

Chapter 2

Basic Water Chemistry

2.1 Overview

Before we delve into water conservation, it is useful to have an understanding of the basic concepts in water chemistry and ions commonly found in water.

Water is known as the *universal solvent* due to its power to dissolve virtually all substances to some extent. The key to this phenomenal ability is its *structure*. The water molecule consists of two atoms of hydrogen and one atom of oxygen with a slight positive charge near the hydrogen atoms and a slight negative charge near the oxygen atom. This polarity enables the water to dissolve all ionic and polar substances. Non-polar compounds such as hydrocarbons are insoluble in water.

For this reason *pure water* is not found in nature. It always contains impurities, which impart colour, clarity, taste, smell and feel. The types of impurities found in water and wastewater can be divided into four groups: dissolved, physical, microbial and radiological (Table 2.1).

Impurities in natural waters depend on the source of water. Wells and spring waters are classed as *ground water* while rivers and lakes are known as *surface waters*.

Ground water picks up impurities as it seeps through the rock strata, dissolving some parts of (or almost all) it makes contacts with. However, the natural filtering effect of rock and sand usually keeps water free of suspended matter.

Wastewater may contain a myriad of substances depending on the source and can range from inorganic to organic substances. For example, effluent from food processes have high levels of organic matter, and leachate from landfills contains organic substances, ammonia as well as heavy metals.

Solubility principles, some common substances found in commercial and industrial water systems, and water-quality guidelines are discussed below. It is by no means a complete list; however, it gives the reader an appreciation for the types of contaminants and their impacts on water systems.

Table 2.1 Types of impurities found in Water

Types of impurities	Examples
<i>Dissolved</i>	
Positive ions (cations)	Calcium, magnesium, sodium
Negative ions (anions)	Carbonate, bicarbonate, phosphate, chloride, cyanide, nitrate
Disinfectants	Chlorine
Heavy metals	Copper, nickel, chromium, lead, mercury
Gases	Oxygen, carbon dioxide, ammonia, hydrogen sulphide
<i>Physical</i>	
Colour	Dissolved organic matter, iron, manganese, dyes, algae
Taste and odour	Geosmin, sulphide, chlorine
Appearance	Silt-suspended solids, plankton, oil fats, petroleum hydrocarbons
<i>Microbial</i>	
Bacteria	<i>E. Coli</i> , <i>Campylobacter</i> , <i>Legionella</i>
Viruses	Adenovirus, Reovirus, Hepatitis A
Protozoa	<i>Cryptosporidium</i> , <i>Giardia</i>
Other	Cyanobacteria (blue-green algae)
<i>Radiological</i>	
Naturally occurring	Radium, uranium

2.2 Solubility Principles

The solubility of a substance in water is a function of

- temperature
- pressure
- pH
- redox potential and
- the relative concentrations of other substances in solution.

In a natural environment these variables are related in such a complex manner that exact solubilities cannot always be predicted. However, some general rules can be formulated.

Common dissolved substances can be segregated into gases and minerals. Dissolved gases are primarily oxygen and carbon dioxide. Sometimes ammonia will be present in certain wastewaters. Ground water may contain hydrogen sulphide gas. Their concentrations are typically expressed in milligrams/litre (mg/L) or in parts per million (ppm).

2.3 Common Substances Found in Water

2.3.1 pH

Water molecules ionise into H^+ and OH^- . The concentrations of these ions are very small. The concentration at room temperature is 1×10^{-7} grams

of per litre or one part of hydrogen ion to 10 million parts of water. This concentration can also be expressed as

$$\text{pH} = -\text{Log} [\text{H}^+] = -\text{Log} (1 \times 10^{-7}) = 7 \quad (1)$$

The pH of 7 is considered neutral. A pH between 0.0 and 7 is acidic. A pH between 7 and 14 is basic. Strong acids have a pH of 1, which means one part H^+ ion in 10 parts of water. A change in pH to 2 is a tenfold decrease in H^+ concentration, which equates to one part H^+ in every 100 parts of water. This simple concept is important in understanding the changes ionic substances have on water.

The majority of living organisms operate at a pH of 7 and natural water has a pH between 6.5 and 9.5. Drinking-water guidelines generally specify a pH of 6.5–8.5. Seawater has a pH close to 8 and acidic hot spring water has a pH of 1.8. The normal pH for irrigation water is 6.5–8.4. Dissolved substances, temperature, microbial activity, however, can change this balance. Figure 2.1 shows these pH ranges for the different types of water.

pH has a strong influence on

- corrosion of metals
- concrete and other infrastructure
- scaling potential inside pipes
- heat exchangers or boiler tubes and
- the mobility of metal ions.

Generally $\text{pH} < 6$ is corrosive to metal piping and $\text{pH} > 8$ may cause scaling (due to precipitation of calcium and other metal ions with anions such as carbonates, phosphates and sulphates). These effects can be magnified in the presence of dissolved gases and ions. For this reason, many industrial water systems are generally controlled between a pH range of 7 and 10 including trade waste discharges to the sewer.

Only a few ions such as sodium (Na^+), potassium (K^+), nitrate (NO_3^-) and chloride (Cl^-) remain in solution through the entire range of pH values found in water.

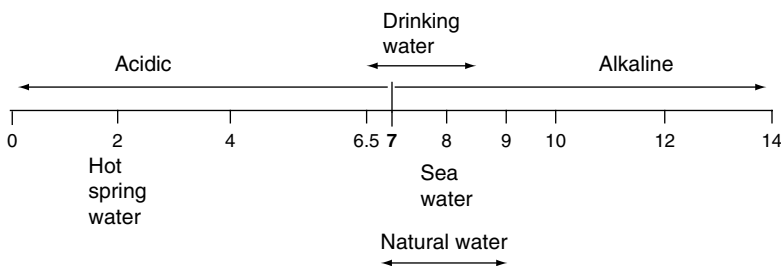


Figure 2.1 pH scale

2.3.2 Dissolved Gases

The dissolved gases of interest to the water chemist are carbon dioxide, oxygen, ammonia and hydrogen sulphide. These gases are discussed below.

2.3.2.1 Carbon dioxide and Alkalinity

The atmosphere contains 78% Nitrogen (N₂), 21% Oxygen (O₂) and 0.033% Carbon dioxide (CO₂).

Despite the low concentration of CO₂ in the atmosphere, due to its higher solubility (about 30 times that of oxygen), it plays a major role in water chemistry.

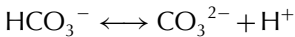
Alkalinity is a measure of the buffering capacity of water or the capacity of bases such as carbonates to neutralise acids.

CO₂ dissolves in water to form carbonic acid (H₂CO₃) decreasing the pH and increasing the acidity of the water. As such, at a pH of 4.2–4.5 and below, all CO₂ is in the form of H₂CO₃ and no alkalinity is present. Above pH of 4.5, H₂CO₃ is present in the form of bicarbonates (HCO₃⁻) and carbonates (CO₃²⁻). These reactions are shown below.



At a pH greater than 4.5, alkalinity is a combination of H₂CO₃ and HCO₃⁻. As the pH increases, the HCO₃⁻ ion becomes the dominant ion.

At pH greater than 8.2–8.4 there is no more free CO₂ gas left – and all alkalinity is in the form of HCO₃⁻ ion and the more alkaline CO₃²⁻ ion.



At pH greater than 9.6, no HCO₃⁻ is present and all alkalinity is in the form of the CO₃²⁻ ion. Further increases in pH results in hydroxyl ions also appearing and therefore hydroxyl alkalinity can be measured above pH of 9.6.

The total alkalinity of water = $\sum \text{HCO}_3^- + \text{CO}_3^{2-} + \text{OH}^-$ concentrations.

Table 2.2 and Figure 2.2 shows how the pH of a solution dictates the form of alkalinity that will be dominant in the solution.

This remarkable ability of CO₂ to exist in many forms gives the water its unique buffering capacity. In a buffer solution, the pH varies only marginally with the addition or removal of H⁺. Waters with low alkalinity are very

Table 2.2 Forms of alkalinity

pH	H ₂ CO ₃ /CO ₂ gas	HCO ₃ ⁻	CO ₃ ²⁻
<4.2–4.5	dominant	absent	absent
4.3–8.3	present	dominant	absent
>8.3	absent	present	dominant
>9.6	absent	absent	dominant

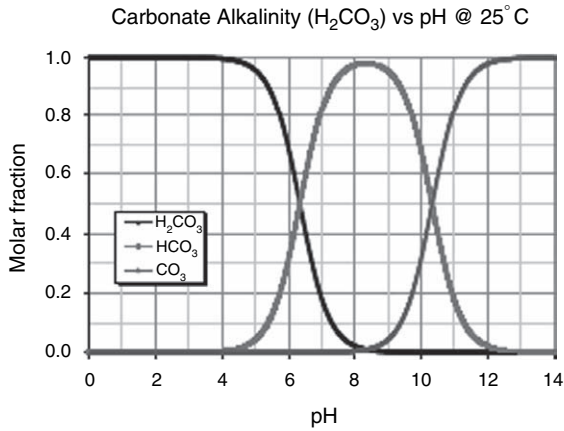


Figure 2.2 Alkalinity and pH relationship

susceptible to changes in pH. Waters with high alkalinity are able to resist major shifts in pH. High alkalinity is also desirable in boiler water to minimise steel corrosion and scaling of some ions.

Measurement of alkalinity is done by titration. Titrations for alkalinity can also include other ions such as borates, phosphates and silicates and other organic substances. It is customary to express alkalinity as mg/L CaCO_3 .

2.3.2.2 Oxygen (O_2)

While oxygen is required for living organisms, it is the principal corrosive in water systems. It causes pitting corrosion, a form of localised corrosion which leads to rapid failures of pipes and heat exchangers. Solubility of oxygen in water is a function of temperature and pressure. This property is used to remove oxygen in steam systems.

Refer to Chapters 5 and 7 for more details.

2.3.2.3 Ammonia (NH_3)

At high pH, ammonia is present as NH_3 gas. At low and neutral pH, ammonia is found as the ammonium ion (NH_4^+). Natural levels of ammonia in surface water and ground water are usually below 0.2 mg/L [1]. Above 1.0 mg/L, ammonia becomes objectionable in drinking water. In raw sewage, ammonia concentrations are in excess of 10 mg/L. For this reason, the presence of ammonia in water is a possible indication of bacterial, sewage and animal waste pollution. Ammonia in industrial water systems is present as the ammonium ion, or as organic nitrogen in industrial effluent such as landfill leachate, petrochemical plants, food processing plants and in steam condensate systems. It is corrosive to copper and its alloys. NH_3 in the presence of oxygen contributes to accelerated corrosion of copper alloys – even as little as 0.2 mg/L can cause corrosion of admiralty (70/30 Cu/Zn) heat exchangers.

2.3.2.4 Hydrogen Sulphide (H_2S)

The presence of hydrogen sulphide gas is detected by its *rotten egg* smell with a threshold odour level of 0.005–0.025 mg/L [2]. At concentrations of 3–5 mg/L it is considered to be offensive. It is a highly toxic gas which overwhelms the sense of smell (loss of smell occurs at 100–150 mg/L) and go onto overcome the victim and cause death. Found in some well, marshy and wastewaters it is readily oxidised to the elemental sulphur.

2.3.3 Dissolved Ions

Fresh water always contains dissolved ions, which come from the dissolution of minerals such as limestone, magnesite, gypsum and decaying plant materials. The most common ions found in water are given in Table 2.3.

To a lesser extent other cations are present such as

- Iron (Fe^{2+} and Fe^{3+})
- Manganese (Mn^{2+})
- Aluminium (Al^{3+})
- Ammonium (NH_4^+) and
- Copper (Cu^{2+}).

Less common anions are

- Carbonates (CO_3^{2-})
- Hydroxide (OH^-)
- Sulphides (S^{2-}) and
- Phosphates (PO_4^{3-})
- Silicate (SiO_4^{2-}).

2.3.3.1 Conductivity and Total Dissolved Solids

Conductivity is a measurement of the ability of water to conduct electricity due to salts present in water. The higher the dissolved salts content of the water, the higher its conductivity. Monovalent salts have a higher conductivity than divalent salts. Organic compounds like oil, phenol, alcohol and sugar are not ionized in water and therefore have a low conductivity. Conductivity is measured in micro Siemens per centimetre ($\mu S/cm$). Distilled water has conductivity in the range of 0.5–3 $\mu S/cm$. Good-quality drinking water has a conductivity less than 700–800 $\mu S/cm$, [1, 3] whilst animals such as sheep can tolerate

Table 2.3 Common ions found in water

Cations (positively charged ions)	Anions (negatively charged ions)
Calcium (Ca^{2+})	Chlorides (Cl^-)
Magnesium (Mg^{2+})	Bicarbonates (HCO_3^-)
Sodium (Na^+)	Sulphate (SO_4^{2-})
Potassium (K^+)	Nitrates (NO_3^-)

Table 2.4 Comparison of drinking water and mine water to Australian Drinking Water Guidelines (NHMRC) maximum limits

Test description	NHMRC Guidelines	Drinking water Sydney	Mine water
pH	6.5–8.5	7.5–8.9	7.4
Total dissolved salts	500	61–130	8100
Colour (True)	15	<3	
Turbidity	5	0.1–0.5	
Total hardness as CaCO ₃	200	40–68	917
Aluminium as Al	0.2	<0.05	
Ammonia as NH ₃	0.5	0.01–0.45	0
Arsenic as As	0.007	nd*	0.054
Cadmium as Cd	0.002	nd*	0.001
Chloride as Cl	250	15–90	1400
Chromium (VI) as Cr	0.05	nd*	0.3
Copper as Cu	1	0.002–0.25	0.003
Cyanide as CN	0.08	nd*	nd
Fluoride	1.5	0.9–1.2	
Iron as Fe	0.3	0.01–0.09	10
Lead as Pb	0.01	nd*	0.004
Magnesium as Mg	na**	1.5–6.2	120
Manganese as Mn	0.1	0.001–0.005	0.35
Mercury as Hg	0.001	nd*	<0.001
Nitrate as NO ₃	50	0.04–5.6	10
Nitrite as NO ₂	3	<0.003–0.5	nd
Selenium as Se	0.01	nd*	0.017
Silver as Ag	0.1	nd*	nd
Sodium as Na	180	4–53	1600
Sulfate as SO ₄	250	1–20	430
Zinc as Zn	3	<0.008	0.007
Organic compounds	Various	nd*	1500
Free chlorine	5	0.1–1.2	nd
Disinfection by products (trihalomethane)	0.25	0.02–0.11	nd

NB: All units expressed as mg/L or otherwise stated. pH, colour and turbidity are expressed as units, Hazen units and as nephelometric units respectively.

* nd – none detected

** nd – no health or aesthetic value in guideline

higher conductivities up to 16 500 $\mu\text{S}/\text{cm}$. Table 2.4 shows the National Health & Medical Research Council's Australian Drinking Water Guidelines (NHMRC) compared to drinking water quality in Sydney and mine water.

Certain well waters and brackish water (intrusion of sea water into low conductivity water) has a conductivity of 10 000–23 000 $\mu\text{S}/\text{cm}$. Seawater has a conductivity of 50 000 $\mu\text{S}/\text{cm}$ or more.

Conductivity of industrial effluent such as landfill leachate can be as high as 14 000 $\mu\text{S}/\text{cm}$. On the other hand, water suitable for use in the electronics and microelectronics industry for purposes such as the washing and rinsing of semiconductor components in cleaning and etching operations require extremely high purity water and for this reason is expressed as resistivity

megaohm-cm. It is the inverse of conductivity. A Ultrapure water (type E-1) has a resistivity of 18 megaohm-cm. The dissolved contaminants are measured in $\mu\text{g/L}$ or ng/L (parts per billion or trillion). Thermal power plants too require high-quality water in their high-pressure steam systems (Chapter 7 discusses steam system water-quality requirements).

The relationship of conductivity and total dissolved solids (TDS) is given below:

$\text{TDS} = 0.55 - 0.8 \times \text{conductivity}$. The average is 0.64.

Other units of expressing TDS are given in Table 2.5.

The dissolved solids content of water can adversely impact plants ability to absorb water from the soil. Most plants cannot tolerate conductivities in excess of $2300 \mu\text{S/cm}$. Table 2.6 shows guidelines for salinity of irrigation water [4].

Some common salts and ions that contribute to dissolved solids are discussed below.

2.3.3.2 Hardness, Calcium and Magnesium

Calcium (Ca^{2+}) and magnesium (Mg^{2+}) give water its *hardness*. Hard water is difficult to lather and therefore *hardness* is a measure of Ca^{2+} and Mg^{2+} ions. Calcium typically accounts for two-thirds of total hardness in surface water and is usually in the range of 2–200 mg/L as Ca. Sea water may contain as much as 400 mg/L as Ca [1]. The typical concentration for Mg^{2+} in surface water is about 10–50 mg/L as Mg. However, in well and in sea water Mg^{2+} can be about four to five times that of Ca^{2+} . Hardness is typically expressed as mg/L CaCO_3 . Most common Ca^{2+} and Mg^{2+} salts are bicarbonates, sulphates, chlorides and nitrates. Other alkaline earth elements of this group of interest are barium and strontium. Typically barium is found in some well waters with typical concentrations between 0.05 and 0.2 mg/L. Strontium is found in certain well waters. Typical concentrations are less than 15 mg/L.

Salts of Ca^{2+} and Mg^{2+} (except for Cl^- , NO_3^- , HCO_3^-) are sparingly soluble or insoluble in water. The solubility product (K_{sp}) of a substance shows the solubility of a given substance in water and is a constant. The higher the K_{sp} of a substance the greater its solubility in water. The K_{sp} for

Table 2.5 Common conversion factors for expressing total dissolved solids

Unit	To convert	Multiply by	To obtain
Conductivity	$\mu\text{S/cm}$ (microS/cm) or $\mu\text{mho/cm}$		
	(when $<5000 \mu\text{S/cm}$) (when $>15000 \mu\text{S/cm}$)	0.64 0.8	mg/L mg/L
TDS	mg/L	1	ppm
Water salinity	deciSiemens/metre (dS/m) or millimho/cm	1000	$\mu\text{S/cm}$ or $\mu\text{mho/cm}$

Table 2.6 Guidelines for salinity of irrigation water

Class	Comment	Electrical conductivity $\mu\text{S/cm}$	Total dissolved solids mg/L
1	<i>Low-salinity.</i> Water can be used with most crops on most soils with little likelihood that a salinity problem will develop.	0–280	0–175
2	<i>Medium-salinity.</i> Water can be used if moderate leaching occurs. Plants with medium salt tolerance can be grown, usually without special control for salinity control. Special care needs to be taken when irrigating salt-sensitive crops with sprinkler.	280–800	175–500
3	<i>High salinity.</i> Water that cannot be used on soils with restricted drainage. Special considerations required even with adequate drainage.	800–2,300	500–1,500
4	<i>Very high salinity.</i> Water not suitable for irrigation water under ordinary conditions. Soil must be permeable and salt-tolerant crops must be selected.	2,300–5,500	1,500–3,500
5	<i>Extremely high salinity.</i> Water may be used only on permeable, well-drained soils with good management practices.	>5,500	>3,500

Adapted from Agriculture and Resource Management Council of Australia and New Zealand. *Guidelines for Sewerage Systems – Reclaimed Water*. February 2000.

CaCO_3 is 4.8×10^{-9} , indicating that it is not very soluble in water when compared to a K_{sp} 36 for common salt (NaCl). When the concentration of CaCO_3 exceeds its solubility product, K_{sp} limit, it precipitates. This is shown by

$$[\text{Ca}^{2+}] \times [\text{CO}_3^{2-}] > K_{\text{sp}}[\text{CaCO}_3] > 4.8 \times 10^{-9}$$

As Table 2.7 shows there are less soluble substances than CaCO_3

The Ca^{2+} and Mg^{2+} ions react with various anions such as SO_4^{2-} , CO_3^{2-} and PO_4^{3-} to form scale in various applications such as on reverse osmosis membranes, boiler tubes and in cooling water heat exchangers. The greater the hardness of water, the greater the scaling potential of the water as shown in Table 2.8.

Build up of scale reduces heat transfer in heat exchangers, boiler tubes and other heat transfer equipment leading to production losses and more frequent turnarounds. For example, in a water tube boiler, a scale thickness of 0.8 mm (1/32 in.) can result in heat loss of 8% and increased fuel consumption of 2%.

Another characteristic of these salts is that unlike most water-soluble salts they have an inverse relationship with temperature. Salts such as sodium

Table 2.7 Solubility products for some common scalants at 20° C

Salt	Formula	Solubility product, K_s
Calcium sulphate	CaSO_4	2.3×10^{-4}
Magnesium carbonate	Mg CO_3	1.0×10^{-5}
Calcium hydroxide	Ca(OH)_2	8.0×10^{-6}
Calcium hydrogen phosphate	CaHPO_4	2.0×10^{-7}
Calcium carbonate	CaCO_3	4.8×10^{-9}
Barium sulphate	BaSO_4	9.2×10^{-11}
Calcium fluoride	CaF_2	3.2×10^{-11}
Magnesium hydroxide	Mg(OH)_2	3.4×10^{-11}
Manganese hydroxide	Mn(OH)_2	4.0×10^{-14}
Manganese sulphide	MnS	1.4×10^{-15}
Ferrous hydroxide	Fe(OH)_2	4.8×10^{-16}
Ferrous sulphide	FeS	4.0×10^{-19}
Aluminium hydroxide	Al(OH)_3	8.5×10^{-23}
Ferric hydroxide	Fe(OH)_3	3.8×10^{-38}

Adapted from Judd S. and Jefferson B. *Membranes for Industrial Recovery and Reuse*. 2003 [5].

Table 2.8 Relationship between hardness and scaling potential of water [3]

Hardness as mg/L CaCO_3	Description
<60	Soft but possibly corrosive
60–200	Good quality
200–500	Increasing scaling problems
>500	Severe scaling

chloride (NaCl) increase in solubility with temperature. CaCO_3 solubility, however, decreases with a rise in temperature. This decreasing solubility with an increase in temperature is the reason for scale formation on the hottest surfaces of heat exchangers or boiler tubes.

In cooling water or boiler water analyses, expressing ions as CaCO_3 is particularly useful.

To convert an ion into the CaCO_3 form:

$$\text{Ion as CaCO}_3 \text{ mg/L} = \frac{\text{Concentration of M}^n \text{ mg/L} \times 50}{\text{Equivalent weight of M}^n}$$

where

50 – Equivalent weight of CaCO_3

M^{n+} – represents any ion (cation or anion).

Example 1

Calculate the total hardness in mg/L CaCO₃ for a solution with the following cation concentrations shown in Table 2.9

$$\text{Ca}^{2+} \text{ (CaCO}_3\text{ mg/L)} = 80 \times 50/20 = 200$$

$$\text{Mg}^{2+} \text{ (CaCO}_3\text{ mg/L)} = 35 \times 50/12.2 = 143.4$$

The total hardness of the solution = 200 + 143.3 = 343.4 mg/L CaCO₃.

Another useful conversion is that from mg/L to milliequivalent per litre (meq/L). This is derived at by dividing the concentration by the equivalent weight of the ion or substance.

$$\text{Milliequivalent/L} = \frac{\text{Concentration of ion in mg/L}}{\text{Equivalent weight of ion or substance}}$$

where the equivalent weight = atomic weight/valency

Worked example

Convert 100 mg/L of Ca²⁺ to meq/L. The atomic weight is 40 and valency is 2.

To convert 100 mg/L to milliequivalent/L = 100/20 = 20 meq/L.

2.3.3.3 Chlorides

Chloride (Cl⁻) is highly soluble and for this reason is a common constituent of water. In drinking water, Cl⁻ becomes noticeable above 200 mg/L [1] and the World Health Organisation recommended upper limit in drinking water is 250 mg/L. Cl⁻ ions accelerate corrosion of metals especially stainless steel even at concentrations as low as 50 mg/L. To mitigate against the possibility of stress corrosion cracking of austenitic stainless steels, limits are put on Cl⁻ concentrations. For type 304 stainless steel at temperatures below 60° C, the Cl⁻ concentrations are limited to 200 mg/L [6] and for type 316–1000 mg/L. Generally the more susceptible a metal is to general corrosion; the less susceptible it is to Cl⁻ attack [7].

Cl⁻ also impact on salt-sensitive plants especially with sprinkler irrigation. Generally a Cl⁻ concentration less than 70 mg/L is safe for all plants and concentrations above 350 mg/L can cause severe problems [8].

Table 2.9 Cation concentrations

Cation	Concentration mg/L	Molecular weight (MW)	Valency (V)	Equivalent weight = MW/V
Ca ²⁺	80	40	2	20
Mg ²⁺	35	24.3	2	12.2

A related ion is fluoride ions. Normally injected to municipal water supplies at 2.5 mg/L, fluoride levels in excess of 5 mg/L can cause mottling of teeth.

2.3.3.4 *Sodium*

Sodium (Na^+) salts are highly soluble and do not cause scaling but cause corrosion of metals and at high concentrations reduce the clay-bearing soil's permeability as well as affecting the soil structure. Sodium has the capacity to disperse clay particles thus making the soil more prone to crusting and reducing its permeability. The sodium adsorption ratio (SAR) shows the degree of sodium adsorption by a soil from a given water and is expressed as:

$$\text{SAR} = \frac{\text{Na}^+ \text{ meq/L}}{\sqrt{[(\text{Ca}^{2+} \text{ meq/L} + \text{Mg}^{2+} \text{ meq/L})/2]}}$$

Water with SAR values greater than 18 is unsuitable for continuous irrigation [8].

2.3.3.5 *Iron*

Although less common than Ca^{2+} and Mg^{2+} , Iron (Fe) occurs naturally in water, usually at <1 mg/L, but can be as high as 100 mg/L [3] in oxygen-depleted well water especially below a pH of 7. Above 0.3 mg/L iron imparts a metallic taste to water and for this reason drinking water is limited to a maximum of 0.3 mg/L.

High concentrations of iron

- stains laundry and fittings in toilets
- forms deposits and corrosion in pipes, boilers and cooling systems and
- causes odours.

Iron exists in two forms. The water-soluble form is known as ferrous (Fe^{2+}). In non-aerated well waters, Fe^{2+} behaves much like Ca^{2+} and Mg^{2+} in that it can be removed by ion exchange or through precipitation. Upon aeration the Fe^{2+} gets converted to the more insoluble ferric (Fe^{3+}) form. Being colloidal in nature, Fe^{3+} in concentrations as little as 0.05 mg/L iron can cause fouling in paper mills, ion exchange resins and front end of reverse osmosis (RO) membrane systems.

2.3.3.6 *Manganese*

Manganese (Mn) is a water contaminant present in both well and surface waters with levels up to 3 mg/L. Like iron Mn also imparts a metallic taste to water. It is present in organic complexes in surface waters. Like Fe it is soluble in oxygen-free water. Upon exposure to air forms black deposits (MnO_2). It creates stains with concentrations in excess of 0.1 mg/L [3]. The limit for drinking water is 0.05 mg/L. Similarly in RO membrane systems it is controlled below 0.05 mg/L in the feed water.

Manganese also causes pitting corrosion of stainless steel. In beverage and food processing industry, Mn can impair taste and promote chemical deterioration of products [9].

2.3.3.7 Silica

Silicon is the second most abundant element on the surface of the Earth. Most common is silica (SiO_2), ranging from 1 to 100 mg/L in natural waters. Higher concentrations are found in waters with significant volcanic activity. The *total silica* levels are comprised of *reactive silica* and *unreactive silica*.

Reactive silica (silicates SiO_4) is dissolved silica that is slightly ionised and has not been polymerised into a long chain. Silicate scale is formed when soluble silica reacts with Ca^{2+} and Mg^{2+} to form various complex silicates at high temperatures. For this reason silica concentrations are controlled below 150 mg/L in cooling water systems. In boiler water, silica concentrations are a function of pressure.

Unreactive silica is polymerised (or colloidal silica), acts more like a solid than a dissolved ion. In steam systems, silica as SiO_2 forms glassy deposits on steam turbine blades. In RO membrane plants colloidal silica causes fouling of the front end of the membrane elements.

2.3.3.8 Phosphate

Phosphate (PO_4^{3-}) is found in domestic and industrial wastewaters. PO_4 contributes to algal blooms and for this reason most modern laundry formulations do not contain phosphate. In industry, PO_4 are used in cooling water, boiler water treatment and in the metal finishing industry. In high concentrations, PO_4 forms calcium phosphate scale.

2.3.3.9 Nitrate

Nitrate (NO_3^-) ions are highly soluble and are present as a result of the nitrogen cycle. Found naturally, high concentrations are an indication of biological decomposition of organic waste or due to agricultural runoff. The recommended drinking water limit for NO_3^- is 44–100 mg/L as NO_3^- . To express NO_3^- as nitrogen (N), divide the NO_3^- concentration by 4.43.

2.3.3.10 Boron

Boron in freshwater is normally present at concentrations of 0.1 mg/L and in sea water it is found at concentrations of 5 mg/L. In recycled water (from laundry detergents containing perborate formulations) and industrial run off, boron is present at much higher concentrations. It is essential to plants at low concentrations but toxic at high concentrations as much as 0.75 mg/L for onions and peach [8].

2.3.3.11 Cyanide

Cyanide (CN^-) is found in many industrial wastewater streams such as in plating, metal cleaning, is a by product of coke oven gas processes and used in gold-mining applications. As the acid HCN it is highly toxic.

2.3.4 *Suspended Solids and Turbidity*

Suspended solids are referred to as suspended and colloidal sediment matter or coarse particles. These solids settle out of standing water. The concentration of suspended solids in water is determined by passing a known quantity of water through a $0.45\text{-}\mu$ membrane filter and determining the weight of solids collected on the filter. The weight of solids collected divided by the quantity of water passed through the filter gives the suspended solids concentration in mg/L.

Suspended solids contribute to the fouling of process and heat transfer equipment. Suspended solids can harbour micro-organisms which can result in health-related risks as well as corrosion of materials known as microbiologically influenced corrosion.

Turbidity is a measure of the cloudiness of water. It is an indirect measurement of suspended solids. The cloudy appearance is caused by the scattering and absorption of light by these particles. Turbidity cannot be directly correlated with suspended solids concentrations since the light scattering properties of suspended matter vary, and turbidity measurements only show the relative resistance to light scattering not an absolute measurement of concentration of suspended matter. Low turbidity concentrations are commonly expressed as Nephelometric Turbidity Units (NTU). It measures the intensity of light scattered at 90° as a beam of light passes through a water sample. Clear water has a value of 1 NTU. Slightly muddy water has NTU of 5. The drinking water standard for turbidity is below 5 NTU. Turbidity in excess of 1 NTU may shield some micro-organisms from disinfection. Steam systems also require water with very low turbidity.

Other units of turbidity are Jackson Turbidity Units (JTU) and Formazin Turbidity Units (FTU). They are not correlated.

2.3.5 *Colour*

The colour of natural water is influenced by decaying organic matter such as tannins, lignin, iron or manganese salts. Dye house or paper mill effluent frequently gives rise to coloured water. Colour due to organic substances such as fulvic and humic acid poison ion exchange resins in steam systems and causes brightness problems in the paper industry. Colour is typically measured as Hazen units (HU) or in Pt/Co units. 1 Pt/Co unit is equal to 1 Hazen unit. Drinking water standards have adopted the Hazen unit and 10 Hazen units are barely noticeable in a glass of water. The limit for drinking water is less than 15 HU [1, 3, 10].

Natural waters range from <5 in very clear waters to 1200 mg/L Pt in dark, peaty waters [10]. For true colour measurement the water samples need to be filtered using a 0.45- μ filter to eliminate the light-scattering effect of suspended solids.

2.3.6 Organics in Water

Organics are found in freshwater and wastewater systems. These can be categorised as soluble organics, which include natural and synthetic organic chemicals. Most naturally occurring organic matter are negatively charged colloids and will be degraded by the action of micro-organisms. Some man-made organics do not degrade naturally; these are known as bio-refractory compounds and for this reason regulatory agencies strictly limit their discharge. Examples are aromatic and chlorinated hydrocarbons and dioxins from paper mill effluent.

Organic concentrations are typically expressed as biochemical oxygen demand (BOD) or chemical oxygen demand (COD).

2.3.6.1 Biochemical Oxygen Demand

Biochemical oxygen demand (BOD) is the amount of oxygen in mg/L used by micro-organisms to consume biodegradable organics in wastewater under aerobic conditions over a 5-day period at a temperature of 20°C. The 5-day test equates to 2/3 of the total BOD demand. Regulatory authorities require that BOD be below 10 mg/L for most reuse applications.

2.3.6.2 Chemical Oxygen Demand

Chemical oxygen demand (COD) measures the total organic content that can be oxidised by potassium dichromate ($K_2Cr_2O_7$) in a sulphuric acid solution. Some organic substances such as aromatic hydrocarbons and pyridines are not oxidised by the COD test under any circumstances. Nitrogen compounds are also not oxidisable. Therefore this test may give falsely low readings where these substances are present. The attractiveness of COD over BOD is that it can be carried out in three hours rather than 5 days. However, the main limitation of COD is that it does not reveal whether the organic matter is biodegradable or non-biodegradable. Bio-refractory compounds need to be treated using physical and chemical methods rather than biological methods. The COD also includes inorganic oxidisable compounds.

The ratio of BOD/COD can be used to assess the biodegradability of organic compounds. For example, for municipal sewage the BOD/COD approximates to 0.68. Generally if the BOD/COD is greater than 0.4, then the substance is readily biodegradable.

Another common term used is 'total organic carbon' (TOC). The TOC is a non-specific test that measures the amount of carbon bound in organic material. All of the organics are oxidised to carbon dioxide and water.

Organics contribute to the effluent load of wastewater streams and is covered in Chapter 8. Organics also contribute to foaming in boilers and corrosion of steam piping. In cooling-water systems it serves as nutrients for micro-organisms.

2.3.7 Micro-organisms

Micro-organisms can be classified into two categories. First, those that pose a threat to human health (pathogens) and secondly, those which contribute to fouling and corrosion of equipment (but are non-pathogenic).

The most common human microbial pathogens found in water are enteric in origin. That means that enteric pathogens enter the environment in the faeces of infected hosts and therefore these are commonly found in sewage-contaminated water. Enteric pathogens can be viruses, bacteria, protozoa and Helminths. There are other pathogens that are not related to sewage contamination such as *Legionella* sp. *Legionella Pneumophila* bacteria found in cooling water systems is responsible for a type of pneumonia known as Legionnaires' disease.

2.3.7.1 Viruses

Viruses are the smallest of the pathogens found in water with diameters ranging from 20 nanometers ($\text{nm} = 10^{-9}$ meters) to 85 nm [11]. In comparison a human red blood cell averages 7600 nm in diameter. The viruses associated with faeces are known as enteric viruses and are more than 100 entities. They can cause poliomyelitis, hepatitis and gastroenteritis to name a few diseases. The infectious dose can be as low as 10 viral particles or less. Many viruses are resistant to standard methods of disinfection. Viruses that infect bacterial cells are called bacteriophages. Bacteriophages are more abundant in wastewaters than viruses and for this reason the presence of bacteriophages are used as a proxy for virus concentrations with the results available in 5 days.

2.3.7.2 Bacteria

Bacteria are the most common and numerous of the microbial organisms in water. They can be pathogenic such as *Shigella dysenteriae*, *Campylobacter jejuni* and *Salmonella* or non-pathogenic such as *Pseudomonas*. Infectious dose can vary from as low as a few hundred cells for *Shigella dysenteriae*, *Campylobacter* to greater than a million in the case of other bacteria. *Salmonella* and *Campylobacter* bacteria are responsible for causing much of the food poisoning in the world. Figure 2.3 shows a scanning electron micrograph of *Salmonella* bacteria invading cultured human cells.

The presence of indicator organisms such as *E. coli* sp. or thermotolerant coliforms and/or total coliforms in drinking water indicates its faecal contamination. In cooling water systems, apart from the health risks caused by *Legionella*, bacteria such as *Pseudomonas* causes fouling and acts as biofilm

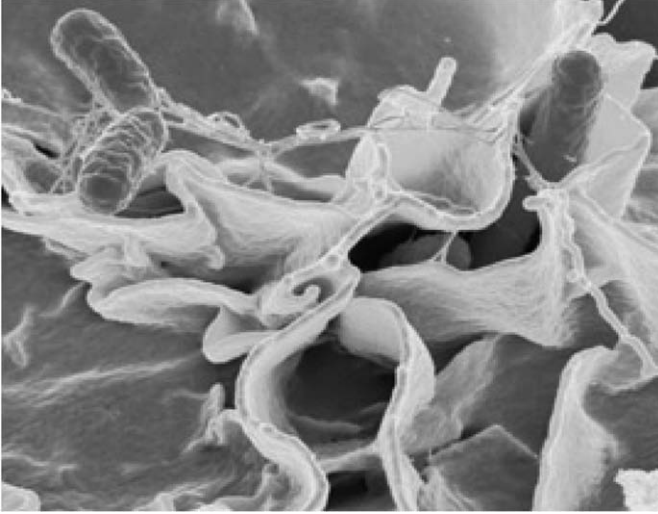


Figure 2.3 Scanning electron micrograph of Salmonella bacteria

Courtesy of Illinois department of Public Health.

for under deposit corrosion to occur. For this reason, total bacterial counts are closely monitored to minimise fouling. Bacteria that cause corrosion of metals are referred to as ‘microbiologically influenced corrosion’ (MIC). Both Sulphate Reducing Bacteria (SRB) such as *Desulfovibrio* sp. and *Clostridium* sp. belong to the MIC group. The SRB uses the conversion of iron-to-iron oxide to create energy. *Clostridium* sp. excretes hydrogen ions, which react with water to form strong organic acids. The common result is pits in the surface of the metal that are hidden under tubercles of iron oxide. Colonies can attack all types of ferrous metals including iron, mild steel, galvanised and stainless steel.

There are, however, beneficial uses of micro-organisms in sewage and industrial wastewater treatment plants. For example, bacteria can break down steel mill coke ovens gas contaminants such as cyanide, phenols and thiocyanate to undetectable levels.

Finally, floc-forming bacteria metabolise organic compounds in biological wastewater treatment plants. These aspects are discussed in Chapter 8.

Bacterial colonies are quantified as ‘Colony Forming Units’ (CFU/mL). It is a measure of the total viable plate count of the bacterial population.

2.3.7.3 Protozoa

These are unicellular organisms. Amoeba is the best example of this class of organisms. In water, wastewater systems organisms of interest are enteric pathogenic protozoa such as *Entamoeba histolytica*, *Giardia intestinalis* and *Cryptosporidium parvum*. All human protozoans are more infectious than

the pathogenic bacteria. They are associated with faecal runoff. Filters with pore sizes smaller than 1 μm remove the oocysts.

2.3.7.4 *Algae*

These are both unicellular and multicellular organisms comprising of bacteria (blue green algae) and plants without roots, leaves or flowers. A characteristic of algae is their ability for photosynthesis. In cooling water systems they block nozzles.

2.3.7.5 *Helminths*

Helminths are parasitic worms and nematodes such as tapeworms. Other Helminth parasites of concern in reclaimed water are hook worm, round worm to name a few.

2.3.7.6 *Fungi*

Moulds are a class of fungi. Fungi produces spores. In cooling water systems mould causes wood rot.

2.3.8 Heavy Metals

These are commonly found in effluent streams of electroplating, textile dyeing, steel, petrochemical and other industrial plants. Whilst chromium is the most widely used heavy metal, cadmium, lead and mercury constitute the most toxic metals to humans. They have an attraction towards sulphur compounds found in enzymes. For this reason heavy metal concentrations are regulated by the EPA and water utilities.

2.3.8.1 *Chromium*

Chromium is a naturally occurring element found in rocks, animals, plants, soil and in volcanic dust and gases. Chromium is present in the environment in several different forms. The most common forms are as the element chromium(0), chromium(Cr^{3+}) and chromium(Cr^{6+}). No taste or odour is associated with chromium compounds. Chromium(Cr^{3+}) occurs naturally in the environment and is an essential nutrient. Chromium(Cr^{6+}) and chromium(0) are generally produced by industrial processes.

Chromium(Cr^{6+}) and chromium(Cr^{3+}) are used for chrome plating, dyes and pigments, leather tanning and wood preserving.

Whilst chromium(Cr^{3+}) is an essential micronutrient, contact with chromium(Cr^{6+}) can cause skin ulcers and ingesting large amounts of chromium(Cr^{6+}) can cause stomach upsets and ulcers, convulsions, kidney and liver damage, and even death.

Various metal finishing processes contribute chromium to the wastewater. Among these are chromium plating, chromating, bright dipping, chromic acid anodizing and chromium stripping.

The United States EPA has set a limit of $100\ \mu\text{g}$ for chromium (Cr^{3+}) and chromium (Cr^{6+}) per L of drinking water [12].

For methods of removal refer to Chapter 8.

2.3.8.2 Cadmium

Cadmium is a relatively rare element in the earth's crust and found in concentrations of $0.2\ \text{mg/kg}$ [13]. It is usually found as a mineral combined with other elements such as oxygen (cadmium oxide), chlorine (cadmium chloride) or sulphur (cadmium sulphate, cadmium sulphide). The major use of cadmium is in the manufacture of nickel-cadmium batteries, electronic components, nuclear reactors, pigments, plastic stabilizers and in metal plating operations. Drinking water contains very low concentrations of cadmium in the order of $0.1\ \mu\text{g/L}$. Polluted well waste may contain as much as $25\ \mu\text{g/L}$ [13]. Exposure to cadmium happens mostly in the workplace where cadmium products are made. The general population is exposed from breathing cigarette smoke or eating cadmium-contaminated foods.

Cadmium and its compounds are classified as carcinogens. They damage the lungs, can cause kidney disease and may irritate the digestive tract. Eating food or drinking water with very high levels severely irritates the stomach, leading to vomiting and diarrhea. Long-term exposure to lower levels of cadmium in air, food or water leads to a build-up of cadmium in the kidneys and possible kidney disease. Other long-term effects are lung damage and fragile bones.

The EPA has set a limit of five parts of cadmium per billion parts of drinking water (5 ppb). EPA does not allow cadmium in pesticides [12].

The United States Food and Drug Administration (FDA) limits the amount of cadmium in food colours to 15 parts per million (15 ppm).

2.3.8.3 Lead

Lead is a naturally occurring bluish-grey metal found in small amounts in the earth's crust. Lead can be found in all parts of the environment. Much of it comes from human activities including burning fossil fuels, mining and manufacturing.

Lead has many different uses. It is used in the production of batteries, ammunition, metal products (solder and pipes) and devices to shield X-rays. Because of health concerns, lead from gasoline, paints and ceramic products, caulking and pipe solder has been dramatically reduced in recent years.

Lead concentrations in drinking water range from $1\ \mu\text{g/L}$ to $60\ \mu\text{g/L}$ [14]. The effects of lead are the same whether it enters the body through breathing or swallowing. Lead can affect almost every organ and system in the body. The main target for lead toxicity is the nervous system. Exposure to high lead levels can severely damage the brain and kidneys in adults or children and ultimately cause death. Lead is not a carcinogen.

The EPA limits lead in drinking water to $15\ \mu\text{g/L}$.

2.3.8.4 Mercury

Mercury is a naturally occurring metal and exists in three oxidation states as the element, metallic mercury (+) and mercury (2+). The metallic mercury is a shiny, silver-white, odourless liquid. If heated, it is a colourless, odourless gas.

Mercury also combines with oxygen, sulphur chlorine to form inorganic salts and with carbon to make organic mercury compounds. The most common organic compound is methylmercury, is produced mainly by microscopic organisms in the water and soil. Metallic mercury is used to produce chlorine gas and caustic soda, and is also used in thermometers, dental fillings and batteries.

The nervous system is very sensitive to all forms of mercury. Methylmercury and metallic mercury vapours are more harmful than other forms, because more mercury in these forms reaches the brain. Exposure to high levels of metallic, inorganic or organic mercury can permanently damage the brain, kidneys and developing foetus. Effects on brain functioning may result in irritability, shyness, tremors, changes in vision or hearing and memory problems.

Short-term exposure to high levels of metallic mercury vapours may cause effects including lung damage, nausea, vomiting, diarrhea, increases in blood pressure or heart rate, skin rashes and eye irritation.

The EPA has set a limit of 2 µg/L in drinking water (2 ppb).

2.3.9 Radionuclides

Drinking water contains naturally occurring radionuclides such as radium-226 and uranium-238. Wastewater streams discharged from hospital laboratories and nuclear power and research facilities contain radionuclides such as uranium and radium-226. The naturally occurring form of Uranium is as the Uranyl ion UO_2^{2+} . Uranium, while it may be radioactive, is actually more serious as a toxin to the kidney. At high enough levels, it can cause permanent kidney damage. The current US EPA standard for Uranium in drinking water is 0.1 mg/L [15]. Similarly other national drinking water standards provide specific limits to be observed.

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