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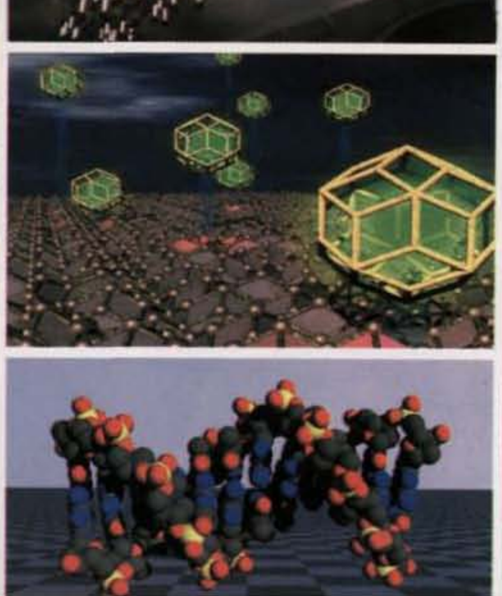
WATER CHEMISTRY

INDUSTRIAL AND POWER STATION WATER TREATMENT

K.S. Venkateswarlu



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Industrial and Power Station Water Treatment

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PREFACE

After my long association with the Bhabha Atomic Research Centre, Trombay, several colleagues suggested that I should write a book on Water Chemistry, considering my deep involvement with the development of this subject. Since I felt that writing a book would be no easy task, I deferred it. Three years later during my recovery from surgery, which restricted my outdoor movements my wife persuaded me to start this task. In deference to her wishes and that of other friends, I made a beginning and soon found that M/s Wiley Eastern Ltd. would be willing to publish it. From then onwards, there was no going back and the result is this monograph, "Water Chemistry and Industrial Water Treatment."

Around 1970, it was realised in the Department of Atomic Energy, BARC and Power Projects, that water chemistry research and development is essential for the smooth and safe operation of India's nuclear power reactors, as they all make use of light or heavy water as the heat transfer medium at high temperatures and pressures. To co-ordinate the effort, a Working Group on Power Reactor Water Chemistry (PREWAC) was set up, which was later transformed into a Committee on Steam and Water Chemistry (COSWAC). I was associated with this effort from the beginning as the Convenor, PREWAC, Member-Secretary COSWAC and subsequently as its Chairman until the end of 1989. The International Atomic Energy Agency, reflecting the world wide emphasis on this subject in the nuclear industry, conducted several co-ordinated Research Programmes on Water Chemistry in Nuclear Power Stations during the 80s. I was privileged to be associated with this effort on behalf of the Department of Atomic Energy. In terms of infrastructure, BARC has set up a dedicated Water and Steam Chemistry Laboratory at Kalpakkam (Near Madras). In addition to chemical programmes, studies on marine biofouling were also initiated. These experiences have given me a close feel for this interdisciplinary subject.

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INTRODUCTION

In her engrossing pictorial volume titled "Eternal India", Mrs. Indira Gandhi quotes a translation of Rig Veda's "Hymn of Creation" thus:

"Then even nothingness was not, nor existence. What covered it ? In whose keeping ? Was there cosmic water in depths unfathomed ? ... All of them was unillumined water, that one which arose at last, born of the power of heat."

The association of water with heat energy dates back to hundreds of million of years, if not to two billion years. There was a time in the very distant past when the earth and its environment were so different from what we experience now. It was a time when the atmosphere was not very dissimilar to the composition of the gases emanating from volcanic eruptions and contained much water vapour. A time when the north east corner of present day South America fitted snugly into West African coast. It was a time when the isotopic composition of uranium (U) was such that the more easily fissionable U-235 was about 3 per cent and not the present value of 0.7 per cent. As the temperature of the earth's surface cooled down to below 100°C, water vapour in the atmosphere started to condense and there were "rains". Rain water began to accumulate and flow over the surface of the earth. When this happened over an area now known as Oklo in Gabon, W. Africa, the water streams surrounded the "low enriched" uranium mineral deposits and a nuclear fission chain reaction ensued, releasing considerable quantities of energy. When the surrounding water evaporated due to the heat generated by the fission process, the chain reaction stopped, since water which acted as a neutron moderator was lost. Subsequent "rains" would restore the chain reaction. This pulsating system, known as the Fossil Nuclear Reactor, generated about 10^{11} KWH of thermal energy. This was at a time when there was no fire as there was no vegetation. Neither were there combustible gases such as hydrogen or methane in the atmosphere, which was any way not a supporter of combustion due to its low oxygen content.

Skipping over the chasm of two billion years, to April 1986, it was the short supply of cooling water relative to the accidental production of excess heat energy in the Chernobyl nuclear reactor No.4 in Ukraine, which led to the world's worst nuclear accident. Unlike at Oklo, in the Chernobyl plant in addition to low enriched uranium, a combustible material, graphite, and the metal zirconium were available in plenty. While graphite caught fire, zirconium reacted violently with the high temperature steam, producing hydrogen that combined with oxygen leading to a devastating explosion. There was also speculation that contact of high temperature water with the molten core of uranium oxide led to a steam explosion in parallel with the hydrogen burn.

Thus, the power of heat and the power of water are always competitive as well as complementary. Their safe co-existence in modern industrial systems having multi metal surfaces, is the subject matter of this monograph.

In nature, the purity of water varies all the way from relatively pure rain water to sea water with high salt content. Even in the case of rain water, depending upon the location and the prevailing environmental conditions in the atmosphere, some impurities such as dissolved gases, (oxides of nitrogen and sulphur), are present. With heavy industrialisation, one hears of "acid rain". Theoretically, pure water is characterised by as low a conductivity as possible, the limit being dictated by the dissociation constant of water at that temperature. At 20°C the theoretical conductivity of water is 0.05 micro siemens per cm (μS/cm). At this limit, the only "impurities" would be the hydrogen and hydroxyl ions formed as a result of such a dissociation. Thus, high or ultra pure water is only a laboratory curiosity and in nature a rain drop in a clean atmospheric environment is the nearest to such an ideal. Once rain falls on the earth's surface, the water becomes loaded with dissolved impurities leached from the surface and the subsurface as the rain water percolates into the soil. Surface waters such as rivers and lakes have relatively less dissolved solids, as compared to ground waters such as bore wells. Geothermal waters have a high salt content as well as dissolved gases. Sea water contains the maximum content of dissolved electrolytes, specially sodium chloride. There are many examples of rivers picking up impurities as they flow over different terrains, so that if at one place calcium (Ca) is more than magnesium (Mg) at another location, it might just be the reverse. The level of dissolved salts in natural waters is important since it determines the use to which the water is put, viz., drinking, agriculture, horticulture, health spas, etc. Different facets of the physical and chemical characteristics of natural waters are reviewed in this book.

The basic physico-chemical properties of water are dependent upon the temperature. As is well known, water can be kept in the liquid phase even above 100°C by the application of pressure. Thus, high temperature water (say at 275°C) implicitly means that it is also under high pressure. If it is in a boiling condition, it will be a two phase system. Being under pressure also means that water or a steam-water mixture at high temperatures will always be a closed system.

In general one might say that water becomes an aggressive fluid at high temperatures. The information that is needed to appreciate this added aggressiveness needs to be discussed. The consequential problems of material compatibility and corrosion in high temperature water and steam are of extreme importance in the smooth functioning of the steam generating industry. The role of dissolved electrolytes, either added intentionally or picked up from surfaces or through unexpected contamination is equally relevant. Surface oxidation, release of corrosion products and their subsequent redeposition depends upon the changing thermal and chemical environment. These are of special importance in nuclear power stations.

The largest volume of water used in the industry is for cooling in chemical processes. Process-water heat exchangers and cooling towers are employed for this task. Depending upon the source of water and the seasonal variations in its composition, a cooling water treatment programme is adopted, which is compatible with the materials employed in the circuit. On the other hand, power plants employ water for cooling the condensers, These are generally once-through systems, although the use of cooling towers to dissipate heat are coming into vogue at inland locations due to the limited supply of water, as well as environmental considerations. Even with sea water cooled condensers, treatment is essential for combating biofouling and corrosion. In fact marine biofouling is so diverse and so persistent that studies to evolve counter measures would take years at each of the coastal sites, inspite of common features.

Natural waters need to be demineralised wholly to make them fit for use in a high temperature heat transfer circuit. A number of techniques have been developed over the last five decades. In addition to distillation, high purity water can be produced on a large scale through ion exchange, while a lower order of purity can be achieved by reverse osmosis. A combination of these two techniques is also being advocated for use in the industry. Special techniques have been developed to prepare ultra-pure water for use in the semi-conductor industry. However, this book deals only with ion exchange and reverse osmosis techniques.

Since the physico-chemical properties of water are a function of temperature and pressure, there is some difference in the feed and boiler water treatment for low and medium pressure industrial boilers as against the high pressure boilers employed by the electricity generating sector. Depending upon the requirements of the chemical process industry, both hot water and process steam are supplied by the former class, while in thermal power stations, the output is high pressure steam that drives the turbine. In other "high tech" industries such as fertilisers and oil refineries, high pressure steam is also used for motive power, as well as in processes such as naptha cracking. The quality of steam is of paramount importance in all these activities. As an example, for modern high pressure turbines, the level of sodium and chloride have been specified to be less than 5 ppb each*.

Co-generation is an attractive concept, in which both the power and the process heat requirements of industries such as fertilisers and petrochemicals

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* Impurities are expressed as 'parts per million', (ppm) or at a still lower level as 'parts per billion', (ppb). In subsequent chapters the units used are mg/l and µg/l which are more or less equal to ppm and ppb respectively. When the specific gravity of water under consideration is nearly 1.0, both sets of units mean the same. In saline waters, milligram/litre (mg/l) is a more appropriate unit.

can be met by a single plant with considerable fuel savings. In this practice, while the high pressure steam drives the turbine for power production, a part of the exhaust steam, which is at a low pressure is used to provide the process heat. Such systems make use of what are known as extraction condensing turbines. The effects of the changes in the steam chemistry within the system due to the changes in pressure can be overcome by adhering strictly to the steam purity limits needed at the high pressure end.

As the steam generating system operates round the clock for prolonged periods, material compatibility with high temperature, high pressure water/steam is vital. The issue is taken up from the design stage itself and is finally reflected in the selection of material and water chemistry control. Nuclear powered steam generators and their primary heat transport systems have their own additional and specific problems in terms of the radioactivity of the fission and corrosion products. Limiting radiation exposure to operating personnel is the primary objective of water chemistry control in a nuclear power station. In addition the life of the plant is extended by providing protection against equipment corrosion.

An attractive as well as an additional source of energy is available from geothermal wells. This natural resource is confined to a few places around the world and is a useful supplement. Even if a geothermal well is not steaming, the hot water effluent can still be made use of for district heating, in addition to being a source of valuable inorganic chemicals. Hydrogen sulphide (H_2S) contamination of geothermal waters is a serious problem. Since, chemical control cannot be easily effected, the designers of equipment look for materials that are suitable in the working environment of geothermal fluids.

No discussion on water chemistry is complete without reference to the chemical and instrumental techniques that are needed for monitoring the properties of water and the measurement of the levels of dissolved impurities. In modern power stations, on-line instrumentation for chemical monitoring and computer controlled chemical addition are becoming more popular. A water chemist would have to make a variety of measurements to enable him to render useful advice to the management. Thus, it is necessary to detail the chemical and instrumental techniques needed by a water chemist.

Desalination of brackish waters, as well as sea water, has gained considerable importance in water starved areas like the desert states around the Arabian Gulf. With its high salt content, sea water poses special problems, in desalination through multiflash evaporation or membrane technology. In India, reverse osmosis is steadily gaining ground, especially as a precurser to ion exchange in water demineralisation, and providing safe drinking water in villages under a Technology Mission. An appreciation of the chemical problems in this area has been provided in this volume.

In view of the increasing concern about polluting our environment, particularly the aquatic environment through the discharge of liquid effluents, it has become absolutely necessary to devise effluent treatment processes that trap the harmful pollutants, while the treated water is recycled. This will be a means of water conservation, as water is a precious resource.

2

PHYSICO-CHEMICAL CHARACTERISTICS OF NATURAL WATERS

A multiplicity of water characteristics is encountered in nature. This is more significant from a chemical point of view than from a physical perspective. From relatively clean and pure rain water with little dissolved impurities, either electrolytes or gases, the chemical contamination stretches upto sea water with a very high dissolved salt content. On the other hand, the temperature ranges only from above 0°C for surface waters to a little over 100°C for geothermal waters.

According to United States Geological Survey(1), most of the fresh water (84.9 per cent) is locked up as ice in glaciers. Of the balance, 14.16 per cent constitutes ground water, while that in lakes and reservoirs amounts to 0.55 per cent. Another 0.33 per cent is in form of soil moisture and atmospheric water vapour. Thus, only a very small fraction of fresh water, viz., 0.004 per cent flows through rivers and streams. The volume of sea water is fifteen times greater than that of fresh water. Hence, the need for the conservation of available fresh water is obvious.

Natural waters can be classified into two categories, viz., sea water (inclusive of estuarian water) and fresh water. At ambient temperature they find maximum use in industry and agriculture. Nearly 90 per cent of the water employed in industry is for cooling purposes and the balance for steam generation. Surface waters might possess colour, odour, taste, suspended solids etc. Ground waters are expected to be free from organic odour and have a relatively less variable composition at the same source. Industry employs water from all types of water resources. This is not the case with agriculture or domestic use. The water quality requirements are somewhat different for different uses. The important characteristics that signify water quality are described below.

2.1 WATER QUALITY

Experience has shown that many diverse factors will have to be taken into account before making comments on water quality. For this reason the concentrations of inorganic and organic substances dissolved in a body of water and their spatial and temporal variations need to be monitored. This exercise should cover not only the major dissolved constituents, but also the minor ones such as heavy metals, detergents, pesticides etc.

The United States Geological Survey(2) has classified different waters on the basis of their Total Dissolved Solids (TDS) content as given in Table 2.1.

Table 2.1 Water Quality vs. Total Dissolved Solids(2)

Water Quality	TDS (mg/l)
Fresh	Less than 1000
Slightly saline	1,000 to 3,000
Moderately saline	3,000 to 10,000
Very saline	10,000 to 35,000
Briny	Greater than 35,000

The underlying chemical relationships between pH, alkalinity, hardness, the ratio of sodium (Na) to that of calcium (Ca) and magnesium (Mg) etc. determines the buffering capacity, deposit formation and corrosive nature of water. The seasonal variations in the quality of some surface waters could be large enough to make the use of such waters more problematic. Under this category comes silt and suspended solids, in addition to dissolved salts. The bacterial content, specially the presence of pathogens, the self purification capacity and the water intake structure also have a bearing on quality. Whatever might be the quality of water available to a user, it can certainly be upgraded by properly designed and executed treatment procedures. It is not advisable to condemn a particular body of water as unsuitable, which may be the only available source at that location.

The United States Geological Survey(2) has given the significant concentration, with respect to several chemicals that might be present in natural waters. Above these levels, such chemicals can cause undesirable effects.

Table 2.2 Chemical Constituents of Significance in Natural Waters (2)

Chemical Constituent	mg/l
Bicarbonate	150 - 200
Carbonate	
Calcium	
Magnesium	25 - 50
Sodium	60 (Irrigation) 20 - 120 (Health)
Iron	Less than 3
Manganese	Less than 0.05
Chloride	250
Fluoride	0.7 - 1.2
Sulphate	300 - 400 (Taste) 600 - 1,000 (Laxative action)

Note : The above are however not to be taken as drinking water standards.

2.2 DRINKING WATER SUPPLIES

The quality of water for domestic use is judged from its total dissolved solids content. The World Health Organisation has stipulated that drinking water should have a TDS content of less than 500 mg/l, although this can be relaxed to 1500 mg/l, in case no alternative supply is available(3). For domestic animals, the limits are the same as for human consumption, although the upper limit may go up to 5000 mg/l, provided the increase is not due to the admixture of industrial effluents containing trace toxic constituents such as chromate. Drinking water should also be free from colour and turbidity. It should have no unpleasant odour (dissolved gases) or taste (absence of certain dissolved solids). A case in point is the smell of chlorine that is once in a way detected in domestic water supply, as a result of excessive chlorination. With an increase in the hardness of water (Ca, Mg, carbonate, sulphate), its suitability decreases with respect to cooking, cleaning and laundry jobs. One of the well documented problems concerning drinking water, is the presence of fluoride. In India, the Technology Mission on Drinking Water laid special emphasis on fluoride, as well as iron contamination in rural water supplies(4). There is also a certain amount of avoidable confusion, since the beneficial effects of a little fluoride in dental care are also known. What is not well publicised is the temperature effect on the fluoride limits in drinking water(5). These are as follows : The lower control limit of 0.9 mg/l at an ambient annual average air temperature of 10°C is reduced to 0.6 mg/l at a temperature of 32.5°C. The upper control limit for fluoride in the same temperature range is reduced from 1.7 to 0.8 mg/l. Thus the flexibility in the range of fluoride control limits in India (as well as in other tropical countries) is much less than say in England or Canada. This is due to the dependence on temperature of the rate of the biological uptake of fluoride by body fluids.

The WHO guidelines for the quality of drinking water (1984) as given in Table 2.3, refer to constituents of significance, both inorganic and organic as well as of microbiological nature to health(6). Under the US law, the Environmental Protection Agency is charged with the task of conducting a regular review of the guidelines for drinking water as applicable in the USA. A result of this is the formulation of National Interim Primary Drinking Water Standards (NIPDWS) in 1985(7), which are slightly different from those issued by WHO in 1984 (Table 2.3). In addition WHO has also issued guidelines for the "aesthetic quality" of drinking water (1984), which are a little difficult to quantify. These are summarised in Table 2.4.

2.3 WATER FOR IRRIGATION

The chemical parameters that are important for water used in irrigation are, the total dissolved solids, the relative proportion of sodium (Na) and potassium (K) to divalent cations such as Ca and Mg and the concentration of boron and other toxic elements. Less than 500 mg/l of TDS is usually satisfactory, between 500 to 1500 mg/l needs special management, while above 1500 mg/l is not suitable for irrigation except under severe constraints(3). The presence of toxic elements usually arises due to contamination by effluents discharged from nearby industries.

Table 2.3. Constituents of Drinking Water Having Significance to Health[6,7]

Constituent	Unit	Limit of WHO Guideline (1984)	Limit of NIPDWS Guideline (1985)
Mercury	mg/l	0.001	0.002
Cadmium	mg/l	0.005	0.01
Selenium	mg/l	0.01	0.01
Arsenic	mg/l	0.05	0.05
Chromium	mg/l	0.05	0.05
Silver	mg/l	—	0.05
Cyanide	mg/l	0.1	—
Lead	mg/l	0.5	0.05
Barium	mg/l	—	1.0
Fluoride	mg/l	1.5	1.4 to 2.4*
Nitrate	mg/l	10.0	10.0 (as N)
Hexachlorobenzene	μg/l	0.01	—
Aldrin	μg/l	0.03	—
Heptachlor	μg/l	0.1	—
Chlorodane	μg/l	0.3	—
1-1-dichloroethane	μg/l	0.3	—
DDT	μg/l	1.0	—
Carbon tetrachloride	μg/l	3.0	—
Lindane	μg/l	3.0	—
Benzene	μg/l	10.0	—
Gross α	pci/l	—	15.0
Ra226 + Ra228	pci/l	—	5.0
β + photon emitters	mrem/y	—	4.0

* Level variation with climatic conditions.

Table 2.4. WHO Guidelines (1984) for Esthetic Quality of Drinking Water [7]

Constituent	Unit	Guideline Value
Aluminium	mg/l	0.2
Chloride	mg/l	250
Copper	mg/l	1.0
Hardness	mg/l	500 (as $CaCO_3$)
Hydrogen Sulphide	—	Odour not to be detected at all
Iron	mg/l	0.3
Manganese	mg/l	0.1
pH	—	6.5 to 8.5
Sodium	mg/l	200
Sulphate	mg/l	400
Turbidity	NTU	5
Zinc	mg/l	5

Sodium and Potassium ion concentrations in natural waters are relevant to irrigation as these cations reduce the permeability of soils. On the other hand,

---

* Equivalents per million (epm), is obtained by dividing mg/l (or ppm) by the equivalent weight of the ion under consideration.

Ca and Mg ions, being divalent, are preferentially taken up by the exchange sites in soil, thus reducing Na and K uptake and helping to restore soil permeability. A factor known as the Sodium Absorption Ratio (SAR), also called Sodium Hazard, is defined as,

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \tag{2.1}$$

The concentrations are expressed in equivalents per million (epm)*, which is the same as milli equivalents per litre⁽⁹⁾. Since Ca and Mg concentrations are also governed by presence of bicarbonate and carbonate ions (i.e. partial precipitation), another criterion that has been used is known as RSC (range of soil carbonates). This is defined as,

$$RSC = \left(CO_3^{2-} + HCO_3^{-}\right) - \left(Ca^{2+} + Mg^{2+}\right) \tag{2.2}$$

The concentrations are again expressed in epm. If RSC is greater than 2.5 epm, the water is not suitable for irrigation; the optimum RSC spread being from 1.25 to 2.5 epm.

2.4 SALINE WATERS

Sea water is not suited for domestic and irrigation purposes. Sea water with a salinity of 35 g/l has an average density of 1.0281 kg/l at 0°C. A variation in salinity of 1 g/l causes the density to change by 0.0008 kg/l. In recent decades, desalination of brackish as well as sea water (an industry by itself) has come into vogue in arid and desert locations, for producing drinking water. Also made use of, is coastal saline groundwater. This is used for horticulture rather than for agricultural purposes. Sea water is used for cooling power plant condensers, when the power station is on the coast. In this context, the biofouling characteristics of sea water at that particular location are of much greater relevance than the chemical parameters.

2.5 ORGANIC LOAD

Natural waters contain organic matter in addition to inorganic substances. This poses several problems with respect to power station water chemistry. The two main areas of concern are as follows :

(a) It can lead to blocking of functional groups of the ion exchange resins of water treatment plants because of irreversible absorption, leading to reduction in the ion exchange capacity as well as damage to the resins.

(b) When carried into the boiler with the deionised water, it may get decomposed into acidic products which can affect not only the boiler water pH, but also its tendency to foam. This can lead to steam entrainment of boiler water, salination of super heaters and turbines. In addition, corrosion in the condensation zone can also result because of volatile decomposition products.

Several techniques have been developed to isolate organic substances from water and to estimate them quantitatively⁽⁸⁾. However, most of these methods are expensive in terms of time involved as well as equipment. Therefore, power plant laboratories usually determine only the potassium permanganate value. The Association of Boiler Manufacturers, Germany, (VGB) found that ultra violet (UV) spectrophotometry carried out in the range of 200 to 340 nm may furnish very useful information about these organic substances (humic acid, lignin sulphonic acid etc.) without the need of isolating, identifying and quantifying the individual constituents.

The breakdown of organics in steam generating systems is leading to problem situations in several power stations. Consequently more and more electrical utilities are switching over to the determination of Total Organic Carbon (TOC), rather than depending on potassium permanganate value of the raw water. Sophisticated analysers are marketed for this task.

In principle it is advantageous to separate organic substances from the raw water through an appropriate pre-treatment. For this, addition of preliminary purification stages ahead of DM plant is recommended. These are flocculation, flocculation-decarbonization and use of anion exchangers as absorbers. Oxidising agents such as chlorine or ozone can also be tried. Under certain conditions, however, it is possible to carry out the ion exchange as well as organic substance removal within the plant.

2.6 CHEMICAL PARAMETERS GOVERNING WATER QUALITY

The quality of surface water from rivers and lakes is important to industry, as it determines the chemical or demineralisation treatment needed, to make it compatible with the construction materials of cooling and heat transfer circuits. Since, water quality varies with location and seasons, water quality monitoring is an essential activity for any industry that makes use of a water source. Biofouling due to surface water is also a problem that has to be tackled. In certain instances, sub-surface or groundwater (from a borewell farm) is also used. In view of variations expressed due to blending of water from different borewell farms, there are instances where the industry experiences changes in water quality on a day to day basis. Thus, more care needs to be exercised.

It is essential to appreciate the significance of limits set on chemical parameters defining water quality. The hydrogen ion concentration is represented by the pH value. By and large the pH of natural waters lies in the neutral range. For drinking water a pH of 6.5 to 8.5 is recommended, while for irrigation the range can be slightly wider viz., 6.0 to 9.0. There are instances when, due to contamination of dissolved gases such as sulphur dioxide or oxides of nitrogen, rain water would have a pH in the acidic region, leading to the phenomenon of "acid rain". Some surface waters passing over areas that are rich in sodium and potassium exhibit an alkaline pH. Such examples of acidic or alkaline water, are however, not common. Clean sea water usually has a pH of 8.0 to 8.2.

The electrical conductivity (EC) of water is related to its total dissolved solids content. Since it is easy to measure this parameter, it is a very useful indicator and is expressed as microsiemens/cm at 25°C. The water quality is usually judged on the basis of its value, as given in Table 2.3⁽⁹⁾.

Table 2.5. Specific Conductivity vs. Water Quality(9)

Specific Conductivity (μS/cm)	Water Quality
Less than 250	Excellent
250 - 750	Good
750 - 2000	Permissible
2000 - 3000	Needs treatment
Greater than 3000	Unsuitable for most purposes

A commonly indicated water quality parameter is its hardness, due to presence of Ca and Mg in combination with anions such as carbonate and sulphate. The presence of these two divalent cations is essential for ensuring soil permeability as well as for the growth of crops. Thus, one measures what is known as Ca hardness, Mg hardness and the sum of these two viz., the total hardness. The measurement of Ca and Mg is through simple volumetric procedures. While hardness per se is not harmful to health, it is better to avoid hard water for drinking. On the other hand, extra hardness will mean the consumption of more soap in washing and also scale formation in cooling water circuits and boilers. It should be remembered that very soft water induces corrosion in iron pipe line. In terms of hardness, the water quality is designated as shown in Table 2.6(9).

Table 2.6. Hardness vs. Water Quality(9)

Hardness expressed as mg/l of $CaCO_3$	Description of Water
0 - 50	Soft water
50 - 100	Moderately soft
100 - 150	Neither hard nor soft
150 - 200	Moderately hard
200 - 300	Hard water
Greater than 300	Very hard

As against the above, the United States Geological Survey Classification of Waters(2) based on hardness [expressed as calcium carbonate ($CaCO_3$) mg/l] gives 0-60 as soft, 61-120 as moderately hard, 121-180 as hard and above 180 as very hard.

At concentrations above 3000 mg/l, Mg is toxic. In the presence of large concentrations of Mg, soluble silica would cause the precipitation of magnesium hydroxy silicate.

Chemical Oxygen Demand (COD), represents the total consumption of potassium dichromate during hot oxidation of water samples and covers a majority of organic compounds and oxidisable inorganic species.

Alkalinity is usually defined in terms of bicarbonate, carbonate and hydroxide ion concentrations. Bicarbonate alkalinity is also called methyl orange alkalinity or M-alkalinity, while P-alkalinity (Phenophalien alkalinity) signifies the presence of carbonates and hydroxide ions. As defined P-alkalinity includes all the hydroxides, but only half of carbonate content. Higher alkalinity causes the precipitation of Ca and Mg leading to the problem of scaling on heat transfer surfaces.

Coming to the presence of other anions in natural waters, chloride takes precedence over others, especially for domestic use. If chloride is present at over 250 mg/l, it is not suitable in food processing and if it is over 1000 mg/l, the water is not suitable for industrial cooling because of the corrosive effects of the chloride ion on several metallic surfaces.

While nitrates are needed for increasing agriculture productivity, more than 50 mg/l is not to be allowed in water for domestic use. The problem of fluoride has already been dealt with. In waters meant for irrigation, boron concentration should not exceed 1 mg/l, as otherwise it is harmful to plant growth.

A discussion on water quality is not complete unless mention is made of the biological monitoring of surface waters(11). In this technique a number of fish are maintained in a channel through which a part of water stream is diverted and their physiological responses are recorded for symptoms of stress. The fish swimming against the stream of water in the test channel emit signals of the order of 10 to 15 μA. Their muscle potentials are of the order of 60 to 80 mV which are attenuated by the dielectric constant of water. By suitable amplication and integration, the normal activity of the fishes can be recorded. If the water quality deteriorates (low dissolved oxygen, presence of toxic chemical etc.), the fish will be affected and this will be reflected in the record of their emitted electrical impulses. While such systems have been used in many countries for monitoring the quality of flowing river water, the best results are obtained in less dynamic laboratory applications and in monitoring the quality of cooling tower water in industry.

2.7 CLASSIFICATION OF WATER QUALITY

Using the specific conductivity and the SAR value of natural water, a salinity hazard diagram has been constructed to classify waters meant for irrigation. There are five groupings in terms of conductivity and four in terms of SAR. Consequently, water quality is often referred to as C_1S_1 (Excellent) --- C_2S_4 (Bad) etc.(10).

The geochemical system of water quality classification rests on the basis of the predominant cations and anions that are present in equivalents per million. This leads to five types, viz. (a) Calcium bicarbonate, (b) Sodium bicarbonate, (c) Calcium chloride, (d) Sodium chloride and (e) Mixed type.

Another classification makes use of the specific conductivity and Biological Oxygen Demand (BOD) as the defining parameters(3). BOD is the quantity of oxygen consumed at 20°C and in darkness during a fixed period of time, through the biological oxidation of organic matter present in water samples. By convention, BOD or BOD_5 is indicated, which is the quantity of oxygen consumed during 5 days of incubation.

The BOD of a water body, although its practical determination is open to a number of reservations, is the most satisfactory parameter for characterising the concentration of organic matter. WHO has imposed a limit of 4 mg/l on the BOD of raw water to be used for pubic supply. If BOD is greater than this value, a part of the organic matter carrying bacteria and pathogens is likely to escape removal and pass into the water distribution system. The presence of toxic substances inhibits bacterial life and gives a low BOD which is not necessarily a sign of clean water fit for consumption.

Considering specific conductivity and BOD together, natural waters have been divided into five classes as shown in Table 2.7 :

Table 2.7 Classification of Natural Waters(3)

Specific Conductivity	BOD	
	LOW	HIGH
	95% of the time less than 4 ppm	More than 5% of the time above 4 ppm
Low (95% of the time less than 750 μS/cm)	Class 1	Class 4
Intermediate	Class 2	
High (95% of the time more than 2250 μS/cm)	Class 3	Class 5@

@ All toxic Constituents come under this class.

Class 1 : Suitable for public consumption as well as other uses.
Class 2 : Suitable after some treatment, but not fit for irrigation if a better source is available.
Class 3 : Not suitable without proper treatment for any purpose, except for watering cattle.
Class 4 : Suitable for irrigation, but treatment required for drinking and for industry.
Class 5 : Unsuitable for all purposes.

2.8 EXAMPLES OF SURFACE WATER QUALITY IN INDIA

To illustrate some of the points discussed above, water quality data assembled by different organisations in India, are presented below. These are only typical examples and a voluminous data is available on water quality of surface and ground waters in India.

2.8.1 River Waters

In a study of the Cauvery river by the Soil Mechanics and Research Division, PWD, Government of Tamil Nadu(9), it has been shown that all along its course, the water is of the calcium bicarbonate type, except at certain locations in Salem and Tiruchirapally districts where the discharge of industrial effluents into the river, turns it into sodium bicarbonate type. Obviously water drawn from these locations, will be less suitable for irrigation. The water quality as a function of the beginning and end of flow season in the river all along its course indicated that TDS is less at the end of the flow season. A study was also conducted of the water quality in 14 reservoirs and an attempt was made to correlate the electrical conductivity with either bicarbonate, chloride and sulphate. In most cases, the correlation was good with bicarbonate, while some showed a good correlation with chloride. There was one reservoir which showed sulphate correlation with EC. The reservoir waters are mostly of the C_1S_1 or C_2S_1 type. Interestingly the C_1S_1 type were mildly acidic in nature, while C_2S_1 type were alkaline.

The Maharashtra Engineering Research Institute has carried out water quality studies of Krishna, Godavari, Bhima and Tapi rivers as well as of several reservoirs(12). Krishna, Bhima and Tapi river water was mostly of C_1S_1 or C_2S_1 type with only a few locations showing C_3S_1. On the other hand the water quality in the Godavari ranged all the way to C_5S_1 indicating that in some locations, the river water is not suitable for irrigation because of salinity. In addition, heavy pollution was noticed down stream at Nasik.

Several variations of water quality can be seen from the data on Godavari and Tungabhadra river waters at relatively unpolluted locations. This study by the Andhra Pradesh Engineering Research Laboratories(13), clearly shows the effect of rainfall on the water quality of the Godavari at the sampling locations as shown in Table 2.8.

Table 2.8. Data of River Water Monitoring in Andhra Pradesh(13)

Parameters		Godavari River		Tungabhadra River	
		April '82	June '82	July '82	Sept. '82
Temperature °C		39	31	28	29
pH		7.9	7.6	7.5	8.0
Sp. Conductivity		1380	920	550	400
Ca	mg/l	134	68	20	47
Mg	mg/l	18	24	18	5.5
Na	mg/l	182	180	64	62
K	mg/l	14	—	—	—
HCO_3^-	mg/l	348	464	201	189
Cl^-	mg/l	298	120	39	50
SO_4^{2-}	mg/l	127	137	104	47
NO_3^-	mg/l	1.8	0.6	5.1	2.4
F^-	mg/l	1.4	1.3	0.8	0.4
Silt	mg/l	117	186	—	—
SAR	—	3.9	4.9	2.4	2.3

In Godavari's sample locations, the rainfall lowered the specific conductivity, calcium and chloride, while an increase is seen in bicarbonate and silt. At Tungabhadra's sample location, however, the parameters do not vary much between the beginning and the end of the rainy season indicating scanty rainfall. These studies were extended to locations down stream of paper mill discharges into both the rivers. It was seen that the change in water quality after mixing with the effluents was more marked for Tungabhadra than with Godavari. While the bicarbonate value dipped from 44 percent to 17 per cent of the total anions, the chloride went up from 9 to 13 percent(13).

2.8.2 Coastal Wells

Intrusion of highly saline water into the wells along the coast is a fairly well known phenomenon. The quality of otherwise good groundwater in wells is brought down by such intrusion due to excessive withdrawal. A study of 334 wells along the coast line of Dakshina Kannada district, Karnataka is illustrative of this phenomenon (Table 2.9)(14).

Table 2.9. Saline Water Intrusion into Coastal Wells in Karnataka(14)

pH	5.5 - 6.5 (113)	6.5 - 7.0 (101)	7.0 - 7.5 (61)	7.5 - 8.0 (48)	> 8.0 (11)
EC (µS/cm)	200 (142)	200 - 500 (75)	500 - 800 (49)	800 - 1200 (38)	> 1200 (30)
Chloride (mg/l)	30 (175)	30 - 70 (60)	70 - 150 (47)	150 - 300 (15)	> 300 (37)

Note : The number within parentheses indicates the number of well in the range of the parameter measured.

Similar studies on sea water intrusion have been reported from Thane District in Maharashtra(15).

2.8.3 Highly Saline Ground Waters

In the arid and semi-arid regions of India, there are numerous examples of wells where the groundwater is highly saline, so that they may be termed as "brine wells". About 50 km southwest of Delhi, in the Gurgaon District of Haryana, a number of such brine wells exist and are being used as a base for thriving salt industry. The chemical composition of some of these well waters is given in Table 2.10(16).

Table 2.10. Chemical Composition of Some Brine Waters, Haryana(16)

Constituent in mg/l	Sultanpur	Muharikpur	Basirpur
TDS	28,182	29,312	24,555
Chloride	16,210	16,300	12,670
Sulphate	2,400	2,530	3,320
Calcium	11,500	930	11,400
Magnesium	2,110	1,760	1,350
Sodium	5,970	7,480	5,540

2.8.4 Cooling Water Quality in Electrical Utilities in India

As mentioned earlier, large quantities of natural waters are employed by the electricity generating units for cooling condensers(17). From the same source of raw water, they make use of a smaller amount for the production of demineralised water. As such it would be instructive to have data of the type of water quality available to such utilities. Table 2.11 gives six examples of raw water quality from different parts of India(18).

A few comments on the data in Table 2.11 are required. Source A although it is from a canal drawn from a big river, is also a partial dumping ground for the sewage of a metropolis. This is clearly reflected in higher value of specific conductivity, as well as the highest permanganate value amongst the set indicating a high organic load.The latter poses problems for the demineralisation plant.

Table 2.11. **(River) Raw Water Analysis with Seasonal Variations as used by Electricity Generation Industry, India[18]**

Chemical	A			B			C			D			E			F		
Parameters	Jan.	Apr.	Sept.	Jan.	Apr.	Sept.	Jan.	Apr.	Sept.	Jan.	Apr.	Sept.	Jan.	Apr.	Sept.	Jan.	Apr.	Sept.
Specific Conductivity μS/cm	438	479	277	158	136	84	85	126	177	470	400	306	970	771	877	309	348	278
pH	8.0	8.0	8.0	7.2	7.5	7.4	7.9	8.0	7.5	8.6	8.6	8.2	7.3	7.6	7.3	8.5	8.6	8.6
Total Hardness mg/l as $CaCO_3$	102	146	119	83	76	60	49	51	32	92	98	85	268	222	523	113	112	101
Total Alkalinity mg/l as $CaCO_3$	146	156	112	72	63	49	59	65	43	126	120	127	257	247	233	123	134	121
Chloride mg/l	34	34	35	10.8	11.9	10.8	5.5	5.0	5.2	48	50	45	245	146	50	17.4	19.5	15.6
Permanganate Value meq/l	4.5	2.2	7.3	1.0	—	1.8	2.6	3.1	0.7	—	—	—	0.6	0.6	0.6	0.8	0.9	0.8

A :	River water by the side of an urban metropolis in North India.
B .	River water in East India.
C :	River water in Central India with other industries nearby.
D :	River water in South India.
E :	Ground water (Borewell farm) in South India by the side of an urban metropolis and sea.
F :	River water in Western India.

Sources B and C are fairly clean. Organic load is seen in Source C, probably due to the locations of industries nearby. Source D, although river water, has a greater content of dissolved impurities as seen by high values for specific conductivity and chloride. Source E is from a groundwater farm (typical borewell waters) and one can readily see the high salt content. This imposes a considerable load on the demineralisation plant of the utility. Source F is moderately "clean". The power plant condensers are cooled by the same raw water in case of A,B,C,D and F, while at location E, the condensers are cooled by sea water. Apart from E, in all other cases, seasonal variation is seen. In general, the values of specific conductivity are lower in September, indicating the general dilution effect of the monsoon.

A nuclear power station located near an artificial reservoir created by a dam on a river in India uses raw water whose typical analysis is shown in Table 2.12(17).

Table 2.12. Typical Analytical Data of Impounded Raw Water from a Reservoir, India (19)

Specific conductivity uS/cm	275
pH	8.2
M Alkalinity	110
P Alkalinity	Nil
Total dissolved solids mg/l	145
Total suspended solids mg/l	5
Silica in mg/l as SiO_2	10
Turbidity in mg/l in silica units	5
Total hardness mg/l as $CaCO_3$	90

Ions	Cations mg/l as the ion	mg/l as $CaCO_3$	Ions	Anions mg/l as the ion	mg/l as $CaCO_3$
Ca	22	54	Bicarbonate	134	110
Mg	9	36	Chloride	11	16
K	2	3	Nitrate	2.5	2
Na	21	45	Sulphate	10	10
Total	—	138	Total	—	138

This type of analytical information is needed for designers of demineralisation plants, where the balance between cations and anions is clearly established, as well as the nature of these ions. While all the cations belong to what is known as the class of strong cations, the major anion, the bicarbonate, belongs to the class of weak anions. As seen later, during the demineralisation process, bicarbonate decomposes after the passage of water through a strong acid cation exchanger giving rise to carbon dioxide which needs to be vented off.

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3

PROPERTIES OF WATER AT HIGH TEMPERATURES AND PRESSURES

The physico-chemical properties of water arise as a result of the structure of the water molecule and its ability to form hydrogen bonds in condensed phases. The two hydrogen atoms are bonded to the oxygen at an angle of 104.5°; close to that expected in a tetrahedral arrangement. The O-H bond length is 0.957 AU. The two lone pairs of electrons on the oxygen are positioned to give a psuedotetrahedral arrangement. The bent shape of the water molecule bestows it with a high dipole moment and high dielectric constant. These two properties make water an excellent solvent in which elctrolytes such as NaCl dissociate into ions, which in turn are hydrated (specially the cations) due to the co-ordinating ability of the lone pair of electrons on the oxygen. The hydrogen bonding often leads to he formation of a secondary shell of hydration, around the first hydration shell.

An important example of anion solvation is the formation of a hydrated electron (commonly referred to as the solvated electron) wherein the positive ends of the water dipoles surround the electron. These properties are unique to water. The only other substances that have such proclivity to a limited extent are liquid ammonia and liquid hydrogen fluoride.

3.1 THERMOPHYSICAL AND THERMOCHEMICAL PROPERTIES OF WATER

The thermophysical properties of water are listed in Table 3.1(1).

When water is employed in industry for cooling, through the use of cooling ponds, cooling towers etc. in combination with process water heat exchangers, the temperature of water ranges from the ambient to about 60°C. In view of this, properties of water at higher temperatures (well beyond 100°C) under pressure are of no consequence in this segment of water use. On the other hand, when water is used to make steam, the temperature in the boilers and the associated steam turbines is in the range of 250-320°C. Thus when one considers steam generation either for production of electrical or motive power, the properties of water and steam at high temperatures and pressures become relevant for understanding the chemistry involved.

Table 3.1 Thermophysical Properties of Water (1)

Property	Liquid	Vapour
Heat of formation at 25°C K.cal/mole	-68.32	-57.8
Energy of formation at 25°C K.cal/mole	-56.69	-54.64
Sp. Heat cal/g/°C	0.998	1.007
Critical temperature, °C	-	374.15
Critical pressure, Kg/cm^2	-	212.2
Critical density, g/cm^3	-	0.32
Critical volume cm^3/g	-	3.28

In view of the temperature difference between cooling water systems and the steam generating systems, it is appropriate to consider the dependence of the physical and chemical properties of water in two temperature ranges, viz., upto 100°C and the other beyond 100°C where pressure is to be applied to keep water in the liquid phase, either fully or in equilibrium with the steam phase. The behaviour of water and steam beyond the critical point of 374°C is also of interest.

3.2 PROPERTIES OF WATER BELOW 100°C

In the temperature range of 0 to 100°C, the density of water is maximum (1.000) at 4°C, while at 0°C it is 0.9999. This is due to the collapse of some of the hydrogen bonds and the release of water molecules trapped in the cavities. Beyond 4°C the density decreases to 0.9971 at 25°C and 0.9584 at 100°C. The decrease in density results in a decrease in the surface tension and viscosity, as shown in Table 3.2:

Table 3.2 Changes in Surface Tension and Viscosity of Water with Temperature(1)

	0°C	25°C	100°C
Surface tension (Dynes/cm)	75.6	72.5	58.9
Viscosity (Centipoise)	1.79	0.89	0.28

The combined effect of such decreases in density, surface tension and viscosity of water (25 to 100°C) is to increase the mobility of the cations and anions present. In the case of high purity water, this would mean an increase in the mobility of H^+ and OH^- ions that are present due to water dissociation. At ordinary temperatures, the ionic product (K_w) of water is very small (pK_w or $-\log_{10}K_w = 14$). The pH is defined as $\log_{10}H^+$ and K_w is the product of $[H^+]$ and $[OH^-]$ concentrations. Thus a simultaneous and equal increase in the values of $[H^+]$ and $[OH^-]$ due to the increased dissociation of water with temperature, would mean that the pH scale, as well as pH as defined will be effected by an increase in the temperature of water. The known range of the pH scale of 0 - 14 at 25°C begins to contract with increase in temperature. For example, the ionic product, whose value at 25°C is 1 x 10^{-14}, increases to 52 x 10^{-14} at 100°C. Consequently, the pH of pure neutral water defined to be 7.0 at 25°C decreases to 6.25 at 100°C. It should be made clear at this juncture that pure water at 100°C will continue to remain neutral and because of the compression of the pH scale at 100°C, the neutral point shows only an apparent decrease. The very fact that the hydrogen ion concentration increases with temperature in pure water, makes it much more aggressive to metallic surfaces at higher temperatures than at room temperature.

As is well known, electrolytes such as sodium chloride dissociate into their component ions on dissolution in water, due to its dielectric constant. This important property of water also undergoes a change with temperature. At 0°C,the value of the dielectric constant of water is 88.0, which decreases to 78.5 at 25°C and to 55.3 at 100°C (and 760 mm Hg.) This means that water loses its ability to effect the dissociation of electrolytes and a fraction of the dissolved substances remains as an undissociated or neutral chemical species. While in the temperature range under consideration this effect might not be of that much importance for strong electrolytes such as NaCl, for weaker electrolytes such as the hydroxides of corrosion products, it has some relevance. Examples are $Fe(OH)_3$, $Zn(OH)_2$ and $Ni(OH)_2$.

The overall effect is that pure water at 50 to 60°C is a more aggresively corrosive fluid than at room temperatures and steps will have to be taken to keep the corrosion rates in the cooling water systems within acceptable limits. This will be dealt with in greater detail in a later chapter.

3.3 PROPERTIES OF WATER ABOVE 100°C

In steam generating systems operating at temperatures well above 100°C, the need for thermal efficiency requires the application of pressure, so that a higher temperature can be reached. Pressure in itself has only a marginal effect on the water chemistry (except with respect to the elevation of its boiling point), but has a profound effect on what has come to be known as steam chemistry. In the two phase system of water and steam, the distribution of solutes is a fucntion of temperature and pressure, rather than temperature alone. The thermophysical parameters and other properties of water as a function of temperature and pressure are given in Tables 3.3, 3.4 and 3.5(2,3).

Table 3.3 Thermophysical Parameters of Water as a Function of Temperature and Pressure(2)

Parameter	Specific Volume cm^3/g		Gibbs Free Energy KJ Mol^{-1}		Entropy J Mol^{-1} ^{o}K^{-1}		Enthalpy KJ Mol^{-1}	
Pressure K. bar	1.0	1.5	1.0	1.5	1.0	1.5	1.0	1.5
Temperature 0°C								
100	1.000	0.984	1.18	2.07	15.7	15.1	7.03	7.72
200	1.084	1.060	-1.29	0.33	33.1	32.3	14.4	14.9
300	1.213	1.169	-5.36	-4.28	47.8	46.5	22.0	22.4

Table 3.4 Variation in the Properties of Water with Temperature and Pressure$^{(2)}$

Property	Thermal conductivity mJ m^{-1} sec^{-1} ^{o}K^{-1}				Static dielectric constant Farad Steradiam per meter					Viscosity* µN Sec mm^{2}		
Pressure K.Bar	0.1	0.25	0.6	0.75	0.1	0.25	0.5	0.75	1.0	0.1	0.5	1.0
Temp. ^{o}C												
100	689	694	703	712	55.7	56.2	57.0	57.8	58.4	287	296	308
150	697	706	719	733	-	-	-	-	-	185	194	205
200	677	690	713	736	34.8	35.4	36.4	37.3	38.0	137	148	162
250	629	650	684	718	27.1	28.1	29.4	30.5	31.4	110	121	132
300	554	582	628	674	20.1	21.5	24.2	25.2	25.3	@	101	113
350	-	-	-	-	-	14.8	17.7	19.3	20.5			

*** To convert values into centipoise multiply by 10^{-3}**

@ Phase transition

Table 3.5 Density of Water : Variation with Temperature and Pressure(3)

Density of Water at 4 K bar		Density of Water at 500°C	
Temp °C	Density gm/cc	Pressure Bar	Density gm/cc
100	1.10	10	0.01
200	1.05	10^2	0.10
300	0.95	10^3	0.50
400	0.87	10^4	1.00
500	0.82	10^5	2.00

In the temperature range of interest to the steam generating sytems, viz., 250 to 300°C, the density of water decreases from 0.6 gm/cc at 250°C to 0.5 gm/cc at 300°C, both measured at a constant pressure of 100 kg/cm^2 (1450 psi). The decrease in density and viscosity coupled with the increase in the dissociation constant of water with increase in temperature results in increased conductivity of pure water as given in Table 3.6. Compared to a value of 4.5 x 10^{-8} µS/cm at 25°C, the conductivity of pure water at 275°C increases to 7.6 x 10^{-4} µS/cm. This in turn makes water very aggressive to the metallic surfaces with which it comes into contact and thus promotes corrosion.

Table 3.6 Specific Conductivity of Water at Different Temperatures

Temp 0°C	Sp. Conductivity µS/cm
20	4.5 x 10^{-8}
31	2.1 x 10^{-7}
49	1.1 x 10^{-6}
86	7.2 x 10^{-6}
156	5.3 x 10^{-5}
274	7.6 x 10^{-4}

The limiting equivalent conductances of several ions in water have been determined as a function of temperature at saturation vapour pressure. Of the different ions, hydronium (H_3O^+) and hydroxyl (OH^-) ions show a large increase in λ_0. Since the number of ions of a given electrolyte are proportional to the dielectric constant (due to increase in temperature), the effect of increased ionic mobility due to the reductions in density and viscosity gets nullified at a certain temperature. In other words, the conductivity of an elctrolyte, like NaCl in water, goes through a maximum when measured as a function of temperature. It so happens that the maximum conductivity of different electrolytes in water, lies in the temperature range of interest (235 to 325°C) to steam generating systems of power stations.

3.4 EFFECTS OF TEMPERATURE ON THE ION PRODUCT OF WATER

The effects of high temperature are nowhere more striking than on the pH value or the pH scale of water and alkalising weak electrolytes such as ammonium and lithium hydroxides dissolved in water. Figure 3.1 shows the temperature

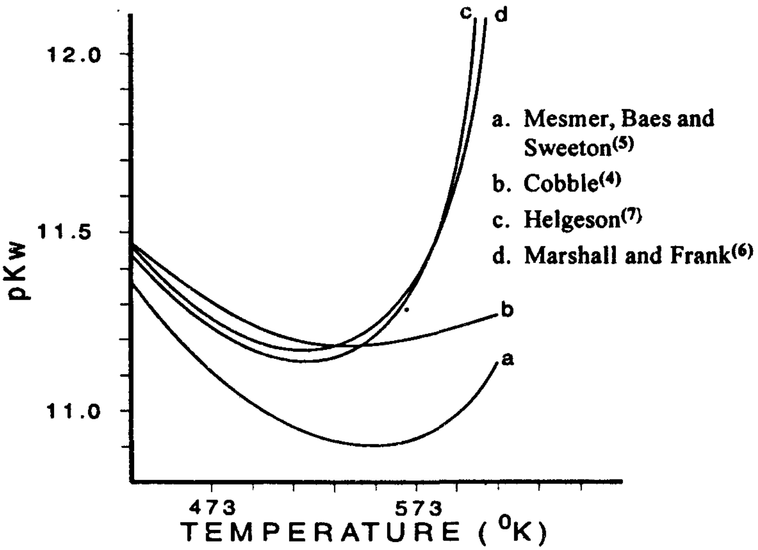

Fig. 3.1 Plot of pKw of Water Vs. Temperatures(8)

dependence of the exponential of the ion product of water (pK_w) in the range of 170 to 340°C. Although there is some difference in the pK_w values as determined by different workers, the trend is the same, viz., the pK_w of water decreases (or K_w increases) upto a certain temperature and then increases (or K_w decreases) as the temperature is increased further. The minimum of pK_w (or maximum of K_w) lies in the temperature range of 230 to 250°C. As seen earlier, since the pH scale and the point of neutrality of pure water are defined in terms of pK_w and the minimum of pK_w value as seen in Figure 3.1 being a little over 11.1, the neutral pH value of high purity water at say 240°C is 5.55. Thereafter the neutral point shifts to higher values. It is once again emphasised that pure water will continue to remain neutral under such conditions, though both H^+ and OH^- concentrations will be at their maximum in equal measure. Thus, water would be most aggressive in the range of 230 to 250°C. An ammonical solution of water that exhibits a pH of 9.5 at 25°C is reduced to 6.4 at 220°C. Similarly water spiked with LiOH that shows a pH of 10.5 at 25°C is lowered to 7.76 at 220°C (Table 3.7). The consequences of such changes are discussed later.

Table 3.7 Changes in pH of Water, Ammonium and Lithium Hydroxide Solutions as a Function of Temperature

Temp °C	Pure Water	NH_4OH	LiOH
25	7.00	9.50	10.50
100	6.16	7.77	8.80
156	5.83	6.96	8.12
218	5.67	6.41	7.76
306	5.89	6.28	8.12

The dielectric constant will continue to decrease with increase in temperature in the range of 100 to 300°C. On the other hand, the dielectric constant of steam will increase with an increase in presssure required to maintain such a temperature. At the critical temperature (374.2°C), the ratio of the two dielectric constants (DC of steam / DC of Water) is unity. In other words, under such a condition, a given solute will be distributed equally between the two phases. However, this is a limiting condition. What is of greater interest is the range of 235-320°C, in which the ratio is a function of temperature and pressure. The vapour transport of solutes like silica are attributed to this dependence and the higher the ratio, the greater is the solute content of the steam phase, which deposits the solute at a different part of the steam water circuit where temperature and presssure are lower.

It is obvious from the above discusssion that the properties of water undergo significant changes as a function of temperature and presssure. In natural systems such phenomena are encountered in geothermal waters/steam, volcanic activity etc. In modern industrial practice, we come across the behaviour of high temperature - high pressure water from the classical steam engines used for locomotion, to highly complex steam-water circuits of power plants, whether they are fired by fossil fuels or nuclear energy. A certain amount of individuality characterises each system that arises from the interaction of specific materials of construction of the steam-water circuit. However, there are enough common points to broadly discuss and understand the application of the basic concepts of physical chemistry of water and its dilute electrolyte and non-electrolyte solutions to industrial practice, so as to achieve maximum efficiency and economy in energy generation..

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4

WATER CHEMISTRY, MATERIAL COMPATIBILITY AND CORROSION

Water chemistry is a relatively new sub-branch of physical and inorganic chemistry, that signifies different things to different professional chemists. On the other hand, corrosion signifies essentially the same to all professional metallurgists and chemists. Material compatibility is the interface between the two specialities of water chemistry and corrosion since what one is concerned with is basically an interfacial phenomenon, between a metallic or a fine oxide surface (solid) and water (liquid) and steam (gas)(1).

To an environmental chemist, water chemistry would mean the analytical determination of impurities especially the trace toxic inorganic and organic contaminants in water and the detoxification processes thereof. For a chemist involved in a chemical process industry, water chemistry is equivalent to effluent chemistry and effluent treatment. On the other hand to a chemist in a power plant or other industries such as fertilisers, water chemistry would immediately signify the chemical regime that is required to be maintained in the steam-water circuits so as to minimise corrosion and material transport. The latter, although on a very small scale is of serious concern to the chemists associated with the nuclear power industry. Here it would lead to the generation of radioactive nuclides and their transport to unshielded locations where maintenance and repair are needed(2). The focus of the present monograph is on water chemistry in such a high technology based industry, while effluent treatment and environmental chemistry of natural waters is touched upon only for the sake of completeness.

4.1 CORROSION IN AQUEOUS SYSTEMS

Corrosion in an aqueous system occurs due to the interaction between the surface of the materials which come into contact with the aqueous environment, many times under conditions of stress. The stress could be chemical in the sense that the aqueous environment may be acidic or alkaline. The chemical stress can be viewed or understood in terms of thermodynamic and electrochemical concepts. The stress could be metallurgical in the sense that the material surface has defects, either inherent or as a result of the manufacturing process. It might be thermal stress as in a steam generating system. In reality, corrosion would be the consequence of a combination of all the above stress factors. To avoid or minimise corrosion, great care has to be taken in selecting the construction materials as well as in controlling the chemistry of the aqueous environment. The problems posed by faulty water chemistry or material incompatibility are the same in thermal and nuclear power stations as well as in chemical process industries such as fertilisers(3).

Basically, corrosion is a process where the metal atoms leave their location on the surface and stabilise in the form of ions in solution. In high purity water, where no other electrolyte is present to any significant extent, it is the solubilising action of water on a metal surface like iron, which is the first step in the corrosion process. The polarisability of the water molecules on contact with the iron surface leads to the weakening of the O-H bond and gives rise to reactions below, which show the combined effect of solubilisation and hydrolysis(2).

$$\text{n Fe (Bulk)} \rightarrow \text{(n - 1) Fe (Bulk)} + Fe^{2+} + 2e^- \quad (4.1)$$

$$Fe^{2+} + 6H_2O \rightarrow [Fe(H_2O)_5 OH]^+ + H^+ \quad (4.2)$$

The primary corrosion product is $[Fe(H_2O)_5 OH]^+$, which gives the second hydrolysis product, $Fe(OH)_2$, Fig 4.1. These two chemical species appear later, in many forms due to secondary reactions as shown in Fig.4.2.

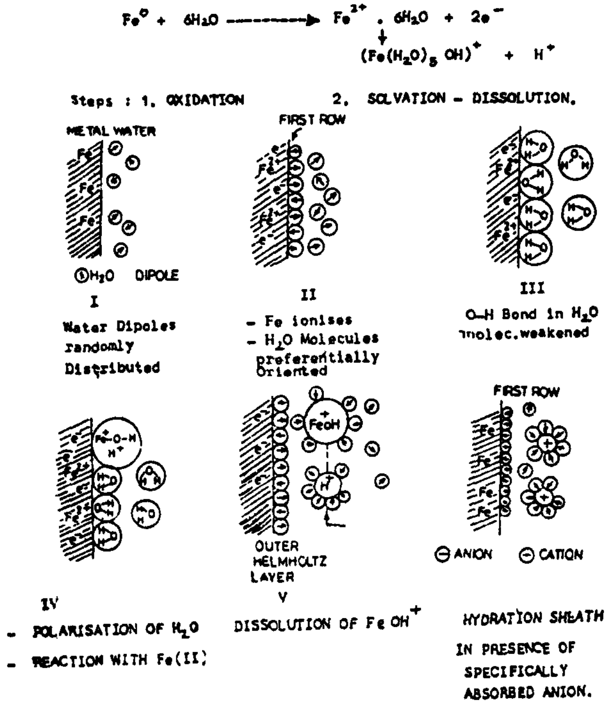

Fig. 4.1 Mechanism of the First Step in Iron Corrosion

The secondary products are FeO.OH, FeO, Fe_3O_4, Fe_2O_3 etc. These secondary reactions being pH dependent, the percentage of iron present in each of the above forms also shows a pH dependence. Reaction (4.1) in terms of the fundamental galvanic dissociation of metal atoms (in this case Fe) from a surface in contact with water is anodic. Corresponding cathodic reactions may be written as,

$$2e^- + 2H_2O \rightarrow 2OH^- + H_2 \qquad (4.3)$$

$$2e^- + {}^1/_2O_2 + H_2O \rightarrow 2OH^- \qquad (4.4)$$

Reaction (4.3) points to the possibility of hydrogen formation in a corrosion process, while reaction (4.4) gives a clue as to the role of dissolved oxygen present in water. The lower the dissolved oxygen content of water, the smaller will be the cathodic reaction (4.4). In general, corrosion is less, if the water is deoxygenated.

In high temperature, slightly alkaline and deoxygenated aqueous environment, the principal corrosion product formed on an iron surface (carbon steel, stainless steel) is magnetite, Fe_3O_4 (Fig.4.2). Under the conditions specified, there is a possibility for Fe $(OH)_2$ to exist as neutral molecules in solution, which get converted to magnetite in a short time.

$$3\,Fe\,(OH)_2 \rightarrow Fe_3O_4 + H_2 + 2H_2O \qquad (4.5)$$

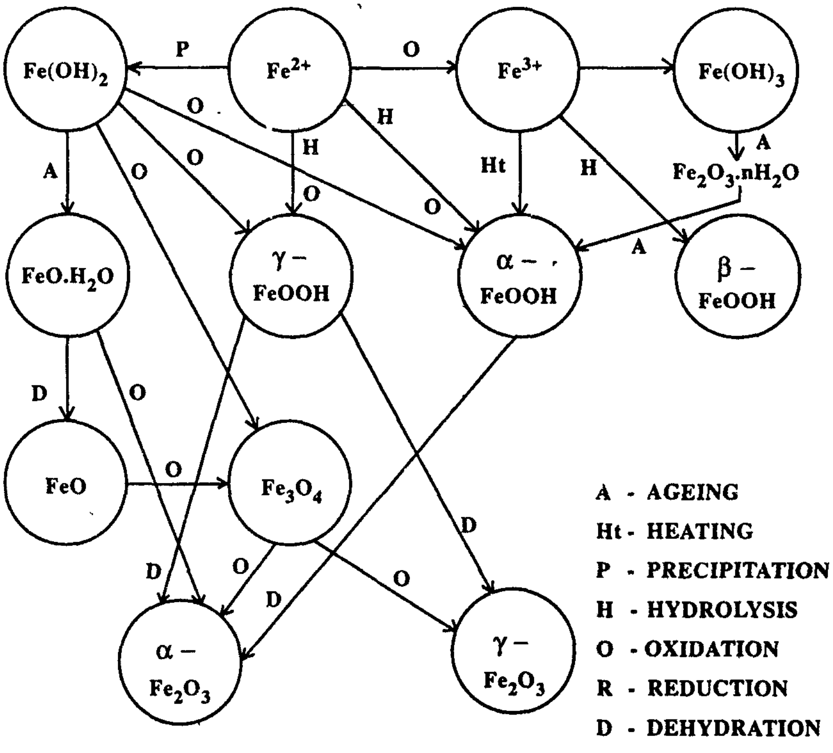

Fig. 4.2 Possible Species of Iron under Aqueous Environment

This reaction is known as Schikkor reaction(4). with a thermodynamically favoured standard free energy change, ΔG^0 of -9.9 kcal at 298°K (25°C).

The hydrogen generated in reaction (4.5) is in addition to that from (4.3). In actual practice, the determination of the hydrogen content of steam (in view of the very limited solubility of H_2 in water) serves to monitor the overall corrosion process in the steam water cycle. There is evidence to indicate that magnetite is also formed directly on iron surfaces as follows :

$$3\,Fe + 4\,OH^- \rightarrow Fe_3O_4 + 2\,H_2 + ne^- \qquad (4.6)$$

$$H_2O\ (Bulk) + ne^- \rightarrow H_2 + nOH^-\ (Bulk) \qquad (4.7)$$

Compared to the bulk density of Fe (~8g/cc) that of magnetite is lower (~5.2 g/cc). Hence the direct formation of Fe_3O_4 on an iron surface leads to a sudden volume expansion.

On stainless steel surface, Fe_3O_4 undergoes a series of substitution reactions with the alloying elements (Cr and Ni) and complex ferrites such as $CrFe_2O_4$ and $NiFe_2O_4$ have been identified in the corrosion products.

Before dealing with the behavior of magnetite and other oxides in high temperature aqueous environment, it would be advantageous to complete the discussion on corrosion, which as noted earlier could have its origin in chemical, electrochemical and metallurgical parameters. What was discussed so far is a general attack occurring uniformly over metallic surfaces on contact with water. There are other specialised forms of corrosion(5). Pitting is one such, extremely localised attack resulting in pits and even pin holes such as in chloride induced pitting of stainless steel under stagnation. Another form is known as stress corrosion caused by a synergistic effect of tensile stress and corrosive environment. Examples are, caustic cracking of boiler, tubes, cracking of stainless steel in a chloride environment etc. Concentration of impurities in crevices and under deposits leads to an attack termed as crevice corrosion If two dissimilar metals / alloys are in contact through an aqueous environment, galvanic action will cause one of the surfaces to corrode rapidly. The use of sacrificial electrodes is a direct application resulting from this form of corrosion. From a metallurgical view point, intergranular corrosion and selective leaching need to be mentioned. The former is a localised phenomenon occurring along the grain boundaries such as the corrosion of stainless steel in heat affected zones of a weld. The de-zincification of brass is an example of selective leaching from an alloy, as a result of which porosity is developed. A purely mechanical form of attack is the erosion - corrosion, as experienced at inlets of condenser tubes of a sea water cooled power station.

4.2 SOLUBILITY OF MAGNETITE (FE_3O_4)

In the temperature range of interest to power station water chemistry the solubility of magnetite and other corrosion product oxides is proportional to the temperature and pH(6,7). Since pH scale as defined undergoes a change with temperature, one must be very clear about what is specified by pH, e.g., measured at 25°C or say at 300°C, as illustrated in Figs. 4.3 and 4.4

Different sections of the steam water circuit are at different temperatures. Thus changes in solubility of magnetite would mean that in a closed, but circulating heat transport system, magnetite gets transported (solubilised and redeposited) from relatively hot to cold sections of the system. Thus, a process of material transport, although on a small scale, is set up in the closed, circulating

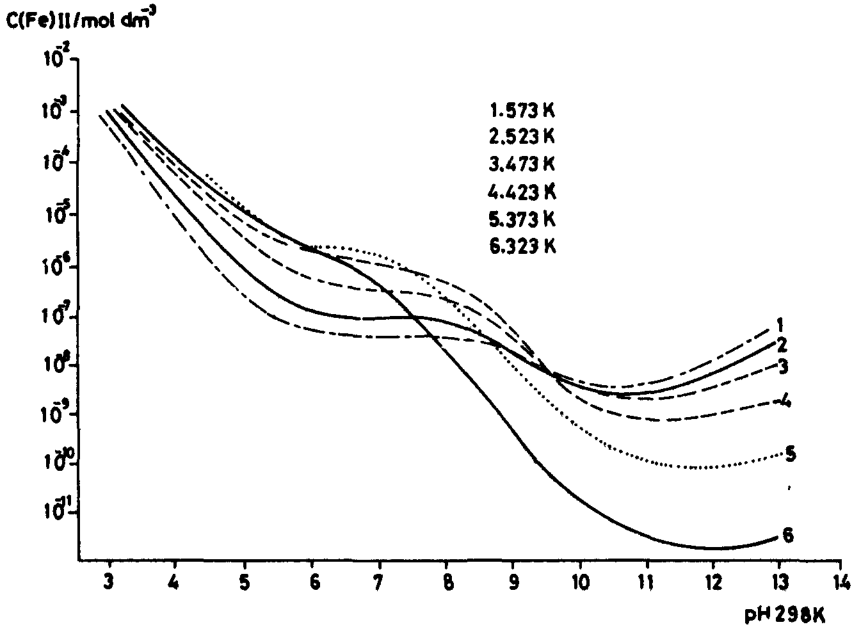

Fig. 4.3 Solubility of Magnetite in the pH Range 3 to 13 (6)

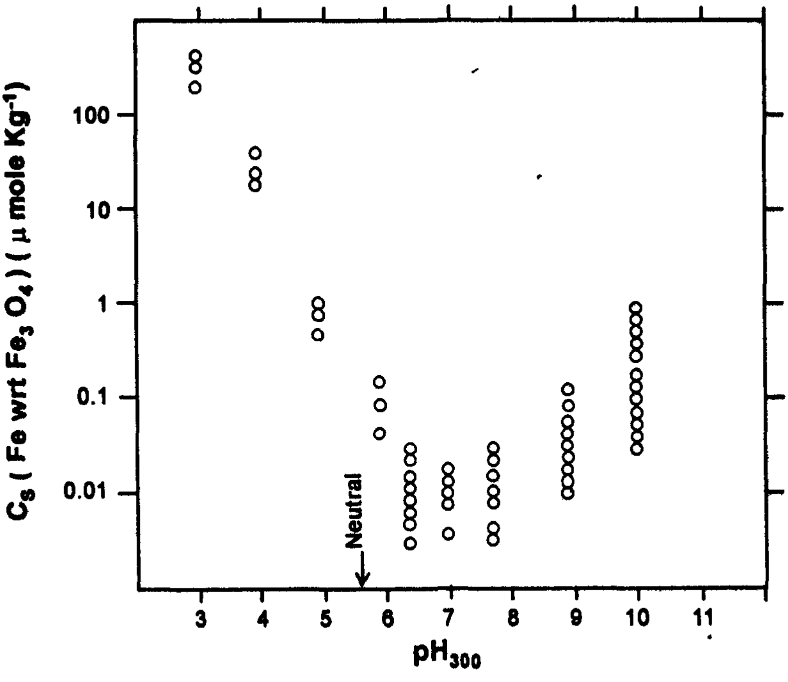

Fig. 4.4 Solubility of Magnetite at 300 °C vs. pH_{300} (7)

high temperature and high pressure water (and steam) circuit. In fossil fuelled power stations, this phenomenon is of no serious consequence, except that under deposit attack is promoted by the formation of deposits all over the place. However, in a nuclear power station, this would mean the transport of corrosion products through the reactor core and their activation by neutrons, leading to radioactive nuclides. These are transported to out-of-core surfaces and get deposited on them, thereby contributing to a radiation field which prevents accessibility to the system for maintenance. This is popularly known as the 'man-rem' problem and is a direct consequence of water chemistry at high temperatures(2).

4.3 DEPOSIT FORMATION VS. ROLE OF ZETA POTENTIAL

The deposit forming species are oxides, hydroxides and frequently hydrous oxides. The latter are as a result of normal chemical, electrochemical and metallurgical factors operating at the interface of a metal and high temperature water(8). Two major forces are responsible for the deposition of such particles, viz., the mass forces and the surface forces. The mass force is directly proportional to the mass of the particles (i.e., to the cube of the diameter of the particles), while the surface forces is proportional to the surface area of the particles (i.e. square of the diameter of the particles). As the size of the particle decreases, the surface forces prevail over the mass forces. When any solid is in contact with an electrolyte solution, it acquires a surface charge which is balanced by an equal and opposite charge in the liquid layer near the surface, but arranged in two layers which is known as the electrical double layer. The first one is the adherent monoionic layer of counter ions held by chemical forces and immovable with respect to the solid. The second one is a diffuse outer layer of counter ions mobile with respect to the surface as shown Fig. 4.5.

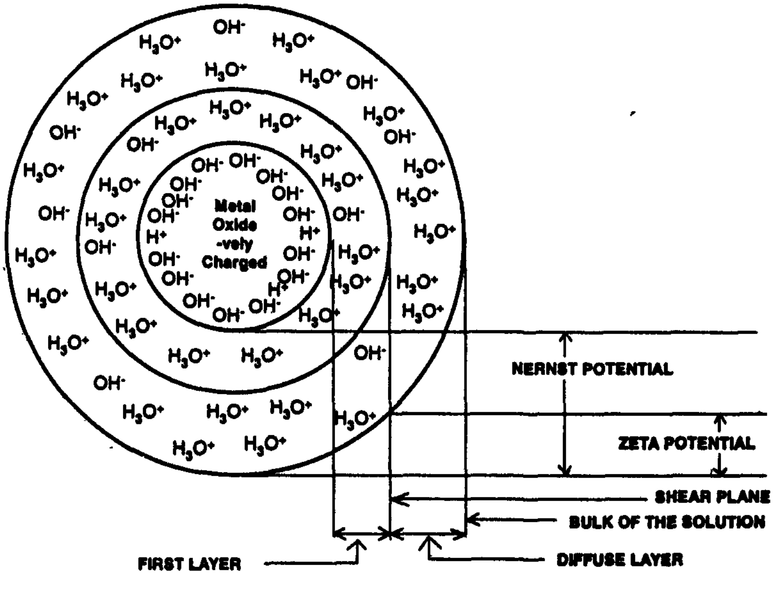

Fig. 4.5 Conceptual Reprentation of Electrical Double Layer(8)

The difference of potential existing between the shear plane and the bulk of the solution is called the Zeta potential (ζ.) The magnitude of ζ is a measure of surface charge on the solid surface and its sign is the resultant of the charge on the surface and the charge on the first layer.

Primary corrosion products, as seen earlier, have MOH groups at the surface. The acidic property of these MOH groups becomes pronounced as the pH decreases. At a particualr pH, ζ and hence the surface charge becomes zero and this pH is known as the Point of Zero Charge(PZC) of the oxide. At PZC, the surface has an equal tendency to release H^+ or OH^- ions. Hence, ζ at a constant temperature can be represented as

$$\zeta = K\ (PZC - pH) \qquad (4.8)$$

Where K is the proportionality/constant and pH is that of the aqueous phase in contact with the oxide surface. From equation (4.8) it can be seen that the oxide surface is positively charged when pH is less than PZC and negatively charged when pH is greater than PZC. Table 4.1 lists the PZC values of several corrosion product oxide and hydroxide species, with H^+ or OH^- as the only potential determining ion$^{(8)}$.

Table 4.1 PZC Values of some Corrosion Product Species$^{(8)}$

Metal	Species	PZC at 30°C	PZC at 90°C
		(in pH units)	
Cr	hydrous Cr_2O_3	7.0	-
Mn	$Mn(OH)_2$	7.0	-
	MnO_2	4.0 to 4.5	-
Fe	FeOOH	5.4 to 7.3	-
	$Fe(OH)_2$	12.0 ± 0.5	-
	α - Fe_2O_3	6.7	-
	γ - Fe_2O_3	6.7 ± 0.2	-
	Fe_3O_4	6.85	5.4
Co	CoO	11.5	10.8
	$Co\ (OH)_2$	11.4	-
Ni	NiO	10.3 ± 0.4	-
	$Ni\ (OH)_2$	11 to 12	-
Cu	$Cu(OH)_2$	9.4 ± 0.4	-
	CuO	9.5 ± 0.4	8.2 ± 0.4
	Cu_2O	8.44	7.36

The apparent decrease in pH of water and dilute aqueous solutions is also seen in the values of PZC as a function of temperature, since PZC is expressed in units of pH.

4.4 DISTRIBUTION OF IMPURITIES BETWEEN WATER AND STEAM

While efforts are made to keep impurities such as NaCl, NaOH and SiO_2 at minimum values in the water phase of a steam water circuit, they can never be brought down to zero level. By implication, a steam generating system promotes concentrations of such impurities in the water phase. Depending upon their solubility in the steam phase under the conditions of pressure and temperature of the steam, the distribution of such impurities between the two phases is of special relevance to the performance of the turbine. This is so since the pressure and temperature decrease in the various stages of the turbine leading to the deposition of substances like NaCl and SiO_2 on the turbine blades. If allowed to go unchecked, such deposition will lead to the failure of the turbine blades. Hence the basic information on solubilities of salts and metallic oxides in steam and their distribution coefficients, needs to be discussed for a proper understanding.

The distribution coefficient K is defined as the weight ratio of the concentration in the steam phase to that in the water phase.

$$K = \frac{ppm(steam)}{ppm(water)} \quad or \quad K = \frac{mole\ /\ Kg.steam}{mole\ /\ Kg.water} \tag{4.9}$$

For neutral compounds such as oxides, the distribution coefficient depends only upon the solubility. On the other hand, for electrolytes such as NaCl, NaOH etc., an equilibrium between the neutral form and the respective ions also comes into play. As seen earlier decrease in the dielectric constant of water with temperature will effect this equilibrium in favour of the neutral species. Thus in general, K increases with temperature which would automatically involve the pressure of the steam phase. Martinova[9] has described what are known as the carry over coefficients into steam from water as a function of pressure. This is generally known as a 'ray diagram' and is shown in Fig. 4.6.

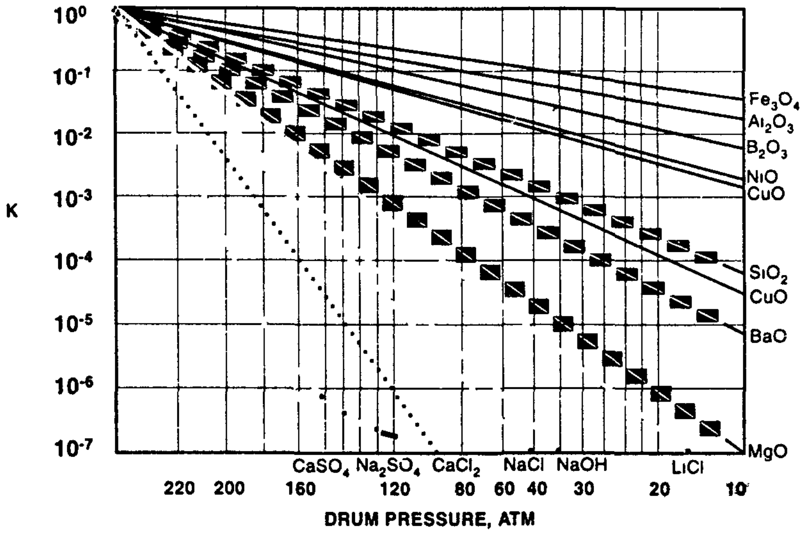

Fig. 4.6 Ray Diagram of Carryover Coefficients of Salts and Metal Oxide Contaminants in Boiler Water[9]

From Fig. 4.6 it may be noted that in general, the carry over of metallic oxides to the steam phase is much greater than of salts. This is to be expected since in the water phase also, the oxides exist as neutral molecules. In the context of a power plant, the carry over coefficients of Fe_3O_4 and other Fe oxides, SiO_2, NaCl and NaOH are of special importance.

The International Association for the Properties of Steam has compiled extensive data on the distribution coefficients and other relevant information pertaining to Fe_3O_4, SiO_2, NaCl and NaOH in steam-water cycles of power plants[10,11]. The data are basic in nature and valuable in understanding the vapour carry over of oxides and salts. As an example Fig. 4.7 shows the solubility data of NaOH on pressure(P), temperature (T) coordinates.

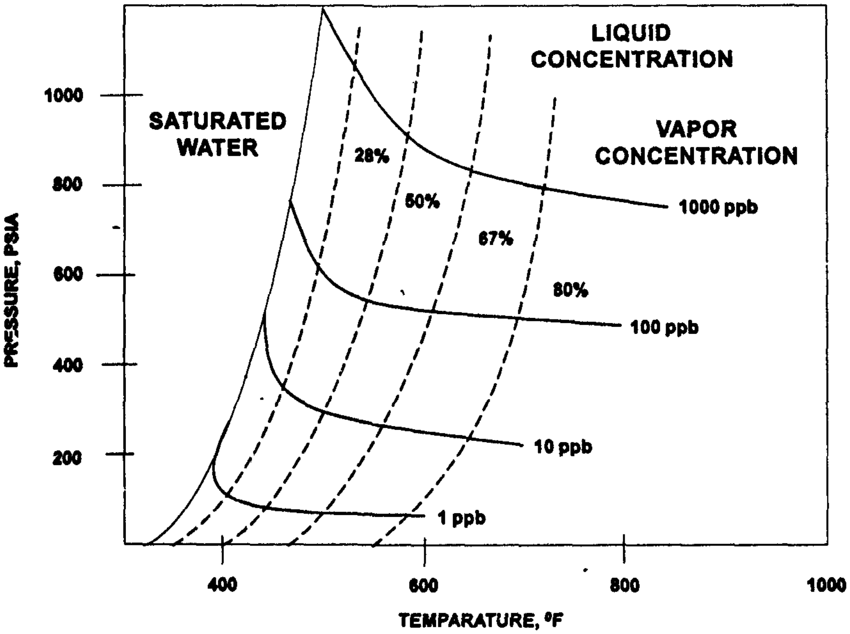

Fig. 4.7 Caustic Solubility Data Shown on P, T Coordinates(10)

The caustic solubility constant composition lines approach the saturation curve asymptotically. If one considers only those areas with a very small amount of superheat, concentrated caustic solutions are possible at virtually every stage of pressure decrease (turbine expansion) that crosses the saturation lines. Calculated data on the vapour pressures of concentrated caustic solutions are also shown in Fig. 4.7. The same data and extrapolations are shown in Fig. 4.8, on a Mollier diagram. The overall conclusions are the same through either method of data representation. If one proceeds from the assumption that the concentration in the liquid phase can attain very high values locally, considerable quantities of the substances can be carried over into steam. Thus from Fig. 4.8, it may be seen that at 290°C (550°F) and a concentration of 50 percent in the water phase, upto 1000 ppb of NaOH can be expected to be present in the steam.

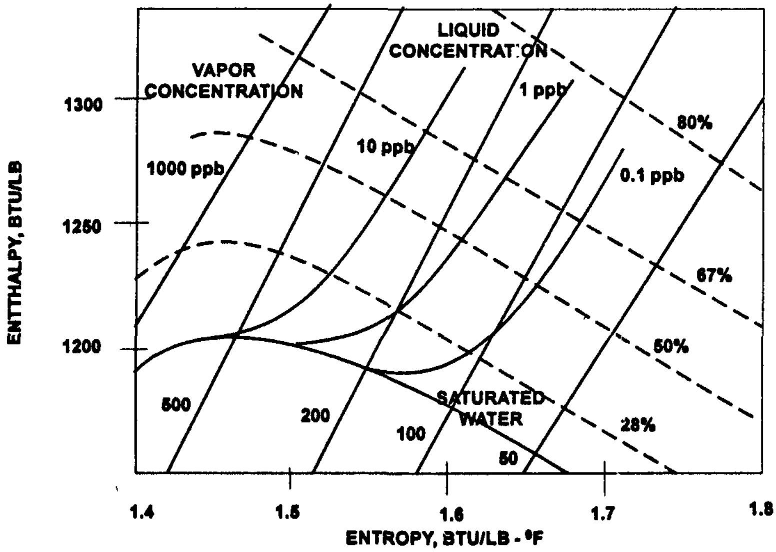

Fig. 4.8 Caustic Solubility Data shown on a Mollier Diagram(10)

Silica is one of the impurity deposits that causes considerable damage to turbine blades. The steam carry over of SiO_2 is essentially due to the distribution of this compound between high temperature water and steam phases. Table 4.2 shows the data on this distribution coefficient as a function of pressure.

Table 4.2 Distribution of Silica between Steam and Water Phases

(Kg/cm^2) ← Pressure →	(psig)	Conc. of SiO_2 in Steam / Conc. of SiO_2 in water
86.0	1273	0.0045
103.0	1529	0.0075
121.1	1793	0.012
137.8	2039	0.020
148.2	2193	0.030
172.3	2550	0.050
190.2	2815	0.080
206.7	3059	0.160

Since the solubility ratio decreases noticeably with decrease in pressure (a condition in the steam turbines from the inlet of steam to its exhaust) deposits of silica on the turbine blades are to be expected. Suffice to say here that increasing concern for low pressure turbine blade and rotor damage by stress corrosion and corrosion fatigue has caused new limits on allowable steam contamination by NaCl, NaOH and SiO_2 to be recommended. Such limits have an impact on the required purity of steam generator feed water.

4.5 ROLE OF ALKALINITY IN STEAM-WATER CIRCUITS

It has been known for some time that mild steel or carbon steel (one of the main components of the steam-water circuit) exhibits a minimum rate of corrosion at 25°C in the pH range of 8 - 10. Thus it has been a practice to make use of volatile alkalising agents such as ammonia, morpholine and hydrazine,(11) in the cycle. The volatile compounds, as compared to the non-volatile alkalies such as NaOH have the advantage of being easily carried over into the steam phase. They thus give corrosion protection to that part of the cycle where steam comes into contact with the surface of the construction materials. Because of their differing dissociation constants, different quantities of each of these reagents are required to attain the same pH, as given in Table 4.3.

Table 3 Relationship between pH values at 25°C and Concentrations of Alkalising Agents(11)

pH Value	Concentrations in mg/l		
attained	Ammonia	Morpholine	Hydrazine
7.5	-	0.05	0.02
8.0	0.03	0.20	0.08
8.5	0.075	1.00	0.60
9.0	0.30	10.00	5.50
9.5	1.0	80.00	50.00

Bearing in mind the role of dissolved oxygen in promoting corrosion, hydrazine is often added as an oxygen scavenger. Somehow, its role in increasing the pH of the water - steam circuit has not been well recognised.

A study of the distribution coefficients of these three volatile compounds between water and steam showed that for ammonia, the ratio (concentration in steam / concentration in water), decreases sharply in the region of 25°C to 100°C after which it decreases asymptotically with temperature. This means that sufficient alkalisation in the condensing phase is not achieved with ammonia. On the other hand, the value of this ratio for morpholine increases with temperature. However, the magnitude of the ratio is smaller than that for ammonia. Thus while pH is upgraded during the condensation process, the concentration of morpholine required is more than that for ammonia. Hydrazine, on the other hand is a good compromise candidate. Its distribution ratio increases with temperature, while a concentration lower than morpholine, but higher than ammonia is required to attain the same pH value in the condensate. Despite this obvious advantage, hydrazine is rarely considered as an alkalising agent in the steam generating industry, because of its tendency to decompose under the conditions of temperature prevalent in the boiler side(12, 13). The main decomposition reaction is,

$$3\,N_2H_4 \rightarrow 4NH_3 + N_2 \qquad (4.10)$$

A small part also decomposes as

$$N_2H_4 \rightarrow N_2 + 2H_2 \qquad (4.11)$$

The typical values for the half times of the decomposition reaction (4.10) of hydrazine and the associated rate constant are given in Table 4.4.

Table 4.4 Thermal Decomposition of Hydrazine[12]

Temperature °C	$t_{1/2}$ (Sec)	k (sec^{-1})
160	307.7	0.0025
200	41.0	0.0169
250	6.5	0.1066
300	1.5	0.4620

Thus in the temperature range of interest (250°C - 300°C), hydrazine decomposes faster and the need for replacement will be high, if employed as an alkalising agent.

4.5 DEOXYGENATION

As mentioned earlier, dissolved oxygen is the main culprit in causing corrosion of iron and ferrous alloys on contact with water, especially at high temperatures. To minimise this problem, deoxygenation is an established practice. At present hydrazine and several forms of catalysed hydrazine are employed for this purpose[12,13].

The deoxygenation reaction is given as,

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O \tag{4.12}$$

Although the above equation denotes a simple bimolecular homogenous reaction, there are several parameters which have a marked effect both on its rate, as well as on its initiation; these include temperature, pH, reagent concentration, presence and concentration of catalysts etc. The reaction has a period of induction and proceeds very slowly at room temperature.

Two additional mechanisms appear to operate during the process of deoxygenation in addition to the one given in equation 4.12. A heterogeneous surface absorption (on metal or metallic oxides) reaction has been postulated.

$$N_2H_4 \rightarrow \underset{\text{Surface}}{[N_2H_4.O_2]} \rightarrow N_2 + 2H_2O \tag{4.13}$$

Another heterogeneous process is where heamatite (Fe_2O_3) in the steam-water circuit is reduced to Fe_3O_4, which further reacts with oxygen.

$$\begin{gathered} N_2H_4 + 6\,Fe_2O_3 \rightarrow N_2 + 2H_2O + 4\,Fe_3O_4 \\ 4\,Fe_3O_4 + O_2 \rightarrow 6\,Fe_2O_3 \end{gathered} \tag{4.14}$$

Experience indicates the involvement of all three mechanisms.

Coming to the parameters that govern the deoxygenation the effect of temperature is appreciable. While the reaction is hardly perceptible at 20°C, it is complete in a few seconds at 170°C. The deoxygenation is most effective in the pH range of 9 - 10. As the purity of water increases, the rate falls showing that impurities present in water catalyse the reaction. The effect of hydrazine concentration is very pronounced. Thus, while 10 percent excess hydrazine requires 40 hours for scavenging dissolved oxygen (at a particular temperature), the time is reduced to less than 10 hours with 200 percent excess. In general, metal ions are found to catalyse the reaction. This is especially true of Cu^{2+} and other 3d transition element cations. It has been observed that certain organic additives (derivatives of quinione) also catalyse the process. Catalysed hydrazine is available in the market.

The discussion in this chapter clearly indicates that water chemistry and corrosion are closely interlinked, leading to a favourable material compatibility (or the lack of it) in high temperature and high pressure water-steam circuits. A large amount of basic physico-chemical information has been generated and collated. The proceedings of several conferences organised by the International Association for the Properties of Steam, provide, valuable data in this regard.

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5

TREATMENT OF NATURAL WATERS FOR INDUSTRIAL COOLING

Water finds extensive use as a heat trasfer and cooling medium in chemical process industries and power generation through the deployment of heat exchangers, condensers and cooling towers. In addition, after special purification procedures, it is also made use for generating high pressure steam in thermal and nuclear power stations. It has been roughly estimated that 90 percent of all the water used by industry is for heat transfer and cooling while about 8 per cent is used for process requirements and about 2 percent for steam generation. The water quality criteria and hence the treatment procedures are different for these three end uses. Stringent control of water chemistry, is essential for steam generation, while this is not so for the other two uses. In this chapter, attention will be focussed on the chemical treatment and quality of water needed for industrial cooling.

Although water from a particular source may be acceptable for drinking or for agriculture, certain suspended and dissolved impurities present in it, will have to be removed by suitable pretreatment procedures, so that it is acceptable for industrial cooling with or without further chemical conditioning. The type of treatment to be adopted depends upon the quality of the available source of natural water, as well as on the capital and operational costs and environmental requirement of the industrial location. Thus, some site-specific variations of the general water treatment procedures are unavoidable. Efforts are constantly being made to envolve improved water conditioning programmes that are environmentally friendly, efficient and cost effective.

Water from rivers, lakes and even underground borewells, is employed for all the three purposes mentioned above, after proper chemical treatment(1). On the other hand, sea water is used only for cooling the condensers and process water heat exchangers (once-through) of power plants and other heavy chemical industries such as petrochemicals located along the coast. Because of the large volume of running sea water in once-through systems, there is no question of a chemical treatment. Only at a few locations, depending upon the material of condenser tubes, a chemical treatment of sea water is practised. On the other hand, biofouling problems are severe with sea water applications and antifouling practices are all pervasive$^{(2)}$. Surface and groundwaters also experience biofouling, though of a different nature and magnitude. We shall first deal with the problem of biofouling encountered in the use of natural waters for cooling condensers, heat exchangers etc.

5.1 BIOFOULING IN NATURAL WATERS

Power stations at inland locations make use of surface waters from rivers, dams and lakes for condenser cooling, with or without the aid of cooling towers. Such raw waters contain their natural flora and fauna. The flora mainly comprises phytoplankton in association with bacteria and fungi fed by nutrients like nitrates, phosphates, iron, silica and carbonic acid present in these waters. Sunlight penetrates the low depth turbid water systems like lakes and river banks and supports the photosynthetic activity of the phytoplankton consisting of different types of algae such as the blue greens, greens and the diatoms.

In India, power stations located at Dhuvaran, Tarapur and Trombay on the west coast and Ennore, Kalpakkam and Tuticorin on the east coast make use of sea water for cooling the power plant condensers and process water heat exchangers$^{(3)}$.

The conventional and the widely practised method for controlling biofouling is through the chlorination of the coolant water$^{(4,5)}$. Since large volumes are involved in once through systems, no other method appears to be economically viable. At the same time this imposes the need for handling bulk quantities of hazardous chlorine, mostly in the form of pressurised gas cylinders round the clock. Residual chlorine present in water from a cooling tower basin could be detrimental to fresh water ecosystem when the blowdown water is drained into the environment. It has been observed that residual chlorine present in the combined form and as chlorinated organics is detrimental to fish, invertebrates and algae in natural water. The effect is a function of the size of the organisms, the period of exposure, the water quality, (e.g. pH) temperature and the nature of the chlorine species. Hence there is a need to regulate the release of chlorine content in the effluents$^{(6,6a)}$. Environmental concerns have led to the lowering of the allowable discharge limits to less than 0.3 mg/l or even 0.2 mg/l of chlorine at the condenser outfall. Such discharges are permitted for not more than 2 to 3 hrs in a day. For continuous chlorination, the discharge limits are set much lower at 0.05 mg/l.

When chlorine gas is added to water, hypochlorous (HOCl) and hydrochloric (HCl) acids are formed.

$$Cl_2 + H_2O \rightarrow HCl + HOCl \qquad (5.1)$$

The oxidising property and the disinfecting action of chlorine is due to HOCl. Hypochlorous acid dissociates to give hydrogen and hypochlorite (OCl) ions depending on temperature and pH of the water; the dissociation is considerable above a pH of 6.5 (Fig 5.1). The OCl^- is not as effective as HOCl(4). Chlorine also reacts with ammonia present in water producing chloramines, which possess a disinfecting property, 300 times less than that of HOCl. Chlorine reacts with nitrogenous compounds like proteins, and other organic matter forming chlorinated compounds or oxidised products. Chlorine present as HOCl and OCl^- is termed free residual chlorine and that existing in the form of chloramines etc., is termed combined residuals. The current practice consists of intermittent chlorination upto 1 mg/l of free residual chlorine for 20-30 minutes, two to three times a day. In order to get the free residual chlorine, it is necessary to know the chlorine demand of the water, that is, the amount of chlorine consumed by the organics and inorganics, (e.g., Fe^{2+}) present in water before free residual chlorine is detectable in water.

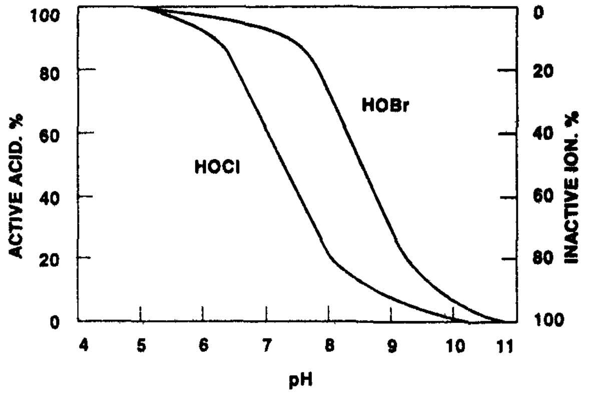

Fig. 5.1. Dissosiation of HOCl and HOBr as a function of pH(15)

It has been suggested that death of bacterial cells results from a chemical reaction of HOCl or a chlorine compound with an enzyme system essential for metabolic activity. The difference between various disinfectants is attributed to their ability to penetrate the cell. The effectiveness of HOCl as compared to other forms of chlorine species could be due to its small molecular size and electrical neutrality which allows it to penetrate the cell wall. The lesser bactericidal effect of OCl^- could be due to its negative charge, which may impede its penetration into the cell. Chloramines have comparatively slow diffusion through the cell wall, however, these are of importance in water chlorination due to their persistence in water for a longer period of time as compared to HOCl.

From this, it is obvious that chlorination is quite an effective antifoulant measure in fresh water systems, where the pH is in the range of 6 to 7, while in slightly alkaline waters (8 pH), it is less effective. The question that needs an answer is the universal observation that chlorination of seawater, which has a pH of 8.2, is still effective in controlling marine biofouling. Herein comes the role of dissolved bromide in sea water.

The presence of 68 mg/l of bromide in seawater, results in a complex chemistry of chlorinated seawater(6). This is because chlorine (HOCl) releases

HOBr from bromide. Hence at the pH of seawater, chlorination leads to the formation of hypochlorous acid, OCl^- ion, HOBr and OBr^- ion, plus the bromamines, which co-exist with chloramines. Hence total residual chlorine in seawater always refers to a mixture of HOCl, HOBr, OCl^-, OBr^-, chloramines and bromamines.

The dissociation of HOBr to form H^+ and OBr^- (hypobromite ion) is also pH dependent; with the equilibrium shifting to a higher pH value. Upto 8.0 to 8.2 pH, 90% of bromine is in the form of HOBr and the percentage drops to 10% only, at 9.5 pH (Fig. 5.1). HOBr is a superior biocide as compared to HOCl. Consenquently, the chlorination of seawater which leads to HOBr, is a successful method of controling marine biofouling(7). At a coastal power station this practice should be optimised depending upon the nature of the fouling community and the chlorine demand of the seawater in the intake area. The chlorine demand varies somewhat with the season and the sea currents and needs to be analytically determined at regular intervals so that the total chlorine dose needed can be evaluated.

As briefly mentioned above, HOCl reacts with both inorganic and organic nitrogenous compounds present in natural waters (a major fraction of the chlorine demand). Examples of such compounds are ammonia, nitrates, amino acids, proteins and humic acid. While the reaction of HOCl with ammonia is comparatively fast, that with organics is slower and depends upon the contract time. The formation of chloramines, stepwise is a follows.

$$HOCl + NH_3 \rightarrow NH_2Cl + H_2O \qquad (5.2)$$

$$HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O \qquad (5.3)$$

$$HOCl + NHCl_2 \rightarrow NCl_3 + H_2O \qquad (5.4)$$

Similar equations can be written for organic nitrogen compounds. The reaction between chlorine and organic nitrogen is relatively slow. The product of chlorine demand and contact time is a characteristic of the water under examination and is given by,

$$D = K\,t^n \qquad (5.5)$$

In Eq.5.5, D is the final chlorine demand (initial chlorine dose - final residual chlorine) in mg/l, K is the chlorine demand in mg/l at the end of one hour (initial chlorine dose - (minus) chlorine residual at the end of one hour), t is the contact time in hours and n is the slope of the curve that is obtained on plotting the experimentally determined chlorine demand at different time intervals vs. contact time in hours(4,6,8).

A significant development following chlorination of natural waters for industrial use, is its reactions with the ever increasing number of man made chemicals of undetermined toxicity discharged into the aquatic environment. The majority of the reaction products are chloro-organics (hydrocarbons, phenols, aromatic acids etc.). The cumulative effect of the potentially carcinogenic chloro-organics is a matter of concern. Thus, in once-through systems, lot of care is to be exercised in regulating the chlorination practice so that the discharged water contains as little total residual chlorine as possible.

Turning to the biological aspects of chlorination, the general efficacy of chlorine as a bactericidal agent is universally accepted. Work on algae indicated that while the effect of chlorine is algistatic, that of bromine is algicidal. Reduced marine phytoplankton productivity in chlorinated seawater has been observed. Similarly reduced carbon uptake (using C-14) and depression of photosynthesis were noted. Branacles are one of the common macrofouiants and their response to chlorine has been well studied. Eighty percent average mortality of Balanus larve was recorded after five minutes exposure to seawater at a chlorine level of 2.5 mg/l of total chlorine. Marine mussels, typified by Mytilus edulis, Mytilus virdi and Mytilus californicus, are the most important of the fouling organisms that restrict the cooling water flow. Macrofouling by branacles and mussels have been the focus of many investigations, including studies at Bombay and Kalpakkam, India(9-12). The time to achieve a 100 percent kill has been related to the temperature and residual chlorine level through a generalised regression equation. It has been realised, of late, that instead of intermittent moderate chlorination (2.5 to 3 mg/l of free residual chlorine), practised once in eight hours, a continuous chlorination level of (0.2 to 0.4 mg/l of free residual chlorine) appears to be more effective in combating mussel fouling. Chlorine interferes with the process or thread of filament formation by the mussel larve, that is vital to the growth of these organisms.

5.2 OPERATIONAL PRACTICE OF CHLORINATION IN POWER STATIONS - USE OF BROMINE

The Central Electricity Generating Board (CEGB) U.K., carried out a systematic study on various antifouling methods used in cooling water circuits. They found that chlorination is the most economical method for combating all biogrowth in power station circulating water systems(13). According to the CEGB, code for chlorination is as given below :

(a) Unless local pollution of seawater is severe it should be assumed that marine fouling is likely.

(b) A thorough census of fouling organisms must be carried out before the erection of a power station.

(c) Chlorination plant must be ready before water is admitted to the circulating water culverts. Chlorine injection must be such that residual chlorine is distributed uniformly throughout the intake water.

(d) Residual chlorine of 0.2 ppm must be maintained at the condenser outlet.

The Tarapur Atomic Power Plant consumes 2500 - 3000 kg. of chlorine everyday. The duration of chlorination is 15-20 minutes in each shift of eight hours with 2-3 mg/l of residual chlorine at the condenser water box. There are four bays at the intake. Each bay is subjected to a shock dose of chlorine that results in 2 to 3 mg/l residual chlorine for 1 hr./week.

While all the seawater cooling systems are once-through, a number of fresh water cooling systems are not. In fact it is becoming the norm to use cooling towers to dissipate heat into the atmospheric environment. Thus, they are recirculating systems, where most of the cooling water is recycled between the cooling tower basin and the heat exchangers or condensers. Fresh make up water is added only to compensate for the evaportion losses from the cooling tower and the blow down is discharged into the aquatic environment, so that a balanced chemical conditioning is maintained in the recirculating cooling water. Biofouling is again a problem area in these systems in which chlorination is invariably used to combat(14). Since, it is a recirculating system, once in a while additional biocides can also be used without economic penalty.

Micro organisms, dead or alive, form slime, which acts as material for cementing particles together. It is, therefore, essential that they are dispersed in water using surface active agents. Dispersed biological matter also makes the chlorination programme effective, by allowing chlorine to interact easily with the binding material. It has been found, for example, that algae and bacteria can be flocculated using cationic polymer. Biocides used in water treatment programmes are mostly cationic surface active agents. Recently it has been established that chlorination and the use of low molecular weight cationic polymers alone can control biofouling of cooling water systems, and the use of biocides can be eliminated.

In fresh water cooling systems,the trend is towards a programme of chemical conditioning of the circulating water, whose pH is maintained towards the alkaline side. Under such conditions, as seen earlier, chlorination loses its efficacy and research was focussed on the use of alternative biocides. Keeping the experience with seawater in mind, the application of bromine (in the form of bromide or other bromine compounds) as a substitute for chlorine is coming more and more into use(15). Bromine chemistry offers reduced corrosion and environmental hazard. The efficacy of HOBr as a biocide over that of HOCl has been well established facilitating dose reduction. Rapid decay of bromine and its compounds such as bromamines, minimises the environmental impact of the biocide on the receiving aquatic eco-system. In addition to HOBr, bromine is available in different chemical forms which can be added as a biocide. One such compound is bromochloro dimethyl hydantion (BCDMH) which is commercially available. At about 2 mg/l equivalent of chlorine, BCDMH and HOBr are about 100 times more effective than HOCl towards pseudomona in alkaline cooling waters. Brominated propionamides like, 2,2-dibromo - 3 - nitrilo propionamide are extremely potent broad spectrum microbiocides. The compound is an oxidising type microbiocide and is unstable with increasing pH and temperature. Thus, the cooling water dosed with this chemical can easily be detoxified before being discharged into the natural aquatic environment.

Equally effective are the bromamines. In addition, the reaction leading to the formation of bromamines can be made reversible by lowering the pH. Thus they are less persistant than the corresponding chloramines. Electrochemical measurements with copper alloy condenser tubes such as Cu : Ni = 90 : 10 showed that in the presence HOBr, their oxidative corrosion is much less than in the presence of HOCl, especially around pH 7.5 - 8.2. It is shown that manganese fouling of 304 stainless steel (SS) condenser tubing is arrested on switching over to bromine based biocides(15). In case, the required bromine biocides are not available, recourse can be taken to adding a few mg/l

(5 mg/l) of sodium bromide to the recirculating cooling water (pH about 8 or more) and carrying out chlorination as usual. As in seawater chlorination, the chlorine will release bromine in the form of HOBr as an effective biocide.

Manufacturers of cooling water chemicals offer a number of proprietory biocides, These are recommended to be used once a week, while chlorination is suspended for that day. Their effectiveness depends upon site specific studies and no generalisation can be made. Tin - organic biocides made a major entry into the market, but of late, environmental considerations have imposed servre constraints on their large scale application. Methylene bis-thiocyanate is another biocide that is effective against algae, fungi and bacteria. The compound is made use of in combination with a dispersant to enhance its penetration of algal and bacterial slime layers.

5.3 MATERIALS IN A COOLING WATER CIRCUIT

Before considering the chemical treatment and conditioning of cooling water, it would be appropriate to look briefly at the materials with which such treated water comes into contact. From the early stages, brass was used to serve as the material for the condenser and heat exchanger tubes. Admirality brass or Naval brass is used for fresh water systems, while aluminium (Al) brass is the preferred material for seawater systems. Subsequently cupronickels were developed and the 90-10 alloy found wide applications in seawater systems. The 70 - 10 alloy is better suited, but is not much used in view of its high cost. In all these copper based alloys, the release of cupric ions due to corrosion is considered to be a good antibiofouling measure, in view of the toxicity of copper to such organisms. When the need for total leak proof condensers arose, titanium (Ti) came into use as the tube material. However, it has no resistance to biofouling. Another equally good alloy is stainless steel, especially some of the new stainless steels that were developed with this specific application in mind. Again stainless steel has no in-built resistance to biofouling. In most cases the tube sheet is of carbon steel, sometimes overlaid with materials like stainless steel and titanium.

For seawater applications employing either Cu-Ni or Ti or even SS, there is no chemical treatment for erosion and corrosion prevention. However, with Al brass being a widely used material, a chemical treatment was found that is effective against such types of attack.

Leakages in condensers, where water with a high salt content is used for cooling, have almost always given rise to serious effects in the operation of power stations(16). However, immediate damage bears no relation to the possible consequential damage. In extreme cases, on the spot intrusion of cooling water containing sodium chloride leads to equipment breakdowns such as a tube burst in the boiler or breakages of turbine parts in areas having contact with wet stream. A prolonged search for leak detection and fixing becomes necessary. The major part of the damage to condensers was substantively due to the corrosion of the condenser tubes. When copper alloyed tubes were used, the damage was caused by local corrosive attack on the tubing. The resistance to corrossion of copper alloyed tube materials in braekish or seawater is said to be due to the formation of a natural covering film of cuprous oxide. If the thickness of this film is inadequate in aggressive cooling waters, it is necessary to add agents which will create additional protective layers which are sufficiently strong and adhere over the internal tube surfaces.

5.4 FERROUS SULPHATE INJECTION

The use of ferrous sulphate as an inhibitor of the corrosion of aluminium brass was first described by Bostwick(17). He produced detailed statistical data relating to the addition of ferrous sulphate versus the number of tube failures(18,19). By way of explanation, Bostwick envisaged the iron additive acting as compensation for the loss of 'natural' iron which had been available from the water boxes prior to installation of cathodic protection. Ferrous sulphate dosing is now widely practised, but there is still no agreement on the mechanism of protection. One way to look at this situation is by considering the principle of Point of Zero Charge (PZC) of the original oxide layers and its interaction with iron hydrous oxides having a different PZC. Iron may also act as a cathodic inhibitor or can be incorporated into a cuprous oxide (Cu_2O) film, by a mechanism similar to that found when iron or nickel are incorporated from cupro-nickel alloys. This gives it a greater passivity. Other workers believe that a relatively thick film of hydrated ferric oxide if formed which reduces the erosive action of seawater and enables a protective film to form on the brass itself. This view implies that the iron film is effective in the commissioning stage of condenser operation and that there after iron neither contributes to the passivation action nor is necessary. There may then be a possibility of reducing or discountinuing iron additions to the cooling water once service conditions are well established. However, this has not been realised in practice at all.

Of the many conceivable and proposed measures, the presence of ferrous oxide layers has proved most efficient in many respects. It is basically of no consequence whether these oxide layers are consciously produced, for example, by ferrous sulphate ($FeSO_4$) injection or by making use of sacrificial anodes, or whether uncontrollably formed, for example, via the corrosion of steel tubes in the cooling water feed lines. The main thing is that conditions of uniform distribution, good adhesion and reconstitution of the film are maintained.

With regard to development of layers via ferrous sulphate injection, several procedures have proved successsful for continuous operation :

- Injection of 1 mg/l Fe^{2+} in cooling water for the duration of one hourday.
- Injection of the same concentration twice per day, but for half an hour at a time.
- Continuous injection to values in the 10 µg/l range.

What concentrations and sequences are finally chosen will depend on the organic matter and sulphide content in the cooling water; especially during back washing of the condensers. Small quantities will be chosen as far as possible because of the formation of slime.

The injection of concentrated $FeSO_4$ solution (21 percent $FeSO_4$, 20°C) should be effected shortly before entry of cooling seawater into the heat exchangers or condensers, since longer dwell times result in premature oxidation which from flaking Fe (III) compounds. In the case of large size condensers, an additional injection into the return water boxes can be advantageous.

The incorporation of iron takes place through negatively or positively charged colloids of hydrated iron oxides, either under the influence of the electric field of the Cu_2O covering film with a positive Zeta potential, or by electrolytic precipitation on the cathode surface of the epitactic layer. It is therefore not expedient to inject $FeSO_4$ directly into pickled tubes, i.e., tubes deprived of their own natural covering film.

Depending on the injection method, brown uniform layers of varying structure are formed on the inner surfaces of the tubes after some weeks. The thickness of these layers is 75 microns. On continuous cleaning with sponge rubber balls or brushes, glossy reddish-brown films with a thickness of only a very few microns appear. The thickness and roughness of the films increases proportionally to the length of the cleaning interval. Automatic cleaning methods lead to a consolidation and homogenization of the external covering layers. There are difference of opinion with regard to the cleaning intervals for condenser tubes having ferrous sulphate injection. Whilst some aim for a firmly adhering and consolidated external protective layer with continuous cleaning, others are of the opinion that, on account of the formation of natural oxide films, a cleaning period of only one hour at a time is acceptable. There is also a body of opinion against the sponge ball cleaning after the treatment with ferrous sulphate.

After a longer injection period, the layers show up as two lamellae on the metallographic picture. Over the natural Cu_2O covering film is a homogeneous, closely meshed layer of ferrous oxide, the crystalline content of which consists of gamma-FeO OH. In isolated cases, $FeCuO_2$ has also been radiographically diagnosed. According to the results obtained by electron microscopy this hybrid oxide seems to occur as a thin intermediate layer to which adhesion-enhancing properties are ascribed.

Ferrous sulphate treatment has been successfully applied not only to brand new tubes, but also to condensers that were in service for some years and which were damaged by pitting and erosive corrosion. It is desirable to inject ferrous sulphate throughout the operating period and at an increased level and frequency after a shut down maintenance. This ia due to the tendency of thc layers to split on drying and peel off in some places.

Electrochemical characteristics of the corrossion of Ni-Resist type 2 alloy in seawater, dosed with ferrous sulphate have been investigated(20). The alloy underwent a uniform cathodically controlled corrosion and no alteration in the stress corrosion cracking suceptibility of the alloy was observed. Electrochemical measurements have shown that on Cu:Ni (90:10), the protection offered is meager (very thin layer) and hence it is not worthwhile to practise this treatment. The procedure has been also advocated for Ti and SS tubes, but has not found acceptance.

5.5 COOLING WATER TREATMENT

Cooling water treatment of a power station or a heavy chemical industry is to be organised from the very inception(14). Unless the required site specific water quality assessment is carried out well ahead of time and suitable chemical treatment procedures evolved, problems such as reduced flow in heat exchanger tubes, failure of equipment etc. would certainly crop up during operation of the plant (Fig.5.2). Thus the most important part of the study is togather data on water quality, over a two year period.

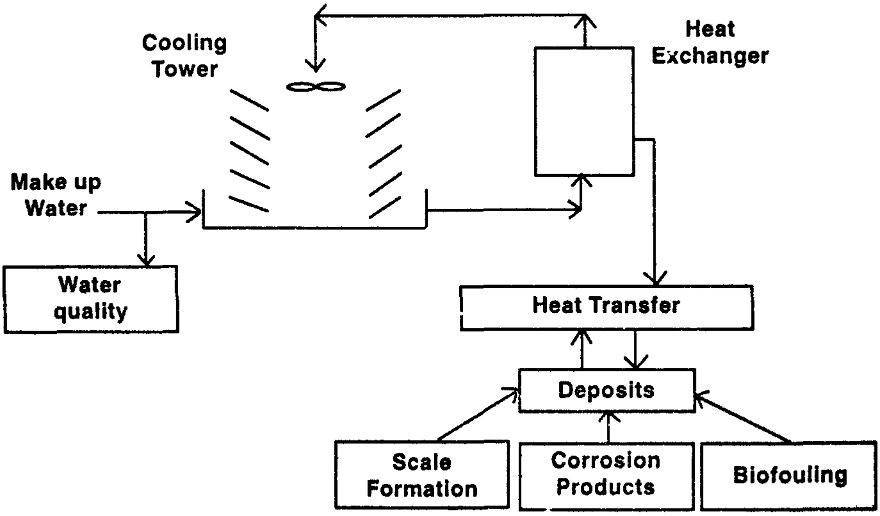

Fig. 5.2 Impor'ant Problem Areas in Cooling Water System(1)

As discussed in detail earlier, in once-through cooling, very little chemical treatment is made use for economic reasons. Of more interest are the recirculating systems with or without a cooling tower. The open recirculating cooling water systems invariably have a cooling tower from which water is lost due to evaporation and mechanical dispersal due to the sprays in the tower. This will result in concentration of impurities and intentionally added chemicals in the cooling tower water. In order to maintain an appropriate level of the chemicals, a part of the water is blown down from the tower. The combined loss due to evaporation, mechanical factors and blowdown is made up by adding the requisite quality of fresh water.

In view of the concentration of impurities in the cooling tower due to evaporation losses, the circulating water contains greater levels of both cations and anions as compared to the make up water. The ratio is known as the concentration cycle. One can take any pair of ions in both streams to arrive at the concentration cycle. It is usual to take chloride ion ratios as chloride deposition is the least. The cooling towers usually operate with concentration cycle in the range of 2 to 3.

The preliminary steps in the treatment of raw water consists of,

(a) Control of biofouling by chlorination, and

(b) Removal of suspended solids.

The first step has already been dealt with. The suspended solids are removed usually with the help of a flocculator, by adding the necessary coagulants(21). The process, known as clarification, makes use of alum or ferric sulphate. The hydroxides of the trivalent ions, neutralise the surface charge of the suspended particles and facilitate their agglomeration. An important problem in flocculation, is the generation of sludge, which is bulky due to a high content of water. This has to be dewatered and disposed of. Another problem is the carry over of the finely divided hydroxide flocs into the clarified effulent. Such problems, arising out of the use of inorganic coagulants alone, has been overcome to a large extent by the use of organic polyelectrolytes in conjunction with them. These are water soluble, long chain polymers with attached active groups and having molecular weights in the range of 10^7. The ionisation of the active group confers a charge on the bulky molecule as a whole. Based on the sign of the charge, these are classified as cationic or anionic polyelectrolytes. Also available are non-ionic or so called neutral polyelectrolytes. Based on site specific experimentation, a polyelectrolyte or a combination thereof is selected. These compounds help in neutralisation of the surface charges of the suspended fine particles by the inorganic coagulants. This results in the formation of microflocs and subsequenttly in macroflocs. It was seen that the use of polyelectrolytes reduced the volume of sludge by as much as 75 percent allowing it to be readily dewatered. The carry over problem is thus minimised. Although organic in nature, the use of polyelectrolytes does not add to the organic fouling of the treated water. Lesser quantities of inorganic coagulants have been found to be adequate.

The dissolved chemical constituents present in the cooling water could result in(1) :

(a) Interaction with materials of contruction leading to corrosion,

(b) Reactions such as precipitation among themselves that could lead to scale formation (such reactions depend upon concentration, temperature etc.) and

(c) Acting as nutrients to the biological species present in the system, thus aggravating the problem of biofouling.

The constituents present in water fall broadly under four categories:

(a) Suspended impurities like clay, silica, organic matter etc.

(b) Dissolved impurities, such as Ca^{2+}, Mg^{2+}, Na^+, NH_4^+, HCO_3^-, Cl^-, CO_3^{-2},SO_4^{-2}, silica, besides traces of iron, NO_3^-, and soluble organic matter, (e.g., humic substances).

(c) Micro-organisms such as algae, different types of bacteria (sulphate reducers, iron bacteria, etc.) and fungi.

(d) Dissolved gases like O_2, CO_2, NH_3, H_2S, etc.

In general scale forming salts have inverse solubility characteristics and tend to get precipitated when saturation is reached due to local changes. These include temperature, concentration due to evaporation, presence of ions which cause precipitation etc. Calcium, magnesium, carbonate, sulphate, phosphate and sometimes silica contribute to this effect. Based on thermal conductivity, the loss of heat transfer due to scaling has been estimated as, SiO_2 : 0.2 to 0.5, $CaCO_3$: 0.5 to 1.0 and $CaSO_4$: 1.0 to 2.0 (in k.cal/m.h.°C)

Constituents like carbonate, sulphate, phosphate and organic compounds from cooling tower serve as nutrients for the micro-organisms. The presence of ammonia or nitrate also contributes to the metabolic activity and can change the water chemistry of the system considerably.

Dissolved CO_2 in the water, which depends very much on the temperature and pH of the water, is an extremely significant factor in chemical reactions involving precipitation of calcium and magnesium salts as scales. Dissolved O_2, and CO_2 contribute to the increased corrosion of system surfaces.

Amongst the added chemicals, that contribute to scaling in cooling water systems is the degradation of metaphosphates to orthophosphates.

In general it is very difficult to predict in isolation the part played by the dissolved constituents in promoting corrosion, biofouling and scale formation. Sometimes one of the reactions can aggravate the other processes.

5.5.1 Deposit Formation and Control

In a cooling water system, an efficient transfer of heat from process fluid to cooling water is possible, when deposition on heat exchanger surfaces is minimised(1,14). Presence of sparingly soluble salts (e.g. $CaSO_4$) having inverse solubility, results in scaling (Table 5.1). Corrosion of construction materials leads to the deposition of corrosion products (mainly different forms of iron oxides) on heat exchanger surfaces. Deposit of dead bacteria, algae, etc., also impair heat transfer. A cooling water treatment programme should effectively control the above mentioned deposition processes.

Table 5.1 Solubility Trends among Scale Forming Calcium Salts.

	Approximate solubilities, mg/l.			
Temperature °C	$CaSO_4$ anhyrous	$CaSO_4$ 0.5 H_2O	$CaSO_4$ $2H_2O$	$CaCO_3$
0	High	V. High	1775	90
40	2800	High	2050	50
100	750	2200	1700	15

Crystallization of scale forming salts precedes the deposition step. Formation of crystals takes place initially by nucleation followed by crystal growth. Nucleation in a cooling water system occurs either in solution or on rough surfaces, once the water is supersaturated with any scale forming salts, e.g., $CaCO_3$. Crystals grow either in solution and subsequently get deposited or grow on the surface itself. Deposition can be controlled during the crystal growth stage by use of surface active agents. These chemicals may increase the time of nucleation but cannot prevent it.

As noted earlier, surface active agents such as polyelectrolytes are classified as cationic, anionic and nonionic depending on the functional groups possessed by them. As a consequence of the absorption of surface active polymers on the suspended particles, flocs are formed which get deposited very loosely on the surfaces. It is also possible that the surface active agents occupy lattice sites of the growing crystals resulting in the formation of distorted crystals having large internal stresses.. These modified crystals do not adhere to the surface on which they are first deposited.

The effectiveness of the surface active agents is not the same for all types of deposit forming compounds. The various surface active agents should be screened for their effectiveness for the different deposits encountered in the cooling water system. Sometimes the final deposit may result through an *intermediate compound, e.g.* Mg $(OH)_2$. *The inhibitor chosen should be more* effective for the intermediate compound than for the final product.

5.5.2 Scaling Indices

As against the principles of cooling water chemistry discussed so far, let us see how the treatment programmes have evolved in practice. The most common scale present in cooling water systems is calcium carbonate, derived from the decomposition of calcium bicarbonate that is normally present in natural waters. Thus it is obvious that when the circulating water has higher levels of calcium hardness and bicarbonate alkalinity, this problem becomes acute. Since the solubility of calcium carbonate shows a decrease with increase in temperature, the inner surface of the heat exchanger will be prone to scale formation. To predict the scale forming tendency of a cooling water with respect to calcium carbonate several techniques are employed, the foremost of which are the Langlier (or saturation) index, the Ryznar (or stability) index and the Puckorus (or modified stability) index$^{(14)}$. It is required to calculate pH of saturation (pH_S) for calcium carbonate. The calculation being involved, nomograms have been developed for the use as ready reckoners. The Langlier equation is formulated with pH of saturation (pH_S) as,

$$pH_S = (pK_2 - pK_S) + pCa + p\,Alk \qquad (5.6)$$

Where pCa and pAlk are the negative logarithms of their respective concentrations (as in pH with respect of hydrogen ions). pK_2 and pK_S are the second dissociation constant and the solubility product constant of calcium carbonate respectively. The Langlier Index is then defined as,

$$LSI = pH\ actual - pH_S \qquad (5.7)$$

and can have a positive or negative value. The former indicates a tendency for scaling while lateer signifies a tendency for corrosion by the cooling water. The Ryznar Stability Index is given by

$$RSI = 2\,pH_S - pH\ actual \qquad (5.8)$$

Under this classification, a value of 6 for RSI indicates stable water, i.e. no scaling or corrosion, values less than 6 would lead to scaling, while above 6 would result in scale dissolution, i.e. corrosion. The Puckorious Modified Stability Index is formulated as

$$PSI = 2pH_S - pH_C \qquad (5.9)$$

Where pH_C is the equilibrium pH based on total alkalinity. Usually the former two indices are made use of for on site evaluation of the scaling and corrosive tendency of natural cooling waters. Since temperature gradients are site and design specific, a variable in the operator's control is pH, which is often adjusted to keep the cooling water in a slightly scale forming condition, rather than on the slightly corrosive side. This was an early way of cooling water treatment; modern treatment programmes depend upon inhibition of scaling as well as corrosion by chemical additives. However, both Langlier and Ryznar indices still serve as initial guidelines for evolving a proper chemical treatment, as well as spot checks later.

5.5.3 Chemical Additives

Chlorination being very effective in the pH range of 6 to 7, coupled with the need for reducing the bicarbonate alkalinity, acid addition is a common practice. Concentrated sulphuric acid is used for this purpose and addition is usually done in the cooling tower basin. Although there is a constant flow of water movement in the basin, it is possible that mixing of the acid may not be uniform, particularly if the slopes in the cooling tower basin are not proper or altered by sedimentary deposits at selective locations. Such a situation could lead to acidulated water directly getting into the heat exchanger tubes. Adequate controls need to be exercised by measuring pH at different locations of the cooling tower basin especially at the basin's outlets. It must also be mentioned that handling of concentrated sulphuric acid is a hazard at all times, and more so during night shifts. The workers have to be given proper training in safety consciouness and remedies for treatment of acid burns must be available on hand. Since chlorination is effective at a lower pH, acid addition should precede chlorination when practised on an intermittant basis, i.e., once a shift.

Addition of sulphuric acid to the cooling water automatically raises the level of sulphate. Depending upon the calcium, level of sulphate needs to be guarded against, given the fact that its solubility decreases with decrease in pH and increase in temperature.. Fortunately, calcium carbonate is more insoluble than calcium sulphate under such conditions and thus will be deposited first. A useful guideline is to see that the product of ionic concentrations of calcium and sulphate does not exceed 5 x 10^5.

There are two aspects for any cooling water treatment by chemical addition. One is the need to prevent scale formations and other types of fouling, the other is to prevent or inhibit corrosion of the system materials. These will be considered separately.

As will be seen later, inorganic phosphates have been widely used as corrosion inhibitors. Consequently when considering prevention of scaling, in addition to calcium carbonate and calcium sulphate, the possibility of calcium phosphate scales also needs to be considered. The other hardness ion, magnesium, figures occasionally as scales in combination with silicate. In high silica waters, the scales could contain silica (SiO_2) itself or in the presence of Mg appear as magnesium hydroxy silicate.

A good way to minimise scale formation is to add chemicals that will keep the scale forming constitutents in solution. For Ca and Mg, polyamino-polycarboxylic acids such as ethylene diamine tetracacetie acid on its di sodium salt (EDTA) and polymeric phosphates like sodium hexameta phosphate have been made use of. At present polyacrylates, copolymers of sulphuric and acrylic acids, organophosphonates, polyelectrolytes etc. in proprietary combinations are available and are widely used for the inhibitation of scale formation(22,23). To keep Ca in solution a little less than 5 mg/l of a polyacrylate with a molecular weight in the range of 1000 is sufficient. Both carbonate and sulphate scaling is prevented. Inorganic polyphosphates have been effectively replaced by organic phosphates and phosphate esters. The former class are quite effective for Ca scale control. The frequently used among them are amino methylene phosphonic acid (AMP) and 1-hydroxy-ethylidine 1, 1-diphosphonic acid (HEDP). As seen earlier, since AMP contains aminonitrogen, chlorine could attack it and destroy its effectiveness. Thus AMP addition to the cooling tower basin or any injection point has to be done out of phase with chlorination. Since HEDP does not have this disadvantage, it is preferred over AMP. Both these phosphonates have a tendency to dissolve copper from circuit materials. Thus when these are added to prevent scaling, it is necessary to add an inhibitor to minimise copper corrosion. The phosphonates are also taken up by the iron corrosion product that is always present in the system, thus reducing their effectiveness.

The principle behind scale control by crystal modification was discussed earlier(24). Sulphonated polystyrenes and polymalac acids which are water soluble polymers, have been used for this purpose. At a concentration level of 0.5 to 2 mg/l they are very effective in modifying the cubic form of calcium carbonate to spherical sludge particles. These polymers are also effective against calcium sulphate and phosphate. The sludge so formed can be conveniently removed.

As the cooling tower is exposed to the environment the wind borne particulates get trapped. Due to the absence of a clarifier or its malfunction, some mud or silts will also get into the tower basin. The basin more or less acts as a trap for all sorts of insolubles and fine sediments are usually formed. There is always a chance of these getting into the heat exchanger tubes and causing fouling. Periodic clean up of the basin, provision of a side stream filter, use of dispersing chemicals and removal of sludge are some of the techniques employed for overcoming the problem. In many plants, the location of the cooling tower is such that exhaust gases or those gases arising out of plant leaks get dissolved in the cooling tower spray and thus alter its chemistry. A typical example is a fertiliser plant, where the ambient atmosphere around the cooling tower could contain ammonia and sulphur dioxide. Changing local wind direction would result in these gases being blown into the cooling tower and there are many examples, where pH of the cooling water gets altered as a result. The wooden planks in the cooling tower are subject to biodeterioration. One of earlier practices was to spray an aqueous solution of sodium pentachlorophenate on such surfaces.

In Chapter No. 4, the general aspects of corrosion have been considered and the characteristics and causes of different types of corrosion described. To recapitulate briefly, the anodic reaction, in the case of iron is,

$$Fe^{0} \rightarrow Fe^{2+} + 2e^{-} \qquad (5.10)$$

while the cathodic reaction is represented by

$$2e^{-} + 2H^{+} \rightarrow H_2 \qquad (5.11)$$

If one breaks or inhibits either, or both the path ways, corrosion will be minimised(14). Thus one can have anodic inhibitors and cathodic inhibitors with which the cooling water system can be dosed. Best known among the former are chromate and orthophosphate, while zinc and polyphosphate are well known cathodic inhibitors. When both are used in combination such as chromate - Zn, the treatment is known as dinodic. Among the anodic inhibitors, chromate was widely used untill recently. It is very effective over a wide pH range and gives excellent protection to mild steel at concentration levels of 300 to 500 mg/l. However, with restrictions on chromate discharge into the environment throughthe blowdown route becoming mandatory, such high concentrations could no longer be employed. Thus a low chromate treatment, in fact a dinodic treatment has come into vogue. In this practice, the pH is adjusted between 6 to 7 and chromate (20 - 25 mg/l), polyphosphate (10 - 20 mg/l) and zinc (1 - 3 mg/l) are added. This combination is one of the best available, but still suffers from the disadvantage that the limit of discharge of hexavalent chromium into the environment is 0.5 mg/l. Efforts have been made to evolve a blowdown treatment process that either reduces chromate to trivalent chromium or recovers chromate by ion exchange. The later is preferred due to various reasons.

In view of the above difficulties, the chromate treament is gradually going out of use. A number of non-chromate treatments have been evolved(21). These are essentially extensions of the scale inhibition techniques discussed earlier. Polyphosphates and aminomethylene phosphonate figure in this treatment. The idea is to inhibit corrosion by the formation of a fine scale in alkaline conditions(pH 7 to 8.5), but at the same time to control excessive scaling by use of chemicals like AMP, total phosphate levels can be upto 15 mg/l in the case of polyphosphates and 1 to 2 mg/l of zn is also added as a cathodic inhibitor, while the possibility of Mg silicate scale is minimised by adding an acrylic polymer. Proprietary formulations are available in the market. It has to be emphasised that cooling water treatment in the alkaline region is much more delicate than the procedure in the 6-7 pH range and needs better chemical control. Programmable chemical addition and frequent monitoring of chemical parameters are required.

Among other corrosion inhibitors mention has to be made of nitrates and orthosilicates on the anodic side and molybdates and polysilicates on the cathodic side. In fact chromate and polysilicate in combination offer excellent protection to steel, copper and aluminium components of the cooling water circuit. Polyphosphate and zinc offer equivalent protection to steel only.

In conclusion, a cooling water treatment programme has to effectively counter biofouling, scaling and corrosion. A variety of procedures are available and many of these are site specific and dependent upon the water quality. Since ninety percent of the industrial usage of water is for cooling,this segment of water treatment has special importance and can in no case be neglected.

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6

DEMINERALISATION BY ION EXCHANGE

The purity of water that is fed to a steam generating system is of utmost importance, since by its very nature a boiler concentrates impurities. Hence the lower the level of impurities, i.e., dissolved solids, the better. Of course, this applies equally rigorously to suspended solids and to an extent to dissolved gases, especially carbon dioxide and oxygen.Thus, every unit of an electricity generating industry installs, as part of its equipment, a water purification system, more commonly known as a Dimineralisation(DM) Plant(1). Raw water after proper pretreatment steps such as floculation, clarification, chlorination etc. is the source for the DM plant(2). The process of demineralisation(getting water free of all its dissolved cations and anions) squarely rests on ion exchange. In fact water purification is the largest single application of the ion exchange technique. Synthetic ion exchange resins have become available over the last fifty years. At present a variety of resins serve the needs of industries as diverse as power generation to purification of life saving drugs.

Use of semi permeable membrances by the reverse osmosis technique for water purification has become important. Since the last two decades drinking water is being produced by this method.

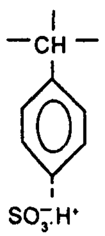
As noted in an earlier chapter, drinking water contains dissolved salts, with permissible levels being specified. Obviously, this water is not fully demineralised. However, if the raw water available to a power plant has a salt content, higher than normally expected, it might be economically advantageous to have the Reverse Osmoss(RO) plant precede the DM plant. This will reduce the load on the latter and enhance the useful service life of the costly resins. But this would mean, two plants based on different priniciples and techniques. Reverse Osmosis is also a very useful technique in waste water treatment, especially in the treatment of low level radioactive effluents.

In this chapter, the application of ion exchange for water purification is discussed, while reverse osmosis is dealt with later on under Desalination.

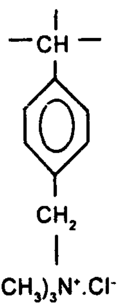
6.1 ION EXCHANGE RESINS

Natural zeolites of the type $[M_a/n\ (Al0_2)_b\ cH_2O]$ are known to possess ion exchange properties. In fact, some of these materials sold under the trade name of Permutit, were being used for water softening. Steam locomotives fill up such softened water at railway stations to avoid scale formation in their boiler internals. By softening is meant that hardness causing cations such as Ca^{2+} and Mg^{2+} are replaced by Na^+ in the water under treatment. The synthetic ion exchange resins developed during the thirties and forties are based on water insoluble organic polymer matrices, with exchangeable sites(2). They are essentially solid electrolytes and reversibly exchange their mobile ions with ions of like charge from the surrounding liquid medium. Divinyl benzene crosslinked with styrene forms the matrix for strong acid cation exchange resins and strong and weak base anion exchange resins. Divinyl benzene crosslinked with acrylic or methyl acrylic acid forms the matrix for the weak acid cation exchange resins. The terms "strong" and "weak" have the same connotation as in the case of simple acids and bases. For example, while HCl is a strong acid, propionic acid is a weak acid. Similarily, while NaOH is a strong base, ammonium hydroxide is a weak base. It is the nature of the dissociating functional group in the resin that is indicated by these terms.

The strong acid cation exchangers are produced by the sulphonation of the polymer skeleton. The sulphonic acid group, $-SO_3^-$ gets fixed on to the matrix while H^+ ions are retained as mobile exchangeable ions. The anion exchange resins are produced by chloromethylation followed by amination of the polymer matrix. This leads either to the formation of quarternary or tertiary ammoniacal nitrogen in the polymer matrix. Since tetracovalent nitrogen is always +ve, the former would contain N^+ in the matrix and is neutralised by a mobile anion such as OH^- or Cl^-. The resin that has tertiary ammonical nitrogen needs protonation in the acid medium to act as an anion exchanger(2).



Strong acid
cation
exchanger



Strong base
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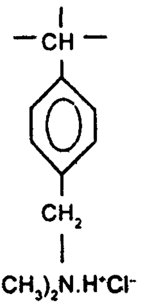
exchanger



Strong base
anion
exchanger

Secondary and primary ammonium resins are also available. These are weak base anion exchangers that can only function in an acidic medium. In the weak acid cation exchange resins, the functional group is usually -COOH in place of $-SO_3H$, in an acrylic -DVB matrix.

6.2 ION EXCHANGE PROCESS

The exchange eqilibria can be illustrated by the following reactions, taking commonly present ions in natural waters as examples:

$$-RSO_3^-.\ H^+ + Na^+ \Leftrightarrow -RSO_3^-.\ Na^+ + H^+ \quad (6.1)$$

$$-R_4N^+\ OH^- + Cl^- \Rightarrow -R_4N^+.Cl + OH^- \quad (6.2)$$

$$H^+ + OH^- \rightarrow H_2O \quad (6.3)$$

Since the dissociation constant of water is very small and as the reaction of H^+ with OH^- is extremely fast, reaction 6.3 goes to completion instantaneously, which in turn acts as the driving force to push reactions in 6.1 and 6.2 in a fast forward direction. When all the exchange sites that originally held H^+ or OH^- ions are occupied by Na^+ or Cl^- (or any other cations or anions) respectively the resin is said to be exhausted. The resin can then be regenerated by equilibration with a suitable acid or a base.

$$-RSO_3^-.\ Na^+ + HCl \Leftrightarrow -RSO_3^-.\ H^+ + NaCl \quad (6.4)$$

$$-R_4N^+.Cl^- + NaOH \Leftrightarrow -R_4N^+.\ OH^- + NaCl \quad (6.5)$$

The reactions in equations 6.1, 6.2, 6.4 and 6.5 being equilibrium processes, can be moved in the forward direction. As a result, the ionic impurities in water are exchanged and retained in the resins. Thus when ordinary water, say tap water, is passed through a bed of a cation exchanger, all the cationic impurities such as Na^+, Ca^{++}, Mg^{++} are exchanged for the hydrogen ions of the resin. Obviously, the effluent will be acidic. When this is passed next through an anion exchanger, all the anionic impurities such as Cl^-, NO_3^- and sulphate are held by the exchanger, releasing OH^- in turn. The hydrogen and hydroxyl ions combine to form water molecules and the effluent becomes neutral water again. The total equivalents of cationic impurities are balanced by the total equivalents of anionic impurities in natural waters. Thus, in principle, the ion exchange capacity is exhausted in both the resin columns to the same extent. But in practice, it is somewhat different, because of the presence of bicarbonate and carbonate ions in natural waters. When water is passsed through the cation resin, we have seen that it becomes acidic. The hydrogen ions interact with these anions and the resultant carbonic acid so formed decomposes into water and carbon dioxide.

$$H^+ + HCO_3^- \rightarrow H_2CO_3 \rightarrow H_2O + CO_2\uparrow \quad (6.6)$$

Thus, a part of the anioic load is removed in the gas form reducing the load on the anion resin bed. This causes a lot of bubble formation, almost like frothing. It is necessary to degas this effluent, usually by blowing air through it before it is led into the anion resin columns.

Since ion exchange is an electrostatic(ionic) phenomenon, it is to be expected that multivalent ions rather than monovalent ions, in the aqueous phase will be preferred by the resin phase. Thus there is a selectivity series. For strong acid and strong base resins, the selectivity for the ions commonly present in water is.

$Fe^{3+} > Ca^{2+} > Mg^{2+} > Na^{+}$ and Sulphate> chloride>Bicarbonate.

The strong acid and strong base resins function over the entire pH range of the medium. The weak acid cation exchange and the weak base anion exchange resins function best in basic and acidic pH ranges respectively.As a corollary, strong anions such as sulphate and chloride are most preferred by the weak base anion exchangers.This has led to an important application in water treatment, whereby ions like sulphate and chloride are first removed by a weak base anion exchanger(since the medium at that point is going to be acidic as seen earlier) and the so-called weak anions such as silicate are taken up in a second column containing a strong base anion exchanger.

6.3 PROPERTIES OF ION-EXCHANGE RESINS

A reference was made earlier to ion exchange capacity and its exhaustion. The capacity is theoretically defined as the number of exchangeable sites present for one mole of the resin. In practice it is expressed as milliequivalents per gram(meq/gm) of the dry resin. Because the resins are always made use of in a wet condition, the capacity is always less than the value in the dry state. For strong acid cation resins, the capacity in the dry state could in principle reach 5.0 meq/gm. The capacity of the weak acid cation resin is much higher than this, while that of anion exchange resins in general is somewhat lower than 5.0 meq/gm. The capacity in the wet state is determined experimentally and it is usually of the order of 65 percent of its value in the dry state(3).

Another important property of the ion exchange resins is the degree of crosslinking, which more or less corresponds to the percentage of the crosslinking agent, viz., divinyl benezene present in the resin. Commercially available resins have a range of crosslinking from 2 to 12. It is obvious that the greater the cross linking, the greater will be the mechanical strength of the resin and hence its swelling behaviour.It also determines the pore or the channel size.

Other physical characteristics of the commercial ion exchangers are density, effective bead size, uniformity co-efficient and the percentage of whole beads in the material(3). For $-SO_3H$ type resins, the apparent wet density is about 0.85 g/ml, while for the -COOH type it is about o.7 g/ml. For anion resins, the apparent wet density is again around 0.7 g/ml. A good sample of the resin contains not less than 70 percent of whole beads, their uniformity coefficient being 1.7(max.).

Some of the relevant properties of the standard resins are given in Table 6.1.

When the resin is in use, it experiences different cycles of treatment over prolonged periods. For example a cation exchange resin would be cycling between the -H form and the -Na form, while an anion exchanger would cycle between -OH form and -Cl form. This leads to a periodic swelling and contraction of the resin beads, at least once in 24 hours. This is known as the osmotic shock. Resistance to osmotic shock(resin beads should not crumble) is a very important criterion for judging resin performance. Resins with low cross linking experience this shock more than those with a high cross linking; however, the latter are brittle. Sulphonated resins are more resistant to osmotic shock than aminated resins (CER > AER).

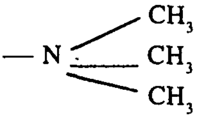
Table 6.1 Characteristics of Standard Ion Exchange Resins[4]

Type and functional group	Bead size (mm)	Moisture content (%)	Total exchange capacity (eq/l)	Max. recommended Temp. (^0C)	Swelling (%)
SAC	0.45	4.4	1.9	120	Na^+__H^+
_SO_3H	to 0.6	to 4.8			(7)
SBA	0.38	4.2	1.4	60	Cl^-__OH^-
_$N(CH_3)_3$	to 0.45	to 4.8			(19)
WAC	0.33	4.3	3.5	120	H^+__Na^+
_COOH	to 0.50	to 5.3			(10)
WBA	0.36	4.0	1.9	100	OH^-__Cl^-
_NH OH	to 0.46	to 4.5			(10)

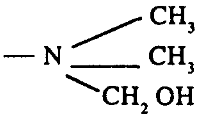
In the table the abbreviations stand for,

SAC: Strong Acid Cation Exchanger,
SBA: Strong Base Anion Exchanger,
WAC: Weak Acid Cation Exchanger,
WBA: Weak Base Anion Exchanger.

There are two types of strongly basic anion exchangers, Type I and Type II. Both have quarternary ammonium groups as the active exchange sites. In Type I, the groups attached to the nitrogen are usually alkyl groups, while in Type II, one of the groups is an alkanol thus,



Type - I



Type - II

Usually Type II resins are used in water purification, since they are cheap. However, they do not effectively remove silica, and are also susceptible to organic fouling[2].

Two varieties of ion exchange resins are commercially available for water purification. They are classified on the basis of their porosity, (a) the gel or the microporous type and (b) the macroreticular or macroporous type[3]. The former are clear, transparent and glassy in appearance. As their name implies, the pores have a small diameter. The beads are spherical with a diameter ranging from 0.1 to 1.0 nm. The pores tend to get clogged with organics, which are relatively large molecules. The macroporous resins on the other hand have pores whose diameter is of the order of several thousand angstroms with large surface areas(~100 m^2/g).The macroporus resins are opaque in appearance and exhibit a good resistance to osmotic shock. Large size neutral molecules such as organics can easily pass through them and hence flows are not reduced in service. These organics subsequently decompose in the boiler.

6.4 DEMINERALISATION OF NATURAL WATERS

The feed to a demineralisation plant is clarified raw water, free from chlorine and nearly purified of organic and bilolgical material. In principle, what one needs from that point would be a cation exchange column,(often referred to as bed) a degasser where air is usually blown through the effluent to drive off carbon dioxide and an anion exchange bed, with facilities for regeneration of the spent resins(4). In practice, it was realised that the water effluent from the anion exchanger outlet was not pure enough; its specific conductivity ranges from about 10 to 20 μS/cm, with the pH being in the alkaline range(upto 9.0). Hence it becomes necessary to add one more bed of ion exchangers, called a mixed bed wherein, as the name implies, a mixture of cation and anion exchangers are in place. This additional bed improves the water purity and one can get water whose specific conductivity is less than 0.5 μS/cm with a pH between 6.5 to 7.5. Silica is reduced to less than 0.02 mg/l, with the total electrolytes being less than 0.1 mg/l.

It has been more or less established by experience that the cation exchange part of the demineralisation process does not pose many problems. The performance of a DM plant really depends upon the performance of the anion exchanger and that of the mixed resin bed. From the input water side, the organic content plays a significant part in the efficiency of the anion exchange. In several countries, the current practice is to have two anion exchange beds. The first contains a weak base anion(WBA) exchanger, while the second is made up of a sttrong base anion(SBA) exchanger. The former has a better affinity for chloride, nitrate and sulphate. Its bed volume, height etc. are to be determined from what is known as negative M alkalinity, which represents the total equivalents of these three anions. If this value is greater than that of bicarbonate, in the raw water, it is essential to have a WBA column. The SBA bed which follows it will then effectively pick up silica and the effluent from this anion exchange bed will have a lowest specific conductivity and reduced silica slip.

6.4.1 Organic Load vs. Anion Exchange

For several years, water technologists all over the world have been preoccupied by the problem of the fouling of strong base anion exchangers. Some of the conclusions available in literature are(1),

(a) In type I strong base anion resins, the fixation of organic matter depends upon the dried matter content of the resin.

(b) Macroporous exchangers of the corresponding variety do not show specially high fixation of organic matter as compared to gel type resins.

(c) The removal of organic matter over a period of time is far from complete and leads to partial, but irreversible fouling of the resin. Hence type I strong base anion exchangers are not well suited for the treatment of water having a high organic load. This conclusion is all the more true if the raw water contains detergents even at low concentrations of 1 mg/l.

(d) On the other hand, when type II strong base anion exchangers are used, the quality of water from anion bed outlet has shown a distinct improvement for about the same conditions of organic and detergent fouling.

(e) Investigations have indicated that condensation exchange resins(weak base type) perform well in water containing a high percentage of organic matter.

(f) Macroporous polystyrene weak base anion exchangers have their own limitations and have been shown to be fouled up by water heavily charged with organic matter.

(g) Experience shows that the presence of a weak base anion exchanger with a reasonably dry solid content will protect the strong base exchange resin column that follows it.

6.4.2 Mixed Beds(MBs)

In order to acheive the required quality of DM water as make up for the high pressure boilers, a mixed bed of cation and anion exchange resins becomes essential. The mixed bed is to be used as a final polishing unit and should be operated with higher levels of regeneration. The plant should produce an effluent that is essentially neutral. The cause of the poor quality of the water coming out of the mixed bed is contact with the sulphuric acid, which is employed for regenerating the cation resin with some of the anion resin in the bed. A strongly basic anion resin picks up acid in the form of the bisulphate ion which is easily hydrolysed later resulting in the leakage of acid into the treated water. This difficulty can be eliminated by using hydrochloric acid as the cation resin regenerent. The strongly basic anion resins take up HCl as the chloride and the chloride form of the resin is not suspectible to hydrolysis which could lead to acid formation and its leakage.

6.4.3 Regeneration Technique

It is customary to effect regeneration by passing the regenerant through the bed of ion exchange resins in the same direction as the raw water being treated(1,2). This is known as 'co-current' regeneration. It has been shown theoretically, as well as in actual practice, that if the co-current regeneration is effected (downward flow), the bottom layers of the exhausted columns are poorly regenerated, unless a very large amount of regenerant-acid or alkali is used. On the other hand, if the regeneration is effected counter-current, that is, in the direction opposite to that selected for the exchange cycle, the bottom exhausted layers of the resins are more efficiently regenerated. This process results in reducing the leakage of sodium to very low levels in the case of cation exchanger and of silica in the case of anion exchanger during the exchange cycle. Apart from increased regeneration efficiency, economy in regeneration (in terms of consumption of chemicals) can be acheived by this technique.

With a strong acid cation exchange resin in service, when the diffusion process has reached equilibrium, it is known that the relative concentration of Na^+ in the resin and in the liquid phase are not identical and their concentration ratio or distribution coefficient is a characteristic of the resin. Sodium leakage,$(Na)_l$ is expressed in terms of this distribution coefficient, K and the ratio R of H^+ in the last layers of the resin bed to its total capacity, thus,

$$(Na)_l = \frac{S}{1 - \frac{KR}{100 - R}} \tag{6.7}$$

where S represents the total Na. From eq. 6.7, it is evident that if R is close to 100, the last layers are that much nearer to a state of complete regeneration. This is however achieved by counter current regeneration.

Water of very good quality can be obtained with counter-current regeneration, whereas co-current systems require a finishing column, to give the same result. With counter-current regeneration system, the quality of the treated water is not influenced by the nature of the influent water and by the regeneration rate; the factor with maximum effect on water quality being the selected sodium leakage rate at which the cycle is stopped.

It has been demonstrated that the performance of type II resin can be improved by the counter- current regeneration. Silica leakage from type II resin can be made to be on par with that of type I resins, if regeneration is made counter-current.

Following the idea of counter-current regeneration, extensive studies have been made on using the fluidised bed technique for demineralisation. In this process the raw water to be treated is passed upwards and regeneration is carried out by a downward flow of the regenerant.

Regeneration of a mixed bed has been a challenge for a long time. For an efficient in-situ regeneration of the resins, the separation of the anion and cation resin should be perfect and clean, which cannot usually acheived in practice. Due to improper seperation during regeneration, a small layer of cation exchange resin at the interface between the two resin phases is converted into the sodium form during the regeneration of the upper layer of anion exchange resin. Also a part of the cation exchange resin is present in the anion exchange resin bed and gets converted to the sodium form.(Fig.6.1). This improper regeneration results in reduced operational capacity (Na-slip) of the mixed beds cycle after cycle.

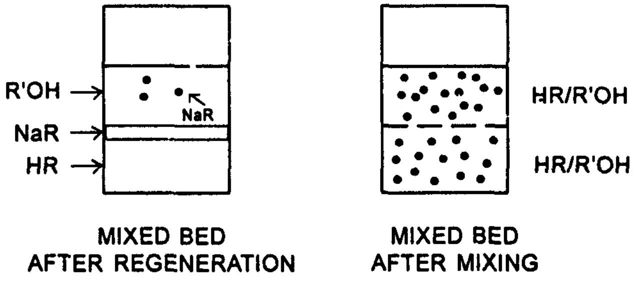


Fig. 6.1 Sodium Contamination in Mixed Bed Regeneration (Schematic)

This problem has been ingeniously overcome by introducing a layer of inert resin with carefully selected buoyancy properties, so that it acts as buffer layer to seperate the two zones of active resins when the regeneration and rinse down cycles are operating (Fig.6.2). This involves a careful selection of the density of the inert material and control of the density of the cation and anion exchange resins. The inert material is an organic polymer(for example, polystyrene) which possesses no ion exchange properties and is physically and chemically inert to most solvents and reagents, particularly to those normally used for regeneration purposes(2).

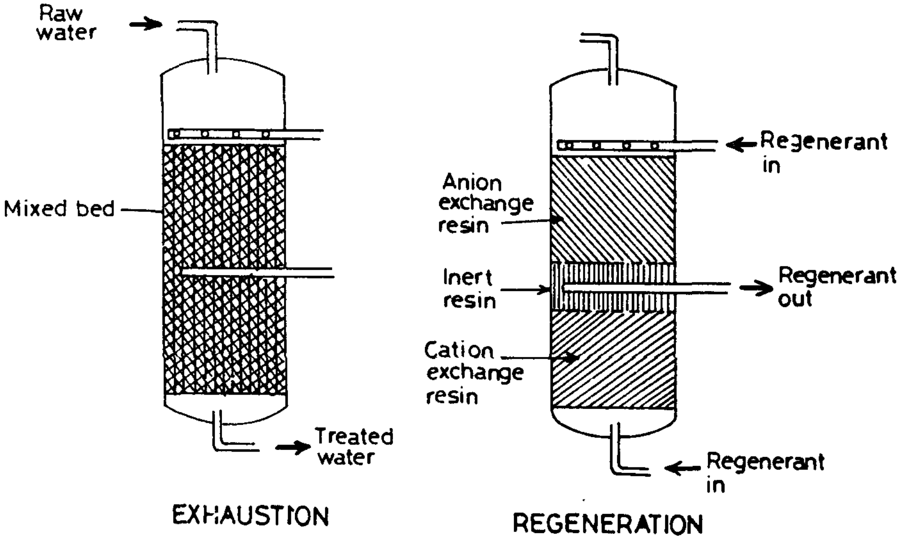


Fig. 6.2 Schematic Diagram of 3-Resin Mixed Bed System

Economy in the production of deionised water can be achieved by the use of stratified beds which consist of superimposed layers of resins of the same polarity. One of them is weak acid or base, while the other is a strong acid or base. During regeneration, the weak acid resin, which is lighter than the strong acid resin is placed at the top of the bed (Fig.6.3). The counter-current regenerant flow will then pass upwards through the bed, encountering first the strong acid resin, followed by weak acid resin. Thus the former is thoroughly regenerated(2).

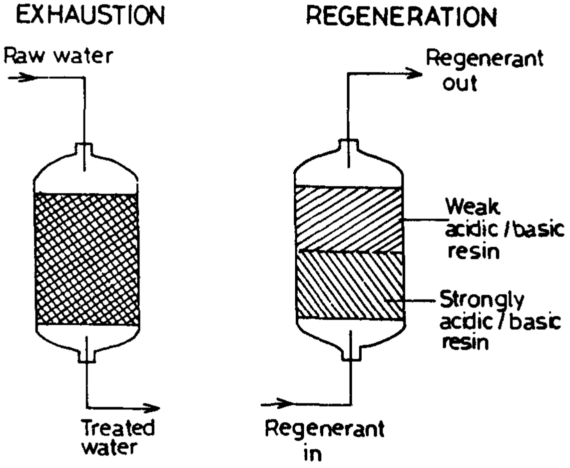


Fig. 6.3 Schematic Diagram of Stratified Bed

In comparision with a single exchanger(weak or strong) regenerated by counter-current flow, stratified beds have a higher operating capacity per installed litre. Less resin is therefore required to treat the same volume of water, and the efficiency of the process is improved in terms of less regenerant consumption.

The ratio of weak acid(carboxylic) resin volume to total bed volume in the case of a stratified system will be larger, the shorter the cycle time and the higher the alkalinity/TDS and total hardness/alkalinity ratios. The performance of stratified beds also depends on a good seperation between the two exchangers. This means that the flow pattern within the column should be optimum in order to have a clear seperation between the two resins during regeneration which necessitates a careful selection of the particle size of the two resins.

In the case of anion exchangers, type II resin can be used as a strong base exchanger. The SiO_2/TDS ratio must be less than 20 percent, otherwise the low regeneration rates used entail a risk of fouling by silica. For a good seperation between the two resins, the particle size range must be carefully selected.

It has been mentioned that a high level of regeneration of the polishing mixed bed is desirable in order to ensure the highest possible quality of water. To acheive this the so called thoroughfare system of regeneration can be used.This system involves passing the regenerant required for the preceding cation or anion units, firstly through the coresponding resins in the mixed bed. The quantity of the anion resin in the basic demineralised unit will be at least five to ten times the quantity of the corresponding resins in the mixed bed. As such the regeneration level in the mixed bed will be correspondingly higher without any additional consumption of regenerants. In addition, temperature is also important when removal of silica from mixed resin bed is considered. At regeneration levels greater than 100 gm of NaOH per litre, the influence of temperature is pronounced. It is important to remove as much silica from mixed resin as possible, since silica in the treated water is dependent upon the amount of silica left in the mixed bed after regeneration. When this type of regeneration is used with either acid or alkali, it is implicit that the mixed bed be regenerated at the same time as the preceding cation or anion exchange column. The quantity of water passing through a mixed bed unit per regeneration being known, it is possible to calculate the permissible amount of silica and other solids in the treated water, that can be taken care of by the mixed bed during normal operation, from the preceding units.

Resin fouling is a major irritant in DM plants(5). One often comes across fouling of the cation exchanger by iron, manganese and copper. These impurities, particularly, iron, comes along with regenerant chemicals. For example, commercial hydrochloric acid usually contains iron. Thus, it has become a practice to specify the iron and chlorine contents of HCl used for regeneration. Once in way the cation exchanger is also fouled up by precipitates such as calcium sulphate. As mentioned earlier, the anion exchangers are fouled up by organics in addition to colloidal silica. Both resins are fouled up by oil,grease, microbes, silt and clay which get in due to improper pretreatment procedures. To overcome the different fouling problems, cleaning up of the resin beds is required. The sequential procedure includes, backwashing, acid wash (10 percent inhibited hydrochloric acid), 15 percent NaCl solution mixed with 5 percent NaOH, or 15 percent NaCl solution mixed with 5 percent sodium hypochlorite (to give about 3 percent wt/v of free chlorine) and 0.5% solution of formaldehyde. The solution or solutions to be used for overcoming the problem of fouling depend upon the nature of fouling. In each case appropriate test procedures are available to judge the efficacy of the treatment.

Some special problems are also encountered in the mechanics of demineralisation. In counter current flow units, it is most essential to maintain the compactness of the resin bed at all times during regeneration and preferably during the service regime also. Any disturbance of the cation bed always leads to an unacceptable leakage of sodium. Counter current flow units should be operated in such a way that sodium and silica end points for cation and anion units are not exceeded. It is also essential that the feed to the DM plant after pretreatment be free from any residual chlorine, introduced earlier(6).

In modern power stations, where the operation of the high presssure boiler and turbine requires the highest quality feed water, it is becoming a standard practice to include the polishing of the steam condensate(partly or even fully) by ion exchange resins(7,8). This is specially necessary, if the steam condenser is cooled by brackish or sea water, since condenser leaks result in an unacceptable level of impurity intrusions. Condensate polishing is strongly advised, if the salinity of the cooling water exceeds 2000 mg/l. Since large quantity of condensate needs to be polished, the purification system operates under a pressure much greater than that of the usual demineralisation plant. Thus, in order to withstand the pressure and flow, attrition strength of the resin bead becomes an important criterion. Particle size and grading are also important to reduce pressure drops. In some condensate processing systems, very fine size resins(25 micron diameter) are used as precoat materials on pressurised filter media before the deep bed polisher. The precoat filters are non-regenerable. If the condensate is near neutral, experience has shown that it is possible to acheive and maintain feed water conductivity below 0.07 μS/cm and total metals around 2-3 μg/l. However, if the condensate, contains alkalising additives such as ammonia, hydrazine or morpholine, the condensate polishing becomes a very complicated process, due to the relative affinity of ammonium type of cations as compared to say that of sodium for the resin sites. As a result, it is difficult to achieve a conductivity value as low as that mentioned above.

6.5 QUALITY OF DM WATER

One can take a specific conductivity of 0.1 μS/cm as the basis for the DM water and can be sure that a very low concentration of electrolytes are present (theoritical conductivity of water at 20°C being 0.05 μS/cm). However, due to ion slip in the DM plant, specific conductivities higher than 0.1 μS/cm are often observed at the outlet of mixed bed filters. These slips do not have much influence on the feed water conductivity in condensate recycling power plants whose requirements of make up water are below 1 percent of the hourly steam output. On the other hand the conductivity of the DM water for industtrial steam generation plants with a large quantity of make up water is an exceptionally important parameter. Increased electrolyte input in this case invariably leads to damage, particularly in once-through boilers and superheaters.

It has often been said that the performance of a demineralisation plant is crucial to the over all water chemistry in a thermal power station. This emphasis is due partly to the installation of a number of once-through boilers in advanced countries and partly to the increasing requirements of steam purity for high pressure turbines. Power stations in India have been making attempts to improve the performance of DM plants. One way to assess this is to monitor critical chemical parameters of the mixed bed output water. Table 6.2 presents data of some case studies carried out by the author in this context.

Table 6.2 Comparison of Mixed Bed Performance(9)

S. No.	Chemical Parameters	A			B			C			D		
		J	M	S	J	M	S	J	M	S	J	M	S
1.	Input												
	Sp.Conductivity µS/cm.	4.3	7.3	7.5	30	40	40	8.8	8.5	6.2	4.8	13.0	4.0
2.	Output												
	Sp.Conductivity µS/cm	0.15	0.15	0.19	0.25	0.25	0.5	0.40	0.44	0.36	0.43	0.42	0.40
3.	Output pH	6.8	6.8	6.9	7.0	7.0	7.0	6.7	6.8	6.8	6.8	6.8	6.9

S.No. 1 represents the Sp. conductivity at the anion exchanger outlet.
A,B,C & D represent the power stations under study.
J,M & S represent January, May and September in the year of study.

It is usual for DM plant manufactures to claim a specification that the specific conductivity of the output water from the mixed bed is less than 0.2 µS/cm. It is evident from Table 6.2 that only in case A and to some extent in case B is this specification met. There is much room for improvement in performance in cases C and D. On the other hand, in case B, the anion exchanger effluent (S.No.1) shows a high value of conductivity, twice that of the specifications usually given for that parameter. Investigation revealed that at B, the anion bed was contaminated with some cation exchanger leading to the higher value. Despite this, the MB performance is not far from optimum, indicating that MB regeneration is being carried out in an efficient manner.

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7

WATER CHEMISTRY IN FOSSIL FUEL FIRED STEAM GENERATING UNITS

7.1 WATER SIDE CORROSION AND DEPOSITION PROBLEMS

For a world in need of energy, the use of water to generate steam for running turbines of power plants is a most important activity. Whether the steam generated is from burning fossil fuels or from nuclear heat, or whether it is to be directly employed for steam cracking of naptha in fertiliser plants, the steam quality is of utmost importance. This has been realized during the last 10 to 15 years, in a full measure all over the world. If one has to meet this requirement, there is no alternative to a well considered and integrated water treatment programme at all steam utilities. For securing better thermal efficiencies, high temperatures and pressures are employed in the steam water circuit, the latter comprising of feed water, boiler water, steam and condensate in contact with surfaces of different materials. The words boiler and steam generator are synonimous, though the former term finds a larger usage in fossil fuel fired power plants, while the latter term is frequently used in the nuclear power sector.

In fossil fuel fired boilers, the boiler tubes are usually of carbon steel. In the case of nuclear steam generators, stainless steel 304,Monel-400, Incoloy-800 are employed as tube materials. In view of what was said in Chapter 4 and also because of the chemical incompatibility of copper with respect to carbon steel under the conditions of a steam-water circuit, there is a marked tendency to eliminate copper alloys from the feed train. Condenser tube materials used include brasses, cupronickels, stainless steel and lately titanium. The steam turbine makes use of a variety of alloy steels.

A block diagram of the water and steam circuit is shown in Fig. 7.1.

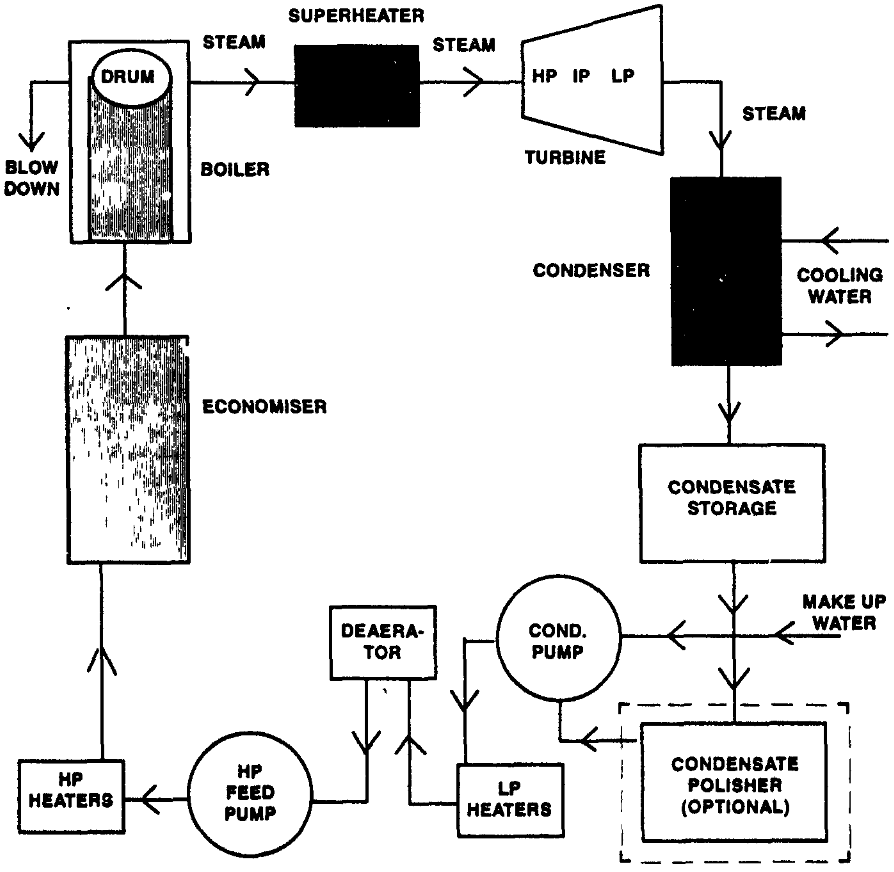

Fig. 7.1 A Simplified Water-Steam Circuit in a Power Plant

In high pressure boilers that make use of fossil fuels, the failure of boiler tubes due to internal corrosion and external 'hot' corrosion, is of concern. The subject matter in this book deals with the former rather than with the latter which is metallurgical in nature. Boiler tube failures result in reduced availability and reliability of the steam generating unit and impose an economic penalty. In India, the Central Board of Irrigation and Power conducted a five year research programme on water chemistry and boiler tube failures in thermal power stations across the country and published their findings in two reports*(1,2).

Protection against internal corrosion by the boiler water is primarily provided by the thin magnetite (Fe_3O_4) film formed on the tube surfaces during the early stages of operation. As long as the adherent film is there, corrosion is prevented or greatly minimised. If the film is damaged, internal corrosion starts again. The corrosion of carbon steel is minimal in the pH range of 8.5 to 10.5(3). The corrosion rate increases more rapidly with decrease in pH from 8.0, than with increase in pH from 11.0. Consequently, the efforts are directed towards

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* As the Expert Coordinator for the study on water chemistry, the author was responsible for Coordinating all the technical work carried out. This chapter is partly based on that experience.

maintaining boiler water pH around 9 to 9.5. The actual range depends upon the nature of other constructional materials in the circuit, specially copper alloys. In all ferrous systems, which is the modern practice the pH is maintained around 10.0 ± 0.5. When the pH is excessively high or low, the magnetite layer is partly destroyed and internal corrosion starts.

Under high pH conditions, excess OH, in the form of NaOH, gets concentrated in the pores resulting in metal wastage, wall thinning of the boiler tube at that point; finally leading to tube rupture(4). This type of attack is often called caustic gauging and the resulting failure is known as ductile failure. Tube thinning is a characteristic of this class and could be detected earlier through ultrasonic in-service inspection. A more frequent type of failure of boiler tubes is due to internal corrosion that occurs in the low pH region. The hydrogen produced in corrosion process gets trapped in the film and diffuses into the metal. There it combines with carbon present in boiler steels and generates methane. The combined pressure exerted by hydrogen and methane within the metal results in grain boundary fracture. This results in tube failure, which may occur explosively, throwing out bits of metal. Ultrasonic inspection might not reveal the trouble-spot early enough to effect a tube replacement.

The cause of pH fluctuations can be traced to leakage in the power plant condenser, resulting in contamination by raw water, cooling tower water or sea water depending upon the location. The internal deposits resulting therein cause tube failures.

The internal deposits being poor thermal conductors, can also lead to over heating of boiler tubes at the spots where such deposits exceed a certain thickness.In other words, the heat transfer from the fire side through the tube to the boiler water is reduced at such spots which becomes over heated. Consequently blisters appear on the boiler tube, which ultimately burst. This type of failure takes place not only with boiler tubes but also with tubes of the superheater and reheater(in units where they exist). To avoid deposit formation in these sections,it is essential that the attemperator or desuperheating spray water be of high quality. The deposit analysis usually shows oxides of Fe, Cu, Ni and Zn which originate from the components bearing these metals in the preboiler section. The causative factors are pH and dissolved oxygen, the latter being more significant than the former(5). As the preboiler section operates at relatively low pressure, air ingress is often the cause of an increase in dissolved oxygen in the feed water. This can be controlled (to values less than 5mg/l) by dosing with hydrazine. This will also help in minimising pitting corrosion, which frequently occurs close to the welds due to internal stresses at such points.

While talking of water side corrosion, the influence of the chloride ion has to be considered. Of the various alloys present in the system, stainless steels are most susceptible to chloride attack, through stress corrosion cracking, specially in the presence of dissolved oxygen. Fortunately, the extent of stainless steel surfaces exposed to feed and boiler water and condensate in a fossil fuel power plant is limited. However, just like NaOH, NaCl would also concentrate in the crevices of a boiler. In general, chloride being a corrosion promoter, it is monitored and kept under control through blowdown. With increasing pressures, the vapour phase carryover of sodium chloride into the turbine and deposition on the turbine blades is a matter of serious concern, as is the behaviour of silica.Thus sodium chloride and silica are to be looked at from a different view point, viz. the turbine. The only way to control them in the steam fed to the turbine is to control them in the feed and boiler water(6). It may also be mentioned that stress corrosion cracking is a serious problem on the water side of nuclear powered boiling water reactors where stainless is used extensively.

7.2 CHEMICAL TREATMENT OF WATER FOR INDUSTRIAL AND POWER PLANT BOILERS

Boiler water chemical conditioning and its control is aimed at:

(a) Avoiding internal boiler tube corrosion.
(b) Preventing deposit formation on heat transfer surfaces.
(c) Ensuring the quality of steam acceptable to the turbine.

Boiler water chemical treatment and its control have evolved over the decades and the process is related to the increasing temperatures and pressures obtained in boilers, as well as to changes in the boiler design itself. Recirculation drum type boilers with blowdown facilities were the first to appear on the scene. There were improved designs over a period for increasing pressure. The water quality requirements changed as a result of this. At a later date, once-through boilers or steam generators came up. In these there is no drum to hold boiler water with a higher content of dissolved solids than feed water nor is there a blowdown facility to regulate the chemistry. This group of boilers require almost zero TDS in feed water.

After the steam loses most of its energy in driving a high pressure turbine, it is condensed and the condensate forms the main bulk of feed water to the boiler, after being reheated and repressurised. The high purity DM water serves only as a make-up to take care of losses(or more usually the boiler blowdown). A very large number of utilities use the condensate without further purification. However, with the increasing technical requirement of a minimum amount of dissolved solids as practicable for feed water, condensate polishing by mixed bed demineralisers has come into vogue.

7.2.1 Low and Medium Pressure Boiler Water Treatment.

Low and medium pressure boilers find extensive use in the chemical industry, serving as a source for both process heat and steam. Low pressure boilers are by convention those operating upto 15 to 20 kg/cm^2 (~300 psig). Above this working pressure, but below 64 kg/cm^2 (~ 900 psig) are the group of medium pressure boilers.During the last 30 years the design of the boilers has undergone improvements in all directions, necessitating a superior quality of feed water.The boilers operate at high heat transfer rates and have evaporation capacities in the range of 10,000 kg/h. The two problems faced under such conditions are scaling and corrosion. The required feed water quality is not attainable by the conventional base exchange softening plant as the water has to be completely soft and clear. In addition to scaling, these boiler internals are also susceptible to corrosion by dissolved carbon dioxide and oxygen(7).

The boiler water quality in the boiler drum as specified for low pressure boilers is given in Table 7.1.

Table 7.1 Water Quality Specifications for Low Pressure Boilers(7)

Total dissolved solids	:	Less than 3000 mg/l
Total alkalinity	:	20% of the TDS (Less than 600 mg/l as $CaCO_3$)
pH	:	10 to 10.5
Total hardness	:	Less than 5mg/l as $CaCO_3$
Sulphite	:	30 - 50 mg/l
Phosphate	:	30 - 50 mg/l

Sulphite is added for deoxygenation,while phosphate is a corrosion inhibitor.

Since the boiler is an evaporator, that too at very high rates (as compared to a cooling tower), it is possible to maintain the above boiler water quality only by a process of feed and bleed. The bleed is known as blowdown and is possible only in the case of drum type boilers. The quantity of boiler water to be blown down can be calculated from the quality of feed water (that acts as a diluent) and the equilibrium quality of boiler water that needs to be maintained despite evaporation. The formula applied is,

$$B\,(in\ M^3/h) = \frac{E \times S}{C - S}\,(in\ M^3/h) \qquad (7.1)$$

Where B is the blowdown rate, E is the rate of evaporation, S is the amount of dissolved and suspended solids in mg/l and C is the maximum permissible amount of dissolved and suspended solids in mg/l in the drain. In fact, it is highly desirable that the amount dissolved or suspended solids in S and C be close to zero.

It is obvious from the above discussion that the amount of blowdown (in terms of a percentage) will be inversely related to the quality of feed water. Since blowdown means loss of heat and improvement in feed water quality is more expensive, a balance is struck on the basis of cost effectiveness. As a rule of thumb one can say that if the blowdown can be maintained at below 10 percent, preferabley at 5 percent, a normal base exchange softening system for feed water along with chemical conditioning is sufficient. If the blowdown works out to be greater than 10 percent it is necessary to install a more elaborate feed water purification system.

Since alkalinity is a controlling parameter and an excess of it would lead to scaling, one aspect of the boiler water treatment for low and medium pressures is to control alkalinity. Earlier practices included acid dosing (as in the cooling water treatment) and lime soda softening. However, the increasing quality requirements have supplanted these procedures and the use of ion exchange resins in one way or another has become the common practice(7,8). Two cases in raw water quality may be distinguished:

(a) Alkalinity in raw water is high and the total hardness less than the alkalinity,

(b) Alkalinity in raw water is high and the total hardness more than the alkalinity, as well as most of the hardness is permanent.

In the first situation, the dealkalisation is carried out by the use of a weak acid cation exchange resin in the hydrogen form. As mentioned earlier, these resins have -COOH as their functional group. The cations tesponsible for hardness viz., Ca^{++} and Mg^{++} are exchanged and replaced by H^+ in the water under treatment. The carbonic acid formed, such circumstances is removed through a degasser. This method of treatment leaves the levels of sodium, chloride and sulphate uneffected in the water. The total dissolved solids content is reduced by a factor corresponding to the removal of Ca and Mg carbonates and the product water is of low hardness and low alkalinity. The exhausted resin is regenerated by one to four percent of mineral acids like hydrochloric or sulphuric acid.

In the second case it becomes necessary to achieve partial demineralisation as well as softening. This is usually realised through the use of two streams (independent and parallel) of ion exchange columns. One contains a strong acid cation exchanger in the hydrogen form, while the other is loaded with a strong acid cation exchanger in the sodium form. Ca^{++} and Mg^{++} get exchanged in both the columns, while H^+ and Na^+ are released from the two columns respectively. Both streams are mixed and led through a degasser. By this process the total solids are reduced to an extent equivalent to the alkalinity in raw water, which is also softened. The resins are regenerated by the usual procedures. As an alternative, the soft water from the sodium form of the cation resin is fed to a strong base anion exchanger in the chloride form. There would be no cation bed in the hydrogen form. The bicarbonate and carbonate ions are replaced by chloride. The advantage lies in the regenerant, viz. sodium chloride rather than acid. The effluents are easy to handle, environmentally speaking(8,9).

The degasser used to remove carbon dioxide in the ion exchange set-up, saturates the water stream with dissolved oxygen. Since this accelerates corrosion, it needs to be eliminated in the water circuit. This can be done either by the use of a thermal deacrator or by chemical dosing with a reductant, such as sodium sulphite. In the former case, the temperature of the water is raised and sprayed through a tower, so that most of the dissolved oxygen is given off. This is an efficient method, but energy input is needed. On the other hand, in chemical addition, the sulphite gets oxidised to sulphate leading to a low level of dissolved oxygen. This procedure while being simple, does contribute to the total dissolved solids.

As mentioned earlier, the medium or intermediate pressure boilers are those that operate between 300 to 900 psig (20 to 64 kg/cm^2). The guideline values for the chemical quality of boiler water are given in Table 7.2.

Table 7.2 Water Quality Limits (Max.) of Medium Pressure Boilers(10)

Chemical	Working Pressure in kg/cm^2		
Parameters	20	40	64
Sp. Conductivity + µs/cm	10,000	5000	2500
p value ++ mval/kg	12	6	3
Silica mg/kg	70	30	10
Phosphate mg/kg	10 -20	15	15

\+ Sp. Conductivity measured at 25°C after neutralisation with HCl with phenolphthalein as indicator.

++ 1 mval/kg of value = 40 mg of $CaCO_3$/l or 0.04 gm NaOH/l.

Working curves that relate the admissible levels of conductivity, silica and p-alkalinity to the working pressure are available in literature. The very fact that the p-alkakinity is allowed to be present in the boiler water means that NaOH is added and the system is under alkaline operation. This chemical regime has been evolved to minimise the corrosion of iron and other ferrous alloys in the boiler circuit that come into contact with water. A sudden switch over to polymer based treatment is not advisable without proper precautions like a heavy blowdown. In fact, the sulphonated and the carbonxylated polymer along with a copolymer are being recommended for sludge conditioning in boilers upto 900 psig or even a little higher. In low pressure boilers, a programme of using chelants like nitrilo tri acetic acid (NTA) and ethylene diamine tetra acetic acid (EDTA) to keep Ca and to some extent Mg, Fe and Cu in solution has been proposed. At the required residuals of the chelants, scale and sludge problems are minimised. There are other advantages as well, but monitoring of the chelant concentrations in boiler water is difficult. Alternatively polymers have also gained attention as sludge dispersants. Early dispersants include potato peels, saw dust, tanin, lignin etc. Subsequently synthetic polymers have been used to distort crystal growth, reminiscent of cooling water treatment. New polymers that incorporate sulphonic and carboxylic functional groups are proving better than the earlier straight chain polymers such as polymethyl methacrylate.

The best aqueous environment in which boiler steel can form and maintain a protective oxide layer that protects the metallic surface from further corrosion, is realised by maintaining a controlled degree of alkalinity with sodium hydroxide, aided by the presence of sodium orthophosphate. While problems crop up with such a type of control in high pressure systems, for boilers in the medium or intermediate pressure range, this treatment offers enough protection against corrosion,provided dissolved oxygen is controlled. As seen earlier, hydrazine is a better dissolved oxygen scavenger than sodium sulphite and is widely used in high pressure systems. Medium pressure boilers have also started to make use of hydrazine to control dissolved oxygen. However, as fears surfaced of hydrazine being a possible carcinogenic agent, a number of substitutes for hydrazine have come into the market. Among these are hydroquinone, carbohydrazide, diethyl hydxylamine, methyl ethyl ketoxime and erythorbic acid. The last one has FDA approval, which allows its application in the food processing industry where steam comes in contact with food products.

7.2.2 High Pressure Boiler Water Treatment

All the boilers or steam generators operating above 64 kg/cm^2 (900 psig) come under the category of high pressure boilers. They are of two types, a) Drum type recirculating and (b) Once- through.Apart from steam, there are three varieties of water in the steam water circuit. These are boiler water (which boils), condensate water and feed water (condensate+makeup water). The blowdown is from the drum, in other words its composition corresponds to boiler water at the time. Makeup water is the high purity water that comes from the demineralisation plant and as the name implies will take care of the losses due to blowdown and any other leaks. We are now in a position to consider different facets of water conditioning in the steam water circuit of high pressure boilers.

Prior to 1950, there were two types of chemical conditioning for boiler water in recirculation type boilers. The first one was based on the presence of free caustic so that the boiler water is in the pH range of 10 to 11. As it is not advisable to have such a pH value in the presence of copper alloys in the circuit, a pH range of 9.5 to 10.0 was considered acceptable. In addition,a few mg/l of residual phosphate as trisodium phosphate was also added to the boiler water. This would be of use, if any hardness salts enter the feed train due to condenser tube leaks or contamination of makeup water. As operating pressure increased, this treatment was found to lead to two corrosion problems, namely 'caustic embrittlement' and 'caustic gauging' of the boiler internals(4).

Fifty years ago 'caustic embrittlement' was a major problem. This type of attack was due to concentration of alkali in certain locations of the boilers. It was commonly found in areas around the riveted seams of boiler drums and in the highly stressed areas where tubes were rolled into the drum. Flashing of steam in and around the sensitive areas produced localised high concentrations of NaOH in the adjoining crevices. A number of inhibitors were tried and found unsatisfactory. On the design and fabricaton side, improvements were made such as welding boiler drums and the elimination of 'cold' work practices.

'Caustic gauging' persists in modern high pressure boilers, where sodium salts are used in one or other form. It is normally a pitting phenomenon and occurs underneath the deposits of boiler tube internal surfaces. Metal wastage can be very rapid once caustic gauging starts. Due to high concentration factors, NaOH is built up under the porous oxide deposit. This points to the need for very close control and monitoring of Na^+ and OH^- in the boiler water. In boilers operating at pressures greater than 160 kg/cm^2 (2300 psig) is the boiler water contains more than 3 mg/l of caustic, its solubility in steam is such as to exceed the primary target.

To combat the two corrosion problems mentione above, a different concept called the co-ordinated phosphate-pH control came into vogue forty years ago(11). Simply put, in this type of boiler water treatment, there is sufficient phosphate to prevent the formation of 'free caustic', thus reducing the risk of 'caustic embrittlement and gauging'. As this method continues to be in wide use even today, the process and the mechanism will be discussed in some detail. The value of pH in boiler water is maintained by phosphate. The observed pH has to be less than what would have been attained, if an equivalent of Na_3PO_4 alone was present in the water . A lower pH value ensures the absence of free alkali. The relevant data are given in Table 7.3.

Table 7.3 Referance Data for Conventional Coordinated Phosphate Treatment

pH Value	Na_3PO_4 (mg/1)
10.05	10
10.35	20
10.65	40
10.90	80
11.00	100

Working curves are available in literature(11).

Chemical control is maintained by adding trisodium phosphate mixed with Na_2HPO_4 and NaH_2PO_4 and not by itself. The addition of trisodium phosphate alone will produce OH^- due to a reversed hydrolysis reaction$^{(11)}$,

$$PO_4^{3-} + H_2O \Leftrightarrow OH^- + HPO_4^{-2} \qquad (7.2)$$

The degree to which this reaction proceeds depends upon the pH of the solution at equilibrium. It stands to reason that with increasing pH (excess of OH^-) or increase in HPO_4^{2-} concentration, the reaction proceeds in the backward direction due to the mass action effect. Since the question of increase in pH does not arise, as in fact, the whole exercise is to remove free OH^- from boiler water, the only course open is to add HPO_4^{2-} in the form of Na_2HPO_4 to the system. In the theoretical formulations, the question of the hydrolysis of HPO_4^{2-} is also to be looked into. This is represented by,

$$HPO_4^{2-} + H_2O \Leftrightarrow OH^- + H_2PO_4^- \qquad (7.3)$$

Table 7.4 gives the percentage of the three species of phosphate as a function of pH at 25°C.

Table 7.4 pH vs. Percentage of Different Species of Phosphate

pH	Percentage of		
	$H_2PO_4^-$	HPO_4^{2-}	PO_4^{3-}
6	93	7	-
7	40	60	-
8	14	86	-
9	3	97	-
10	-	100	-
11	-	95	5
12	-	70	80
13	-	17	83

It is seen from Table 7.4, that in the pH range of 9 to 11 or more specifically 9.5 to 10.5, the phosphate in solution is exclusively present as the monobasic ion, HPO_4^{2-} It is this pH range that is specified in many boilers. It is also observed from, Table 7.4, that the best way of chemical control is to add a mixture of trisodium phosphate and monosodium dihydrogen phosphate. When boiler water pH fluctuates, the ratio of these two salts is so adjusted as to bring the pH into the desired range. For example, when pH drops due to condenser tube leaks, the rate of conversion of the trisodium salt to the monosodium salt is increased and vice versa in case of pH rise.

In the higher pressure range of boilers (175 kg/cm^2) chemical control by using data given in Table 7.3 results in high phosphate values leading to the distribution of the solute between boiler water and steam. Hence, a lower level of phosphate is desirable and the data given in Table 7.5 is to be used.

The guidelines are the same as in Table 7.3-Coordinated phosphate pH control is desirable where the makeup water is from the demineraliser plant. Alkaline buffers other than phosphate in boiler water disturb the phosphate -pH relationship. Since many utilities use ammonium hydroxide as a pH

Table 7.5 Reference Data for Low Level Coordinated Phosphate Treatment for High Pressure Boilers

Phosphate* mg/l	pH (25°C)
1.0	9.15
2.0	9.30
4.0	9.60
6.0	9.80
10.0	10.02
15.0	10.20
20.0	10.30
24.0	10.40
30.0	10.50

* As a mixture of Na_3PO_4 + Na_2HPO_4

regulating agent, the presence of chloride in boiler water will lead to the buffer NH_4OH - NH_4Cl. Its interference in measured pH values after phosphate (tri and mono mixture) addition is to be carefully evaluated, specially in high pressure boilers (where transport of NH_4Cl into the steam introduces a further complication). Thus one important conclusion is that chloride in boiler water is undesirable.

A variation of the coordinated phosphate pH control is known as the congruent pH-phosphate control, which employs a mixture of phosphates as mentioned earlier. The 'free caustic' condition in boiler water is understood not only in terms of its possible concentration but also on the basis that free hydroxide serves no useful purpose in high pressure boilers, where hardness salts(Ca and Mg) are rigorously excluded.

A phenemenon encountered in phosphate treatment of boiler water is its hide-out(11). The solubility of trisodium phosphate increases with temperature upto 120°C, to a value of around 94 gms/100gms of water. It then decreases gradually upto 210°C to a value of 60 gm/100gm and falls sharply thereafter. At 230°C it is only 20gm/100gm of water. The hide-out is due to this retrograde solubility (Table7.6).

Table 7.6 Solubility of Trisodium Phosphate as a Function of Temperature

Temp. °C	Solubility (gm/100 gm H_2O)
38	20
65	45
93	70
120	94
150	82
177	65
204	60
232	18
260	7

Utility and laboratory studies indicate that the compound which crystallises out under hide-out conditions has a sodium to phosphate ratio of less than 3:1. Under operating conditions, this may result in free hydroxide, which is undesirable. When the plant load is reduced, the phosphate is redissolved with a reduction in boiler water pH. Thus phosphate monitoring during load changes is very important for high pressure boilers, to ascertain the extent of hide-out and its implications.

There have been suggestions to make use of potassium phosphate, since it has a much higher solubility than the sodium salt at high temperatures. Although this has been tried(6), there is reluctance to use the potassium salt as evidence shows that gauging type corrosion is more with KOH,than with NaOH. It must be mentioned that sodium phosphate hide-out (crystallisation) can occur on the surfaces of boiler tubes, even if they are in a clean condition, leading to elevation of the tube temperatures. While phosphate hide-out is not desirrable, a number of utilities have operated under cyclic hide out without much damage to boiler tubes, To maintain the corrosion of the boiler at a very low rate the feed water is also specially chemically conditioned by hydrazine dosing, to reduce dissolved oxygen to less than 10 µg/l and maintain its pH in the alkaline range.

While alkalinity is a major factor to be properly controlled in the water steam circuit, it is equally important to control dissolved oxygen to avoid pitting corrosion. It is clear that the phosphate regime has no influence on the dissolved oxygen. With increasing boiler pressures and the introduction of once-through boilers, control of dissolved oxygen and alkalinity by volatile chemicals like hydrazine and ammonium hydroxide or morpholine has been considered(12). The advantage of such an All Volatile Treatment (AVT) is that the reagents being volatile, will also go into the steam phase and get condensed along with it. Thus they give protection to the turbine and condenser surfaces in addition to the boiler internals (See Chapter 4). However the alkalinity that can be reached with ammonia and morpholine is lower and chemical control limits for pH are 9.5 to 10.5 or more usually 9.8 to 10.0 in boiler water.

At high temperatures hydrazine also decomposes to ammonia and hydrogen. Thus the amount of hydrazine to be dosed depends not only on its scavenging action for oxygen, but also on its rate of decomposition under operating conditions. The characteristics and behaviour of ammonia, morpholine and hydrazine were considered in detail in Chapter 4.

A disadvantage of the AVT is the lack of buffering capacity. Consequently, during condenser tube leaks, the alkalinity drops quickly, specially if the condenser cooling water is brackish or seawater. Under such circumstances, it has been suggested that the chemical treatment be switched to coordinated phosphate addition. After the tube leak is plugged, the phosphate can be blown down and the treatment reverted to AVT. Condensate polishing will give some lead time to operators under the above circumstances. In fact, in once-through boilers that operate only under AVT, condensate polishing is mandatory, even if fresh water is used for condenser cooling.

While morpholine is a component of AVT, specially in nuclear power stations, ammonia continues to be made use of in several fossil fuel fired stations and in once-through steam generators. In addition, there are other candidates for alkalinity control such as cyclohexylamine (CHA)and methoxypropylamine (MPA). It is quite possible that MPA would play a leading role in AVT in the years to come.Combination of amines is also being practised in the condensate system. In addition, the use of filming amines such as octadecyl amine is on the increase. These amines have both hydrophobic as well as hydrophilic groups. The monomolecular film formed on the oxide surface inhibits both low pH and oxygen attack but does not protect the pitted surfaces. For optimising protection, a combination of neutralising amines (for alkalinity control/neutralisation of CO_2 in the boiler due to decomposition of organics), filming amines and oxygen scavengers are highly recommended. These are commercially available as blends under different trade names.

7.2.3 Chemical Regimes for Feed Water, Boiler Water and Condensate

Against the above background let us consider the optimum chemical regimes envisaged by different utilities, manufacturers etc. for feed and boiler water and condensate in high pressure steam generating units. At the outset it should be mentioned that the earlier approach was to specify these chemical targets mainly based on corrosion control in the preboiler, boiler and condenser sections. In other words the specifications have been evolved mostly with respect to the water side corrosion. During the last decade, it has been amply realised that this is not an appropriate approach. The current practice is to look at cycle chemistry from the steam side(13). In high pressure turbines, the steam side corrosion and deposition problems have been found to be much more important than the water side corrosion in the other sections of the unit, as failures in turbine components impose a greater economic penalty and unit unavailability. Hence the steam purity has become the guiding principle. To achieve that type of purity, the quality of feed and boiler water has to be upgraded. This ofcourse will automatically ensure that water side corrosion is minimised. Steam side problems are dealt with in the next chapter.

A study of the literature reveals that every organization basically agrees that the important parameters in feed water, are pH and dissolved oxygen. In fact, the Central Electricity Generating Board (CEGB), UK(14), considers dissolved oxygen as a primary target and specifies that at the economiser inlet, oxygen should not exceed 5µg/l. Combustion Engineering (CE), USA, agrees with this low limit(3). CEGB further specifies that at the condensate extraction pump discharge (CEPD), oxygen should be less than 15µg/l. Electric Power Research Institute (EPRI), USA, advises that oxygen at the deaerator outlet be less than 7µg/l, while at CEPD, it should be less than 20 µg/l(15). For 200/210 MWe sets in India, it is generally agreed that oxygen at the economiser inlet be less than 7 µg/l. These figures are based on the deaeration capability of modern plants and are supplemented by the addition of hydrazine as oxygen scavenger. During operation about 10 to 30 mg/l (an average of 20 mg/l) of residual hydrazine would be able to keep oxygen within the specified limits. Since this measure is to control the concentration of iron, copper and nickel corrosion products a limit is set by CEGB, in this respect also as a primary target. At the economizer inlet these should not exceed a combined level of 20 μg/l. CE and ASME agree with this limit, but specify only Fe and Cu (10 μg/l each). Recently EPRI (based on steam purity consideration) reduced the Cu limit to 2 μg/l. From the above resume, it is evident that oxygen and its control is a very important chemical function in operating power plants.

In view of the importance attached to corrosion of Fe and Cu components, pH is another important specification of the feed water chemical reigme. For systems having both Fe and Cu, the pH range (at 25°C) specified by EPRI is 8.8 to 9.3, at the economiser inlet, while for all ferrous systems, it is 9.0 to 9.6. The concentration of the alkalising agents and the specific conductivity should be consistent with this pH range. On the other hand, to make sure that no other soluble impurities are getting into the boiler, the cation conductivity of feed water at the economiser inlet should be less than 0.2 μs/cm (EPRI).

Silica has not been included as a primary target in feed water either by CEGB or EPRI. Combustion Engineering mentions a limit of 20 μg/l for total silica. In case condensate polishing is utilised, at the polisher outlet, silica should not exceed 10 μg/l (EPRI). This is the same limit as for makeup water.

As mentioned earlier, feed water is a mix of condensate (with or without polishing) and a relatively small amount of treated makeup water from the DM plant. Thus their chemical regimes are equally important. The EPRI guidelines are summarised in Table 7.7.

It is noteworthy that pH has not been specified. With both sodium and chloride being at low levels, it is assumed that the pH will be in the neutral range of 6.8 to 7.2.

Table 7.7 EPRI Guidelines for Makeup Water and Condensate(12,13)

Chemical parameter	Makeup water (μg/l)	Condensate pump discharge (μg/l)
Sodium	5	5
Sodium (if condensate polishing available)	-	10
Chloride	3	-
Sulphate	3	-
Silica	10	-
T O C	300	200
Dis. O_2	-	20
Sp. conductivity μs/cm	0.1	-
Cation conductivity μs/cm	-	0.2
Cation conductivity μs/cm (if condensate polishing available)	-	0.3

With the respect to boiler water of the drum type unit,CEGB, UK, makes a clear distinction between units employing NaOH or NaOH/Phosphate or AVT. In case caustic soda alone is employed as the alkalising agent, its level is made dependent upon the level of chloride impurity as NaCl. The chloride specification shows a decrease from less than 6 mg/l to less than 2 mg/l with increase in pressure from 900 to 2350 psi (or 64 to 162 kg/cm^2). NaOH should be 1.5 times that of NaCl, with a minimum of 5 mg/l at 64 kg/cm^2, which is to be reduced to a minimum of 2 mg/l at 162 kg/cm^2. For the coordinated phosphate treatment also, the chloride levels are the same as with free caustic treatment. However, for AVT, the chloride level must be less than 0.2 mg/l by weight, as NaCl for all pressures. CEGB has separate specifications for the high pressure- high heat flux boilers (162 kg/cm^2) cooled by seawater, as given in Table 7.8.

Table 7.8 CEGB Specifications for High Pressure (162 Kg/cm^2) - High Heat Flux Boilers Cooled by Sea Water(14)

In Boiler Water	Units	Primary targets
Chloride	mg/l by wt as NaCl	Less than 0.5
Caustic Soda	mg/l by wt as NaOH	1.5 x NaCl with min. NaOH of 0.5 mg/l
pH	at 25°C	9.8 ± 0.2
Sp. Conductivity	μs/cm at 25°C	Less than 20
Cation conductivity	μs/cm at 25°C	less than 6
Silica	mg/l by wt. as SiO_2	0.2

For 200/210 MWe units in India operating upto a pressure of 160 bar (i.e. comparable to the operating pressures given above by CEGB) the boiler water chemistry specifications appear to be slightly different(16). The pH is mentioned as 9.0 to 9.5 (lower than CEGB value). Free caustic is not permitted at all. This is because of the fact, that mere caustic addition is no longer practised. Phosphate is given as 2 to 4 mg/l, while silica and chloride should be less than 300 and 50 μg/l respectively.

As expected in boiler water in drum type units with or without reheat, the sodium limits are very stringent, since sodium compounds (as hydroxide or chloride) are major boiler tube and turbine blade corrodents. In the 64 to 162 kg/cm^2 pressure range, sodium concentration is specified as 5 to 2 mg/l. The same specifications hold for chloride as well, while that of silica are from 3 to 0.3 mg/l. Sodium to phosphate molar ratio is in the range of 2.3 to 2.8. Working curves have been developed by EPRI for different chemical contaminants vs. pressure so that any situation can be monitored and analysed for target values. Action levels have been prescribed so that when contaminants exceed target values beyond these levels, corrective action, such as increasing blowdown and reducing power can be taken within specified time limits.

Since the guidelines set by EPRI in 1986(15) have been evolved through a long process of consultation between experts, utilities and vendors, in the author's opinion, they should be given enough weightage. If others differ from these guidelines, the underlying arguments for the variation must be clearly spelt out.

A study on the feed water and boiler water characteristics of seven thermal power stations in India,spread over a realistic time span revealed the following features(17). At a seawater cooled power station, the specific conductivity of the feed water was above 1 μs/cm for most of the time, occasionally going as high as 3 μs/cm. This was due to condenser tube leaks. In only two out of the other six stations, where the condensers are cooled by river or dam water, the feed water conductivity was lower (0.3 to 0.4 μs/cm), while in two others it was about 1μs/cm. What was surprising was that at the remaining two stations, the feed water conductivity was higher than at the seawater cooled location, although their condensers were being cooled by fresh water. On comparing the above observed values with the specifications discussed earlier, it was obvious that considerable improvement was needed. For example, at the sea water cooled station, replacement of the Al- Brass by Cu-Ni tubes, improved the feed water conductivity through a better leak-proof situation.

Since feed water is a mix of condensate and makeup, its characteristics were also studied. The problem of high feed water conductivity in the last two stations was traced to condensate contamination and remedial action in terms of cleaning and corrosion protection was initiated.

Other characteristics of feed water studied were the pH (maintained between 8.5 to 9.0), silica (10 to 20 μg/l) and chloride (not detectable, except at the sea water cooled locations).

The concentration factor between feed and boiler water was also studied in terms of the ratio of the respective specific conductivities. The ratio varied from about 10 to 70. It was reasoned that the lower level was due to excessive blowdown, whilst the higher level was a result of feed water contamination. Phosphate treatment was in vogue in all stations.

The above discussion along with the examples, clearly demonstrates the need to monitor the chemical parameters of different components of water as found in the steam generating system and understand the reasons for normal or abnormal varations,only then can corrective action be initiated(18).

It is evident that for once-through boilers, without a drum and blowdown facility, the chemical regime will be much more stringent. The question of caustic and phosphate treatment does not arise at all and OTs depend upon AVT only,with ammonia (in most cases) or morpholine as the alkalising agent and hydrazine as the dissolved oxygen scavenger. Condensate polishing is mandatory and the alkalising agents create special problems in terms of resin selectivity at times of condenser leakage. The type of chemical treatment for feed and boiler water is often referred to as 'Zero Solids Treatment'. At present, the only once-through boiler or steam geneator in India, is the one attached to the Fast Breeder Test Reactor at Kalpakkam. Operational experience on the ammonia cycle is very limited. The specifications for once-through boilers as stated by CEGB(14) are given in Table 7.9.

Table 7.9 CEGB Primary Targets for Once-Through Boilers[14]

Parameter	Limit	Sampling Points
Cation conductivity (μ s/cm at 25°C)	0.1	Condensate polishing plant outlet
pH at 25°C	9.0 - 9.3	After chemical dosing at the condensate polishing plant outlet
Dissolved O_2 (μ g/l)	15	Final stage extraction pump discharge.
	5	Boiler inlet.
Sodium (mg/l by wt. as Na)	5	Condensate polishing plant outlet.
Silica (mg/l by wt. as SiO_2)	20	Condensate polishing plant outlet.
Total Fe, Cu and Ni (mg/l by wt. as Fe + Cu + Ni)	10 (3 as Cu)	Economiser inlet or boiler feed pump discharge.

In conclusion, it needs to be emphasised, that with increasing pressure of the operating units, the chemical conditioning procedures have undergone a change, both in character and rigour. Currently, the chemical targets in the water phase are derived from the chemical control requirements of the steam phase, which will be discussed in the next chapter.

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8

STEAM QUALITY REQUIREMENTS FOR HIGH PRESSURE TURBINES

Steam purity is an important criterion that has received considerable attention from industries in developed nations. The relative distribution of contaminants between boiler water and steam is a function of temperature and pressure. At pressures in the 105 kg/cm^2 (1500 psig) range or below, the steam solubility or vapourous carry over of the soluble contaminants, except that of silica, can be ignored at concentrations which are usually encountered in boiler water. In this range of temperatures and pressures, the salt content of the steam is essentially due to moisture entrainment of the steam. The solvation property of steam increases as the critical point and single fluid phase is approached. For very high pressure recirculating boilers 193 kg/cm^2 (~ 2750 psig), 50 to 90 percent of boiler water soluble contaminants (mostly the sodium salts) are transferred to the steam phase and get deposited in the turbine with decrease in steam pressure. In supercritical pressure boilers copper transport and redeposition in the turbine is also a serious problem. The purity of inlet steam to the high pressure turbines is specified by leading manufacturers to be: Conductivity less than 0.3 micro siemens/cm with sodium and chloride less than 5 µg/l* (Table 8.1).

Manufacturers and the organisations of electrical utilities give specifications for high pressure steam that differ slightly. Those listed in Table 8.1 illustrate the stringent requirements for the purity of HP steam. During the last few years, the tendency is to further tighten these specifications under normal operation. For example, M/s General Electric, USA puts the limit for sodium at 3 µg/l and cation conductivity at 0.2 µs/cm, while M/s Allis Chalmers, USA gives a limit of 1 µg/l for copper. EPRI guidelines, on the other hand, are those evolved through comprehensive discussions(1).

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* µg/l may be taken as equivalent to ppb.at such low levels

Table 8.1 High Pressure Steam Quality Specifications(1,5)

Impurities in HP steam (μg/l)	Normal operation	Limiting conditions of operations 24 hrs.	2 weeks
Sodium	5	10 to 20	5 to 10
Chloride	5	10 to 20	5 to 10
Dis. O_2	10	30 to 100	10 to 30
Silica	10	20 to 50	10 to 20
Cu	2	-	-
Fe	20	-	-
Cation conductivity (μs/cm)	0.3	0.5 to 1.0	0.3 to 0.5

In all drum type boilers, means are provided in the drum to seperate the steam generated in the boiler tubes from water. The required efficiency of this seperation depends to a great extent on the use to which the steam is put e.g to drive a turbine or crack naphtha and whether it is to be superheated or not. Thus one has, 'saturated steam' and 'super heated steam'. In the former case, 0.25 to 0.5 percent of moisture can be tolerated. If the steam is to be super heated, the seperation efficiency should be such that the moisture content is well below 0.2 percent. This is to prevent the moisture carry over of soluble impurities into the steam phase. All this is apart from mechanical carry over of impurities(2).

Detailed studies have shown that reliable performance of high pressure steam turbines depends on the selection of its constructional materials, the stresses to which the components and parts of the system are subjected to during operation and chemical environment, which is high quality steam. While design and availability of improved materials have reduced the contribution of the first two causative factors, the control of steam chemistry has not been achieved to the same extent. In fact steam quality has become a varying parameter in otherwise comparable high pressure turbines. As a result of this, a number of problems have been experienced. To mention only a few, lower quality steam leads to deposit formation in crevices and the consequent loss of thermodynamic efficiency as well as corrosion and erosion of the turbine parts. The variations in steam quality are partly due to lack of stringent control on feed and boiler water quality due to a lack of sufficient appreciation of the basic chemistry involved in the high pressure steam-water cycle(3). As noted in the previous chapter, the feed and boiler water chemistry specifications are arrived at by working backwards from steam quality requirements. This has led to better steam quality. At the same time considerable progress has been made in understanding the steam chemistry as it passes through the turbine(from high to intermediate to low pressures).

As steam expands in the turbine, different impurities present in steam start separating out and get deposited in the turbine as the solubility of most compounds in dry steam decreases with pressure. One can see this from solubility data represented on P, T coordinates or a Mollier diagram (Chapter 4), where the coordinates are entropy *vs.* enthalpy. From this it is deduced that the presence of just 10 μg/l of NaOH is sufficient for the formation of an 80 percent solution of NaOH in the intermediate pressure range(4). It is evident that seperation of concentrated solution of NaOH would adversely effect the turbine parts due to stress corrosion cracking. This would mean that NaOH in dry steam at high pressures ought to be much less. The same is true for NaCl.

Solubililty data of NaOH and NaCl in steam illustrate this point very clearly(4). At 330°C and 1067 psia pressure, the solubility of NaOH in steam is 750 μg/l (in terms of Na), which decreases sharply to 540 μg/l, when the pressure is reduced to 1052 psia at a temperature of 316°C. In the case of NaCl, when the pressure is reduced from 1176 to 1063 psia, the solubility sharply decreases from 680 to 360 μg/l (again in terms of Na) over a narrow temperature range (327.7°C to 325.5°C).

Chemical impurities such as NaOH or corrosion product oxides enter the steam phase from the water phase due to their differential solubility between the two phases. The so-called 'Ray Diagram' of the carry over coefficients from water into the steam phase given by Martinova of the Moscow Power Institute, is widely used to appreciate this aspect of steam chemistry (See Chapter 4). As the density difference between the liquid and vapour phase diminishes and the critical point is approached with dielectric constant of steam on the increse, the transport of materials to the vapour phase steadily increases. Just how clean the steam entering the turbine should be and the mechanisms involved in stress corrosion cracking are still not fully appreciated. An extensively reported study in this context, is the failure of a turbine at Hinkly Point 'A' power station, wherein it was shown that concentrated caustic solutions were deposited in this turbine. For very high pressure (190-200 kg/cm^2 drum pressure) recirculation boilers, the vapour transport of sodium salt may approach 80 percent of the total solids carried. Besides sodium hydroxide, sodium carbonate, sodium phosphate and iron oxides are known to get deposited on all the three states (HP, IP and LP) of the turbine internals. On the other hand, oxides of copper and sodium sulphate are preferentially deposited in the HP and IPstages, while silica & sodium chloride get preferentially deposited from the steam phase in the IPand LP sections(2).

Even though the impurity levels in the feed and boiler water are kept relatively low, the concentration of such impurities in the steam phase within the turbine results in a host of problems. Without such concentration mechanisms, the construction materials can tolerate steam with low levels of impurities. However, the concentration processes operate via deposit formation from super heated steam, evaporation and drying as well as adsorption or inorganic ion exchange on the metal oxide surfaces. It has been shown that iron oxide films concentrate impurities by a factor of 10 to 100 and this might alter the composition of the steam/water phase close to oxide interface. It is known that "dissociative hydrolysis" of sodium chloride into HCl and NaOH at the high temperature oxide surfaces results in the products as such being present in the IP and LP sections of the steam turbines. Chemical analysis of the compounds in steam turbines has shown a wide variety and range of compounds such as potassium trisodium aluminium silicate, calcium aluminium hydroxy sulphate, sodium aluminium molybdenum silicate etc., (which represent some of the highly complex compounds present) on the oxide surfaces in steam turbines, in addition to simple compounds such as sodium chloride, ferric sulphate etc(3). It has been emphasised by Westinghouse Electric Corporation that, " Impurity concentration in dry steam should be below its solubility anywhere in the dry regions of the system (turbine)".

Table 8.2 lists some of the failures in turbine components and the suspected causes behind such events.

Table 8.2 Turbine Part Failures-US Industry Experience(5)

Failure	Probable Cause
HP Turbine bolts (steel)	High Na in steam
HP Discs (Ni Cr Mo)	High caustic in steam
HP Blade (Springs)	- do -
HP Inner cylinder (Cr MoV)	High NaOH, NaCl in steam
LP Blades (SS)	Organic acids in steam
LP Blades (12 Cr hardened)	Inorganic acids in steam

After a detailed study, electrical utilities in USA and other advanced countries have realised that an improvement of steam purity is needed in several operating units inspite of the existence of well established boiler water specifications(5,6). The philosophy behind the recommendations(1) as given in Table 8.1, for superheated/reheat steam is,

(a) The steam quality should be achievable,

(b) The specified limits should be measurable.

The most important cationic and anionic limits are for sodium and chloride. For normal operations, the sodium level has been specified to be less than 5 µg/l, low enough to guarantee that no deposition takes place of sodium hydroxide, sodium chloride or any other compound any where in the turbine. Analytical methods currently available are able to determine sodium in quantities less than 5 µg/l.

The corresponding limit for chloride ior has also been specified to be less than 5 µg/l. On-line chloride analysers using solid state electrodes are available for such measurements. Ion chromatography with ready to use cartridges for concentrating chloride in spot samples is also on the anvil.

If due to some reason or other, these limits of sodium and chloride are exceeded during normal operation, some limiting conditions on operation have been suggested. Sodium and chloride should not each exceed a limit of 20 µg/l in one calender year or in one operating year, in any 24 hour operating period at full power. On the other hand, for a two week operating period at full power, these impurities in steam might range from 5 to 10 µg/l in one calender or operating year.

Measurement of the conductivity of the steam condensate after passing through a cation exchanger, is also used as an important specification. Cation conductivity rather than the total conductivity measurement, will avoid interference due to the presence of ammonia, but will reflect the presence of carbon dioxide. The best way to measure cation conductivity is to remove carbon dioxide by blowing pure dry nitrogen. Under such conditions, the conductivity of the steam condensate must be less than 0.3 μS/cm during normal operation. The limiting conditions are 0.5 to 1.0 μS/cm for 24 hrs, and 0.3 to 0.5 μS/cm for two weeks in a calendar or an operating year.

A 20 μg/l limit for silica in steam has been in vogue for quite some time. However, as a result of the silica hide out phenomenon and in view of the complex silicate formation in turbine deposits, this limit has been lowered to 10 μg/l for reheat units. During adverse operating conditions it can range from 20 to 50 μg/l during a 24 hour period and can be in the range of 10 to 20 μg/l during a two week period. Since the distribution of silica between steam and boiler water depends upon pressure, as well as on the pH of the boiler water, it is desirable to follow the guidelines, given in Table 8.3.

Table 8.3 Maximum Permissible Concentration of Silica in Boiler Water, if the Target of 10 μg/l of Silica in Steam is to be Met

Boiler Pressure	Boiler water silica in mg/l (max.)	
kg/cm^2	pH 9	pH 10
60	4.7	5.5
90	1.6	1.9
120	0.6	0.7
150	0.25	0.28
180	0.10	0.12

Dissolved oxygen is yet another impurity that has been specified to be less than 10 mg/l during normal operations. The limits under adverse conditions were given earlier in Table 8.1.

EPRI guidelines prescribe Action Levels, when the specification limits are exceeded during normal operations(1).

Action level 1 is 2 weeks (14 days), same as noted earlier.

Action level 2 is 48 hrs., twice that noted earlier.

Action level 3 is 8 hrs, after which the persistence of abnormality cannot be tolerated for more than 1 hr and calls for an immediate shut down.

As far as reheat steam is concerned, EPRI guidelines are as given in Table 8.4. It may be noted that EPRI introduced a new chemical parameter, viz., sulphate, whose limits are as tight as that of chloride. While sodium and cation conductivity are to be monitored on-line (continuous), chloride and silica are to be sampled once a shift, while sulphate can be measured once a day.

Table 8.4 Guidelines for Reheat Steam(1)

Parameter	Unit	Normal	A1	A2	A3
Sodium	μg/l	5	5	10	20
Chloride	μg/l	3	3-6	6-12	12
Silica	μg/l	10	10-20	20-40	40
Sulphate	μg/l	3	3-6	6-12	12
Degassed cation conductivity	μs/cm	0.3	0.3-0.55	0.55-1.0	1.0

The author's experience(7) with thermal power stations in India indicates that sufficient attention is not being paid to the chemical monitoring and control of steam chemistry. One of the lacunae noticed was the quality of attemperating water. Unless this is well controlled, there is every likelihood of impurity ingress into the high pressure steam. In fact, because of this type of situation, CEGB, UK requires the sampling of saturated steam, so that the extent of contamination can be monitored. Similarly, EPRI recommends the monitoring of sodium and silica in saturated steam. It is generally recognised that saturated steam is the most complex fluid to be sampled(1). This is primarily due to the differences in density between steam and entrained water droplets.

Coming to the consideration of industrial turbines as distinct from utility turbines, a recent survey indicated that blade deposits dominate the problem area followed by pitting, and corrosion induced cracking(6). The pattern resembles that found in utility turbines. Most of the industrial turbines require an improvement in steam purity. The Mollier diagram has also been applied in these cases to deduce the level of impurities that could be tolerated in steam. The following procedure is recommended for using this diagram.

(a) Steam expansion lines are to be drawn for different types of operation of an individual turbine. By different types, it is meant, whether the turbine is to be operated at low or high load etc.

(b) The solubilities of major chemical impurities in superheated steam are determined at the points where these lines cross the saturation line.

(c) The solubility value at the cross point is the impurity limit. However, this is specific to the turbine under consideration.

The recommended steam purity limits for industrial turbines using non-reheat steam are given in Table 8.5. It is obvious that the above limits are less stringent than for high pressure steam (superheat/reheat) in utility turbines. It is only to be expected, that with decrease in pressure, one can tolerate a higher level of impurity.

Table 8.5 Steam Purity Limits in Industrial Turbines(6)

Industry	Temp. ^0C	Pressure kg/cm^2(psig)	Inlet chemical parameters (μg/1)				Cation conductivity
			Na	Cl	Si	TOC	μs/cm
Pulp/paper	400	33.5(475)	15	10	30	150	0.5
Oil	450	63.4(900)	20	12	40	200	0.7
Waste Heat	315	38.7(550)	40	25	80	200	1.5

Non-reheat units

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9

SPECIAL PROBLEMS OF WATER CHEMISTRY AND MATERIAL COMPATIBILITY IN NUCLEAR POWER STATIONS

At present and in the foreseeable future, the deployment of nuclear power is through water cooled nuclear power reactors(1,2). In nuclear power plants, both light and heavy water, H_2O/D_2O is made use of as a moderator and coolant. As a moderator, the hydrogen or deuterium atoms of the water molecule, reduce the velocities of neutrons generated ~~in~~ fission to thermal energies (0.025 ev) which makes the chain reaction feasible. A solid like graphite can also act as a moderator or one can dispense with the moderator altogether as in fast reactors, wherein the fission chain reaction is sustained by fast neutrons (~1 Mev). However, since the ultimate aim is to generate steam that drives a turbine, the use of high temperature-high pressure water cannot be avoided in any type of nuclear power plant. As far as this part of the operation is concerned in which a steam generator, a turbine and a condenser are the major components, the problems of water chemistry and material compatibility are essentially the same as in thermal power stations(3). The nuclear steam generator tube integrity is however, much more critical than the fossil fuel fired boiler tube integrity, as any rupture in the former would lead to radio-active contamination of the steam water circuit. Consequently, superior materials like stainless steel and high nickel alloy tubes are used in nuclear steam generators.

The all important issue in the safe operation of nuclear power reactors is the accidental release of radioactive fission products from the core and generation of activated corrosion products in the primary water coolant that flows through the reactor core and their redeposition(4). It is equally important that during normal operation and maintenance, the occupational exposure of workers,

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The author was associated with the Coordinated Research Programmes of the International Atomic Energy Agency on Reactor Water Chemistry and the material in this chapter is partly based on that experience.

operators and supervisiors, be kept to a minimum i.e. lower than the radiation exposure dose limits, prescribed by International Commission for Radiological Protection and national regulatory agencies.

Water cooled nuclear reactors can be broadly divided into two groups: boiling water reactors and pressurised water reactors. The boiling water reactors (BWRs) developed in USA, make use of a pressure vessel, lined with stainless steel in which the nuclear fuel elements, in the form of a core of a particular geometrical configuration reside. The fuel elements consist of an array of fuel rods (7x7or 8x8). The fuel rods are made of zircaloy tubes filled with low enriched uranium dioxide (UO_2) pellets and sealed at both ends. The core is surrounded by water, which acts both as a neutron moderator and as the name implies, a boiling (~ 270°C) coolant. The steam-moisture mixture is passed through moisture or steam seperators and the steam is then fed directly to a turbine. In some of the BWR versions, part of the reactor water is fed to a secondary steam generator and the steam which is generated at low pressure is fed to an appopriate stage of the turbine. The exhaust steam after condensing to water is purified through the use of deep bed demineralisers and fed back to the reactor through feed water heaters. The Tarapur Atomic Power Station is an example of this type(5,5a).

The boiling water reactors developed in the former Soviet Union, use graphite blocks as the moderator in which pressure tubes are embedded vertically. The fuel elements reside in the pressure tubes, leaving sufficient space for coolant water to flow through them and boil. The steam generated is collected and fed to a turbine as in western BWRs. The Chernobyl nuclear power station is an example of this type of BWR and is known as RBMK(6).

The other group of water moderated and cooled reactors are known as pressurised water reactors (PWRS). Here again the arrangement is the same as in western BWRs, except that the water is not allowed to boil by the application of higher pressure. The high pressure coolant is fed to a steam generator on its tube side. Steam is generated on the shell side and the rest of the circuit is the same as in a thermal power station. While this type of plant is called PWR in western countries, in Russia and other states of the former Soviet Union and in eastern Europe, it is known as VVER(6). At present in the nuclear power industry PWR/VVER is the dominant reactor. The nuclear core is again made up of low enriched UO_2 pellets encased in zircaloy tubes, which are smaller in diameter than in BWRs.

A third gruop of water reactors has been developed by Canada and are known as CANDU reactors. The Indian nuclear power programme is based on this type of reactor,which have been described as Pressurised Heavy Water Reactors (PHWRs)(5). Argentina. Rumania and S.Korea are the other countries interested in this type of power plant(6).

CANDU/PHWR makes use of zircaloy pressure tubes as fuel channels which are horizontally fixed in a vessel called calandria. This is filled with heavy water which acts as a moderator at about 50°C. A little pressure is applied to maintain the required circulation. The fuel is made up of natural UO_2 pellets clad in zircaloy. The fuel pin clusters or bundles are of much smaller length, than those in BWRs and PWRs. Usually 12 bundles are loaded into each of the fuel channels, through which heavy water at high temperature (~275°C) and pressure flows as the heat transport fluid, without boiling. The outlets of all the fuel channels are combined and this hot heavy water then goes through the tube side of a steam generator. Light water is used on the shell side to generate steam which is then fed to a turbine.

A class of reactors developed in the UK, makes use of graphite as the moderator and Carbon dioxide/Helium as the coolant. Ultimately the coolant gases generate steam. These reactors are the mainstay of the UK nuclear power industry.

In fast reactors where there is no moderator and the fuel is of highly enriched Uranium and Plutonium, the heat of the compact core is removed by molten sodium, which in turn is used as the heat source in a steam generator, either of a recirculating or once through type.

Against the above background, special problems of water chemistry and material compatibility are further discussed. The major issue of concern is radioactivity. The low level magnetite transport in the heat transfer circuit, which is of no consequence in thermal power stations, results in the activation, transport and redeposition of corrosion products in nuclear power plants(7,8). The principal offender is Cobalt-60 (Co-60), a strong gamma-ray (γ-ray) emitter with a half life of ~5.3 years. The deposition of this nuclide on out of core surfaces, along with Co-58 and other radioactive products makes maintenance a serious problem. Skilled maintenance personnel can work at their tasks for only a short period at a time. The radiation exposure limits are such that a welding repair in a thermal power station which takes about an hour of a skilled technician's time might require as many as six welders of equivalent skill on the coolant circuit in a nuclear power station shortly after shut down. In nuclear industry this has come to be known as the Man-Rem problem. Considerable effort of water chemistry control in nuclear power stations is focussed on to this issue(9). Minimising the Man-Rem problem is taken up from the stage of design and materials selection itself. The number of valves and joints is minimised to reduce repair work and materials with as low a Cobalt content as practicable are selected for reducing the radiation dose. Apart from design and material selection, this problem is largely tackled in the primary system by a strict water chemistry control. Maintenance of steady pH in a narrow range effectively controls mass transport during the operating cycle of a nuclear power station.

An equally important issue is the chemistry under accident conditions(10). Unlike in thermal power stations, the core can heat up very fast. In the Three Mile Island nuclear power station, unit 2 (TMI-2) and in the Chernobyl nuclear power station, unit 4 (CN-4), such a sharp and fast rise in clad temperature led to its chemical interaction with water. The highly exothermic reaction resulted in the production of hydrogen.

$$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2 \qquad (9.1)$$

The hydrogen generated in massive quantities can lead to an explosion (muffled in the case of TMI-2 and violent in the case of Chernobyl-4) and spread of radioactivity(11). The major concern even in minor accidents is the release of radioactive iodine and caesium (both fission products). Their chemical forms and hence their dispersal depends strongly on the water chemistry prevalent in that particular situation.

Another problem of serious concern is the rupture of a steam generator tube in PWRs and PHWRs. It is almost impossible to retube such a steam generator which will be radioactive due to the deposition of corrosion products on the tube side. The stress corrosion cracking of stainless steel piping in BWRs is also a matter of serious concern.

A problem of water chemistry that is special to water moderated and water cooled reactors is the radiolysis of water(12). This leads to the production of hydrogen and oxygen, which gives rise to two issues. One aspect would be to ensure that the mixture does not explode. The other concern relates to the increased dissolved oxygen content of water that would result in enhanced corrosion. If the water is heavy water as in PHWR, the additional problem of recovery of D_2 (a costly isotope) has to be tackled.

Because of radiolysis, oxygen and pH control additives such as hydrazine, ammonia or morpholine may not be added to the primary coolant system during operation. However, VVERs do add ammonia as seen later on. A chemical additive which is not required in thermal power stations is boric acid. This chemical (B_2O_3 dissolvrd in H_2O or D_2O) is widely employed in PWR/VVER/PHWR as a neutron absorbing (control) material. The ion exchange purification has to be dovetailed into the maintenance of the required concentration of boric acid in the moderator at any given time. There is no addition of boric acid in a BWR.

Thus the main objectives of reactor water chemistry are,

(a) Reduction in the aggressive action of high temperature water towards the structural materials (stainless steel,carbon steel, zircoloy and high nickel alloys like Monel, Inconel etc.) to condition the chemistry environment such that the mass transport is minimal and in a specific direction, so that activity build up on out-of-core surfaces can be kept to a minimum.

(b) Achievement of the lowest possible occupational radiation exposure by minimising the ingress of incore impurities and out-of-core radioactivity build up.

(c) Prevention of the release of radioactivity into the environment.

(d) Prevention of fuel element surface fouling that could adversely affect heat transfer and corrosion.

(e) Containment of radiolysis products.

Radioactive corrosion products may be generated either directly or indirectly. In the first instance, corrosion would result in the release of neutron activation products from in-core structural materials. In the second case, corrosion products from out-of-core surfaces that get deposited on the incore surfaces, undergo neutron activation and get resuspended into the coolant(13). Since the bulk corrosion product is magnetite, Fe_3O_4, the other corrosion product oxides may be free (e.g.Co_2O_3) or mixed ferrites such as $NiFe_2O_4$ or $CoFe_2O_4$. The radioactivity is due to ^{60}Co, ^{58}Co, ^{51}Cr, ^{54}Mn and ^{59}Fe. Apart from ^{58}Co, the others are generated due to thermal neutron activation of the corresponding inactive isotopes of these elements. ^{58}Co is generated by fast neutron activation of ^{58}Ni. Cobalt is a low level (ppm level) component of stainless steels, nickel alloys such as Monel-400 and Inconel-600, as well as a high level (55 percent) constituent in hard facing materials such as stellite alloys. While the former group of alloys are extensively used, stellite is used only sparingly with relatively low incore surface area. As mentioned earlier the principal concern is ^{60}Co, followed by ^{58}Co. Radioactive and non-radioactive corrosion products may be transported in the coolant both as truely soluble species, as well as inertial (>1 μm)or colloidal (<1 μm) particulate species*. Particulate matter is conventionally defined as that retained by a 0.45 μm microporous filter membrane. Material that is not retained and which goes through the membrane is often classified as 'soluble'. Therefore, the soluble fraction will also contain some colloidal particulates in addition to the truely 'soluble' species. It has been suggested that most of the non-filterable ^{60}Co circulating in a PHWR coolant is colloidal in nature. A contrary view is that true soluble Co transport is dominant when the crud levels are low. It is also often assumed that iron, nickel and chromium species behave in the same way as the cobalt species, with respect to nucleation and precipitation, this however, is not borne out by experience. The behaviour of substituted ferrites is somewhat different from that of magnetite. It is desirable that all such variations be reflected in the evolution of any model for corrosion product transport(14, 15).

A simplified diagram of the processes described above is shown in Fig.9.1.

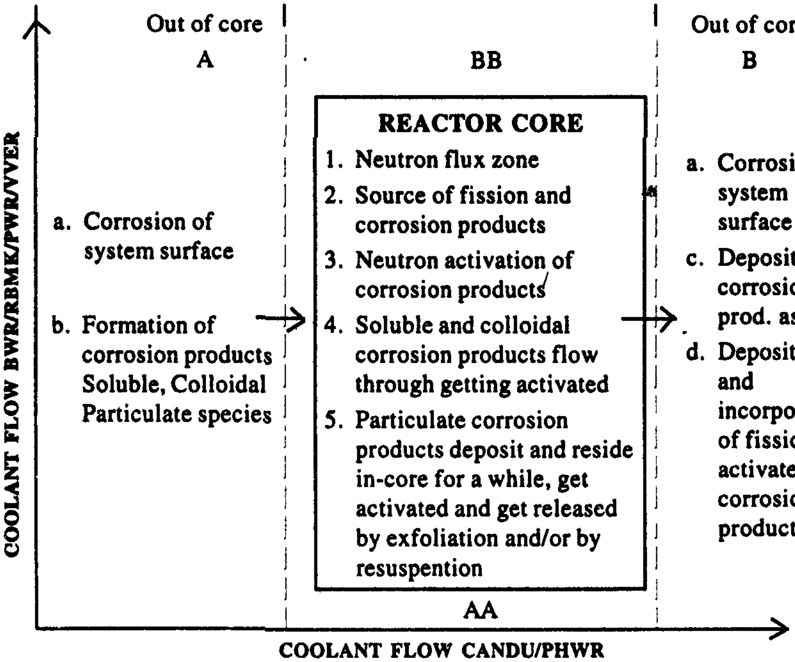

Fig. 9.1. Corrosion and Deposition Process in Water Cooled Nuclear Power Reactor

(Processes in AA and BB are same as indicated in A and B respectively.)

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* Reactor coolant water chemistry literature widelly refers to this as 'crud'. The term appears to have originated in Canada and is reported to be an acronym for Canadian Reactor Unidentified Deposit. It is insoluble and hence, is composed of both inertial as well as collodial particulates.

From the above discussion, it is apparent that in the reactor coolant circuit, a 'source term' and a 'recipient term' coexist which will ultimately result in the transport and deposition of radionuclides. These two terms are inter-dependent. Any change in operational chemistry that affects the corrosion rate has an immediate impact on the 'recipient term' and a delayed effect on 'source term'. Consequently, control of corrosion will lead to the control of the entire activity transport process. The regimes in the primary heat transport system of water cooled reactors have been devised to meet this requirement, viz.,minimising corrosion with a consequential reduction of material transport through the core.

In the harsh environment of the reactor core, both hydrodynamic and radiation field wise the fuel cladding material,viz.,ziracaloy experiences the worst conditions. Fortunately, the corrosion resistance of zircaloys (zircaloy-2 and 4)is very good(16,17,17a) and the neutron absorption cross section of Zr is very low. Consequently,radioactivation and the deposition of radioactive ^{95}Zr on out of core surfaces is not a matter of concern. However, what is of significance is the integrity of the thin fuel tubes, as well as the relatively thick pressure tubes in PHWRs. Development of pin holes or minor cracks in the fuel tube will lead to the release of fission products (like iodine and caesium) to the coolant, which is not acceptable. In fact, when one speaks of fuel performance in nuclear reactors, one is actually discussing the Zr clad integrity. It was found that this is affected more from 'inside attack' than from the outer coolant. Internal hydriding, stress corrosion cracking due to pellet clad mechanical interaction coupled with the chemical interaction between fission product iodine and Zr are some of the reasons ascribed to clad failure both in BWRs and PWRs/PHWRs(18). Hydrogen embrittlement of zircaloy is another problem that has received considerable attention. The failure of a pressure tube in one of the reactors at the Pickering Nuclear Generating Station, Canada is suspected to be partly due to hydrogen percolation into zircaloy pressure tube under special stress conditions.

A wide variety of analytical techniques have been applied in chemical laboratories of nuclear power stations to monitor and control water chemistry. The International Atomic Energy Agency, has collected relevant information from different countries and tabulated the same for easy reference(19).

In boiling water reactors, the dominant material is stainless steel (304, 304L etc.) besides zircaloy. Not only is the pressure vessel lined with SS, but the primary piping is also of this material (steam lines are of carbon steel). The coolant chemistry in BWR adopts a hands-off policy,with no chemical addition, using as pure water as possible(5,a). Thus condensate polishing is mandatory. The main chemical characteristics of the feed water and the boiling reactor water are more or less the same. Differences are essentially due to the concentration factor. The specifications(6) for water quality in BWRs are given in Table 9.1.

As the reactor oxygen level is an equilibrium value depending on the reactor operating power, one has no control over this parameter. Hence, BWRs impose a severe restriction on chloride. This is to avoid the stress corrosion cracking (SCC) of stainless steel. Pipe rupture accidents due to (SSC) have been experienced in BWRs.

Table 9.1 Feed and Reactor Water Specifications for BWRs(6)

Chemical parameter	Units	GE		VGB		RBMK	
		FW	RW	FW	RW	FW	RW
Sp. Conductivity	μS/cm	0.1	1.0	0.15	1.0	0.1	1.0
pH a 25^{0}C	-	6.8	7.2	-	-	6.5	8.5
Chloride	μg/l	NS	200	NS	200	4	100(Cl+F)
Oxygen	μg/l	NS *	NS *	NS	NS	NS	NS
Silica	μg/l	NS	4000	NS	4000	NS	1000
Iron	μg/l	13	NS	25	NS	60	200
Copper	μg/l	2	NS	3	NS	2	50

NS : Not Specified

* Though not specified, feed water dissolved oxygen is not expected to exceed 14 μg/l in Tarapur. In reactor water an equilibrium level of ~ 400 μg/l would be prevalent due to radiolysis and stripping.

The SCC propensity of austenitic stainless steel in relation to chloride and dissolved oxygen in water has been thoroughly studied(20-22) and the interrelationship is shown in Fig.9.2.

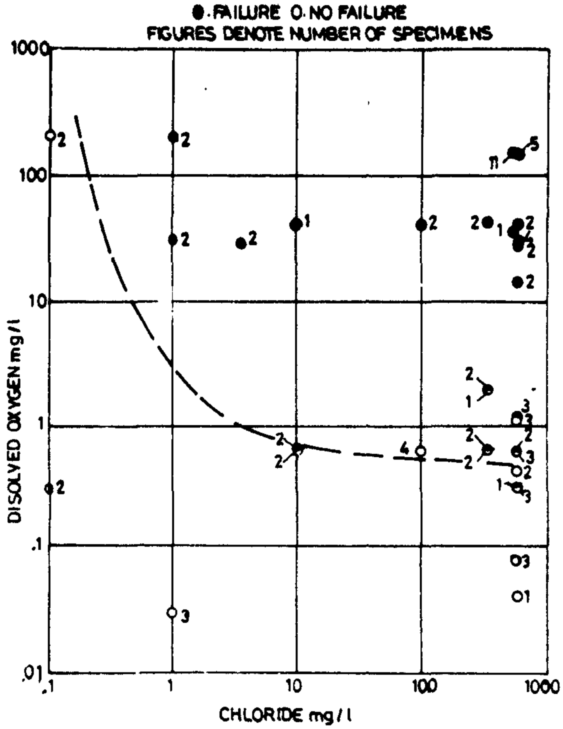

Fig. 9.2 Stress Corrosion Cracking of Stainless Steel-Influence-Chloride and Dissolved Oxygen(20)

One way to reduce dissloved oxygen in a radiation environment is to promote the radiation induced back reaction. This can be achieved by the injection of hydrogen into the coolent water. Production of oxygen can be suppressed through a chain reaction which rapidly eliminates OH, HO_2 and H_2O_2, the precursors of molecular oxygen.

$$H_2 + OH \rightarrow H_2O + H \qquad (9.2)$$

$$H + O_2 \rightarrow HO_2 \qquad (9.3)$$

$$H + HO_2 \rightarrow H_2O_2 \qquad (9.4)$$

$$H + H_2O_2 \rightarrow H_2O + OH \qquad (9.5)$$

Eventually, the chain reaction will lead to the reconversion of the stable radiolysis products, H_2O_2, O_2 and H_2 back to water. Laboratory as well as large scale demonstration experiments have shown this to be feasible, even in a boiling (consequent stripping of hydrogen) condition of the coolant. This type of chemistry control, called Hydrogen Water Chemistry(23), is gradually being introduced in BWRs (though not at Tarapur, India).

Reactor water purification is the key to adequate coolant chemistry control in BWRs. The normal clean up flow is about 2 percent of the feed water flow at full power. The primary coolant, diverted to the purification plant is at a high temperature and pressure. It is usual to reduce the temperature, but purify at a relatively high pressure so as to maintain the desired high purification flow rate through mixed bed demineralisers, preceded by cellulose and/or Powdex* precoat filters. A decontamination factor not less than 10 is acheived. Full flow condensate polishing is mandatory, as stated earlier, for BWRs, using deep mixed bed ion exchange resins.

The primary coolant chemistry of PWR/VVER is more complicated than that of BWRs(6). A specific feature of the chemistry is the presence of boric acid over a wide range of concentrations, to control reactivity. The variations could be from 0 to 1200 mg/l measured in terms of boron. A boron level upto 400mg/l could be encountered under shut down conditions. At operating temperatures (270°C to 320°C), an alkaline pH condition is to be maintained to minimise the corrosion. The presence of boric acid makes it all the more necessary to add an alkali. Here, PWRs differ from VVERs in the nature of the alkalising agent. While PWRs make use of lithium hydroxide, (as ^7LiOH), VVERs employ a mixture of KOH and NH_4OH. Since the mixture is a combination of a strong and a weak base, a sort of buffering action prevails. A pH (300°C) value of 6.9 to 7.4 has been found to be optimum. Since this range of pH cannot be directly measured in a reactor system at 300°C, a set of calculations based on room temperature pH measurement of boric acid-LiOH ,mixtures is made use of. A coordinated boron to Li ratio has been evolved to acheive pH (300°C) of 6.9 to 7.4 throughout the cycle. Similarly in VVERs a pH (260°C) of 7.1 is acheived by adjusting the boron to potassium ratio. Considering that a part of the reactor water is constantly purified by ion exchange, one can see the difficulties involved in maintaining such constant ratios over prolonged periods.

In PWRs, a low level of dissolved oxygen is maintained by injecting hydrogen. On the other hand, in VVERs, in-situ radiolysis of ammonia generates the hydrogen required to keep the level of oxygen low.

The chemical specifications for the reactor coolant water in PWRs and VVERs are given in Tables 9.2 and 9.3(6).

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* POWDEX is a brand name for cation & anion exchange resins made in very fine particle size. These resins mixed with binders in a slurry and cast over porous surface, serve as precoat filters.

Table 9.2 PWR Reactor Water Quality Specifications(6)

Chemical Parameters	Unit	Value	Remarks
pH at 25⁰C	–	4.2 - 10.5	Depends upon H_3BO_3 and ^{7}LiOH concentration
pH at 300⁰C	–	6.9 - 7.4	
Boric acid as boron	mg/l	0 - 1200	
^{7}LiOH as ^{7}Li	mg/l	0.7 - 2.2	
Sp. Conductivity at 25⁰C	µS/cm	1 - 40	As for pH at 25⁰C
Hydrogen	cm^3/kg (at STP)	25 - 35	
Oxygen	µg/l	5	During power operation with H_2 as above
Chloride	µg/l	150	
Fluoride	µg/l	150	

Table 9.3 VVER - 400 Reactor Water Quality Specifications(6)

Chemical Parameters	Unit	Value	Remarks
pH at 25⁰C	–	6.0	
KOH as K^+	mg/kg	2 to 16.5	Depending upon H_3BO_3
H_3BO_3	g/kg	0 to 8.0	
NH_3	mg/kg	5	
Hydrogen	cm3/kg (at STP)	30 to 60	In-situ equilibrium values

Water chemistry on the steam generating side of PWR/VVER is the same as in fossil fuel fired power stations(9). Coordinated phosphate or AVT is employed. In early designs of drum type steam generators, the tubes were of a high nickel alloy, Inconel-600. Stainless steel has also been used as the tube material. Based on long term experience, the present trend is towards the use of Incoloy-800, a relatively low nickel alloy, with additional content of Cr. Inconel-690 is a tube material that is showing great promise.

In several cases, the nuclear heat transport system is coupled to a once-through steam generator, with zero solids treatment and condensate polishing.

The nuclear industry has been conditioned over the years to have dissolved oxygen at levels less than 10 µg/l in the feed water to the steam generators. However an accident in December,1986 in a nuclear power plant opearated by the Virginia Power Company, USA has revived arguments against such low levels. A portion of the carbon steel section of the feed water piping experienced severe thinning from the inside, which escaped in-service inspection. The pipe line suffered a guillotine failure. Water (non-radioactive,as it is in the secondary circuit) flashed to steam. Due to the configuration in that section of the piping turbulence was the main culprit. In the initial stages of the investigation although the low level of dissolved oxygen was blamed for not providing enough of the protective magnetite layer, a full investigation, showed this to be unsubstantiated. The reason for this is that just as on the primary side, dissolved oxygen is to be rigorously controlled on the secondary side as well.

The history of PWR steam generator corrosion is a good example of all the major problems in any steam raising circuit(9). The study led to an understanding of the complexity of the water-steam system at high temperatures vs material compatibility. Phosphate chemistry works well at relatively low temperatures. Temperature increase leads to phosphate hide-out, which results in alkaline stress corrosion and phosphate induced thinning where local boiling temperatures are aroung 280^{0}C. Removal of phosphate, without rigorous removal of chloride, produces excessive corrosion of carbon steel causing tube denting in the baffle plate region. This situation gets further aggravated, if copper alloys and a higher level of dissolved oxygen are present. It could even lead to tube pitting. On the other hand, the advantages of AVT are off set by its inability to provide buffering action in the event of condenser tube leaks, especially if the condenser is cooled by sea water. AVT is also not really compatible with the presence of copper alloys and poses problems in condensate polishing. A boiler water treatment that is being tried out in conjuction with AVT is the addition of boric acid,which is a very weak acid at high temperatures. Its action in reducing corrosion damage results from the incorporation of boron in the thin corrosion films, making them more protective.

The water chemistry in CANDU/PHWR group of reactors(5,6) is in some ways simpler than that of PWR/VVER. However, the use of heavy water as the coolant and moderator imposes special restrictions on operations, sampling and analysis as the presence of the radioactive isotope, tritium(^{3}H) poses an additional inhalation hazard and spillage of the expensive heavy water has to be avoided. As mentioned earlier, Canada and India are the countries where these reactors are the base for nuclear power. All these units are of the pressure tube type, employing zircaloy-2 clad natural uranium dioxide fuel and using heavy water as the moderator as well as the coolant. The latter is in seperate circulating systems that operate under different conditions of temperatrue, pressure and chemistry. The primary heat transport system is comprised of multi metal surfaces, the major components being carbon steel,zircaloy-2 and Monel-400 or Incaloy-800. The objective behind coolant system chemistry is the same as in all other nuclear power reactors,viz.,to minimise the out of core radiation fields by minimising the processes of corrosion and erosion of the heat transfer surfaces(8,24). A prerequisite for achieving this objective is, "Hot Conditioning," of the primary heat transport system during its light water commissioning stage. After cleaning and degreasing the system surfaces, water maintained at pH 10 (by LiOH) and deoxygenated (by hydrazine) is circulated in the system in the temperature range of 220^{o}C-240^{o}C for about 10 days. Such a procedure results in the formation of a thin protective layer of magnetite (Fe_3O_4) especially on carbon steel surfaces(5). This minimises further corrosion of the structural materials and acts as a check on crud inventory. The steady state crud concentration values have been observed to be ~0.01 mg/l, with some transient values during start up and cool down operations. The integrity of the magnetite film is due to a well regulated coolant chemistry and consequently results in a low level of the activity transport. This contributes to low out of core radiation fields(4).

As compared to PWRs or VVERs, the advantage of PHWRs stems from their different moderator system in which boron is added rather than to the coolant. This simplifies the coolant chemistry and in general permits a higher operating pH which is mostly kept constant at 10.2 ± 0.2 (as measured at 25°C) by the addition of LiOH. The specific conductivity of the coolant normally ranges between 15 to 30 μs/cm. A pH of 10.2 at 25°C due to LiOH addition alone means a pH of 7.4 at 270°C - 280°C which is generally the operating temperature in PHWRs. In terms of magnetite solubility the pH and the temperature regimes ensure that the solubility of magnetite is almost minimum. Actually it is a little towards the right hand side of the minimum in the solubility *vs.* pH (280°C) curve for Fe_3O_4 (Fig.4.4). With a positive temperature coefficient, the magnetite solubility increases in the coolant channel from the inlet to the outlet, thus reducing the chance of deposition on the fuel clad surface. It may be mentioned that the adsorption of Co (II) on magnetite is maximum and constant in the pH range. This would mean that the Co adsorbed by the magnetite layer on the fuel clad surfaces has a chance to get activated. On the other hand,with the solubility gradient of magnetite in a fuel channel, Co(II) is expected to be in the suspended or soluble form in the coolant. In short, the operating pH takes care of the integrity of the magnetite film formed during hot conditioning/normal operation. It also keeps the magnetite solubility in the appopritate direction and ensures a lower residence time for Co (II) in the core(24).

Another chemical control that is strictly adhered to is that of dissolved oxygen in the coolant. In a closed system, water radiolysis leads to generation of hydroxyl radicals which end up as dissolved oxygen. The Primary Heat Transport (PHT) system in earlier PHWRs had a large surface area of Monel-400 (steam generator tubes) in contact with the coolant D_2O. The corrosion of this alloy at high temperatures is adversely influenced by dissolved oxygen. In view of the high Ni content of this alloy, Monel surfaces are one of the major sources of cobalt in the system,. Thus it is essential to maintain a low level of dissolved oxygen (10 μg/l), so as to minimise the corrosion of Monel and hence the input of cobalt. Hydroxyl radicals can be scavenged by increasing the partial pressure of dissolved hydrogen in the coolant. In PHWRs, hydrogen injection to a level of 10 to 15 cm 3/kg of D_2O at STP has been found to keep dissolved oxygen at ~10 μg/l. It is also to be noted that hydrogen addition to the coolant does not influence the solubility of magnetite, since the solubility is dependent on the cube root of hydrogen partial pressure(24). Following the development and good performance of Incoloy-800 as the steam generator tube material, Monel-400 is being substituted with this alloy. Incoloy-800 is not all that susceptible to dissolved oxygen transients at high temperatures and having a lower Ni content, will have less cobalt inventory.

The third aspect of the coolant chemistry in CANDU/PHWRs relates to its purification. A part of the coolant (1% of coolant inventory) is withdrawn from the circuit, cooled and then passed through a filter and mixed resin bed. In order to keep the pH of the coolant constant, the Li form of the cation exchanger is employed, while OD (O^2H)form of the anionic resin ensures no degradation of isotopic purity. The use of organic ion exchangers is a cause for a chemical transient, since the intrusion of any of the resin into the system will upset the chemistry due to their thermal and radiation degradation. This is true for all types of reactors.

Against the above background, the experience of coolant chemistry in CANDU/PHWRs has been very satisfactory. Chemical transients are rare. The radiation fields around the steam generator cabinets, measured 24 hours after a shut down are fairly low and constant. On-line γ-monitoring of the outer surfaces of primary piping (over the insulation) indicates that the major contributory radionuclide to the radiation field is ^{60}Co and occassionally,fission products as in other reactor types(4). The replacement of Monel-400 by Incaloy-800 is expected to further reduce the radiation field build up on the out-of-core surfaces that was observed earlier. Models for activity transport have been developed(8).

Typical specifications for the chemical control of the heavy water coolant are given in Table 9.4.

Table 9.4 Chemical Control Specifications for PHT System in PHWRs(24)

Parameter/ Constituent	Sampling frequency	Range/ limit	Remarks
Isotopic purity	3/week	95% min.	From reactivity considerations.
Sp. Conductivity	3/week	30 micro Siemens/cm	Specific conductivity limited by the concentration of lithium hydroxide (LiOH) maintained in the coolant for keeping it's pH within specified limits.
pH 25 °C	1/day	Between 9.5 - 10.5	Adjusted with lithium hydroxide (LiOH). This is the optimum pH range for least corrosion of the carbon steel in the system
Chloride	3/week	0.3 mg/l	To minimise possible stress corrosion.
Fluoride	1/month	0.5 mg/l	Higher concentration of fluoride can have a corrosive effect on zircaloy tubes and fuel cladding.

Contd.

Table 9.4 (*Contd.*)

Parameter/ Constituent	Sampling frequency	Range/ limit	Remarks
Crud	1/week	0.1 mg/l for steady operation	Circulating crud gets activated in the core and will get deposited on the fuel bundles and on the PHT system surface.
Dissolved Oxygen	3/week	10 μg/l during steady operation*	Higher values of oxygen damages the protective magnetic layer and increases the corrosion of boiler tubes specially of Monel-400. Both will lead to problems of activity transport.
Dissolved D_2	1/week	Between 3 - 20 mg/l of D_2 at STP	Maintained by injecting hydrogen to the system when pressurised.

* If the limit exceeds the value, it shall be brought back below the limit in 72 hours, failing which the reactor shall be shutdown.

The heavy water moderator that fills the calandria is in a seperate low temperature (~50°C) circuit. Boron Trioxide dissolved in D_2O is added for reactivity control and the required concentration is maintained by a by-pass ion exchange unit, that also takes care of the purification. The radiolysis of heavy water releases D_2 and O_2 into the He cover gas of the moderator system. This gas is circulated through catalytic recombiners, so that the concentration never exceeds four percent v/V (Volume of D_2/Total volume of cover gas). Other important chemical parameters are the isotopic purity and chloride, the latter because the system components have stainless steel surfaces.

In the secondary system of all CANDU/PHWRs, AVT is being employed with morpholine as the alkalising agent. This poses problems, if condensate polishing is also practised, as would be the case at a seawater cooled power station, (such as MAPS at Kalpakkam, India). Since the condenser tubes are of Al-brass and there is heavy biofouling, there are bound to be condenser tube leaks. Two signigicant developments are worth noting in this context. An interactive software code, "BOIL", stimulates the build up of chloride in different parts of the secondary circuit due to seawater leaks in the condenser(25). It is possible to establish the leak rate by measuring the chloride concentration twice in succession over a period of time in the steam generator and feeding that data to the code. The resulting determination of the leak rate helps the operators to initiate corrective action.

The other development relates to the performance of the condensate polishing unit (CPU)(26). The impact of morpholine is both direct and indirect. The concentration of morpholine is higher (2-3mg/l) for a given pH, as against ammonia (0.5 mg.l.). This results in lesser effluent volume from the polishing bed prior to its saturation with morpholine. As the selectivity coefficient of morpholine (MOR) over sodium on the resin is rather poor, the retention of sodium in the resin is highly dependent on the ratio of Na to MOR. The chloride slip is indirectly controlled by morpholine absorption by the bed; it is minimal untill morpholine saturation occurs. Hence, it is anticipated that the performance of the condensate polishing unit would be poorer in the presence of morpholine than that in the presence of ammonia under the same conditions of resin quality, the ratio in the mixed bed and regeneration characteristics.

Water Chemistry and corrosion problems are experienced not only in power reactors,but in research reactors as well. A couple of examples will illustrate the point. In 1961, when the effects of water radiolysis were not fully appreciated in large systems, 300 mg/l of potassium chromate was added as a corrosion inhibitor, as well as a biocide to primary coolant water (H_2O) of the CIRUS reactor in India. Radiolytically produced H radicals, reduced the chromate to trivalent chromium, which got precipitated as its hydrous oxide on the aluminium clad of the metal fuel. This caused pressure drops and reduced the flow of the coolant leading to fuel failures. A mixture of hydrogen peroxide and di sodium salt of EDTA was used to clean up the coolant channels and fuel clad surfaces. Chromate was also removed from the system, thus solving the root cause of the problem(27). In 1985, due to vibrational problems, the aluminium cladding of the fuel bundles in the DHRUVA reactor in India was getting eroded and corroded at a rapid rate. This led to the formation of aluminium hydrous oxide turbidity in the heavy water coolant. The turbidity was identified as Bayerite aging to Gibsite and the colloid was negatively charged. A magnesium loaded weak acid cation exchange resin was developed to clean the heavy water of its turbidity and associated radioactivity. Magnesium was later hydrolysed in the resin pores. When the contaminated heavy water was passed through such a special ion exchange resin bed, the turbidity was removed and the clean heavy water returned to the reactor(28). For a similar purpose Israel developed a carbon fibre filter material.

In accidental situations, where the primary coolant water (H_2O/D_2O) spills out of the circuit, its chemical condition at that time determines the chemical nature of the volatile radioactive fission products such as iodine and the release behaviour into the containment atmosphere. If the coolant is alkaline as in CANDU/PHWR, most of the iodine will be retained in the aqueous phase as iodide. On the other hand, if it is a BWR neutral coolant, a considerable fraction of iodine will be in the form of I_2 and hence will volatalise. PWR/VVER situation depends on the pH at that time, which is determined by the ratio of lithum to boric acid.

The severe nuclear reactor accidents in NRX, TMI-2 and Chernobyl-4 have brought the role of water and steam chemistry in aggravating the effects into sharp focus(10). The temperature of the core materials will continue to rapidly increase to levels much higher than in the normal operating mode. Consequently, several interactions get initiated at fast rates, when water/steam comes into contact with very hot surfaces. With increasing temperatures, these processes are:

1. $2H_2O + C \rightarrow 2H_2 + CO_2$
2. $H_2O + C \rightarrow H_2 + CO$
3. $3H_2O + 2Al \rightarrow 3H_2 + Al_2O_3$
4. $2H_2O + Zr \rightarrow 2H_2 + ZrO_2$
5. $3H_2O + 2Cr \rightarrow 3H_2 + Cr_2O_3$
6. $4H_2O + 3Fe \rightarrow 4H_2 + Fe_3O_4$
7. $2H_2O + U \rightarrow 2H_2 + UO_2$
8. $H_2O + UO_2 \rightarrow$ More volatile U bearing species.
9. H_2O + Fission products $\rightarrow$ More volatile species.

(Here H_2O signifies water and /or steam depending upon the situation).

Chemical reactions excluding 3 and 7 played important role in CN-4, while reactions 4, 8 and 9 and possibly 5 and 6 were of significance in TMI-2. On the other hand,reactions, 3, 7 and 9 were reported to have influenced the course of the accident in NRX. The net result in all cases except 8 and 9 is the production of hydrogen. In the special case of 2, it would be a mixture of combustible gases. The individual accident scenario will determine the extent to which the above chemical processes involving high temperature water/steam proceed(29).

In the case of loss of coolant, the temperature of zirconium cladding of the affected fuel elements can go up within a few minutes to about 1030 °C due to decay heat. This is the temperature required for the initiation of the self sustaining stage of the zirconium-steam reaction No.4. This exothermic process results in the production of large amounts of hydrogen as well as a further rise in temperature. The consequent pressure build up coupled with a further rise in temperature can lead to the deformation of the zirconium fuel and pressure tubes (coolant tubes) in the reactor. The possibility of the rupture of pressure tubes is always a real one. In such a situation, the steam-hydrogen mixture enters the restricted volume in the reactor vault which houses important equipment. In the absence of mixing and large containment volumes, there is a chance for a hydrogen build-up and its possible deflagration(29). If the environment is inerted, monitoring of hydrogen and oxygen in such restricted volumes on a continuous basis as well as installation of catalytic recombiners as additional back up safety features are expected to mitigate this risk. Hydrogen explosion was one of the causes for the breach of the containment in Chernobyl-4.

Once the irradiated fuel is exposed to the hot steam environment in an accident situation, chemical speciation of fission products will depend upon their interaction with steam. Thus, directly or indirectly those chemical reactions of No.9 will strongly influence the radioactive "Source Term".

Since chemical species in the vapour phase and their transport rates are expected to be influenced by the vapour phase composition, the presence of hydrogen generated in an accident will have a significant impact on the chemical speciation of fission products. Theoretical studies using estimated thermodynamic data for the vapour species and the condensed phases enable predictions to be made on the influence of variable vapour composition, (steam to hydrogen ratio) on the nature of the chemical species and their relative amounts in the gas phase. For example, it has been shown by calculations that in a hydrogen rich environment, the major contributor to the ruthenium bearing species is from ruthenium gas. The total ruthenium content in vapour phase has been shown to be maximum in a steam rich vapour. It decreases progressively with increasing hydrogen content. Thermodynamic calculations indicate(30), the possibility of molybdenum fractionating from the other constituents of the metallic inclusions present in irradiated fuel. This is a function of the hydrogen to steam ratio in the case of severe nuclear reactor accidents, such as the one at Chernobyl-4.

The above discussion clearly brings out the added importance of water and steam chemistry vis-a-vis the special problems that are encountered in the safe operation of nuclear power reactors.

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10

GEOTHERMAL POWER AND WATER CHEMISTRY

The utilisation of geothermal energy is extremely important in the quest for energy resources not based on fossil fuels. A wide gap, however,exists between the availability of this energy source and the amount that is being turned into process or space heat or electricity. The complex water chemistry of the hot geothermal fluid, which interacts with the materials of construction of the steam - water circuit, is a major cause for the under utililsation of this energy resource. The hostile working environment mars the reliability of the equipment. Since the chemical composition of geothermal waters is site-specific, any treatment programme cannot be generalised.

There are two broad categories of geothermal water-steam sources. They are classified on the basis of thermal gradients in a volume of the earth over and above the normal heat flow, and are given below:

(a) *Hot water fields,* in wide areas with moderately high temperature gradients of 30 to 50°C per km depth having surface temperatures below 100°C.

(b) *Steam fields* in narrow zones, of temperature gradients of above 50°C per km depth, having surface temperatures above 100°C.

Some of the important geothermal locations in India(1) are given in Table 10.1.

In some of the locations like Puga, although the surface temperature is a little above 80°C, in view of the height (the boiling point of water at that height being near about 85°C) the geothermal wells can generate steam.

Table 1C.1 Geothermal Locatioins in India(1)

Name and Location	Highest Temp. at surface °C	Name and Location	Highest Temp. at surface °C
Manikaran (HP)	100	Puga(J&K)	82
Jumnotri (UP)	90	Agnigundala (AP)	80
Tapoban (UP)	89	Rajawa· (J&K)	80
Surajkund (Bihar)	88	Chongo (J&K)	78
Sirguja (MP)	88	Duchin (J&K)	78
Khorkum (J&K)	85	Nulna (J&K)	78

10.1 GEOTHERMAL ENERGY UTILISATION

One can visualise two main types of utilisation of geothermal energy on the above basis(2,3). One is essentially electrical energy generation using dry steam, in a few instances, or more usually a steam water mixture. The other type is a mixed system, wherein the hot water is used for space heating, hot house cultivation, supply of low process heat and recovery of chemicals like borax.

The growth of installed capacity (MWe) of geothermal power world wide upto 1990 is given in Table 10.2.

Table 10.2 Growth of the Installed Capacity (MWe) of Geothermal Power

Year	MWe	Year	MWe
1910	0	1965	575
1916	8	1975	1290
1935	56	1980+	3888 (1444)+
1940	250	1990+	5827 (2770)+
1955	380	1995+ (projected)	8967 (3170)+

+From "Geothermal Resources",Encyclopedia of Physical Science & Technology, 2nd Edition, Vol.7, pp 323-360, Academic press (1992). The figures for USA are given in brackets.

Italy, Japan, Mexico, New Zealand, Phillipines and USA are among the countries that generate electricity from geothermal sources. The Geysers geothermal field with several wells in California, is the only one in USA where dry steam forms the dominent resource. Its combined output in 1990 was about 1770 MWe. While the projected increase in installed capacity (MWe) between 1990 to 1995 is modest in the case of Italy and Mexico, in the Phillipines it is expected to rise sharply from about 890 MWe in 1990 to 2165 MWe in 1995.

10.2 CHEMICAL COMPOSITION OF GEOTHERMAL WATERS

The dissolved solid content of geothermal waters ranges from that of ordinary well water upto concentrated solutions as high as 40 percent by weight(4). The principal constituent is sodium chloride. Usually potassium and calcium chlorides are also present, though to a much lesser extent. Thus chloride is the main anionic constituent, the next in importance being bicarbonate. Silica in the form silicic acid is present in the range of 200 to 600 mg/l. Some typical compositions of geothermal fluids are given in Tables 10.3 and 10.4.

Table 10.3 Composition of Some Geothermal Fluids(8)

Location	Components (Appr. Wt. %)				Total
	NaCl	KCl	$CaCl_2$	H_2SiO_3	dissolved solids (mg/l)
Weitap, NZ	72	10	1	19	3,000
Otake, Japan	62	0.5	1.5	23	3,800
Broadlands, NZ	65	10	-	26	4,000
Ahuachipan, El Salvador	82	11	6	2	15,000
Carro Pricto, Mexico	78	9	5	4	20,000
East Mesa, USA	72	7	9	2	24,000
Raykjanes, Iceland	72	8	16	2	29,800

The total chloride and TDS vary considerably not only from region to region but even within the region itself.

The concentration of fluoride in geothermal brines is limited by the solubility of calcium fluoride(CaF_2). Fluoride is readily leached from rhyolite, but it is leached slowly from silicified rocks. The concentrations of both fluoride and bisulphate under saturation conditions in these fluids is inversely related to the calcium concentration.

The pH of geothermal waters is determined by different equilibria in different locations. Published values range from 4.9 to 9.1. The pH and the electrolytic composition exercise a profound influence on the corrosion and material compatibility of geothermal waters.

When geothermal water flashes to steam, a number of gases are released. A major component is carbon dioxide, accounting for about 90 percent or more by volume of the non-condensible gases. The other components are H_2S,CH_4, H_2 and NH_3. In some fields, such as Lake Marvin in Iceland H_2S is one of the major components.

10.3 CORROSION AND MATERIAL COMPATIBILITY

The corrosion of equipment used in the production of power from geothermal water or steam or for hot water distribution is generally due to the hot electrolyte solution entained in the steam, H_2S contamination and the possible presence of oxygen(5). Usually geothermal waters are free from oxygen and as such chloride induced stress corrosion is not problem.

However, if air gets in, as it does in many situations and if the waters are acidic, high surface corrosion rates prevail. Stress corrosion cracking is also possible, H_2S in the steam or liquid phase causes micro cracks on the surface of steels. Copper or cupronickels are not compatible with H_2S. The general corrosion characteristics of geothermal fluids are given in Table 10.5.

Table 10.4 Characteristics of Some Geothermal Steam and Water Phases(4)

Location	Nature of the fluid	Temp °C	pH	H_2S	CO_2	Cl^-	HCO_3^- (mg/l)	So_4^{2-}	NH_3/NH_4^+
Ahuachapan	Turbine inlet steam	156	–	103	2716	2.3	–	–	0.9
	Separated water	156	7.0	–	–	9770	2 4	41	–
Cerro Prieto	Turbine inlet steam	160	–	1500	14100	0.8	–	–	110
	Separated water	160-180	7.7	–	–	16.0	45-74	6	-
Larderello	Turbine inlet steam	183	–	630	42612	1.1	–	–	205
	Separated water	Steam dominated resources.							
Matsukawa	Turbine inlet steam	147	–	586	4153	–	–	–	–
	Separated water	Steam dominated resources.							
	Condensate	25-47	4.0-5.9	57	49	2.2	4.6	3.7	–
Otake	Turbine inlet steam	127	–	61	5347	–	–	–	–
	Separated water	127	6.6-8.4	–	–	1385	46	148	0 06
	Condensate	26-42	5.0-5.7	–	–	5	–	–	–
The Geysers	Turbine inlet steam	177	–	222	3260	–	-	–	194
	Separated water	Steam dominated resources.							
Wairakei	Turbine inlet steam	101-175	–	36.5	1933	3.5	–	–	1.6
	Separated water	101-175	8.2-8.6	2.0	21	2170	–	28	0.16

Table 10.5 Corrosion Characteristics of Geothermal Fluids[5]

Phase	Corrosive components	Materials in contact	Type of Corrosion
Liquids	acidic	steels	Surface
Water-Steam	oxygen	steels	Surface
Water-Steam	O_2 and Cl^-	steels	Stress
Water-Steam	H_2S	steels	Stress
Steam	H_2S	Tempered steel (turbine blades)	fatigue
Condensate	H_2S and O_2	steels	surface

Corrosion experienced in geothermal power plants may be summarised as follows[6]: As the two phase fluid is quite erosive, (in addition to being corrosive), carbon steel valves and elbows have a short in-service life, due to turbulence induced erosion at these points. For steam lines, carbon steel has been found to be satisfactory, provided air (oxygen) in-leakage is prevented. Sulphide induced stress cracking of high strength casing in the pumps used to extract geothermal fluids from underground have been frequent. Geothermal steam has been observed to cause a sharp reduction in the fatigue endurance limit of turbine blades, as compared with high pressure steam from conventional boilers. In such cases, e.g. at The Geysers, where the steam is dry, cracking of 12 percent Cr, steel turbine blades has been reported. Consequently, thicker and heavier blades are found to be necessary. At locations where saturated steam is fed to the turbine, blade cracking is not a problem. Use of special materials such as carbon steel clad with SS 316 as turbine blades, showed a marked improvement.

10.4 CORROSION MONITORING

As mentioned earlier, The Geysers geothermal power plant is the largest in the world and from 1972 onwards a programme of corrosion monitoring and H_2S abatement was implemented. The corrosion monitoring system utilises several techniques to determine corrosion rates and analyse data. The electro-chemical method employs the linear polarization technique for rapid corrosion rate determination. It measures the potential oscillation on electrodes, with or without crevices or pits, for the determination of passivity, pitting and crevice corrosion suceptibility. Electro-resistence methods are also employed. Additionally pipe and plate-type coupons are incorporated as corrosion monitors in in-plant systems.

In The Geysers power plant[7], corrosion monitoring in the hot condensate in three units, without measures for abatement of H_2S indicated that,

(a) Stainless steels and Al alloys are only partly passive

(b) Pitting and crevice corrosion susceptibility of stainless steel is small

(c) Al is susceptible to erosion-corrrosion in areas of high turbulent flow

(d) Corrosion rates are strongly dependent on condensate velocity.

Under the same conditions, the cold condensate imparted some susceptibility to stainless steel for pitting and crevice corrosion.

10.5 THE H_2S PROBLEM

For the abatement of H_2S, at The Geysers[7], initially, direct contact condensers were used where steam from the turbine exhaust was mixed directly with cooling water, containing ferric sulphate as a catalyst, to oxidise H_2S to elemental sulphur. But later on the level of H_2S in steam from new reservoirs being higher the catalyst could not be regenerated quickly enough and the sludge caused severe operating problems. To compound this situation, the corrosion monitoring programme showed substantially increased corrosion rates on stainless steels exposed to the hot condensate treated with the iron catalyst. On the other hand aluminium alloys showed a better performance . This is indicated by data in Table 10.6.

Table 10.6 Corrosion Studies with Reference to H_2S Abatement by Iron Catalyst(5)

Probe	Condensate	Corrosion rate, in miles per year(m p y)	
		Without iron catalyst	With iron catalyst
304 SS	Hot	0.5	0.5 to 2.5
416 SS	Hot	0.5	0.4 to 2.5
6061 Al	Hot	2.8	0.1 to 0.6
3003 Al	Hot	7.4 *	0.1 to 0.4
304 SS	Cold	0.5	0.1
316 SS	Cold	0.5	0.1

*Erosion.

To overcome the corrosion problems caused by H_2S contamination, a new method for its removal is now being practised at The Geysers. Unit 15 is equipped with surface condensers using SS 304 and a Streinford system designed to acheive more than 90 percent H_2S remova!. In this process the non-condensible gases are directed to a unit where H_2S is oxidised by sodium vanadate at pH 9 to elemental sulphur and water. The overall performance of the system has been satisfactory.

The Electric Power Research Institute and the Department of Energy, USA have evaluated two methods for H_2S abatement in all geothermal power plants. Both depend upon an upstream removal of H_2S. The following advantages are expected,

(a) Turbine blade failure caused by fatigue corrosion due to H_2S can be controlled

(b) Turbine efficiency is increased by reducing boric acid deposits on turbine blades.

One demonstration process uses $CuSO_4$ scrubbing. Efficient removal of H_2S dependes upon high pH, copper content, contact time and pressure. The other process is based on condensation and re-evaporation of the steam in a single heat exchanger. Here the non-condensible gases are seperated from the condensate. The shell side of the heat exchanger is made of SS 304 and the tubes are of titanium.

10.6 TURBINE STRUCTURALS

It was mentioned earlier that turbine blades exhibit fatigue corrosion in the presence of H_2S. Chrome iron (12 percent Cr) in the hardened or martensitic state is susceptible to stress corrosion cracking in the presence of geothermal steam. However, in its ferritic form, the alloy enjoys immunity provided that chlorides are present in quantities less than 10 mg/l in residual water droplets of the steam. Thus softened and tempered stainless steel is being increasingly used for turbine blades. On the other hand, in this condition, the blades and other surfaces are susceptible to erosion in the presence of fast moving water droplets in the steam. By a proper choice of the speed of the turbine blade tip, this risk is minimised.

The internal parts of a turbine are normally resistant to attack from geothermal steam. However, during a shut down air ingress might occur, which, in the presence of non-condensable gases remaining in the turbine will lead to serious corrosion. The erosion-corrosion rates at the turbine rotor and casing and nozzle diapharm at Matsukawa, Japan (which has acidic water and H_2S) were computed to be about 20 mil/y. Hence it is preferrable to purge the turbine internals with a stream of hot nitrogen with suitable venting.

10.7 CONDENSERS

From a corrosion view point highly adverse conditions exist in the condenser and gas extraction equipment of a geothermal turbine. Surface corrosion will be exhibited by steels in contact with the condensate from the steam flashed in the unit, due to the presence of H_2S and oxygen. The inner surfaces of the condensers are therefore protected with a coating of epoxy resins or aluminium spray. Austenitic steels are recommended for use as gas extraction rotors, while 99.5 percent pure aluminium has been suggested for the inner cooler tubes. The latter material is said to be resistant to geothermal steam except at high temperatures.

Surface corrosion rates reported for several candidate materials for the condenser tubes are shown in Table 10.7.

Table 10.7 Surface Corrosion rates (MIB/Year) of Materials in Contact with Geothermal Fluids[8]

Geothermal fluid	Temp. °C	Cu & alloys	Ni & Monel	Carbon Steel	Ferretic Steel	Austenitic Steel
Condenste	70	0.2-5	0.4-4	3-4	0.1	0.1
Aerated steam	100	10-40	8-10	18-20	1	0
Well head flushed water	125	0.3-10	1	0.3-0.5	0.1	0
Well head flushed steam	100 to 200	0.3-4	1-4	0.3-6	0.3	0

It is evident that the condenser tubes cannot be of Cu or Ni alloys, as in many fossil fuel fired power plants.

At this point, it is appropriate to mention that in addition to the problems of corrosion, the utilisation of geothermal waters will also lead to a lot of scaling and deposition on surfaces. This is specially so when wet steam under a pressure of 8 kg/cm_2 (100 psig) in the temperature range of 175 to 315°C is made use of. The scale formation affects every aspect of the plant from the production reservoir to the reinjection system. The rate of scale build up and corrosion inside the steam turbines used in flash cycles is not generally known. Extensive field testing is required. In many cases, scaling is only due to calcium carbonate *and silica. It may become necessary to clean up the deposits on turbine blades* and valves. The Salton Sea (USA) geothermal waters have an average of 2,50,000 mg/l of dissolved solids, making them very prone to scaling. A set of pressure-volume - temperature - composition - energy data is required for predicting the conditions of minimum scaling and optimum operating conditions,including reinjection of the spent fluids. The data for NaCl - H_2O analysed by the International Association for the Properities of Steam will serve as a model in this context. As regards prevention of scaling, lowering of the pH to 3.0 reduces the polymerisation of silica and supresses the precipitation of $CaCO_3$ and metal sulphides. Use of organic polymers as antiscaling agents is being tried out. Another approach is to 'sludge scaling', in which finely divided silica is added to the geothermal fluid to promote silica precipitation. This would, however, require the handling of high levels of suspended solids.

When the geothermal water temperature is not much above 100°C, it is impractical to produce steam by flashing. In such cases, a binary cycle is proposed wherein the geothermal water circulating through a heat of exchanger,transfers energy to an organic liquid with a low boiling point like isobutane. The vapour pressure of gaseous isobutane so generated will be enough to drive a turbine and can later be condensed by surface water, with a cooling tower. Recent studies report the use of a direct contact heat exchanger to overcome scaling problems *due to the high salt content of geothermal waters. This type of approach through* a binary cycle, completely eliminates the problem of corrosion in turbines.

10.8 DIRECT USE OF GEOTHERMAL WATERS

At temperatures lower than 100°C at the well head, geothermal waters are not suitable for electricity generation, but can be used for space and process heating. In India, this will probably be the main application sinee, well head temperatures are less than the boiling point of water.

The materials to be used in the heat transport system in such cases could be the same as at Klamath Falls, USA. Here the buried supply pipe is of carbon steel. Fan coil units are conventional copper tube units with aluminium fins. Heat exchangers are of the shell and tube variety using carbon steel shell and copper tubes. Operational experience shows that copper fan coils and tubes give good services in low chloride neutral pH waters free of oxygen. Nevertheless problems arose because of CO_2 and H_2S content. CO_2 apparently produced dezincification of even low zinc brasses in high velocity regions. Experience at Klamath Falls indicated that when H_2S is greater than 0.1 mg/l, the low temperature geothermal water produces excessive scaling on copper tubes leading to under deposit attack.

It is evident from the information presented in this chapter, that in the utilisation of geothermal water/steam resources for the generation of electricity or process heat, the problems due to water and saturated steam chemistry are more severe than in fossil fuel fired plants, because the working fluid is contaminated to a high degree with gases and dissolved solids(8).

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11

ANALYTICAL TECHNIQUES FOR WATER CHEMISTRY MONITORING AND CONTROL

11.1 WATER AND STEAM CHEMISTRY MONITORING

An effective programme of water the steam chemistry monitoring as the basis for exercising the necessary chemical control requires, reliable sampling, good laboratory facilities, a dedicated Chemistry Task Force and on-line analysers with low maintenance problems(1).

United States surveys showed that while more data on the chemical quality of steam and water are required at more frequent intervals, the power plants are deficient to the extent that,

(a) One or more of the important on–line analysers do not exist in a majority of stations,

(b) Effectiveness of most of the on-line analysers is compromised by crud deposition in the sampling lines/nozzles and

(c) A significant fraction of the analysers are not in use.

For prevention or minimising the corrosion in the steam water circuits of a power plant, the major chemical parameters which one monitors, preferably by on-line instrumentation are conductivity, pH, dissolved oxygen, sodium, chloride and silica. In order to evalute the steam chemistry, it is desirable that direct sampling and continuous instrumental analysis of the steam samples from predetermined turbine extraction stages be adopted. Since steam is under high pressure and at a high temperature, pressure reducers and sample coolers form part of steam analysis instrumentation(2).

Chemical specifications are maintained by analysing samples from various points in the system, and by dosing appropriate amounts of various chemicals. The manual method of taking samples, obtaining laboratory analyses and adjusting chemical addition rates in order to correct deviations from the specifications is probably satisfactory for steady state operation of earlier designs. However, it is unlikely that any reasonable sampling frequency could keep specifications to within limits during transient operation or during periods of condenser leakage. For modern units, the most reliable means of achieving an efficient control is by a completely automated chemical sampling, analysis and addition scheme. This calls for a sophisticated design of the entire chemical control system and more importantly reliable maintenance(3,4).

In this chapter, analytical methods in the laboratory based on chemical and instrumental techniques as well as on-line monitoring for different chemical parameters are described. Water chemistry monitoring in a power plant might involve as many as 25 source points from which either the samples are drawn on the spot or sampling lines routed to a central sampling station. Reliable and reproducible sample collection is an essential condition. In case of long sample lines leading to a sampling station, adequate flow ensures that the chance of a blockage is minimised. Sample nozzles must be kept clean and they will have to extend within the flow-line in an inward direction, so that the bulk fluid is sampled. One should always bear in mind that external factors such as dust, humidity and temperature might interfere with the caliberation exercise. A two phase system like that of saturated steam poses difficulties in terms of sampling (as opposed to sample) reproducibility. On the other hand, with single phase fluids such as feed and boiler water (i.e.boiler blowdown) condensate and superheated steam,this doubt on sampling integrity is absent. The problem of sampling superheated steam at the turbine in-let is very exacting and the steam purity so monitored will be the reference point for any other chemical control. There is scope for improvement in sampling of superhead steam.

A very reliable indicator of water purity is its conductivity. The lowest theoritical limit of specific conductivity for water is about 0.05 μs/cm at 25°C Taking this as a reference, the quality of water in different sections of the power plant can be judged. It is best to cool the sample to 25 ± 0.2°C. Very good on-line instrumentation is available and it is becoming a standard practice to install a number of conductivity probes specially in the hotwell section so that early warning of condenser tube leakage is available in the control room. As mentioned in Chapter 6 specific conductivity measurements are also made use of in monitoring the performance of DM plants. The basic principle involves the generation of a current when an AC voltage is impressed upon two electrodes immersed in the aqueous test solutions. The current is measured by an AC bridge. In the conductivity meters, the signal is amplified and measured on the scale in terms of specific conductivity values. The cell constant of the electrode cell is very important and depending upon the range of specific conductivity to be measured, cells with an appropriate cell constant are used. The measurement also has to be compensated for the temperature of the sample, electronically and all conductivity measurements are reported at 25°C. Modern instrumentation measures conductivity automatically with temperature compensation. The cleanliness of the conductivity cell, specially the electrode surfaces is very important. In addition to measuring the specific conductivity, one also measures "Cation Conductivity" wherein all the cations in the sample are removed by passing it through a H^+ form of the cation exchanger. If the sample is degassed (free from CO_2) after it is put through the cation exchanger, it is called "Degassed Cation Conductivity".

Another important instrumental measurement is the alkalinity of the boiler water, for which pH monitoring is essential. It is a less reliable parameter for high purity feed water as compared to specific conductivity. On-line instrumentation gives the pH indication in the control room. In several power stations it has been noticed that pH, as measured in the laboratory is different from on-line measurements. This is possibly due to poor response of the on-line electrodes, and CO_2 ingress in laboratory measurements. The cleanliness of the on-line as well as the laboratory electrode surface is an important parameter in this context. Of the various reference electrodes and junctions available for continuous monitoring, calomel (Hg_2Cl_2)or silver-silver chloride (Ag-AgCl) electrodes with frit junction and unsaturated KCl reference solutions give good results. Ion selective electrodes, sensitive to H^+ can also be made use of for pH measurements. As with specific conductivity measurement, temperature compensation is a must; special precautions recommended include low sample flow, electrode arrangement in parallel pairs and special electrode construction to minimise streaming potentials.

It is desirable to know the sodium level in feed water. Sodium limits in steam have been revised to values as low as 3 μg/l. In fact, the Central Electricity Generating Board, UK envisages the determination of the Na balance in the entire water steam cycle. On-line sodium analysers are available in the market. At sea water cooled power stations such on-line probes, installed in the condenser hot well will suppliment the conductivity instrumentation in detecting the condenser tube leak at a very early stage. On-line sodium analysers are in service in the Madras Atomic Power Station. The sodium ion specific electrode is capable of detecting 0.05 μg/l of Na. Commercial instruments having working range from 0.1 to 1000 μg/l are available.

Equally important is the chloride content of feed water, especially in boiling water nuclear power reactors. Hence a BWR power station laboratory has to analyse a comparatively larger number of samples for chloride than in other stations. Recourse has been taken to make measurements with chloride ion specific electrodes. Not only liquid junction but also solid state ion specific electrodes are in use for the determination of chloride. On-line instrumentation is also employed, though it is some what less reliable than conductivity measurement.

Chloride can also be determined in the laboratory, using Hg^{2+} - Fe^{3+} - CNS^- procedure. M/S Bharat Heavy Electricals Ltd (R & D Unit), India has developed a PVC coated wire electrode containing red HgS - Hg_2Cl_2 as the sensor with Hg - $HgSO_4$ as the reference electrode. With this system, it is possible to measure chloride at level of as low as 5 μg/l, l in a flowing sample. Lower concentration level measurements are possible in combination with an ion chromatograph.

One of the alkaline conditioning agents used in boilers is ammonium hydroxide. Once-through boiler operators only make use of this reagent. In view of the volatility of ammonium chloride, one opinion is that the presence of chloride in steam, in such a situation , is due to the added ammonia. Hence, there is a speicific need to monitor this additive in different sections of the water and steam cycle. On-line ammonia analysers are becoming useful.One such analyser is based on a probe which responds to the partial pressure of ammonia across a gas permeable membrane. The resultant pH change in the probe develops a potential which can be measured and used for judging the partial pressure of ammonia.

Based on electrochemical techniques, on-line instrumentation has been developed for the measurement of dissolved oxygen. Several such instruments are available in the market. These are based on the development of a potential or a current directly proportional to oxygen concentration in water. Silver or platinum serves as the cathode material, while lead is used as the anode. The electrodes are seperated by an oxygen permeable membrane. The oxygen dissolved in the sample diffuses through the membrane, thus creating a potential or current in proportion to its concentration. This is amplified and measured. The electrode reactions are:

At the cathode : $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (11.1)
At the anode : $Pb + 4OH^- \rightarrow PbO_2 + 2H_2O + 4e^-$ (11.2)

The minimum detectable limit is 0.001 mg/l. The Coulometric method can also be adopted as an on-line technique. However the limit of detection is 0.005 mg/l. Another method of determining dissolved oxygen is by its fast reaction with metallic thallium (Tl). This results in the formation of soluble TlOH. The specific conductivity of this solution is directly related to dissolved oxygen in high purity water. In the laboratory, the well established Winkler's test procedure, using colorimetry with 5 cm absorpotion cells will lead to a detectable limit of 0.005 mg/l. An oxygen analyser should find a place in the main condenser area at the discharge of the condensate pump.

Another important constituent which must be monitored is silica. As seen earlier, the distribution of silica between water and steam phase depends upon the temperatures and pressures of the two phases. Since silica from steam has a tendency to deposit on turbine blades, very strict limits are imposed on silica levels in high pressure steam. In addition, the silica level of the DM water from the mixed bed is an important guide in assessing the performance of the anion exchange resins. On-line analysers for silica are now commercially available. It may be mentioned that M/S BHEL (R & D Unit) have developed and introduced into the market a combined on-line analyser for chloride, silica and copper.

In the laboratory, colloidal or 'non-reactive" silica is monitored by the use of a turbidimeter based on the principle of light scattering. To measure reactive silica a number of wet chemical methods are available. The colorimetric procedure recommended by ASME that depends upon the formation of the blue heteropoly silicomolybdate can be used to measure silica upto 20 µg/l, if 10 cm cells are used. Since most of the power station laboratories have 1 cm cells, it is advised to concentrate the blue colour by extracting it into a small quantity of an organic mixture (cyclohexanol and amyl alcohol in the volume ratio of 1:9) containing 0.2 M Aliquat 336. Through this additional step, concentrations of silica lower than 10 μg/l can be measured even with 1 cm cells.

In both steam and feed water, copper has been specified to be kept at very low levels (2 and 10 μg/l). The extractive photometric determination using Neocupron reagent can detect a level of 20 μg/l with 1 cm cells. Use of 10 cm cells or alternatively a copper ion selective electrode gives a detection level of 1 μg/l under ideal conditions.

Other instruments useful in a power station laboratory are the flame photometer and atomic absorption spectrophotometer. Ion chromatograph is proving to be a very useful addition to the range of equipment.

11.2 AUTOMATED CHEMISTRY MONITORING AND CONTROL

On-line chemical instrumentation can be integrated into an automated system for chemical monitoring and control. For steam generators making use of nuclear heat, the main requirements of such a system are

(a) An ability to control the chemistry in the All Volatile Treatment (AVT) mode for long periods,

(b) Reliable detection of condenser leaks and if the leak is large enough, initiation of automatic control of the boiler water chemistry by using phosphate treatment in case of recirculating drum type units and

(c) An abillty to log data and provide the chemist with a summary of post incident steam generator conditions at regular intervals or to diagnose the system chemistry behaviour.

For meeting the above needs, modern power station designs incorporate a dedicated mini computer as the basic component(5). Chemical analysis information is fed to it by commercial on-line analysers located at strategic points in the steam/water circuit. Acting on information from these analysers, the computer actuates valves which control the addition of appropriate chemicals at the correct dosing points. For example, operation of the phosphate system is such that the automatic addition of phosphate to the boiler will begin when a condenser cooling sea water leak is confirmed by a signal from the sodium analysers. The computer controls the phosphate addition by feed back information supplied by on-line analysers measuring the phosphate concentration and pH of the composite boiler blowdown. In addition to initiating stipulated chemical dosing, the computer has to log and display data from all on-line analysers, interpret,give alarms and execute preventive action to correct off-normal trends in water chemistry.

For the instrumental and automated chemical control system, using a computer to operate satisfactorily, a number of on-line analysers and probes are needed. These are in addition to the ones described earlier, viz.,hydrazine analyser amd a phosphate analyser(5).

The computer should be dedicated and possess the following functional abilities:

(a) Acquisition of data from all the chemical analysers on the secondary side

(b) Automatic calibration of the analysers for ensuring accurate measurements and to detect instrument malfunction,

(c) Monitoring for all the system's alarm devices for diagnostic purposes these include temperature and flow indicators on analyser feed lines, flow switches on chemical dosing tanks and other pertinent indicators associated with the steam generator

(d) Detection of a condenser leak via the sodium ion analysers

(e) The starting and maintenance of phosphate treatment upon the detection of a significant condenser leak

(f) Storage and organization of a twenty four hour history of the analyser date and the sections of the controller for display on the CRT screen in a numeric or plotted form; a printed copy unit for selected permanent paper records is also desirable and

(g) Direct digital control of the hydrazine and pH Control loops, if desired.

Two sodium ion analysers are required to be installed for the purpose of rapidly detecting condenser cooling water leakage. One signal per minute from both instruments could be sent to the computer where the following logic sequence is enacted:

(a) Temperature and flow rate of the sample to each instrument is checked

(b) If the temperature and flow rate of the sample to the analyser are within specification limits,the data from the analyser are examined to determine, if an abnormally high level of sodium exists in the condensate,

(c) An affirmative answer by one or both analysers initiates automatic instrument calibration and

(d) If water calibration, both analysers reconfirm the high sodium level and temperature and flow rate of the sample to each are acceptable, a leak is declared detected and phosphate addition begins automatically.

The process of the above logic sequence for positive detection of condenser leak takes about 10 minutes.

11.3 SAMPLE CONDITIONING PHILOSOPHY

Analysers based on electrochemical principles, such as those for measuring pH, conductivity, dissolved oxygen and hydrazine can provide adequate accuracy only if the sample is maintained at a constant temperature. For this purpose it is recommended that each sample is cooled to a constant temperature (20°C or 25°C).

For an efficient chemical control,it is essential that the sample flow to the analysers is always maintained. To make the computer aware of any discrepancy in this respect, Chromel-Alumel thermocouples and flow indicator tramsmitters are needed to be installed ahead of each analyser. Abnormal signals from them will alert the computer to the doubtful integrity of the signal from the associated analyser.

In conclusion, it can be said that on-line monitoring of chemical parameters and their automatic control through a computer, will go a long way in providing reliable operation of the high temperature and high pressure steam generating system, whether in the fossil fuel fired or nuclear heated segments of the electric power industry.

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12

DESALINATION, EFFLUENT TREATMENT AND WATER CONSERVATION

The availability of clean drinking water is still a major problem not only in the semi-arid and desert regions of the world, but also in both rural and urban areas of the developing countries. However, the science of water purification, to make it fit for drinking, has made great strides during the last 30 years. Among these new technologies, Reverse Osmosis (RO) stands out as the one that gained wide acceptance and application(1). S.Sourirajan, who along with his colleagues has pioneered this technique, has this to say about Reverse Osmosis. " In the context of water scarcity in many parts of world and public concern on the quality of our environment, the effective utilisation of RO for the water treatment problem alone would make the social relevance of RO second to none". In addition , RO finds wide ranging application in waste water treatment and consequential abatement of pollution and water reuse(2,3). The Technology Missison on Drinking Water launched by the Government of India has RO as one of the metbods for providing clean and safe drinking water in rural India. Removing the dissolved salts from brackish or seawater to make the water acceptable for drinking is popularly known as Desalination. The standards for drinking water as set by the World Health Organisation are detailed in Chapter 2.

Examples of Osmosis, are the passage of water through cell walls, uptake of soil moisture by the roots of a plant etc. Osmosis is the process whereby, when two solutions having different concentrations of an electrolyte (such as NaCl) are seperated by a semi-permeable membrane, pure water from the solution having lower concentration of the electrolyte flows across the membrane into the one at higher concentration. This continues untill the concentration of the dissolved solute on both sides becomes equal. This flow or diffusion of water is basically due to the difference in the total solvation energy on either side of the membrane and the flow will result in the equalisation of energy on both sides. Since there is a flow in one direction, it would be appropriate to relate it in terms of a pressure and this is called the osmotic pressure. This phenomenon can be easily demonstrated in the laboratory. It is also dependent upon temperature, since basically energy terms are involved.

As the name implies Reverse Osmosis (RO), is the opposite of this process. By exerting hydrostatic pressure on the side of the solution having a high concentration of electrolytes, the flow due to osmosis is at first stopped and then reversed at a higher pressure. Thus it is possible to transfer pure water from a salt solution, like seawater, across a membrane by application of the required pressure. The translation of this principle to large scale application is what makes RO so attractive to desalination and effluent treatment. The required technology has been well developed during the last 25 years(4).

As an approximation, it is noted that the osmotic pressure of a solution having 1000 mg/l of dissolved salts (NaCl etc.) is about 0.7 kg/cm^2 (10psi). Since seawater has a TDS of about 35,000 mg/l, one can say its osmotic pressure is of the order of 25 kg/cm^2 (350 psi). Consequently for the desalination of sea water, a pressure in excess of 25 kg/cm^2 has to be applied in order to over come its osmotic pressure and start giving a reverse flow of desalinated water across the membrane. This flow will increase with an increasing positive difference between the applied pressure on the sea water side and 25 kg/cm^2.

The expression governing the flux of water (W_F) across the membrane is given by,

$$W_F = \frac{KA\ (\Delta P - \Delta \Pi)}{t} \tag{12.1}$$

In the above equation,

W_F : Water flux through the membrane,
ΔP : Differential of the applied pressure, (kg/cm^2)
$\Delta \Pi$: Differential of the osmotic pressure, (kg/cm^2)
A : Membrane area (in sq. cm),
t : Membrane thickness (in microns),
K : Membrane constant.

If one wants to increase W_F, A and/or $(\Delta P - \Delta \Pi)$ have to be increased, while t has to be decreased. These factors have to be optimised to suit the electrolyte concentrations in the water resource, as well as the quantum of drinking water needed per day. The effect of temperature is not noted in the above expression. RO membranes are sensitive to temperature, while the viscosity of water decreases with increase in temperature. These two are opposing effects. Thus at higher temperatures, the membrane performance deterioates while the water flux across the membrane increases. Again one has to optimise.

In an ideal situation, only pure water gets transferred across the membrane. But in reality, a small part of the electrolytes also get transported. To quantify, one uses a term, 'Rejection Level', which indicates the amount of electrolyte left behind in terms of a percentage. Thus, the Rejection Levels of monovalent cations and anions (e.g., sodium, potassium, chloride, fluoride) are about 90-92 percent while those of divalent ions (Ca, Mg, Sulphate) are about 93-95 percent. Most of the membrane have pore sizes around 5 Angstrom units and thickness of about 100 microns.

The earlier type of membranes had a tight but thin surface layer backed up by a thick porous substrate. These are known as asymmetric membranes. The rejection of electrolytes occurs at the thin surface layer and the porous layer acts only as a support. Subsequently thin film composite membranes have been developed and these have helped in reducing the operating pressure. The membranes have been made use of in several geometrical configurations, prominent among them being tubular, spiral wound and hollow fibres. Of these, the later two configurations have found wide application in the water industry. The output of the tubular configuration, which is also bulky, is on the lower side as compared to the other two geometries.

One can conceive the spiral wound geometry as a rolled sandwich. A sheet material that acts as a water carrier is sandwiched between two membrane layers. The three layers are then wound cylindrically over a plastic tube through which the purified water flows out. The plastic tube has perforations on it to allow this to happen. The sandwich layers are seperated by a plastic netting. The membrane configuration is placed in a suitable pressure vessel (cylindrical) made of stainless steel or fibre reinforced plastic. The feed water flows from one end of the pressure vessel to the other and the product (purified water) comes out of the plastic tube along the central axis of the membrane configuration. A good surface to volume ratio is available and is not affected by suspended solids or turbulance.

Another popular configuration is known as the 'Hollow fibre'. As the name implies, extremely thin strands of a hollow membrane, are packed in a U shape in a cylindrical pressure vessel. This configuration bears a close resemblence to nuclear steam generators with a U shape bundle of tubes fixed in a cylindrical vessel. (It may be recalled that the hot primary coolant flows through the U tubes and steam is generated on the shell side). In the hollow fibre RO Unit, the feed water flows around them, while the product water comes out of the fibres. Here again, an excellent ratio of surface to volume is acheived, but the configuration is susceptible to fouling by suspended solids.

While RO is a physical process, water chemistry comes in because of the feed water (raw water). As we saw in the beginning, raw water contains all sorts of impurities and some of these affect the efficiency of RO. It is self-evident that with RO pore sizes in the range of 5 - 10 Angstrom units, suspended material is a serious threat. Suspended solids have to be removed from raw water to the maximum possible extent. In addition to normal clarifying and filtration procedures, the use of a fine 5 micron catridge filter, just before the water enters the RO unit is being advocated. On the chemistry side , calcium salts (bicarbonate and sulphate) pose a serious scaling threat. It was noted earlier that for both calcium and sulphate, the rejection level is very high, being 95 percent, so that they concentrate quickly in the feed side of RO unit. Once the saturation solubility is exceeded, calcium sulphate precipitates out. The counter treatment procedures are essentially the same as discussed under cooling water treatment. To prevent the precipitation of calcium sulphate, the water is dosed with sodium hexa metaphosphate, while the scaling of calcium bicarbonate is prevented by keeping the Langlier Index in the negative range (acid dosing).

Iron and manganese present in raw water have a tendency to get partially oxidised at neutral pH values and the oxidised forms, Fe (III) and Mn (III) might hydrolyse and precipitate. The acid dosing referred to above will be able to overcome this problem.

It is pertinent to point out that the type of chemical treatment noted above is for industrial water (either directly used or fed to a DM plant for further purification). For domestic consumption, the residual chemicals must conform to the tolerances prescribed by WHO for drinking water. Product analysis, before public distribution is therefore an important requirement when RO is used for rural water supply. This would call for the establishment of local chemical testing facilities, based on simple procedures.

The membranes are also subject to biofouling. Once again chlorination of raw water is the only remedy. However, the residual chlorine needs to be removed before the raw water enters the RO unit, as otherwise the membrane will get damaged by chlorine interaction. In this respect cellulose acetate membranes are somewhat better than the polyamide type. On the other hand cellulose acetate membranes are susceticible to hydrolysis, but this is prevented by acid dosing that is done for other reasons mentioned above.

As noted earlier the membrane performance is affected by temperature. While the water flux across the membrane increases with temperature, the membranes deteriorate much quicker. Usually RO operates best at 25°C. One can easily see the limitation it imposes in arid zones, where the daily as well as seasonal fluctuations in temperature are wide.

Economies dictate the utility of a RO unit, when it is coupled to a demineralisation plant for producing high purity water. It is obvious that the capital cost will increase when RO is added. However, it has been shown that operating costs, particularly in terms of the savings effected on regenerant chemicals is such that a break even point can be realised. From a chemical point of view, this break even point is reached when the TDS in the raw water is $\geq$1600mg/l as $CaCO_3$.With marked improvements in membrane performance and technology, this break even point has been reduced to 1100 mg/l expressed as $CaCO_3$. One should bear in mind, not only the cost of regenerant chemicals used in the DM, but also their disposal. In conclusion it can be inferred that RO offers an attractive route for rural water supply and it is also an attractive precourser to a full scale DM plant.

12.1 EFFLUENT TREATMENT AND WATER CONSERVATION

In view of the very large volumes of water employed by industry, it is but natural that attention is paid to two aspects at the back end of any process using such water. Since water is a precious resource, the priority is to conserve it. Another aspect is the treatment to be applied to a stream of industrial effluent or waste water, with due regard to pollution control, before it is discharged into the environment. Apart from legal requirements on the effluent discharges, it is also unethical to discharge such waste water which an unsuspecting public might come into contact with and some times even make use of it, leading to hazardous consequences. Thus industrial effluent or waste water discharge into the environment is as much of a moral issue as one of law and chemistry. The best way is to reclaim as much water as possible even though it may not be of the same quality as the input, for reuse.

Unlike the similarities in the quality of water needed by industry, specially the core industries like power, fertilisers and steel, the effluents generated by an industry are specific to it . As such universally applicable effluent treatment procedures are not avaiable. General techniques such as precipitation, filtration, ion exchange, reverse osmosis and even distillation are made use of to meet the treatment requirements, before the waste water is either discharged into the environment or reused. The tolerance limits of some of the parameters set by the Indian Standards (IS:2490,Part 1,1981), for the discharges to the environment are given in Table 12.1(5).

Table 12.1 Tolerence Limits for Discharge as per Indian Standards (IS: 2490, part 1, 1981)

Constituent/ parameters	Effluent Discharge to Surface	Public sewer	Irrigation
Suspended solids mg/l	100	600	200
Dissolved solids mg/l	2100	2100	2100
pH	5.5 - 9.0	6.5 - 9.0	5.5
Chloride mg/l	1000	1000	600
Sulphate mg/l	1000	1000	1000
Zinc mg/l	5	15	-
Lead mg/l	0.1	1	-
Mercury mg/l	0.01	0.01	-
Ammonical nitrogen	50	50	-
BOD	30	350	100
Oil & grease mg/l	10	20	10
Temperature °C	40	45	-

As mentioned in the begining, large volumes of water are used by industry. The water requirements of some of these, without recycling or reuse are given in Table 12.2(5,6). In the power generation sector, a 210 MW unit consisting of a drum (normal level) with water wall boiler tubes, economiser, superheater and reheater have a water holding capacity of about 320 cubic meters. The full steam water circuit will, of course have a much greater holding capacity.

It has been estimated that in the production of industrial alcohol, viscose rayon, pulp and paper and steel, as much as 50-60 percent of the water can be recovered and recycled.

In this section, a few illustrative examples of effluent treatment in some industries are reviewed.

Table 12.2 Water Requirements for Industrial Operations[5,6]

Industry	Cubic meters of water used per ton of the product
Fertilisers (Ammonia)	
a) Gas based	10
b) Naphtha based	17
c) Fuel oil based	24
d) Coal based	69
Fertilisers (Urea)	6
Petrochemicals (Gasoline)	25
Cement by wet process	12
Chrome leather	32
Industrial alcohol	65
Viscose rayon	160
Pulp and paper	275
Integrated steel plants	150 - 300

It is important to realise, that in power stations, either thermal or nuclear, water is recirculated to a very large extent. If cooling towers are employed for condenser cooling, there will be some loss of water due to evaporation. On the other hand, when river, lake or sea water is used for this purpose, it is directly discharged into a large water body after passing through the condenser. The waste water in power stations could be the boiler blowdown and the cooling tower basin (if it exists) blowdown waters. Simple treatment will make these volumes of water environmentally safe and reusable. For example,the blowdown from boiling water reactors, is purified of its radioactive constituents present at a low level, by ion exchange and effluent is recycled, or discharged into the aqueous environment. The effluents that really need a treatment in a power station are the acidic and alkaline regenerative waste streams coming out of the demineralisation plants. Use of sulphuric acid in place of hydrochloric acid, generally reduces the effluent load. Neutralisation and dilution ponds are available adjacent to the DM plant and usually a treated and neutral effluent water is discharged into the environment. Water conservation is best seen in nuclear power reactors using heavy water as the moderator and coolant. Special instrumentation is available to detect heavy water spills and recovery systems from the ambient atmosphere are installed to recover as much of it as possible. After upgrading, the heavy water is reused. In all nuclear power stations,effulent treatment is one of the important activities, in view of the need for discharging "as low a radioactivity" as possible (ALARA criterion). Reverse Osmosis is finding increasing application in such situations.

In modern fertiliser plants, an integrated approach is adopted for effluent treatment, water conservation and its reuse. The utilisation of chalk which is a by product of the ammonium sulphate production process by Gujarat State Fertiliser Corporation, India is a good example[7]. A slurry of chalk fills a pond known as the chalk pond. The water from this pond is utilised in the phosphoric acid plant for fume scrubbing (which makes it acidic), cooling condensers and other odd jobs. The acidulated effluent is returned to the chalk pond. On the other hand, ammoniacal effluents from ammonia and urea plants are also fed to the chalk pond. Thus the chalk pond serves simulataneously as a neutralisation facility for both acidic and alkaline effluents by using a by product, and functions as a medium for water cycling. Even in making the chalk slurry, contaminated process condensate from an ammonium sulphate plant is used. Of course, this would mean that chalk pond water might contain 1.5 to 2 percent of ammonium sulphate. By making use of this in a phosphoric acid plant, the mineral value could be recovered in the form of diammonium phosphate.

In some plants ammonia and urea bearing effulents are mixed and subjected to thermal hydrolysis at 200°C under pressure with steam. The ammonia and carbon dioxide generated are stripped and recycled, while the treated effluent could be used as make up to the cooling tower. In the steam reformers, where naphtha is cracked, the water coming out of the units contains fine carbon particles. These are collected by using a drum filter and the water is reused.

One of the largest consumers of water per ton of the product is the steel industry, wherein it is used for coke making, scrubbing of blast furnace gases, steel making, rolling etc., in addition to power generation in its captive plant(8). To save on fresh water, saline water is also used (in part) at shore based steel plants. The average percentage distribution of water usage at a shore based plant is given in Table 12.3.

Table 12.3 Water Consumption in a Shore Based Steel Plant(8)

Process	% of the total	Distribution as percent	
		Fresh water	Sea water
Power generation	47.8	10.3	37.5
Blast furnace	14.9	7.1	7.8
Rolling mills	11.6	9.7	1.9
Steel making	8.2	4.3	3.9
Coke making	5.7	3.0	2.7
Sintering	1.1	0.4	0.7
Miscellaneous	10.7	5.7	5.0
Total	100.0	40.5	59.5

Thus, as much as 60 percent of the total water requirement at a shore based steel plant is met by sea water. Consequently material compatibility problems arise that are similar to other situations, where sea water is used. These include corrosion and marine biofouling. The advantage lies in the effluents getting discharged into the sea, where the dilution factor is very high.

In the steel industry, effluents and suspended solids constitute the bulk of pollutants. Chemical and organic contamination is also a common factor in the waste water from tlhe coke oven batteries. The volume and composition of effluents arising out of a coking plant are dependent upon the nature of the coal, the temperature and the process of carbonisation and the recovery of ammonia. A representative range of contaminants from a coke oven plant is given in Table 12.4.

Table 12.4 Chemical Contaminants in the Waste Water from a Coke Oven Plant(8)

Chemical Constituent	Range in mg/l
Free Ammonia as NH_3	20-500
Ammonium compounds as NH_3	100-3000
Chloride as HCl	500-9000
Thiocyanate as CNS	100-600
Thiosulphate as S	100-1000
Chemical oxygen demand	3000

Ammonia is removed from the coke oven gas by contacting it countercurrently with a solution of phosphoric acid in a two stage spray type absorber. The lean solution so produced is recycled into the process. Water washing of the residual gas gives an effluent that is almost free from ammonia. A number of techniques such as ion exchange, electrolysis, adsorption on high surface area, synthetic polymers etc. have been developed to remove the other pollutants, before the water is reused.

Waste waters from organic chemical industries such as refineries, petrochemicals, pesticides, plastics, dye-stuffs etc. require treatment procedures that will effectively destroy the organic contaminants before such waters are reused or discharged into the environment. Among different processes, Wet Air Oxidation (WAO) of the organics has gained favour(8). The process is based on the observation that dissolved or finely dispersed organic compounds in waste water can be hydrolysed and oxidised by bubbling compressed air or high pressure oxygen at elevated temperatures(upto 320°C) and pressures (210 kg/cm^2). There is an induction period, followed by fast oxidation, which slows down with time. The behaviour is typical of a free radical initiated process. WAO is self sustaining at Chemical Oxygen Demand (COD) levels greater than 15 g/l. After oxidation in a reactor (30 to 60 mm) the waste water stream is cooled and depressurised. The efficiency of the process is judged by the percentage reduction acheived in the COD and Total Organic Carbon (TOC) levels of the waste water. A few examples are given in Table 12.5(10).

Table 12.5 Examples of the Efficacy of Wet Air Oxidation(10)

Contaminants in Waste Waters	Efficiency (as percentage) for	
	C O D	T O C
Acrylonitrile	65	-
Amines	-	86
t-Butyl alcohol	-	91
Carbon tetrachloride	-	99
Dye stuffs (composite)	94	94
Epoxy resins	-	86
Formaldehyde	-	97
Herbicides (composite)	79	-
Monoethanol amine	-	88
Pesticides (composite)	97	-
Phenols	97	-
Polythylene	-	90
Polyglycerine	89	83
Sulphides	98	-

An added benefit of WAO is its ability for recovering some inorganic chemicals like sodium carbonate (from black liquor in paper and pulp industry) ammonium sulphate (from coke oven scrub liquids) and chromium (from sludges of glue manufacture).

As noted in Table 12.2, the paper and pulp industry is one of the very large consumers of water per ton of the product. During pulping and bleaching processes, lignin and its degradation products are released which are resistant to biodegradation. A number of chemical processes have been developed to overcome this problem. The chief among them are massive lime treatment (doses ranging from 3000 to 10,000 mg/l of lime) and coagulation with alum and ferric alum. Because of the cost of chemicals specially in the coagulation process, there is a need to explore alternate techniques. A recent process developed in India(11) makes use of the plant's waste cellulosic material as the medium for lignin adsorption under acidic conditions. The acidity which is around a pH of 2 is determined by the zeta potential of the cellulosic fibres. The cellulosic material is suspended in water, which is then acidified (less than pH 2). The lingin containing waste water is then allowed to mix with this. Under these conditions, lignin precipitates out and is adsorbed on the cellulosic matrix, thus freeing the waste water of its contaminants. At an initial COD to fibre ratio of 1, nearly 70 percent reduction has been observed for both COD and colour. Thus the process offers a good alternative to other chemical processes. Wet Air Oxidation can also be adopted to these wastes.

Because of the decreasing availability and increasing cost of water for industrial activities, it is very essential to recycle as much waste water as possible by a proper choice of effluent treatment, which will in addition, considerably reduce the discharge of pollutants into the environment.

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