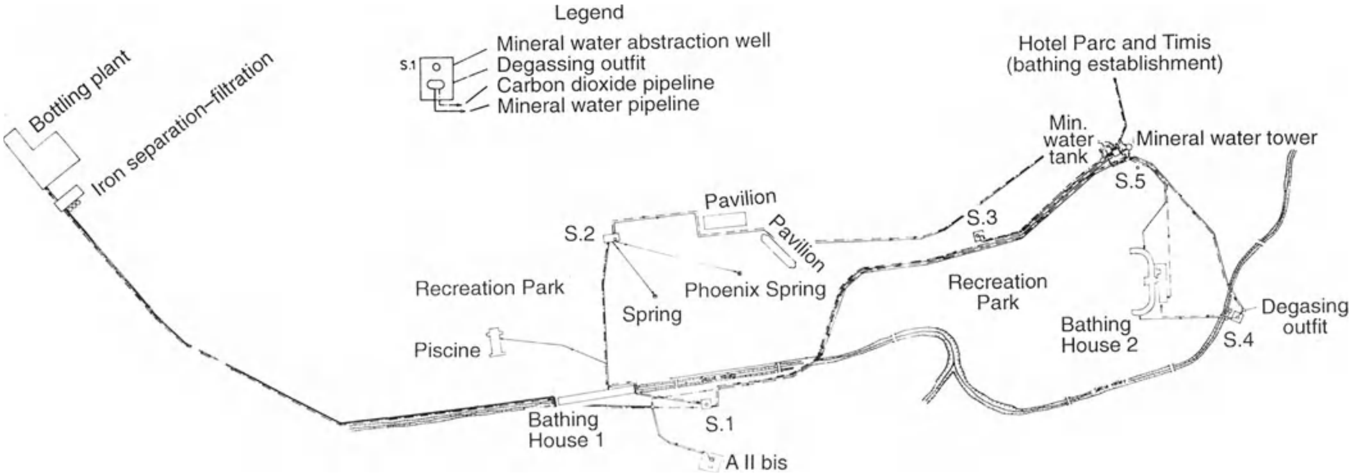

Figure 15.6 Mineral water and carbon dioxide distribution and storage system. (Not to scale.)

15.4.3 Well exploited for bottling

The only well presently exploited for bottling is Apemin II, drilled in 1959 and reconditioned in 1965. The horizons between 76.5 and 77.5 m are in Pliocene deposits and are exploited by pumping. The exploitation rate is 1 l/s for 1 m of drawdown. The water has a CO_2 concentration of 1400–1900 mg/l.

15.5 UTILIZATION OF MINERAL WATERS

The mineral waters are used for bottling and for balneological treatment. They are successfully used for external treatment (in cardiovascular disease, disease of the nervous system, asthenic neurosis and certain occupational diseases) and internal treatment (digestive disorders, kidney and urinary duct disorders and certain nutrition and metabolic disorders). Walking in the park is also recommended as part of the cure, but the consumption of alcohol is not.

The large amounts of free carbon dioxide from the operating boreholes ($>2500\,m^3/d$) are used both for balneological treatment as mofette baths (for cardiovascular disease and diseases of the nervous system) and for the reimpregnation of the mineral waters. Part of the free carbon dioxide is liquefied and bottled into metal containers and used in the food industry.

15.6 OPTIMIZATION OF EXPLOITATION

In order to optimize the exploitation of the mineral waters and the free carbon dioxide, measures were taken to connect all the sources to a complex distribution and storage system (Figure 15.6). This allows efficient administration of the mineral waters, taking into account the daily and seasonal times of maximum consumption. For all the wells under exploitation, degassing devices are mounted and the water and the carbon dioxide are directed to separate ducts.

The preservation of the quality of this important mineral water system is achieved by rational exploitation, established by close monitoring, over a 5-year period for mineral waters, and over 9 years for carbon dioxide, during which time 7000 CO_2 and H_2CO_3 analyses and 4500 discharge measurements have been carried out.

This research has established that, whatever the number of wells exploiting the artesian aquifer horizon, the extracted cumulative discharge of water should not exceed 9.0 l/s. The total exploitable resource of free CO_2 is $2975\,m^3/d$. At these rates, the recharge of CO_2 and water levels can be maintained, with no derogation of the resource.

15.7 PROTECTION AND CONSERVATION OF SOURCES

The development of the resource for balneary treatment and bottling of mineral waters led to an excessive number of wells being drilled in the period 1955–1970, and exploitation was carried out without control. This led to a significant loss of energy in the system, manifested by the decrease in CO_2 contents of the mineral waters in the abstraction wells, from over 2000 mg/l to less than 1000 mg/l, as well as to a decrease of the shallow aquifer heads.

During the period 1972–1975 studies were carried out to establish new protection zones for the mineral sources and to determine optimum abstraction rates. The water chemistry was monitored during the same period.

These studies allowed the design and implementation of a monitoring programme to protect the mineral water resources both against overexploitation and pollution. During this time, the natural conditions of the carbogaseous aquifer were successfully restored, and the dissolved CO_2 concentration returned to the initial values of over 2.0 g/l.

In order to prevent overexploitation, the following rules were established:

- strict limitation of the abstraction rate to the optimum values (9 l/s for the entire resource);
- reduction to the minimum of transport, distribution, storing and handling losses;
- sealing by grouting of some of the drilled wells not in use, to avoid the loss of carbon dioxide;
- closing of the other three wells (S5, S6, S7), to be kept in reserve;
- constant monitoring of the discharge regime and chemical composition of the water.

Protection zones were created to prevent pollution of the aquifers. Romanian legislation provides for three protection zones. Although these zones have slightly different definitions and descriptions from Western European ones, there are obvious correspondences between them (Table 15.2).

For the mineral waters of Buziaş, the zone with the most severe regime (WPZ1) is represented by areas with a diameter of 10–20 m, immediately around the wells. These zones are surrounded by protection fences (Figure 15.5). The outer restriction zone (WPZ2) is mostly occupied by a

Table 15.2 Terminology for groundwater protection zones in England and Romania

Title given to water protection zones (WPZ)		
England		*Romania*
Inner Source Protection Zone	(WPZ1)	Inner Protection Zone with Sanitary Severe Regime
Outer Source Protection Zone	(WPZ2)	Outer Protection Zone with Sanitary Restriction
Source Catchment Zone	(WPZ3)	Hydrogeological Protection Zone

Table 15.3 Restricted activities in water protection zones in Romania

Activity or construction	*WPZ1*	*WPZ2*	*WPZ3*
Any activity or construction which is not related to the abstraction and exploitation of mineral waters	*	0	0
Storage of hazardous substances	*	*	0
Discharge of waste waters	*	*	*
Use of mineral fertilizers, manure, etc.	*	*	*
Digging deeper than 1 m	*	0	0
Drilling operations	–	0	0
Construction or extension of graveyards	*	*	–
Dam construction and irrigation structures	*	0	0
Mining that may cause the destruction of the water protection layers	*	0	0
Construction of pipelines for potential contaminants	*	*	0
Use of explosives	*	*	*
Timber exploitation	*	*	0
Construction or extension of roads; heavy traffic	*	*	*

* Forbidden.
0 Needs special permit.
– No specification.

recreational park with a surface of about 1 km^2. The hydrogeological protection area (WPZ3), with a surface of about 100 km^2, was established for the entire carbogaseous mineral aquifer which includes, together with the catchment area, the area of mixing of groundwaters with carbon dioxide. Table 15.3 lists the activities in all three protection zones that are forbidden or require a special permit.

The Romanian Administration of Mineral Waters (RAMIN) is responsible for the management of mineral waters and therefore for their protection. The role of RAMIN is to propose protection zones and to establish exploitation programmes for mineral water sources. The approval and control of the protection zones, as well as the enforcement of the legislation, are carried out by the National Agency for Mineral Resources together with the Ministry of Health.

16

Optimization of exploitation of geothermal reservoirs in the Pannonian Basin, Romania

Horia Mitrofan and Viorel Şerbu

16.1 INTRODUCTION

Thermal gradients of 40–55°C/km, slightly higher than the continental average, occur in the eastern section of the Pannonian Basin, in Romania. Some 15 low temperature (50–85°C) geothermal well fields (Figure 16.1) exploit aquifers in the Pliocene detrital formations, at depths ranging between 900 and 2000 m (Plaviţă and Cohut, 1990, 1992).

These well fields share several characteristics:

- they tap multilayered reservoirs, consisting of slightly consolidated sandstones interbedded with shales;
- significant pressure decreases have been experienced over the period of exploitation;
- artesian flow rates of 10–30 l/s per well can be obtained, if overexploitation is avoided;
- in order to avoid interference and overexploitation, wells close together in some cases tap distinct aquifers, situated at different depths (and hence having different temperatures);
- reinjection proved to be unsuccessful, due to the extremely high wellhead pressures required (50–90 bar);
- the water has a rather low total dissolved solids (TDS) content (3–6 g/l);
- due to the release of the dissolved carbon dioxide, usually in the upper 100 m of the wellbore, carbonate scaling is liable to occur;

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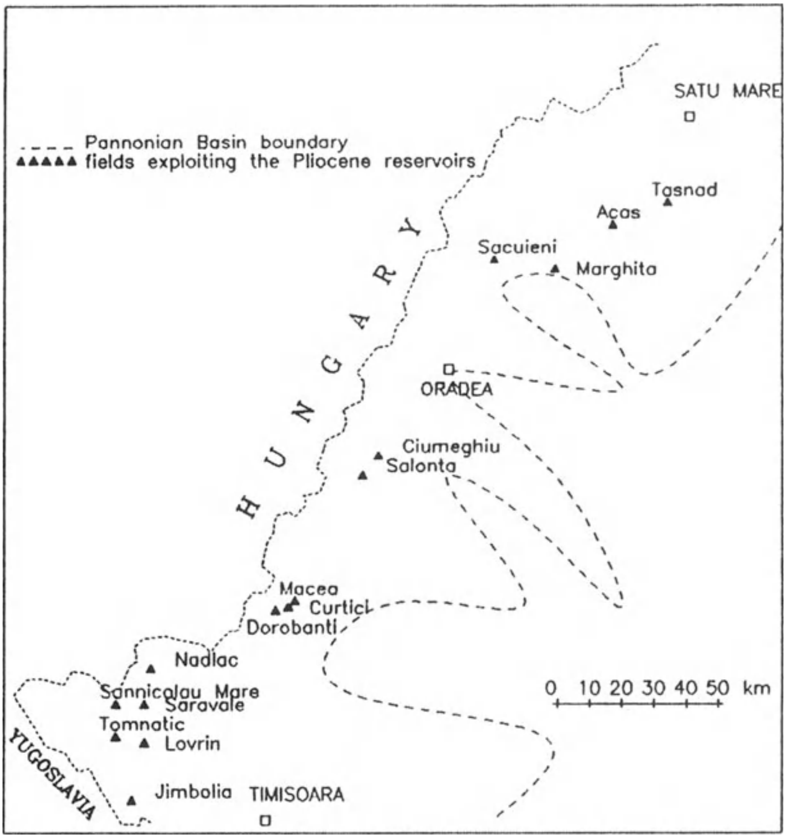

Figure 16.1 Location map showing the Pannonian Basin geothermal field.

- about 1–2 $\mathrm{N\,m^3/m^3}$ of dissolved methane is also released, resulting in extensive two-phase flow within the wellbore.

16.2 RESERVOIR CHARACTERISTICS

Sediment assemblages in the Pannonian Basin are deltaic. The sandstones are channel fills and bars, while the siltstones and shales represent lower energy environments, such as interchannel and levee deposits. Under such circumstances, a one-dimensional (linear) flow geometry is appropriate to describe the hydrodynamic behaviour of the reservoirs. Specifically, the pressure drop recorded during well tests (Figure 16.2) is proportional to the square root of time (Barker, 1988).

It has been generally observed that existing wells tap individual aquifer bodies of rather poor productivity. However, transient tests systematically show that hydraulic properties (permeability, storage capacity and

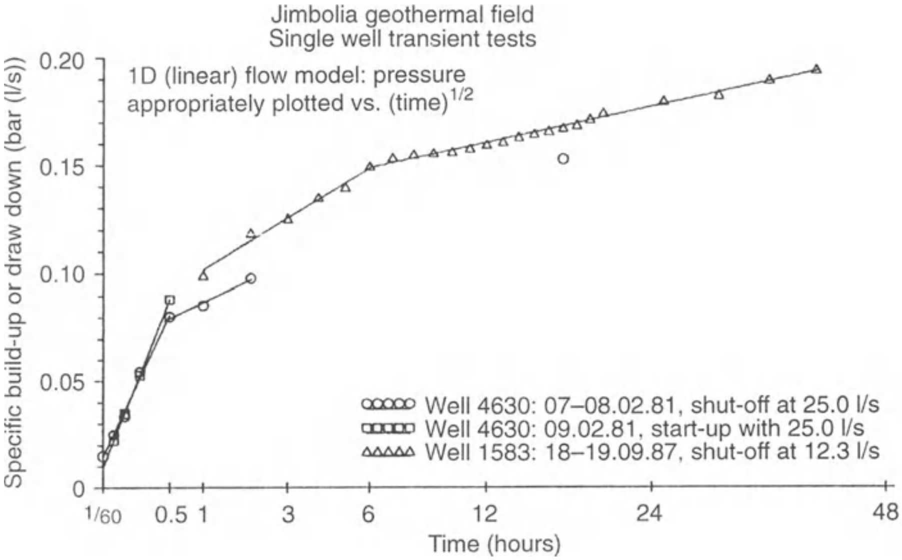

Figure 16.2 Change of specific pressure during well tests.

throughflow area) improve away from the well, as illustrated by pressure build-up diagrams with distinct, increasingly gentle slopes (Figure 16.2). This setting probably reflects a hierarchy in distribution: frequent linear aquifers of low productivity, connected to fewer aquifers of moderate productivity, which in turn are connected to even fewer high productivity reservoir sections. Estimates of intrinsic permeability × throughflow area for high productivity reservoir sections are of the order of 10^6 D m^2, while those for moderately permeable reservoir sections are 10^4–10^5 D m^2.

The correlation between pressure decline, flow rate and time, derived from the late time period of the well tests, was successfully used to simulate the evolution of pressure in the reservoir over the 10–15 years since exploitation started (Figure 16.3). Otherwise stated, long term reservoir pressure decline is also an outcome of the one-dimensional geometry, as suggested by the discussion of Barker (1988) on the influence of the flow dimension on the late-time behaviour of the generalized line source solution.

It is also inferred that the linear aquifer bodies carry water that originated in an area of different temperature from the inflow zones of the wells. This might be the cause of the observed systematic, flow rate-induced variations of the inflow point temperature (Figure 16.4). Such variations are consistent with the temperature distribution in a fluid exchanging heat with the surrounding formations, while flowing along a linear channel (according to relationships derived by Van Genuchten *et al.*, 1984; Rasmuson and Neretnieks, 1986).

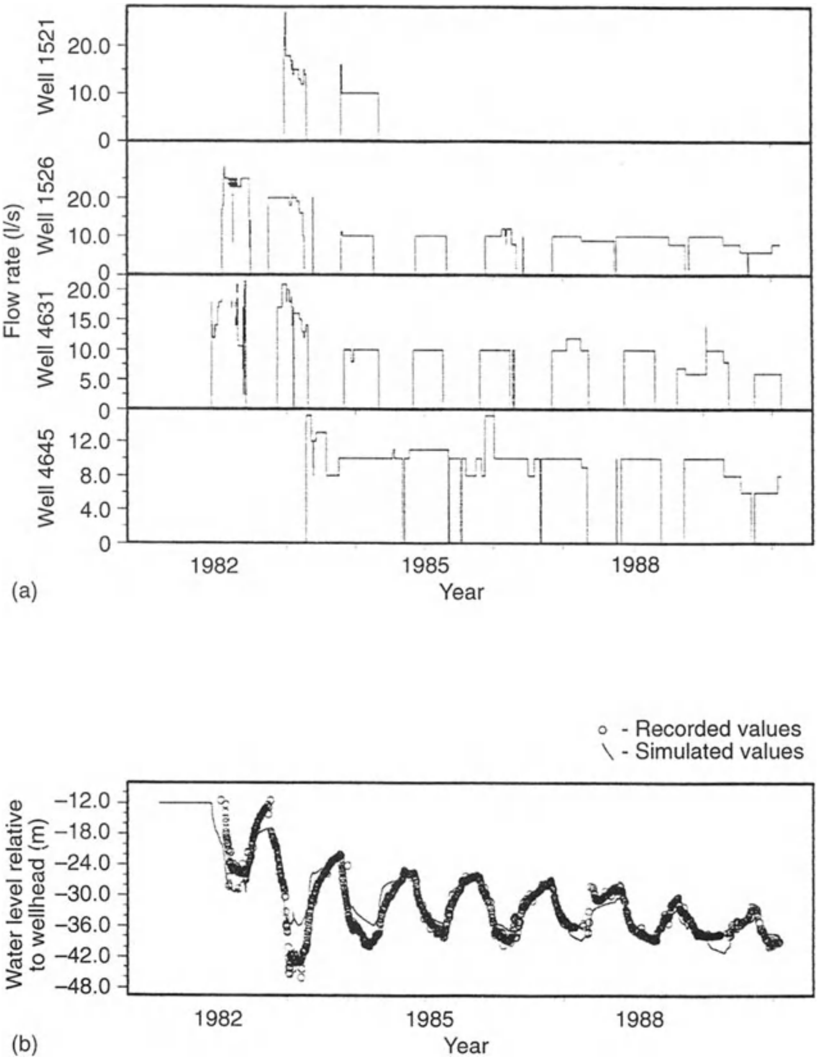

Figure 16.3 (a) Flow rates and (b) recorded and simulated water levels for Well 1522, from 1982 to 1990.

16.3 SPECIFIC MANAGEMENT APPROACHES

Geothermal well fields exploiting the Pliocene reservoirs supply either municipal district heating schemes (Sânnicolau Mare, Jimbolia, Lovrin, Nădlac, Săcuieni, Marghita and Tăşnad), or greenhouse complexes (Tomnatic, Curtici, Macea, Dorobanţi, Acâş and Săcuieni). In recent years the new municipalities and the new owners of the greenhouses have become interested in increasing the exploitation efficiency.

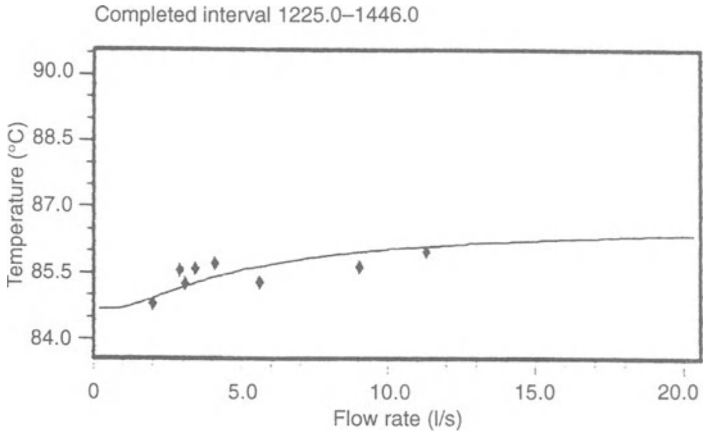

Figure 16.4 Variation of bottomhole temperature with flow rate in Well 4058.

The optimization goals are all cost related.

- To provide the maximum necessary heat output (without pumping, if possible). The effect is a reduction in the cost per unit of heat supplied, by increasing the overall efficiency of a specific investment, and even more by reducing the original investment if, for instance, pumps or peak-load boilers appear to be unnecessary.
- To secure production lifetime for as long as possible. The effect is to extend the period of enhanced profit, after the complete payback of the investment.
- To restrict to a minimum the number of wells involved in the heating scheme. The effect is also a lowering of the cost per unit of heat supplied, as a result of savings on transmission pipes, transmission pumps and maintenance.

To meet these requirements, an integrated reservoir engineering approach is used to evaluate the optimum exploitation schemes. Basically it consists of modelling, in terms of temperature and pressure changes, the separate responses to exploitation of the reservoir and the wellbores. The first step is to calibrate model parameters until a reasonable match to observation data is achieved. Subsequently, responses to various exploitation scenarios are simulated.

For a single well, the assessment normally starts with an evaluation of the instantaneous thermal and discharge performance. At this stage, interference with other wells in the well field, and the possible long term reservoir pressure decline are neglected. An integrated well field analysis next refines the discharge performance assessment, by taking into account interference between wells and the decline of pressure in the reservoir. It provides forecasts of the wellhead pressure evolution in time, based on the abstraction history of the well field and provisional exploitation scenarios. The scenarios which best comply with the desired lifetime of the well field are identified as a result.

In performing the overall analysis, full assistance is provided by the integrated software package GEOTHERM, developed by DATA EXPERT. It essentially consists of a reservoir simulator, interconnected with a wellbore simulator. The considered geothermal fluids are of low temperature (<100°C). Two-phase flow along the wellbore may be accounted for if gases, originally dissolved in the geothermal water, are released. The fundamental scheme of GEOTHERM can be described as follows:

Reservoir behaviour

Temperature

Variable temperature input at the inflow depth is considered, in the form of an inflow temperature versus total extracted flow rate correlation. It allows for:

- a realistic assessment of well thermal performance;
- an accurate simulation of the pressure drop along the well bore.

Pressure

Distinct procedures are available for two basic assumptions:

- time-independent reservoir pressure (the procedure devised for this case also assumes that the effects of interference with other wells in the well field can be ignored);
- reservoir pressure decline during exploitation, by assuming one, two or three dimensional radial flow geometry.

Wellbore behaviour

Cooling

A power law relates the cooling of the geothermal fluid along the wellbore (linear temperature drop assumed) to total extracted flow rate.

Pressure drop

Pressure drop within the actual casing and tubing configuration of the wellbore can be simulated for liquid only and two-phase (either bubble or slug flow) conditions.

The predictions provided by the basic functions mentioned above are integrated into assessments of the wellhead thermal and discharge performance. The overall approach is illustrated by an optimization scheme applied to part of the Săcuieni geothermal well field.

16.4 SINGLE WELL ANALYSIS

Single well analysis usually includes the following (successive) approaches:

- forecasting the wellhead temperature versus flow rate relationship;
- forecasting the wellhead pressure versus artesian flow rate relationship (the ‘output curve’), which also implies assessing the optimum of several

possible wellbore configurations (i.e. casing and tubing diameter and length);
- assessing the heat outputs corresponding to the available range of artesian flow rates;
- investigating whether the discharge flow rate should be additionally increased through pumping: computation of the pump discharge pressure at the surface and of the liquid level during pumping, for specified pumping equipment.

16.4.1 Wellhead temperature forecast

The wellhead temperature is controlled by two flow rate-dependent processes:

- contrasting temperature inflows into the production zone of the well;
- the cooling of the geothermal fluid during its transit up the wellbore, from the inflow depth z_i[m], to the wellhead:

$$Gt = (T_i - T_{wh})/z_i$$

where Gt is the gradient of cooling [°C/m], and T_i and T_{wh} are the fluid temperatures at the inflow depth and at the wellhead respectively [°C].

The two processes are individually quantified by fitting appropriate correlations to observation data (Figures 16.4, 16.5), then the established relationships are connected into a computation of the drop in temperature 'up the wellbore' (from bottom to top). By repeating the temperature drop computation over a selected range of flow rates, a wellhead temperature

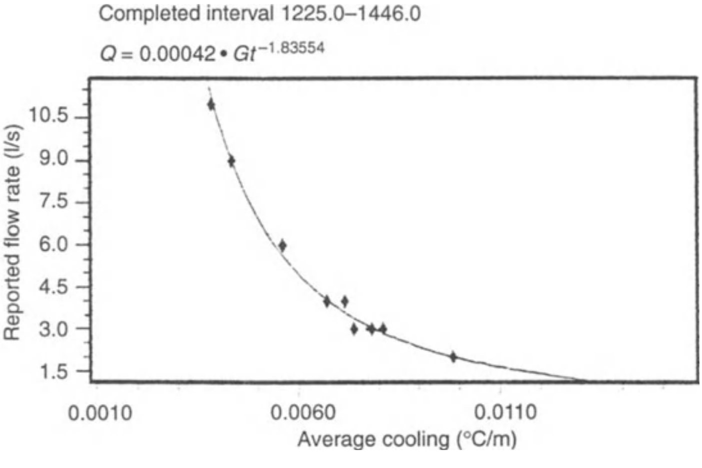

Figure 16.5 Increase of cooling rate up the wellbore as the flow rate decreases.

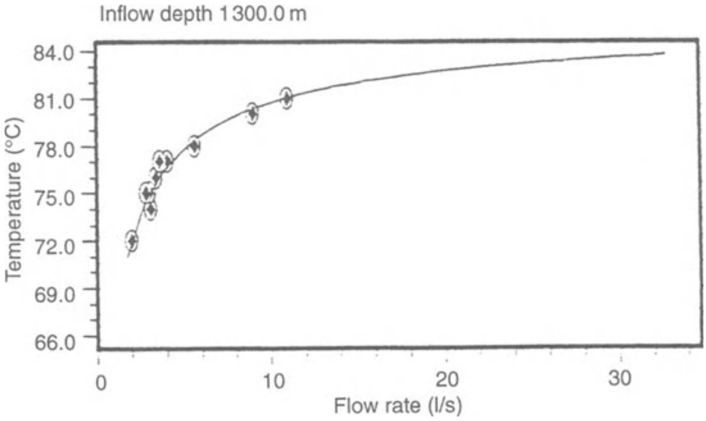

Figure 16.6 Variation of wellhead temperature with flow rate.

versus extracted flow rate diagram is constructed, which is also checked against recorded temperature values (Figure 16.6).

16.4.2 Wellhead (artesian) pressure forecast

Under a preliminary assumption that interference with nearby wells and long term pressure decline could be ignored, the linear correlation between the bottomhole pressures recorded at the inflow depth and the abstracted flow rates is computed by a best fit procedure (Figure 16.7). For a given flow rate, this correlation provides a reference pressure, which is used as a starting value in the simulation of the pressure drop along the wellbore, up to the wellhead.

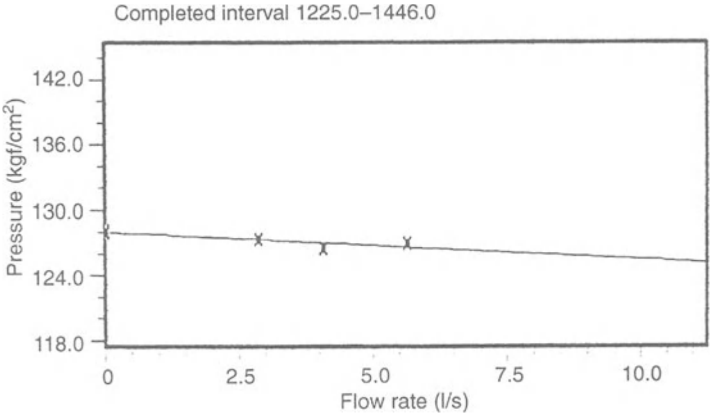

Figure 16.7 Best fit relationship for bottomhole pressure versus flow rate.

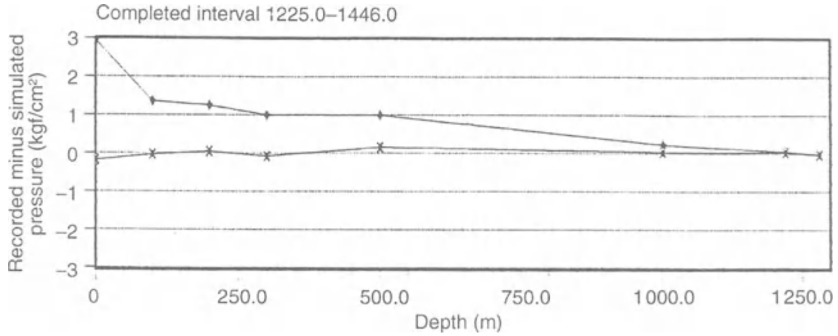

Figure 16.8 Relationship between recorded and simulated pressure with depth.

The wellbore flow regime parameters (roughness and free methane content) are calibrated by checking simulated pressure profiles against recorded downhole pressure profiles (Figure 16.8). In the given example, a first guess of 'zero gas/water ratio' proves to be unsatisfactory: in the upper section of the wellbore, where free gas is presumably released from the solution, the deviation between the simulated and the recorded pressures is extreme. Yet when an appropriate gas/water ratio of 1.85 $\mathrm{N\,m^3/m^3}$ is chosen, the deviation becomes close to zero along the entire wellbore.

The established correlations and parameters are then entered into an 'up the well bore' pressure drop computation, which is repeated over a selected range of flow rates. The result is a diagram of simulated wellhead pressure versus artesian flow rate (output curve), which is checked against measured pressure values (Figure 16.8).

The configuration of an artesian well discharging a two-phase (gas–water) fluid normally includes a production tubing, introduced inside the casing (Figure 16.10). Its main purpose is to force the two-phase flow through an area smaller than that of the casing which, according to the specific conditions, may result in a significantly smaller pressure drop and in correspondingly enhanced artesian flow rates (see below). The tubing can be also extracted periodically, to enable scaling products to be removed.

As a result of complex behaviour due to two-phase flow, optimum tubing selection is a trial and error process, conducted by observing the criterion of 'the highest wellhead pressure for the required flow rate'. Several output curves are simulated (Figure 16.9), by considering alternative tubing configurations (diameter and length) below the wellhead. In the given example, the considered flow rate is 19 l/s, for which Figure 16.9 indicates the $5\frac{1}{2}$ in

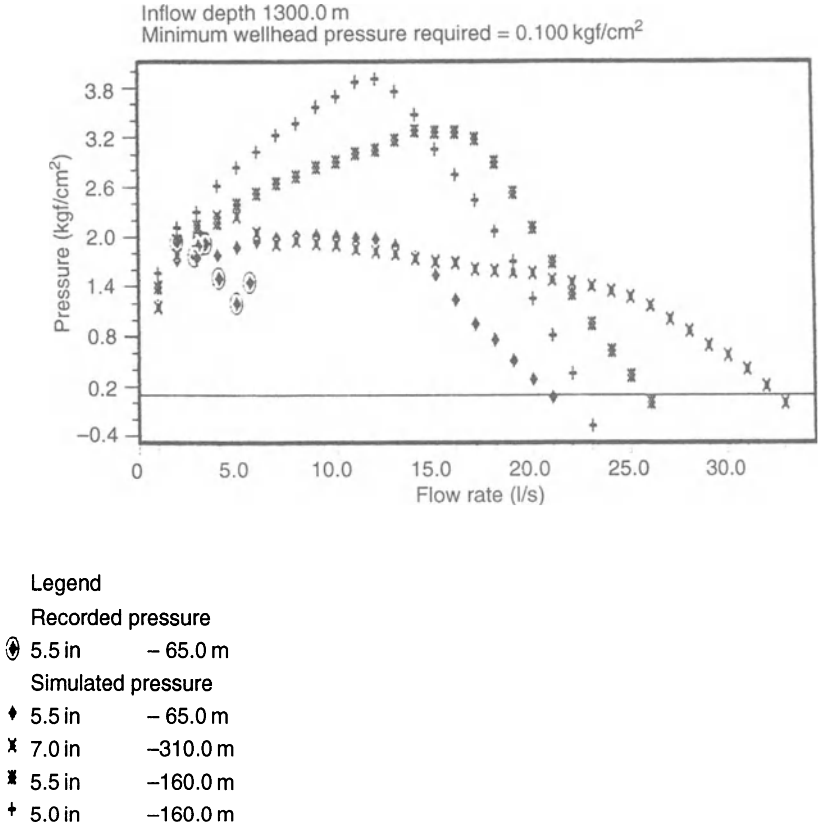

Figure 16.9 Comparison of recorded and simulated wellhead pressures.

(*c.* 14 cm) tubing diameter to be more appropriate than either the immediately narrower 5 in (*c.* 12.5 cm) or the next wider 7 in (*c.* 18 cm) diameters. By simulating, for the required discharge and a given tubing diameter, the wellhead pressures obtained by stepwise increase of the tubing length (Figure 16.11), the tubing length that provides the highest wellhead pressure may be identified.

Notice in Figure 16.9 that at low flow rates the wellhead pressure increases with increasing discharge, which might seem anomalous when the analogy with groundwater wells is considered. In fact, cooling across the wellbore diminishes during the transition from low to high flow rates (Figure 16.5), resulting in a significant increase of the average temperature of the water column of the flowing wellbore. As a consequence, while the discharge is increased, thermal expansion of the water column in the wellbore exceeds the flow-induced drawdown, and the wellhead pressure increases accordingly. Additional effects are induced by the two-phase flow within the wellbore.

Single well analysis

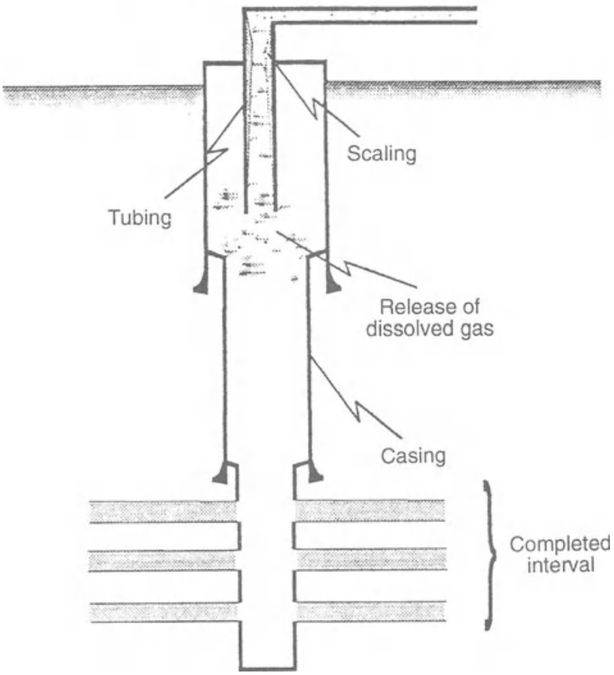

Figure 16.10 Construction of a borehole with artesian flow.

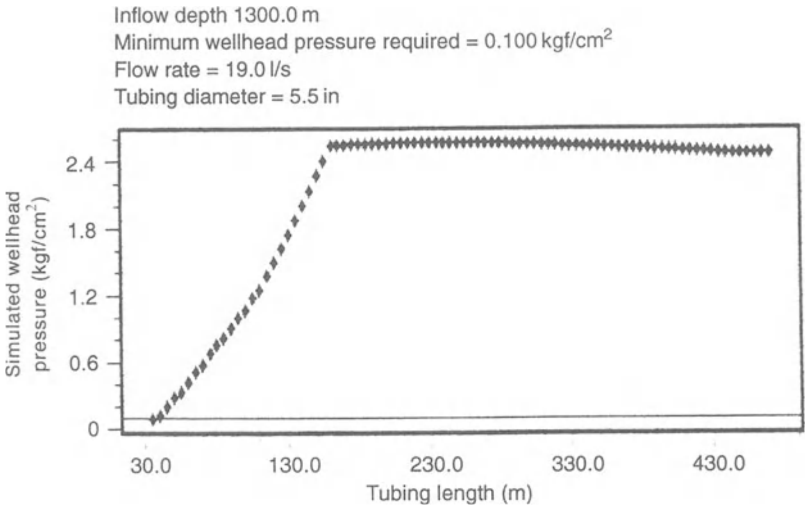

Figure 16.11 Determination of the optimum tubing length.

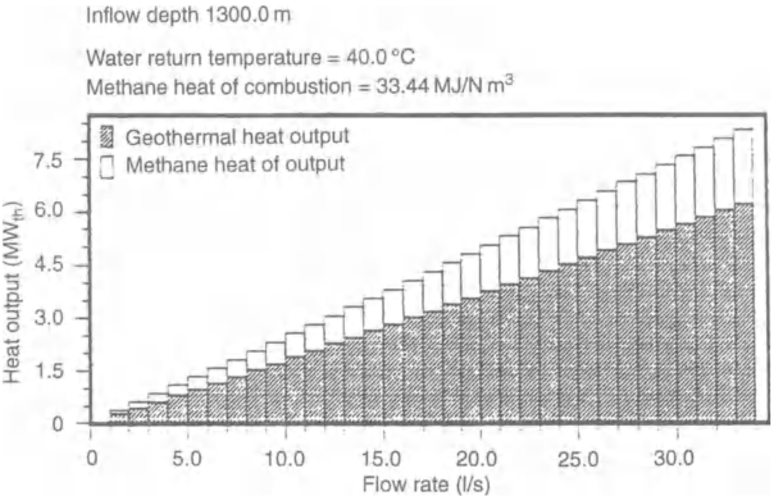

Figure 16.12 Variation of heat output with flow rate.

16.4.3 Assessing the well heat output

The geothermal heat output W_g [MW$_t$] is computed for a specified water return temperature T_r [°C] by considering, for each water flow rate Q [l/s], the corresponding wellhead temperature T_{wh} [°C] (derived as indicated in section 16.4.1):

$$W_g = Q \times 10^{-3}(T_r - T_{wh})c$$

where c = the volumetric specific heat capacity of the geothermal water [J/(m^3 °C)].

The additional heat output W_a that can be provided by methane combustion [MW$_t$] is also computed (Figure 16.12), by taking into account the methane content of the geothermal water GWR (gas/water ratio [N m^3/m^3], estimated as indicated in section 16.4.2), together with the gas heat of combustion m [MJ/N m^3]:

$$W_a = Q \times 10^{-3}\mathrm{GWR}\, m$$

16.5 WELL FIELD ANALYSIS

As a result of reservoir pressure decline, artesian (or even pumping) flow rates estimated by the above single well analysis are applicable over a limited time-span only. The well field analysis prescribes a project lifetime and assesses the sustainability of the necessary artesian (or pumping) flow rates over this period.

The following successive steps are taken:

- deriving, from single well and interference tests, reciprocal drawdown relationships between wells;

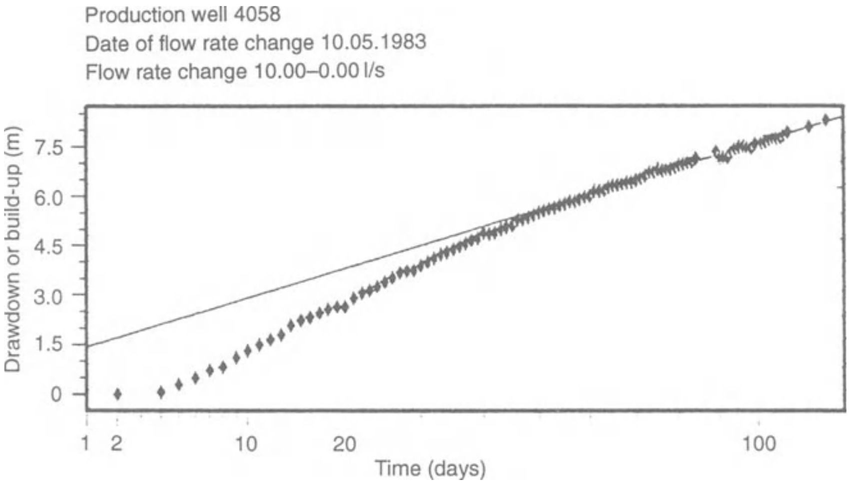

Figure 16.13 Best fit relationship for head change versus time.

- checking the long term validity of the derived drawdown relationships, by reconstructing the pressure decline history of the well field;
- forecasting the wellhead pressure versus time evolution for provisional withdrawal scenarios.

16.5.1 Interpretation of well tests

The pressure build-up (or drawdown) induced under accurately controlled interference testing conditions, plotted versus an appropriate time scale (i.e. the square root), is used to derive reciprocal drawdown relationships between the wells of the well field. In the considered example the well field comprises a single production well (no. 4058), hence only its own reaction to a flow rate impulse is quantified, by fitting an appropriate build-up versus time equation to the observed data (Figure 16.13).

16.5.2 Reconstruction of the history of reservoir pressure decline

The responses of a 'reaction' well to all the wells that 'excite' it (derived in section 16.5.1), are used to simulate the overall response of the considered 'reaction' well to the long term, multiwell exploitation of the well field. Since in this particular case there is only one production well in the well field, the simulated overall pressure response of this specific well obviously takes into account only its own exploitation history (Figure 16.14).

The computation starts from the initial, pre-exploitation water level, and proceeds by superposition of all the drawdowns and build-ups induced

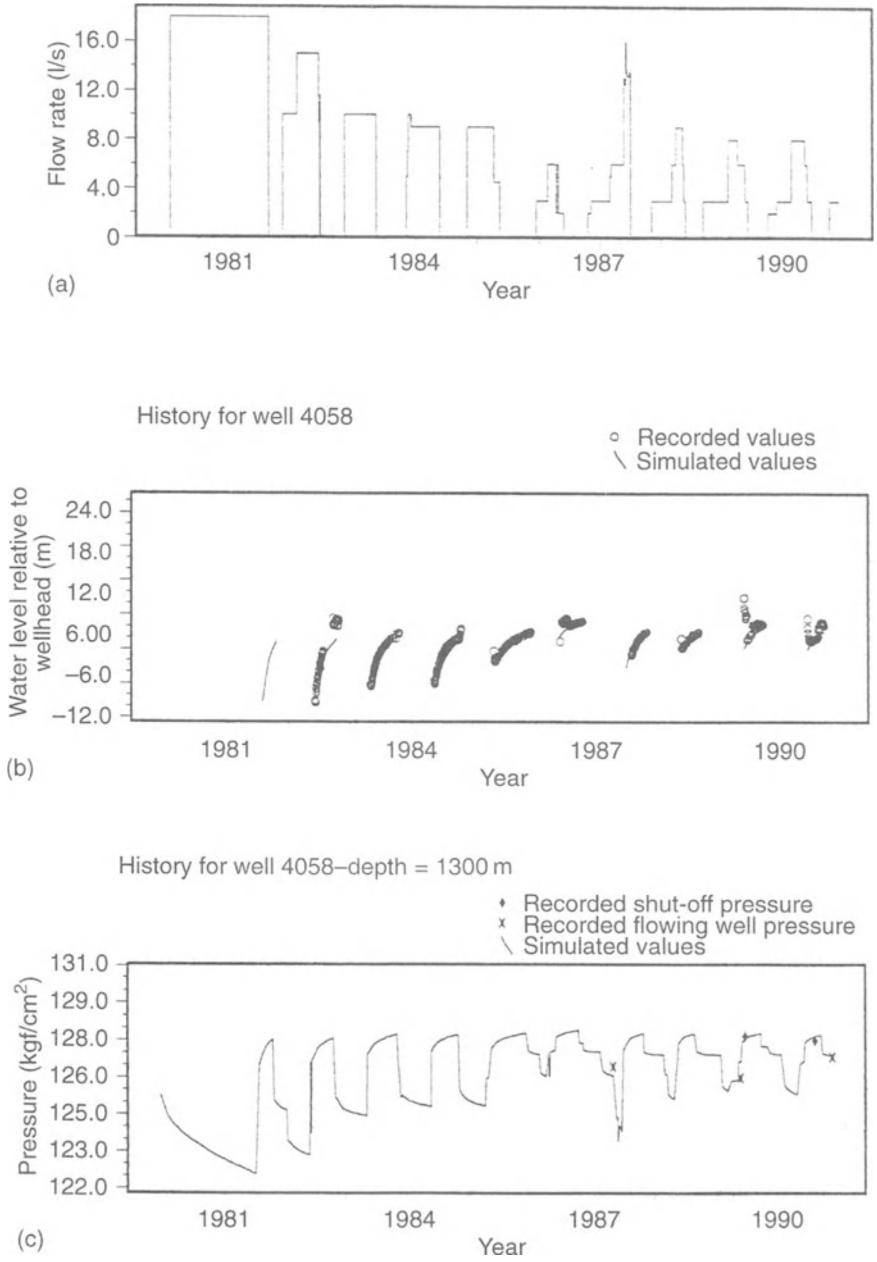

Figure 16.14 Simulation of bottomhole pressure: variation of (a) extracted flow rate, (b) water level and (c) bottomhole pressure for 1981–1990.

during the exploitation period. The results are initially checked against the evolution of the water levels recorded when the considered well is shut off (Figure 16.14).

The coefficients of the drawdown relationships are subsequently multiplied by an average pressure gradient, in order to convert water level equations to bottomhole pressure equations. The average pressure gradient for each well is selected by a least squares procedure, so that the simulated bottomhole pressures for a specified depth match the bottomhole pressures recorded at that depth (Figure 16.14).

16.5.3 Wellhead pressure evolution forecast

Finally, each simulated bottomhole pressure belonging to production periods of the considered well is used as a starting value in modelling the pressure drop up the wellbore. As a result, a wellhead pressure evolution history is reconstructed and checked against recorded wellhead pressures (Figure 16.15). When an overall satisfactory match between the recorded and the modelled pressure values has been achieved, the simulation is extrapolated into the future, according to a hypothetical withdrawal scenario and assuming the most appropriate tubing configuration, selected as indicated in section 16.4.2 and Figures 16.9 and 16.11.

For the considered example the exploitation parameters corresponding to the maximum artesian flow rate that can be sustained during a forecast period of 5 years (starting from 1 December 1990, as illustrated by Figure 16.15), are $Q = 19\,\mathrm{l/s}$, $T_{\mathrm{wh}} = 82.0°\mathrm{C}$, $W_{\mathrm{g}} = 3.3\,\mathrm{MW_t}$ and $W_{\mathrm{a}} = 1.2\,\mathrm{MW_t}$.

The wellhead temperature and the heat output (for a water return temperature of 40°C and a methane heat of combustion of $33\,\mathrm{MJ/N\,m^3}$) are taken from Figures 16.6 and 16.12 respectively.

16.6 FINAL REMARKS

For a long period, the benefits of the existence of tens of geothermal wells in the Romanian part of the Pannonian Basin have been somehow obscured by an inability to control the declining reservoir pressure and to secure the desired artesian flow rates. However, a proper understanding of the influence of each specific factor (the prevailingly one-dimensional reservoir development, the variable temperature inflow into the producing zone of a well, the extensive two-phase flow within the wellbores, etc.) was eventually achieved and integrated in an overall reservoir engineering approach. The GEOTHERM software used can evaluate readily both existing and alternative exploitation schemes and provide recommendations on optimum wellbore configurations and withdrawal rates.

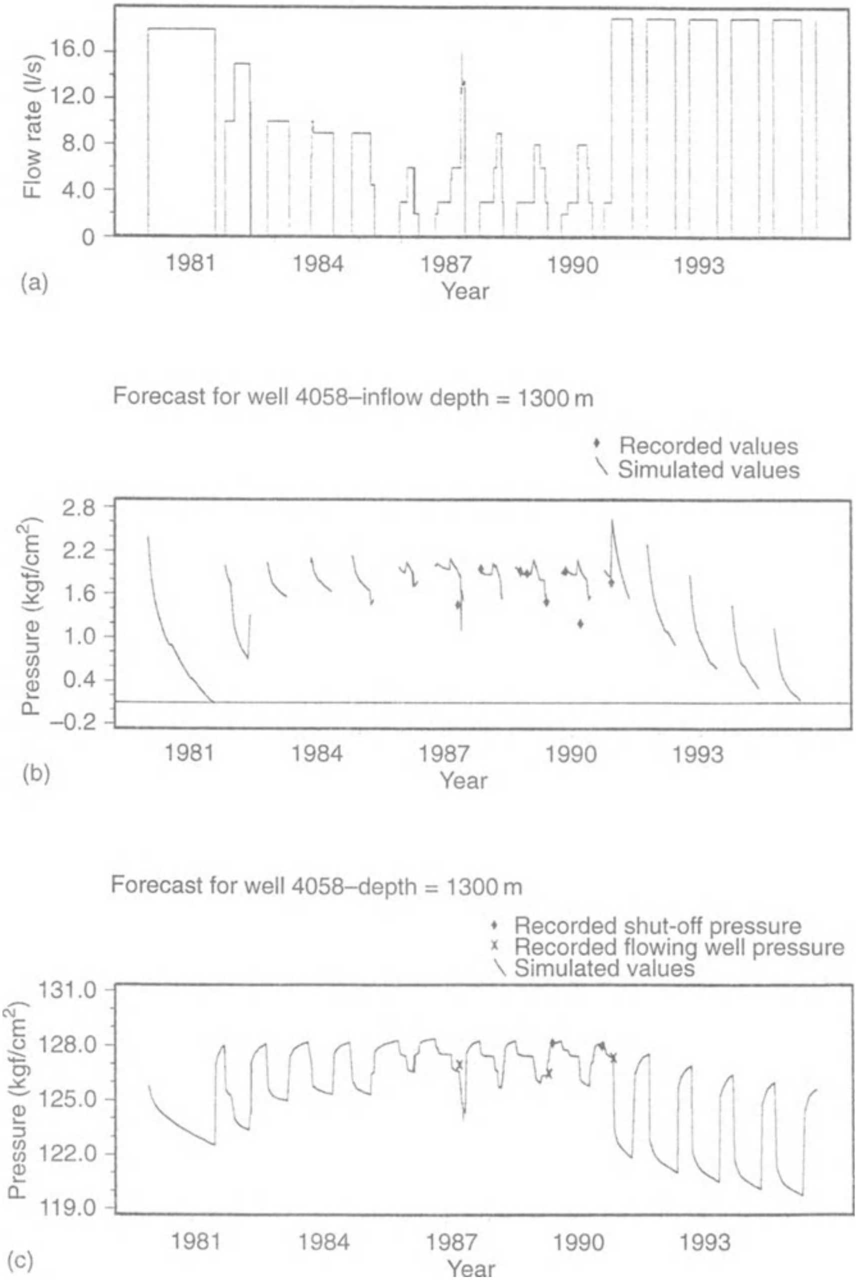

Figure 16.15 Simulation of bottomhole pressure: forecast values. Variation of (a) extracted flow rate, (b) wellhead pressure and (c) bottomhole pressure.

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