

## Chapter 2

# Characteristics of Membrane Concentrate

**Abstract** This chapter discusses the characteristics of membrane concentrate, and the relevance that the concentrate has on the method of disposal. Membrane concentrate from a desalination plant can be regarded as a waste stream, as it is of little or no commercial benefit, and it must be managed and disposed of in an appropriate way. It is largely free from toxic components, and its composition is almost identical to that of the feed water but in a concentrated form. The concentration will depend on the type of desalination technology that is used, and the extent to which fresh water is extracted from the brine. Based on the treatment processes that are used, a number of chemicals may also be present in the concentrate, albeit in relatively small quantities.

**Keywords** Additional discharge streams • Antiscalants • Chemical treatment • Coagulation/flocculation • Concentration factor • Dechlorination • Filtration • High recovery • Membrane cleaning • Pretreatment • Recovery rate

### 2.1 Source Water

The concentrations of seawater and brackish water can vary significantly, and as such there is a difference between the concentrate produced from seawater desalination plants and brackish water desalination plants. Seawater typically has a level of total dissolved solids (TDS) between 33,000–37,000 mg/L. The average major ion concentration of seawater is shown in Table 2.1 along with water from the Mediterranean Sea, and water from Wonthaggi off the southern coast of Australia. Seawater salinity increases in areas where water evaporates or freezes, and it decreases due to rain, river runoff, and melting ice. The areas of greatest salinity occur and latitudes of 30° N and S where there are high evaporation rates,

**Table 2.1** Major ion concentrations of seawater (mg/L)

Ion	Worldwide average	Mediterranean Sea <sup>a</sup>	Wonthaggi, Australia
Chloride, Cl <sup>-</sup>	18,980	21,000–23,000	20,200
Sodium, Na <sup>+</sup>	10,556	10,945–12,000	11,430
Sulphate, SO <sub>4</sub> <sup>2-</sup>	2,649	2,400–2,965	2,910
Magnesium, Mg <sup>2+</sup>	1,272	1,371–1,550	1,400
Calcium, Ca <sup>2+</sup>	400	440–670	420
Potassium, K <sup>+</sup>	380	410–620	490
Bicarbonate, HCO <sub>3</sub> <sup>-</sup>	140	120–161	NR
Bromide, Br <sup>-</sup>	65	45–69	62
Borate, H <sub>2</sub> BO <sub>3</sub> <sup>-</sup>	26	NR	NR
Strontium, Sr <sup>2+</sup>	13	5–7.5	7.6
Fluoride, F <sup>-</sup>	1	1.2–1.55	0.9
TDS	34,482	38,000–40,000	NR

Data from Department of Sustainability and Environment 2008, Gaid and Trear 2007, Suckow et al. 1995

<sup>a</sup> Values for the Mediterranean Sea are taken from Gibraltar and Toulon (France)

**Table 2.2** Concentration (mg/L) of major cations and anions in the brackish water feed to three desalination plants in the Abu Dhabi Emirate, United Arab Emirates

Ion	Al Wagan	Al Qua'a	Um Al-Zumool
Sodium, Na <sup>+</sup>	741.59	451.13	2,482
Calcium, Ca <sup>+</sup>	146.31	162.36	456.40
Magnesium, Mg <sup>+</sup>	112	104	194
Potassium, K <sup>+</sup>	28.46	27.24	110.1
Chloride, Cl <sup>-</sup>	3,827	6,213	9,443
Phosphide, P <sup>3-</sup>	–	0.14	–
Nitrate, NO <sub>3</sub> <sup>-</sup>	8.99	1.57	12.70
Sulphate, SO <sub>4</sub> <sup>2-</sup>	539.22	394.38	1746

Data from (Mohamed et al. 2005)

while there is a decrease in average salinity at the equator where there is a greater amount of precipitation (Millero et al. 2006). Areas of notably high salinity include the Mediterranean Sea and the Red Sea, which in parts can have concentrations of up to 39,000 and 41,000 mg/L respectively (Millero et al. 2006).

The concentration of brackish water is far more variable than seawater. Depending on the location, brackish groundwater can have TDS concentrations ranging from several hundred up to several thousand mg/L. Table 2.2 shows the ion concentrations from the feed of three brackish water desalination plants in the Emirate of Abu Dhabi, United Arab Emirates. It can be seen that even three water sources in the same region can have widely variable concentrations of dissolved salts.

Other components likely to be found in both seawater and brackish water are heavy metals and organic matter, both of which will impact the composition of the concentrate. Heavy metals and other toxic constituents are found in all water sources, but they are more likely to be found in inland water sources rather than

seawater (Del Bene et al. 1994). Metals may also be in the discharge as a result of corrosion. However, while thermal desalination plants are more susceptible to corrosion due to their operation at elevated temperatures, corrosion is not a significant problem in membrane desalination plants. Natural organic matter (NOM) will also be found in source waters, including humic acids and materials generated by algae or other organisms in the source water.

## 2.2 Recovery Rate and Concentrate TDS

The recovery of the feed water will determine how concentrated the final solution is. The recovery ratio,  $R$ , is defined as:

$$R = \frac{Q_P}{Q_F} = \frac{Q_P}{Q_C + Q_F} \quad (2.1)$$

where  $Q_P$  is the product flow rate,  $Q_F$  is the feed flow rate and  $Q_C$  is the concentrate flow rate. The recovery rate changes according to the specific membrane process, and in particular the number of membrane elements in each vessel, the number of membrane passes and stages per pass, the type of membrane that is used, and the quality of the final permeate (Mauguin and Corsin 2005). With lower levels of TDS, brackish water systems are able to achieve higher recovery rates, as the water is able to be concentrated to higher levels before the onset of precipitation, which eventually leads to membrane fouling. Brackish water desalination plants can achieve recoveries of between 65–90%, while seawater desalination plants range from 40–65% (Voutchkov et al. 2010).

Once the recovery rate is known, the TDS of the concentrate can be calculated with the following:

$$TDS_{concentrate} = TDS_{feed} \left( \frac{1}{1-R} \right) - \frac{R \times TDS_{permeate}}{100(1-R)} \quad (2.2)$$

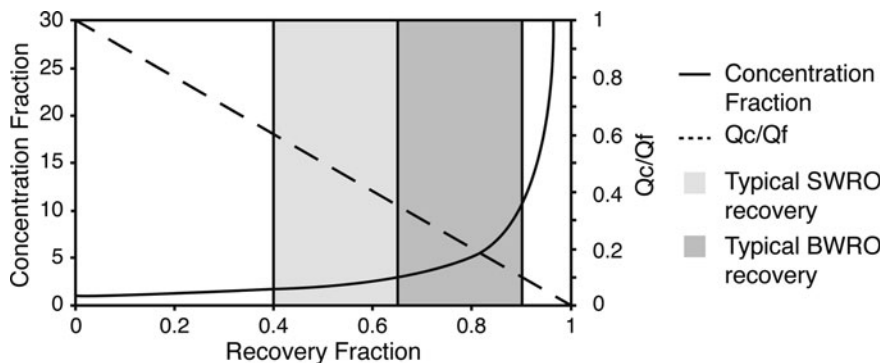
Since the value of  $TDS_{permeate}$  is often very low, it is often approximated as zero, and the above equation becomes:

$$TDS_{concentrate} = TDS_{feed} \left( \frac{1}{1-R} \right) \quad (2.3)$$

The concentration factor of the brine, the ratio of the concentrate and feed concentrations, can also be calculated. It is given as:

$$CF = \frac{TDS_{concentrate}}{TDS_{feed}} = \left( \frac{1}{1-R} \right) \quad (2.4)$$

For example, a plant operating at a recovery ratio of 90% will have a concentration factor of 10 (i.e., the components in the feed solution are concentrated 10 times).



**Fig. 2.1** Increase in concentration factor and decrease in concentrate volume with increasing recovery rate. The shaded regions represent typical recovery ranges for typical seawater reverse osmosis (SWRO) and brackish water reverse osmosis (BWRO) processes

The more water that is extracted, the smaller the volume of concentrate, but the greater the salinity of the brine. This trade off between concentration factor and recovery rate is shown in Fig. 2.1. As recovery approaches 100%, there is a sharp increase in the concentration factor, however the volume of the concentrate relative to the volume of feed,  $Q_c/Q_f$  is shown to decrease linearly. Figure 2.1 provides a useful comparison between the degree of concentration that may be achieved, and the volume of concentrate that must be managed. Higher recoveries are generally more desirable, as more water is recovered and less feed water is required to produce the same amount of water.

In terms of concentrate management, some disposal options are better suited to low volume and high concentration, while others are better suited to high volume with lower concentration. Ultimately there may be a balance between plant performance and disposal suitability. Plants with high recovery rates that produce a more concentrated brine must have the means to dispose of this concentrate in a safe and environmentally friendly manner. When suitable concentrate management is not achievable, the recovery of a plant may need to be compromised.

Additional processing of concentrate to achieve very high recoveries, that eventually approach 100% recovery and zero liquid discharge is possible. The definition of high recovery processing is variable, but it can be generally described as further processing of concentrate to achieve a higher recovery than what would normally be achieved in a single membrane pass. For brackish water desalination, this generally translates to recovery rates of greater than 90%. Many different methods exist for the treatment of brine to achieve high recovery. These involve some form of control over the precipitation of sparingly soluble salts and other potential foulants, so as to be able to remove them from the system at a convenient stage and to allow further treatment.

**Table 2.3** Calculated and actual ion concentrations (mg/L) in the feed and concentrate from the Al Wagan BWRO desalination plant

Ion	Feed	Calculated		Actual	
		Concentrate	Concentration factor	Concentrate	Concentration factor
Sodium, Na <sup>+</sup>	742	2,473	3.33	2,248	3.03
Calcium, Ca <sup>+</sup>	146	487	3.33	367.96	2.51
Magnesium, Mg <sup>+</sup>	112	373	3.33	282.02	2.52
Potassium, K <sup>+</sup>	28	93	3.33	68.44	2.40
Chloride, Cl <sup>-</sup>	3827	12757	3.33	8,946	2.34
Nitrate, NO <sub>3</sub> <sup>-</sup>	9	30	3.33	7.11	0.79
Sulphate, SO <sub>4</sub> <sup>2-</sup>	539	1,797	3.33	1,540	2.86

Data from (Mohamed et al. 2005)

### 2.2.1 Case Example

Data from the Al Wagan BWRO desalination plant (Mohamed et al. 2005) has been used to highlight a typical brackish water desalination scenario. The following has been calculated assuming 200 m<sup>3</sup>/day of brackish water is treated at a recovery of 70%. From Eq. 2.1:

$$0.70 = \frac{Q_p}{200}$$

$$Q_p = 140 \text{ m}^3/\text{d}$$

Therefore the permeate quantity is 140 m<sup>3</sup>/d. The volume of concentrate can then be determined using  $Q_F = Q_P + Q_C$ . With a feed of 200 m<sup>3</sup>/day and a recovery of 70%, the concentrate quantity is 60 m<sup>3</sup>/day. The concentration factor can be found using Eq. 2.4:

$$CF = \left( \frac{1}{1 - R} \right) = \left( \frac{1}{1 - .7} \right)$$

$$CF = 3.33$$

Table 2.3 shows the calculated ion concentrations with a concentration factor of 3.33, and compares them with actual plant values. Note that there are significant differences between the calculated and actual ion concentrations for most species, however this is likely to be a result of the plant operating below the stated recovery rate of 70%. The differences in the concentration factors from the actual plant data (ranging from 0.79 for nitrate to 3.03 for sodium) are largely a result of the different precipitation points for each of the species in the water.

## 2.3 Chemical Treatment and Additional Discharge Streams

The majority of the discharge from a desalination processes is concentrated brine from the membrane process, and this may contain quantities of treatment chemicals used. Treatment of water is necessary in all desalination plans for variety of reasons; feed water treatment, membrane protection, membrane cleaning, permeate treatment and concentrate treatment prior to discharge. Although non-chemical treatment is possible, chemical treatment is widely practiced.

In addition to the concentrated brine, streams from the pretreatment, cleaning, post-treatment and startup processes are also present. The management of these streams, including chemical treatment, must be tailored to suit the specific concentrate management scheme in place. Buffer tanks can be used to store additional discharge streams, thus helping to regulate the flow and concentrate of the final discharge (Mauguin and Corsin 2005). Streams which cannot be disposed of via the same means as the concentrate will require alternative treatment and disposal.

### 2.3.1 Pretreatment

Before any membrane treatment process, the feed water must undergo pretreatment. This is primarily done to reduce fouling caused by suspended solids, microbial growth, and inorganic deposits of silica and precipitated sparingly soluble salts and silica. Fouling reduces the flux of water through the membranes and hence lowers the water recovery of the process. Excessive fouling can incur additional costs for the replacement of membranes. Pretreatment is also used to prevent the oxidation and hydrolysis of the membranes, and remove metals or other chemicals in the feed water as necessary. Typical pretreatment for a reverse osmosis process includes initial screening, or biofouling control (often referred to as chlorination), acid treatment, coagulation/flocculation, media filtration, anti-scalant addition, cartridge filtration and dechlorination (Isaias 2001). A summary of the chemicals that are used for these processes can be seen in Table 2.4. Alternatively membrane pretreatment can be used, reducing the amount of chemicals that are required.

#### 2.3.1.1 Biofouling Control and Dechlorination

Biofouling control is used to prevent the buildup of microorganisms and the formation of biofilms that cause fouling. The oxidants chlorine and ozone can be added as biocides, with chlorine being used most commonly. Chlorine is added in the form of chlorine gas ( $\text{Cl}_2$ ) or sodium hypochlorite ( $\text{NaOCl}$ ) (Fritzmann et al. 2007). The dosage of the oxidant must be high enough to allow for residual oxidant to disinfect the entire pre-treatment processes (Greenlee et al. 2009).

**Table 2.4** Commonly used membrane desalination plant chemicals

Pretreatment process	Typical chemicals
Biofouling control	Chlorine, sodium hypochlorite, calcium hypochlorite, ozone
Antiscalants	Polymeric substances such as polyphosphates, phosphonates and polycarbonic acids
Acids	Sulphuric acid, hydrochloric acid
Coagulants/ Flocculants	Ferric chloride, ferric sulphate, polyelectrolytes
Dechlorination	Sodium bisulphite

Data from (Voutchkov et al. 2010; Committee on Advancing Desalination Technology, National Research Council 2008; Younos 2005)

All oxidants used must be removed in the final stage of the pretreatment process, as they are known to damage most polymer membranes used for desalination. In particular, chlorine is known to be harmful to commonly used thin-film composite polyamide membranes.

When chlorine is used as an oxidant, sodium bisulphite can be used for dechlorination. However, even after the process of dechlorination, free residual chlorine (FRC) may be present in the discharge. The sodium bisulphite used for dechlorination may also cause low levels of dissolved oxygen in the concentrate. For processes which use ozone, not only must it be removed to prevent damage to oxidant sensitive membranes, but also to prevent the formation of bromate, a known carcinogen, in waters containing bromide (Greenlee et al. 2009).

As an alternative to the addition of oxidants, ultraviolet (UV) treatment may be used. UV treatment has found to be less effective than chlorine or ozone in preventing biofouling, however unlike those methods, it does not incur additional downstream processing (Committee on Advancing Desalination Technology, National Research Council 2008; Cotruvo 2005). This eliminates the need for the use sodium bisulphite or other reducing agents and the potential for FRC or ozone to be present in the final concentrate.

### 2.3.1.2 Acid treatment

To increase the solubility of calcium carbonate and reduce its potential for precipitation and hence membrane fouling, the pH of the feed water is lowered through the addition of acid (Greenlee et al. 2009). Sulphuric acid and hydrochloric acid are most commonly used. Acid treatment can also help to improve the coagulation of colloids and slightly increase the solubility of silica (Bergman 2007).

### 2.3.1.3 Coagulation/Flocculation

Coagulants are used to bind together particulate and colloidal matter so they may be filtered from the feed before the membrane process. Coagulants can be either inorganic (such as ferric salts) or organic polyelectrolytes. The correct dosage and

effective removal of coagulants is crucial for the prevention of membrane fouling (Bergman 2007). These chemicals are only likely to be present in the concentrate if the filter backwash is disposed of with the concentrate and does not undergo any additional treatment (Lattemann and Höpner 2008).

#### **2.3.1.4 Antiscalants**

The extent of process recovery is often limited by the fouling of membranes from sparing soluble precipitates. Antiscalants are added during pretreatment to increase the solubility of salts likely to precipitate, enabling the membrane process to achieve a higher recovery before fouling occurs. Antiscalants can be a number of polymeric substances (typically polyphosphates, phosphonates and polycarbonic acids), and as there is no treatment process to remove antiscalant, they will be present in the membrane concentrate discharge.

#### **2.3.1.5 Filtration**

Both media filters and cartridge filters can be used in a pretreatment process. Granular media filters involve the filtration of large particles through different layers of fine particles, usually coal, pumice, sand or garnet (Bonnelye et al. 2004). Cartridge filters act as the final filtration step before the water passes through the membranes, and remove fine particles as small as 1 $\mu$ m.

Although no chemicals are required to pass water through the filter, the filter cleaning process produces a stream of waste known as filter backwash. This discharge is high in suspended solids, but the concentration of dissolved salts is similar to the intake. It will also contain any coagulants or flocculants that were added to the water. This water generally requires treatment prior to disposal with the membrane concentrate (Mauguin and Corsin 2005). Treatment of filter backwash involves the separation of solids from the waste stream to bring the water quality back to a similar quality of feed water. The separated solid waste can be then separated and disposed of appropriately.

#### **2.3.1.6 Membrane Pretreatment**

Microfiltration (MF) and ultrafiltration (UF) membranes can be used as forms of pretreatment for nanofiltration (NF) or reverse osmosis (RO) desalination processes. Membrane pretreatment reduces the amount of chemicals that are required and hence reduces the environmental impact of the final discharge. MF membranes can be used to filter particles with diameters of 0.1–10  $\mu$ m and typically remove bacteria, viruses, precipitates, coagulates and large colloidal particles. UF can remove particles with diameters as small as 0.002  $\mu$ m, and



**Table 2.5** Commonly used cleaning chemicals for the removal of membrane foulants

Foulant	Typical cleaning chemicals
Metal oxides	Citric acid, phosphoric acid
Inorganic colloids	Sodium hydroxide, sodium dodecyl sulphate, sodium dodecyl benzene sulphonate
Biofilms	Sodium ethylenediaminetetraacetic acid (Na-EDTA), sodium triphosphate, trisodium phosphate
Organic matter	Sodium hydroxide, sodium dodecyl sulphate, sodium dodecyl benzene sulphonate
Silica	Ammonium bifluoride, sodium hydroxide, sodium dodecyl benzene sulphonate

Data from (Committee on Advancing Desalination Technology, National Research Council 2008; Lattemann S and Höpner 2003)

typically remove high molecular weight proteins, large organic molecules and pyrogens (Curcio 2009).

Membrane pretreatment can improve the feed water quality and reduce particulate matter to a greater degree than other pretreatment methods. This reduces the required cleaning frequency of the downstream membranes and the amount of cleaning chemicals that are required and subsequently disposed of (Pearce 2007).

Similar to filter backwash, the concentrate from these membranes requires treatment before it can be disposed of with the membrane concentrate. However, the total amount of solids produced after the treatment of filter backwash can be 60–80% greater than MF and UF concentrate due to the addition of coagulants prior to the granular media filters (Bergman 2007).

NF has been also been studied as a potential form of pretreatment for reverse osmosis desalination processes (Hassan et al. 1998, 2000). Based on the feed water, it may be a suitable pretreatment method that allows for operation with little or even no use of antiscalants.

### 2.3.2 Membrane Cleaning

Cleaning chemicals are used to remove membrane fouling. Fouling can include salt precipitation, particulate or colloidal fouling, organic fouling and biofouling. Both acidic and alkaline solution are used to clean membranes based on the foulants that accumulate on the membrane surface. A list of common membrane cleaning chemicals for foulant removal is provided in Table 2.5. Membranes are also disinfected with chemicals such as sodium hypochlorite or hydrogen peroxide (Van Der Bruggen et al. 2003).

Cleaning chemicals are generally discharged in a separate waste stream rather than the concentrate discharge, as additional treatment is often required.

However, because both acids and bases are used in cleaning, it may be possible to store these chemicals in a stirred buffer tank to allow the solution to neutralise. This solution may then be slowly added to the concentrate waste to dilute it and allow for a safe disposal (Mauguin and Corsin 2005). Note that the volume of this discharge is much lower than both the concentrate and filter backwash discharges.

### 2.3.3 Other Discharges

While the plant is in operation, but not producing water that is of the required quality, two additional discharge streams can be produced (Mauguin and Corsin 2005). This usually occurs during the startup of the plant. The first stream is the pretreated water which has not reached an acceptable quality to pass through the membrane unit. Its composition is largely similar to that of the feed, and if membrane processes are not used as pretreatment, its salinity should be the same as feed. The second stream is the permeate which has not yet reached the desired quality of the final water product. This stream will have a lower salinity than the feed, and should not contain great quantities of harmful chemicals. Both these streams should be safe for disposal in the concentrate stream.

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