3-2. Feed Water Analysis

A complete and accurate water analysis must be provided before an RO system is designed. The water analysis report should contain the type and the concentration of all constituents in the water. The constituents are consisted of dissolved ions, silica, colloids, and organic (TOC)

- Typical dissolved anions are as follows :
  bicarbonate(HCO_3^-), carbonate(CO_3^{2-}), hydroxide(OH^-), sulfate(SO_4^{2-}), chloride(Cl^-), fluoride(F^-), nitrate(NO_3^-), sulfide(S^{2-}) and phosphate(PO_4^{2}-)
- Typical dissolved cations are shown below :
  calcium(Ca^{2+}), magnesium(Mg^{2+}), sodium(Na^+), potassium(K^+), iron(Fe^{2+} or Fe^{3+}), manganese(Mn^{2+}), aluminum(Al^{3+}), barium(Ba^{2+}), strontium(Sr^{2+}), copper(Cu^{2+}) and zinc (Zn^{2+}).

Table 1. Solubility Products of Sparingly Soluble Inorganic Compounds

Substance	Formula	Temp.(℃)	Solubility Product
Aluminum Hydroxide	$Al(OH)_3$	20	1.9 X 10^{-33}
Barium Carbonate	$BaCO_3$	16	7 X 10^{-9}
Barium Sulfate	$BaSO_4$	25	1.08 X 10^{-10}
Calcium Carbonate	$CaCO_3$	25	8.7 X 10^{-9}
Calcium Fluoride	CaF_2	26	3.95 X 10^{-11}
Calcium Sulfate	$CaSO_4$	10	6.1 X 10^{-5}
Cupric Sulfide	CuS	18	3.5 X 10^{-45}
Ferric Hydroxide	$Fe(OH)_3$	18	1.1 X 10^{-36}
Ferrous Hydroxide	$Fe(OH)_2$	18	1.64 X 10^{-14}
Magnesium Ammonium Phosphate	$MgNH_4PO_4$	25	2.5 X 10^{-13}
Magnesium Carbonate	$MgCO_3$	12	2.6 X 10^{-5}
Magnesium Hydroxide	$Mg(OH)_2$	18	1.2 X 10^{-11}
Manganese Hydroxide	$Mn(OH)_2$	18	4 X 10^{-14}
Strontium Carbonate	$SrCO_3$	25	1.6 X 10^{-9}
Strontium Sulfate	$SrSO_4$	17.4	2.81 X 10^{-7}
Zinc Hydroxide	$Zn(OH)_2$	20	1.8 X 10^{-14}

Certain combinations of cations and anions form sparingly soluble salts in water and scaling of a reverse osmosis membrane may occur when the salts are concentrated within the RO element beyond their solubility limit. Typical sparingly soluble salts and their solubility product limit are shown in Table 1.

In an RO system the most common sparingly soluble salts encountered are $CaSO_4$, $CaCO_3$ and silica. Other salts creating a potential scaling problem are CaF_2, $BaSO_4$ and $SrSO_4$, though less prevalent. Other ions causing problems are described below. Sulfates are present in relatively large concentrations in most raw waters. Their concentration can be artificially increased when sulfuric acid is added to water to adjust pH. In this case, Ba^{2+} and Sr^{2+} must be analyzed accurately at 1 μg/L (ppb) and 1 mg/L (ppm) level of detection, respectively, since $BaSO_4$ and $SrSO_4$ are much less soluble in water than $CaSO_4$ and moreover, barium and strontium sulfate scales are extremely difficult to redissolve.

Alkalinity consists of negative ions which include bicarbonate, carbonate and hydroxide. Most of the alkalinity in naturally occurring water sources is in the form of bicarbonate alkalinity (HCO_3^-). Below a pH of 8.3, the bicarbonate alkalinity will be in equilibrium with a certain concentration of dissolved carbon dioxide. At a pH greater than 8.3, HCO_3^- will be converted to the carbonate form (CO_3^{2-}). With water sources of pH above 11.3, hydroxide (OH^-) will be present.

Water can dissolve carbon dioxide from the air, forming carbonic acid (H_2CO_3). The acidic water will tend to dissolve calcium carbonate from the ground as it passes over or through the calcium carbonate rock. Most naturally occurring water sources are close to saturation in calcium carbonate which is in equilibrium with calcium bicarbonate, depending on the pH of the water. Calcium bicarbonate is much more soluble in water than calcium carbonate. It the water is concentrated in an RO system, calcium carbonate salt is likely to precipitate in the system. Thus the use of a scale inhibitor or lowering the pH below 8 by an acid injection is required in most RO systems.

Nitrates are very soluble in water and thus will not precipitate in an RO system, Nitrates are a health concern since, when ingested by mammals including humans, they are converted to nitrites which interfere with hemoglobins to exchange oxygen in blood. This can cause serious problems especially for fetus and children. For this reason, it is desirable to maintain a nitrate concentration below 40 mg/L in drinking water. Typical nitrate removal by RO is in the range of 90 ~ 96%.

Iron and manganese are present in water either in a divalent state, which is soluble in water, or in a trivalent state, which forms insoluble hydroxides. The soluble iron (Fe^{2+}) can come from either a well water or the rust of pump, piping and tanks, especially if acid is injected upstream of the equipment. If the iron or manganese concentration is greater than 0.05 mg/L in an RO feed water and they are oxidized by air or an oxidizing agent to the trivalent state, then the insoluble hydroxides $Fe(OH)_3$ and $Mn(OH)_3$ will precipitate in the system, when the water pH is neutral or higher. They can also catalyze the oxidative effects of residual oxidizing agents, possibly accelerating the membrane degradation. Thus iron and manganese must be removed at the pretreatment step (see the pretreatment section).

Aluminum is usually not noticeably present in naturally occurring water sources. With its valence of 3+ like iron (Fe^{3+}), aluminum will form very insoluble hydroxide [$Al(OH)_3$] at the normal operating pH range of 5.3 to 8.5 in an RO system. Because of the high charge characteristics, alum [$Al_2(SO_4)_3$] or sodium aluminate ($NaAlO_2$) is used to coagulate negatively charged colloids in the pretreatment of surface waters. Care must be taken not to employ the coagulant excessively to result in carrying the residual aluminum over to the membranes.

A concentration of aluminum greater than 0.01mg/l in the dialysis water is a health concern for kidney dialysis patients. In this regard, iron [$FeCl_3$ or $Fe_2(SO_4)_3$] may be preferred as a coagulant.

Copper and Zinc are not appreciably detected in natural water sources. Sometimes, it is possible to pick up trace amounts from piping materials. Their hydroxides $Cu(OH)_2$ and $Zn(OH)_2$) will drop out of solution over the operating pH range of 5.3 to 8.5. Because of the low concentrations of copper and zinc, their precipitants will foul an RO system only if allowed to precipitate over an extended period of time without cleaning the system. However, more serious situation may develop, when an oxidizing agent such as hydrogen peroxide is present together with copper or zinc, to degrade the membranes rapidly.

Sulfides are present as a dissolved gas, hydrogen sulfide (H_2S). Hydrogen sulfide gas can be removed by running the water through a degasifier or oxidizing them by chlorine or air to insoluble elemental sulfur followed by media filtration.

Phosphates have a strongly negative charge (3-) and a tendency to react with multivalent cations such as Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+} to give insoluble salts. Calcium phosphate has a very limited solubility at neutral pH and an even lower solubility at higher pH. The use of a scale inhibitor or lowering the pH of the feed water below 7 is a measure to control the phosphate precipitate.

Silica is naturally present in most feed waters in the range of 1-100 mg/L and exists mostly in the silicic acid form [$Si(OH)_4$] below a pH of 9. At low pH, Silicic acid can polymerize to form a colloid (colloidal silica). At high pH above 9, it dissociates into the silicate anion (SiO_3^{2-}) and can precipitate as a salt with calcium, magnesium, iron or aluminum. Silica and silicates are difficult to redissolve. Ammonium bifluoride solutions are somewhat successful at cleaning silica. However, ammonium bifluoride is considered a hazardous chemical posing problems for disposal. Silica present in an RO feed water at a concentration greater than 20 mg/L may pose a potential for silica scaling.

Colloids (Suspended Solids) Analysis

Silt density index (SDI), also known as the Fouling Index(FI), is a good guide line to determine the colloidal fouling potential of RO feed water. The source of colloids in RO feed waters is varied and often includes bacteria, clay, colloidal silica and iron corrosion products. Pretreatment chemicals used in a clarifier such as alum, ferric chloride or cationic polyelectrolytes can also cause colloidal fouling if not removed in the clarifier or through proper media filtration.

SDI measurement should be done prior to designing an RO pretreatment system and on a regular basis during RO operation (at least once a day for surface waters). The test measures the rate of fouling of a 0.45 μm filter membrane by the following procedure.

Place the membrane filter(47 mm, 0.45 μm) on its support, bleed water pressure on carefully, tighten the O-ring seal and fix the support vertically. Adjust feed pressure to 2.1bar (30psig) and measure initial time t_0, necessary to filter 500 mL of sample water (feed pressure to be kept constant by continuous adjustment). Continue filtering the water for 15 min at 2.1bar (30psig). If the filter is plugged up in 15min, use the 10 or 5min measurement. After 15 minutes, measure again time, t_1, necessary to filter 500 mL.

SDI is calculated as follows ;

$$\text{SDI} = 100 \times \frac{1 - t_0 / t_1}{T}$$

T is the time before the second flow measurement (5, 10 or 15 minutes).

The guideline is to maintain SDI at less than or equal to 5 for RO feed water.

Turbidity is another guideline as an indicator for the rate of RO membrane fouling. Turbidometers (also called nephelometers) measure the scattering of light caused by various suspended solids in the water sample. Water samples having turbidity reading greater than 1 will tend to foul the membranes. These readings are typically given in nephelometric turbidity units (NTU). Like the SDI test, turbidity is only an indicator of fouling potential. High turbidity does not necessarily mean that the suspended solid is going to deposit on the RO membrane.

In fact, there are some membrane foulants such as surfactants and soluble polymers that do not scatter light to register a turbidity reading. Although turbidity and SDI are not perfect in predicting the behavior of the colloidal foulants, they are useful for characterizing an RO feed water. For examples, SDI greater than 5 and NTU greater than I strongly suggest that some coagulants should be used in the clarifier step of the feed water pretreatment, followed by media filtration. The feed water with SDI less than 5 and NTU less than I may just require media filtration or cartridge filters without the necessity of coagulation of the colloids.

It is also necessary to have some guidelines for controlling the amount of the coagulant added to the clarifier, since excessive addition of the coagulant should be avoided. Two possible guidelines are zeta potential measurement and streaming current detector.

Zeta Potential is a measurement of the overall charge characteristics of the suspended solids in the water, when the water containing the charged colloids flows in one direction between the oppositely charged electrodes. Most colloids in natural water sources have negative charges which help to repel each other to keep them suspended in solution. In overall, the colloidal water will show negative zeta potential. These negative charges can be neutralized by the addition of cationic coagulants such as aluminum sulfate (alum) and ferric chloride. The coagulants are portionwise added until zeta potential read zero (neutral). The colloids without charges do not repel each other and are more likely to coagulate into larger particulate groups which can be easily filtered out by media filters.

Streaming Current Detector uses a mechanical plunger to create a high water velocity, which causes movement of the ions surrounding negatively charged suspended colloids. It measures the electrical current generated by the moving ions. If the charge of the colloids has been neutralized by the addition of a coagulant, there will be very little current generated by the streaming current detector.

The last constituents in the feed water to be analyzed are bacteria count and organic compounds. There are two ways to count bacteria in the water. One method is to collect bacteria by filtering a measured quantity of water through a membrane filter followed by culturing the retained organisms and counting the developed colonies under low power magnification. The second method is to count the retained microorganisms on the filter plate directly under a fluorescent microscope after staining the microorganisms with dyes such as acridine orange. Direct count methods should be preferred, because they are much faster and more accurate than culture techniques.

Examples of organic compounds in the feed water are oils, surfactants, water soluble polymers, and humic acid. The organic compounds are collectively analyzed by Total Organic Carbon (TOC), Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD). Identification of individual organic substance may require more elaborate analytical tools such as chromatography (HPLC) and GC-Mass spectrometry. Removal of the organic compounds from the feed water at the pretreatment step should be considered when TOC exceeds 3 mg/L.