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# An Introduction to Makeup Water for Industrial Water Systems

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**1. MAKEUP WATER FOR INDUSTRIAL WATER SYSTEMS.** Industrial water systems at many installations use fresh water and, often, potable water. Makeup water, often referred to as “makeup,” is fresh water that is added to an industrial water system to replace water lost by blowdown, evaporation, wind drift, leaks, steam, humidification, or withdrawal from these systems.

**1.1 SOURCES OF MAKEUP WATER.** The usual source of makeup water is the installation's potable water supply. This source is water that has been conditioned and is usually of a very uniform quality from day to day. Other sources of makeup water could include groundwater obtained from shallow or deep wells, or surface water from streams or holding ponds. These sources are not treated to the extent that the potable water source is treated. Still another source is reuse water (i.e., water that is “used” and reclaimed and not rated as potable).

**1.1.1 GROUNDWATER.** The term “groundwater” refers to subsurface water, such as that obtained from wells or artesian springs. This water contains a high amount of dissolved minerals and is often consistent in quality, although it may vary with the seasons of the year and the conditions of the aquifer from which the water is drawn. Treating groundwater can improve its quality.

**1.1.2 SURFACE WATER.** The term “surface water” refers to water found in rivers or lakes. Surface water may vary in quality with the seasons of the year or local weather conditions, with higher turbidity and suspended solids (SS) possible during rainy weather. Treating these waters prior to use can make the quality more uniform, depending on the type of treatment.

**1.1.3 REUSE WATER.** Reuse water is any water that has been previously used. Reuse water helps conserve the precious limited supply of fresh water since less fresh water is needed for an intended use. Treated municipal wastewater is a type of reuse water and can be a source of makeup. In addition to the natural impurities of a fresh water source, municipal wastewater usually contains ammonia, phosphate, and other byproducts of the

waste treatment process. These impurities are factors that affect the usability of reuse water. Other examples of reuse water include cooling tower and boiler blowdown, softener rinse water, plating water effluent, condensate, and reverse osmosis (RO) reject water. Examine each type and source of reuse water and establish its suitability prior to use.

**1.1.4 SOURCE SELECTION FACTORS TO CONSIDER.** Industrial water systems will operate more effectively if the source for water is both reliable and (ideally) uniform in quality. A backup water source should be available for use in case of need.

## **1.2 REASONS AND CRITERIA FOR TREATING MAKEUP WATER**

**1.2.1 REASONS FOR TREATING MAKEUP WATER.** Makeup water is treated to remove or reduce the concentration of any unwanted impurity, including impurities that will cause corrosion, create a deposit or scale in the system, or otherwise interfere with the operation of the industrial water system or limit the use of the original water. The process of treating makeup water often results in water conservation, which minimizes the chemical treatments in terms of frequency and amount of use and the resulting cost.

### **1.2.2 CRITERIA FOR TREATING MAKEUP WATER**

**1.2.2.1 MAKEUP WATER FOR COOLING TOWER SYSTEMS.** To allow the system to operate at a minimum standard, the makeup water needs to be of a minimum standard of quality. Pretreatment of makeup water for cooling towers is not required if the levels of impurities in the water are not excessive.

**1.2.2.2 MAKEUP WATER FOR STEAM BOILERS.** The quality requirement for makeup water often necessitates using water softeners (zeolite or ion-exchange units) to remove water hardness before use. Dealkalizers can be used to remove alkalinity. High-quality steam applications require demineralization or RO, or both. Refer to Chapter 3 for treatment requirements.

**1.2.2.3 MAKEUP WATER FOR HIGH-TEMPERATURE HOT WATER SYSTEMS.** The makeup water for high-temperature (177 °C [350 °F]), high-pressure hot water systems should be softened when its total hardness exceeds 10 parts per million (ppm) as calcium carbonate (CaCO<sub>3</sub>).

**1.2.2.4 OTHER SYSTEMS.** Soften the makeup water for chilled water systems and for dual-purpose (hot and chilled) systems if its total hardness exceeds 250 ppm (as calcium carbonate [CaCO<sub>3</sub>]). For hot water boilers, treat makeup water with sodium sulfite and caustic soda, and soften makeup water used for diesel jacket systems if the total hardness of the raw makeup water exceeds 50 ppm (as CaCO<sub>3</sub>). Refer to Chapter 5 for specific requirements.

**1.2.3 MEASUREMENT OF MAKEUP WATER RATES.** Knowing the use rates of makeup water is essential for calculating proper operating data on cooling towers and steam boilers. You may estimate makeup water use rates by recording the time it takes to fill a container of known volume with water obtained from a blowdown line or, preferably, measured with an appropriately sized makeup meter to provide more accurate values. Filling a container is not a recommended method for measuring hot water streams such as boiler blowdown.

**2. MAKEUP WATER TREATMENT METHODS.** Treatment of industrial makeup water is a process of external water treatment. External treatment involves the treatment, by various processes, of makeup water to remove or reduce hardness, alkalinity, dissolved gases, or other impurities before the water enters the water system (e.g., steam boiler, cooling tower, closed hot water system or chilled water system). This process of external treatment is often referred to as “pre-treatment.” In contrast, internal treatment involves the treatment of water directly within the water system. Both external and internal treatment methods may be used in a given system.

**2.1 EXTERNAL TREATMENT.** External treatment equipment processes and water treatment chemicals reduce or remove impurities contained in the makeup water before the impurities in the water stream enter the internal system. The most effective way to protect the system, reduce boiler problems, and improve operating efficiency is to use a process of removing impurities before they enter a system, particularly a steam boiler. The required treatment methods and equipment are determined by the specific type and amount of impurities that must be reduced or removed from the makeup water. Table 1 lists the various external treatment methods that are available to remove the typical impurities found in makeup water. Figure 1 illustrates the effects of these treatment methods on raw water. The treatment process may be applied to only a portion of the makeup water, in which case the treated water is then blended with raw (untreated) water to achieve a specific quality. Treatment involving this type of blending is known as “split-stream” treatment. Split-stream treatment may also involve the blending of two different treated waters to achieve a specific quality. Paragraphs 2.2 through 2.10 briefly describe external treatment methods. External water treatment is required only for steam boilers and high-temperature hot water systems, but its use may be justified for other industrial water systems as well. Although several types of treatment may be available, Owner installations most commonly use sodium zeolite softening (ion exchange) for treating makeup water. Table 2 provides a guide for selecting external treatment methods or equipment for steam boilers.

Impurity	Removal/Reduction Method
Hardness (calcium & magnesium)	Sodium ion exchange Hydrogen ion exchange Lime-soda softening Evaporators RO Electrodialysis
Alkalinity (bicarbonate & carbonate)	Lime-soda softening Hydrogen ion exchange (followed by degasifying) Dealkalization (chloride ion exchange)
SS/turbidity	Filtration/clarification
Dissolved solids	Demineralization (deionization) Evaporators RO Electrodialysis
Dissolved iron	Aeration (converts to precipitated iron), then filtration Sodium ion exchange (iron will foul the resin)
Dissolved gases (carbon dioxide, hydrogen sulfide, methane)	Aeration Degasifying

Table 1  
 Makeup Water Treatment Methods for Removing Impurities



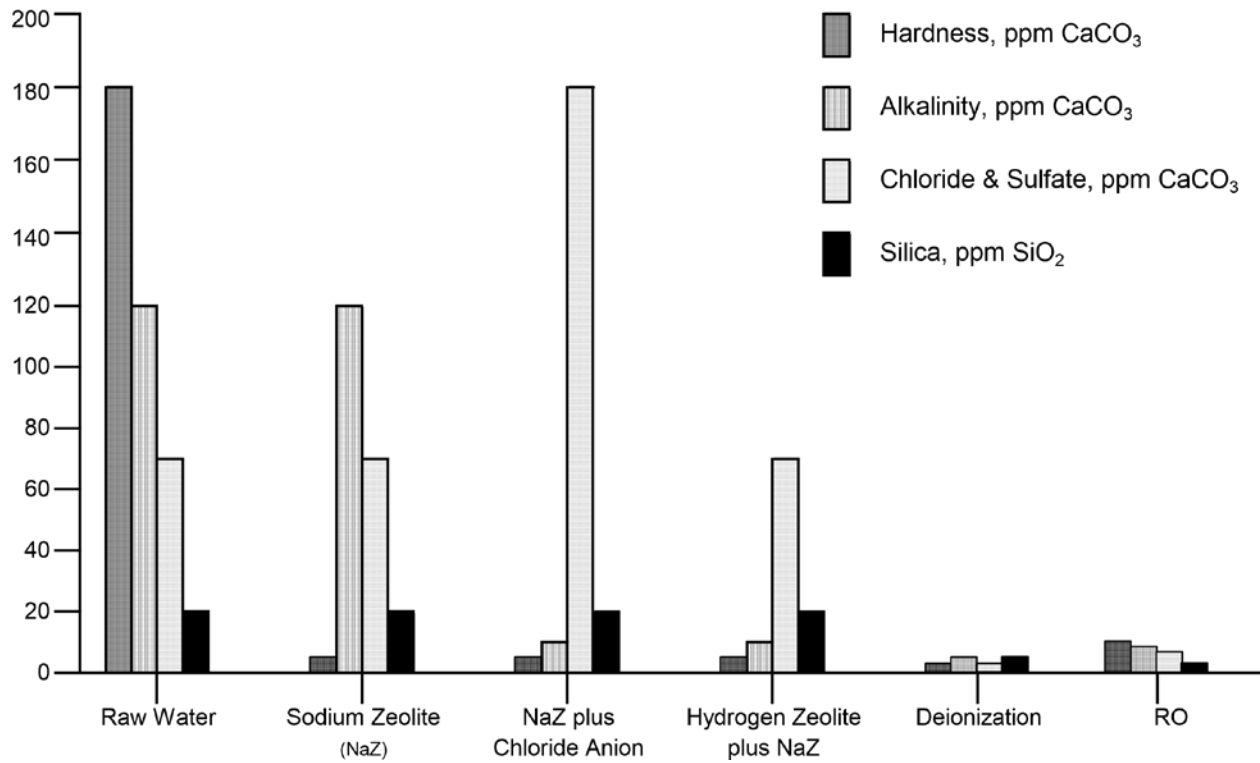


Figure 1  
Effects of Treatment on Raw Water

Makeup Rate l/sec (gpm)	Steam Pressure KPa (psig)	Alkalinity (ppm CaCO <sub>3</sub> )	Turbidity	Recommended External Treatment Equipment
All	< 103 (< 15)	All	< 10	Normally internal treatment only
			> 10	Filtration plus internal treatment
< 6.3 (< 100)	103-138 (15-200)	< 75	< 10	Sodium zeolite
			> 10	Filtration plus sodium zeolite
		> 75	< 10	1. Sodium zeolite plus hydrogen zeolite 2. Sodium zeolite plus chloride/anion exchange 3. Hydrogen zeolite
			> 10	1. Filtration plus sodium zeolite plus hydrogen zeolite 2. Hydrogen zeolite
	138-448 (200-650)	< 35	< 10	Sodium zeolite
			> 10	Filtration plus sodium zeolite
		> 35	< 10	1. Sodium zeolite plus hydrogen zeolite 2. Demineralization
			> 10	1. Filtration plus sodium zeolite plus hydrogen zeolite 2. Filtration plus demineralization
> 6.3 (> 100)	103-138 (15-200)	< 75	< 10	Sodium zeolite
			> 10	1. Filtration plus sodium zeolite 2. Hot-lime soda
		> 75	< 10	Sodium zeolite plus hydrogen zeolite
			> 10	1. Filtration plus sodium zeolite plus hydrogen zeolite 2. Filtration plus demineralization
	138-448 (200-650)	All	< 10	1. Sodium zeolite plus hydrogen zeolite 2. Demineralization
			> 10	1. Filtration plus sodium zeolite plus hydrogen zeolite 2. Filtration plus demineralization 3. Hot-lime hot-sodium zeolite
All	> 448 (> 650) (normally super-heated)	All	< 10	Demineralization
			10-400	Filtration plus demineralization
			> 400	1. Filtration plus demineralization 2. RO 3. Electrodialysis

Table 2  
External Treatment Equipment Selection Guide for  
Steam Boiler Makeup Water

## NOTES:

1. *Table 2 provides only general guidelines. The final choice of treatment system must be based upon complete raw water analysis, feedwater requirements, and overall economics, including both external and internal treatment and blowdown. External treatment may be necessary to reach recommended levels of total dissolved solids (TDS) without exceeding other parameter limits for causticity, silica, or SS.*
2. *Separate deaeration is required for all boilers with pressure over 0.103 megapascal (15 pounds per square inch gauge), except where lime-soda softeners are designed to provide adequate deaeration as well as softening.*
3. *Degasification is required after hydrogen zeolite treatment.*
4. *The filtration process may require clarification and aeration.*

**2.2 AERATION.** Well water can contain high levels of dissolved iron (1 to 5 ppm). Although this quantity of dissolved iron may seem small, it can produce excessive precipitates when the iron comes in contact with air. If these precipitates are deposited in system lines, they will restrict flow and heat transfer. Soluble iron can be removed by filtration after contact with air (aeration), a process that causes the soluble iron to be converted by oxidation to insoluble iron, which then precipitates. Aerators are designed to mix air and makeup water in equipment that contains slats or trays to provide thorough mixing (i.e., aeration of the water). They are usually of the coke tray or wood slat design. Coke tray aerators consist of a series of coke-filled trays through which the water percolates. A forced-draft fan supplies air for aeration during the percolation process, with the water free falling from one tray to the next. Wood slat aerators are similar to small atmospheric cooling towers with staggered slats to break the free fall of the water and thereby increase the surface contact with air. Wood slat aerators can also be equipped with a forced-draft fan to increase efficiency. In addition to oxidizing iron, aeration can also strip or remove dissolved gases such as carbon dioxide, hydrogen sulfide, and methane. Aerators also contribute to a reduction in dissolved manganese by causing it to be oxidized to an insoluble salt.

**2.3 FILTERS AND FILTRATION.** A variety of filters can remove particles in a wide range of sizes, from course to very fine. These solids or particles may include soluble iron that has been precipitated, residual calcium carbonate particles, sand, dirt, debris, and some microbiological organisms.

### **2.3.1 SAND FILTERS**

**2.3.1.1 SAND FILTER DESCRIPTION.** A sand filter is a bed of sand (or anthracite coal) located below a set of distribution headers and resting on a support layer of coarse rock. The collection header, through which the clarified water is drawn, is situated below the sand filter. Water flows downward through the filter bed, either due to gravity or by applied pressure.

**2.3.1.2 METHOD OF ACTION.** The sand or anthracite acts as a support bed for a layer of SS laid down on top of the bed as a result of the filtering process. This layer of deposited solids, formerly SS, does most of the actual removal of solids from the water and is known as the filter cake.

**2.3.1.3 FILTER CYCLE.** As the thickness of the filter cake builds up, the water flow decreases and the backpressure increases. When the flow rate becomes too low or the back-pressure too great, the water flow can be reversed, with the filter cake then being backwashed with the wash water to a waste collection point. The filter is then returned to service and the cycle is repeated.

**2.3.1.4 SAND FILTRATION RATES.** Sand filtration rates are typically 2 liters per second per square meter (3 gallons per minute per square foot). Backwash rates are 8.1 to 10.2 liters per second per square meter (12 to 15 gallons per minute per square foot) for sand filters and 5.4 to 8.1 liters per second per square meter (8 to 12 gallons per minute per square foot) for anthracite filters. A variety of filter types are available.

**2.3.2 CARTRIDGE AND BAG FILTERS.** Cartridge and bag filters are available in various mesh and pore sizes, which determine the size of the particles removed.

**2.3.3 CENTRIFUGE SEPARATORS.** Centrifuge separators represent still another way to remove suspended materials by passing water through a centrifuge chamber where particles are removed due to density instead of size. Using separators is limited to removing very small particulates. An advantage of separators is that they do not require back-flushing or change-outs of filter cartridges or bags.

**2.4 LIME-SODA SOFTENING.** The lime-soda process is often used for treating large volumes of water (i.e., 37,850 liters per day [10,000 gallons per day] or higher) for potable and industrial uses. The process is used primarily to reduce the levels of hardness and alkalinity, but also to reduce the quantity of silica and SS. The process could be applicable to an entire base or facility; usually this process is not practical for individual small site locations. The process is labor intensive and can produce large amounts of sludge from the precipitated materials.

**2.4.1 METHOD OF ACTION.** The process involves adding hydrated lime (calcium hydroxide) and soda ash (sodium carbonate) to the water in an open reaction tank. The calcium and magnesium concentration is reduced by the resulting precipitation of solids. Bicarbonate and carbonate alkalinity is also reduced, as may be some silica. The sludge that is formed is allowed to settle for subsequent removal as a watery sludge. The treated water is filtered prior to use as makeup.

**2.4.2 COLD AND HOT PROCESSES.** Adding lime and soda ash at ambient temperature is referred to as the “cold lime-soda process.” When lime and soda ash are reacted with the water at temperatures greater than 100 °C (212 °F), the process is called the “hot lime-soda process”. The hot process removes a greater amount of the hardness, alkalinity, and silica from the water than the cold process.

**2.5 ION EXCHANGE PROCESS.** Several types of ion exchange units are used at Owner installations. An ion exchange unit is an open or closed vessel containing an ion exchange material, also known as resin, which has been deposited on a gravel support bed. Most ion exchange units operate under pressure, but gravity flow units are also available. Flow rates vary with the type of equipment but are in the range of 4 to 5.4 liters per second per square meter (6 to 8 gallons per minute per square foot of ion exchange material surface). A backup ion exchange unit and a storage tank are typically included to permit an uninterrupted supply of treated water. The manufacturer's recommendations for proper equipment operation should be posted near the softening unit. A typical ion exchange hardness softener unit is illustrated in Figure 2. Figure 3 shows a typical duplex softener.

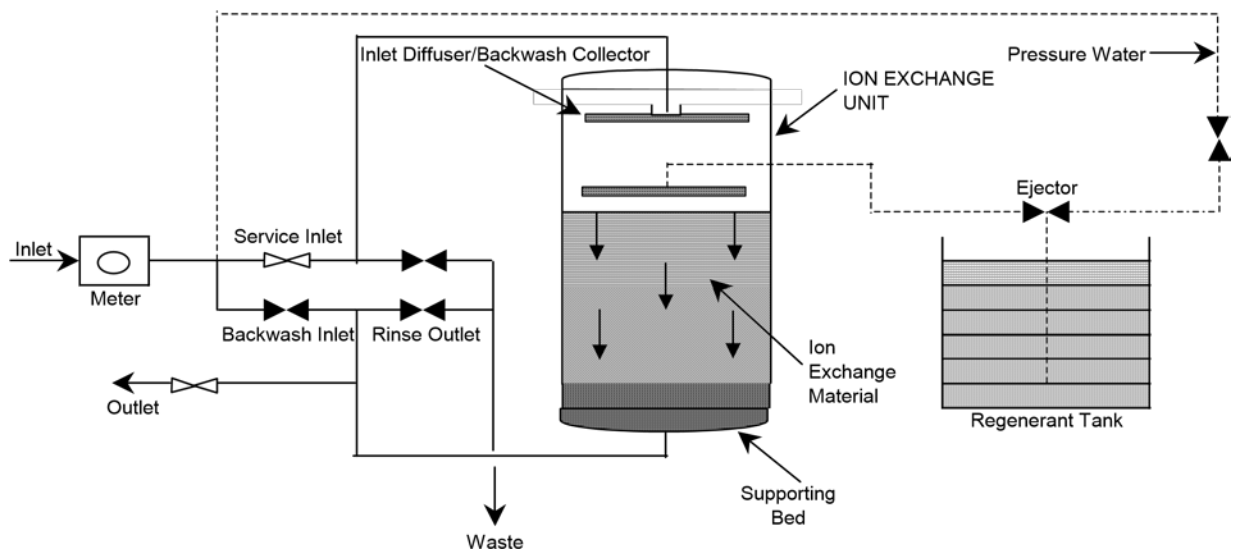


Figure 2  
Typical Ion Exchange Unit

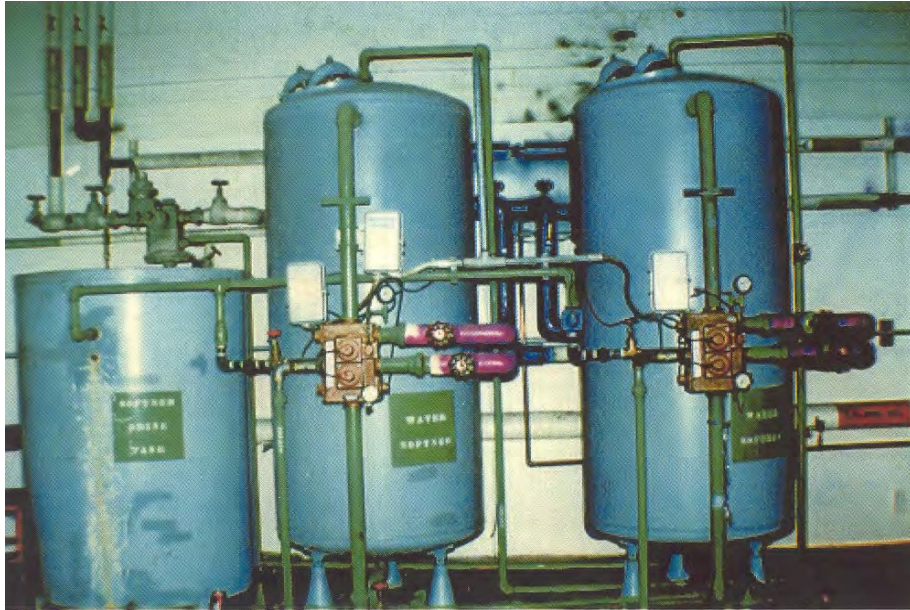
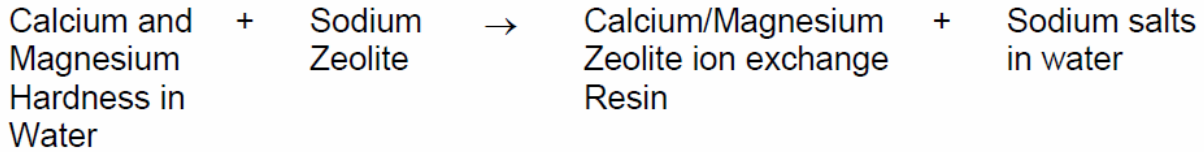


Figure 3  
Duplex Softener

**2.5.1 SODIUM ION EXCHANGE.** The sodium ion exchange process is used on most Owner installations. It is preferred to other softening processes because the equipment is compact, easy to operate, relatively inexpensive, and produces a makeup that is suitable for use in industrial water systems. This system exchanges (removes) hardness (cations) from incoming water with sodium ions contributed by the sodium chloride (salt) used in regenerating the cation ion exchange resin.

**2.5.1.1 SERVICE CYCLE.** The normal operating cycle during which hardness is removed from the makeup water flowing through the softener is determined by calculating the amount of water that can be softened by a given ion exchange material. The operator must consider several factors:

**2.5.1.1.1 SODIUM ION EXCHANGE PROCESS.** The sodium ion exchange process depends upon the exchange of sodium ions in either the zeolite material or synthetic ion exchange resins (whichever is used) for calcium and magnesium ions in the makeup water, as shown below:



**2.5.1.1.2 WATER SOFTENER CAPACITY.** The softening capability or capacity of an ion exchange softener is usually given in units of grains (grams) of total hardness of calcium carbonate (CaCO<sub>3</sub>). The operator needs to know how much water can be softened before regeneration is necessary. The volume of water that can be softened between regeneration cycles is determined by the softener capacity and the hardness in the water. See the example calculations below.

English Units

The maximum capacity of the ion exchange softener is 2,000,000 grains. The water being treated has 257 ppm total hardness. If the softener regenerations cycle is set for maximum capacity, how many gallons of water can be softened before the softener must be regenerated?

$$\begin{aligned} \text{Removal} &= \frac{\text{Capacity, grains} \times 17.12}{\text{Total hardness, ppm, in raw water}} \\ &= \frac{2,000,000 \text{ grains} \times 17.12 \text{ ppm/1 grain per gallon}}{257 \text{ ppm}} \\ &= 133,230 \text{ gallons} \end{aligned}$$

Metric Units

2,000,000 grains x (1 pound/7,000 grains) x (453.6 grams/1 pound)  
= 129,600 grams

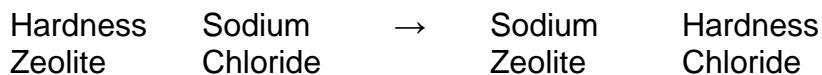


$$\begin{aligned} \text{Removal} &= \frac{\text{Capacity, grams} \times 1000 \text{ mg/gram}}{\text{Total hardness, ppm (mg/liter), in raw water}} \\ &= \frac{129,600 \text{ grams} \times 1000 \text{ mg/gram}}{257 \text{ ppm (mg/liter)}} \\ &= 504,280 \text{ liters} \end{aligned}$$



Thus, for a softener with a rated capacity of 2,000,000 grains (129,600 grams), 133,230 gallons (504,280 liters) of water, with 257 ppm total hardness, can be softened between regeneration cycles.

**2.5.1.2 REGENERATION CYCLE.** Regeneration of the ion exchange resin refers to replacement of the calcium/magnesium hardness that has accumulated on the ion exchange resin as a result of the exchange with sodium ions. The regeneration cycle is a process involving a number of steps during which the softener is taken off-line and backwashed. The resin is regenerated by treatment with a strong solution of salt (sodium chloride) and then rinsed. When the exhausted ion exchange resin material is washed with a strong sodium chloride salt solution (brine), the resin is regenerated by the hardness (calcium and magnesium ions) being exchanged for sodium ions.



The completeness of the regeneration is dependent upon the strength of the salt solution (brine) used and the length of time the solution is in contact with the resin. After the resin is regenerated, it can be used again and again (after regeneration) to continue to remove hardness from water. The following procedure is typical for an ion exchange resin regeneration process.

**2.5.1.2.1 BACKWASH.** Before the exhausted resin bed is regenerated, it must be backwashed by flowing water from bottom to top. The flow rate must be adequate to remove any solids that have been caught on top of the bed. The resin bed volume will also be expanded by about 50% due to the backwash flow; the volume of expansion will be dependent upon the flow rate. The backwash flow rate should be controlled so that it will not sweep ion exchange resin out of the softener to the waste collection area. A backwash rate of 2.72 to 4.07 liters per second per square meter (4 to 6 gallons per minute per square foot) of bed surface for about 10 minutes is normal, but the manufacturer's recommendations should be followed.

**2.5.1.2.2 BRINING.** Next comes the addition of salt, a process known as “brining.” A 10% (by saturation) solution of sodium chloride salt brine is slowly added with a downflow rate of 1.11 to 2.22 liters per second per cubic meter (0.5 to 1 gallon per minute per cubic foot) of bed volume for about 30 minutes. Rock salt is preferred to granulated salt as a brining salt because it is equally as effective, less expensive, and less prone to cake. Some installations may start with a solution of concentrated or saturated brine, which must be diluted before use in the brining step. The salt required and the capacity regenerated is shown for a typical resin in Table 3; however, the manufacturer's instructions should be followed, if available.

<b>Salt Use per liter of Ion Exchange Material kg/m<sup>3</sup> (lb/ft<sup>3</sup>)</b>	<b>Capacity of Ion Exchange Material g Hardness/m<sup>3</sup> (gr/ft<sup>3</sup>)</b>
80 (5.0)	43,450 (19,000)
120 (7.5)	55,130 (24,000)
160 (10.0)	61,615 (27,000)
240 (15.0)*	73,290 (32,000)*

*\* Practical upper limit for exchange capacity. This upper limit and the actual dose per capacity relationship may vary with the resin; the manufacturer's instructions should be followed.*

Table 3  
Salt Required for Regeneration of a Commonly Used Cation Resin

**2.5.1.2.3 SLOW RINSE.** A slow rinse follows the brining step and is performed at the same rate as the brining step. The rinse is performed with downflow through the softener. One to 3 bed volumes of fresh water are used to remove most of the excess sodium and hardness brine from the bed. The volume of fresh water is equal to 1,000 to 3,000 liters per cubic meter (7.5 to 22.5 gallons per cubic foot) of bed volume.

**2.5.1.2.4 FAST RINSE.** In the last step, a fast rinse is used, also with downflow, to remove any traces of the sodium and hardness brines. This is done at a rate of 200 to 270 liters per minute per cubic meter (1.5 to 2 gallons per minute per cubic foot) of bed volume until

the discharge is free of hardness; 4,690 to 13,400 liters per cubic meter (35 to 100 gallons per cubic foot) of bed volume is required. The unit is now ready for another service cycle.

**2.5.1.3 TESTING AND RECORD KEEPING.** Influent water should be tested for hardness on a weekly basis. The softener effluent water should be tested for hardness on a daily basis, every shift (3 times a day), or as required for systems that require frequent (1 to 3 days) or less frequent regeneration. Accurate records should be kept of these tests, including recording the number of liters (gallons) of water that have been treated during each service cycle, and the amount of salt that was used during each regeneration cycle.

**2.5.1.4 OPERATING PROBLEMS.** Several common problems are sometimes encountered during softener operation:

**2.5.1.4.1 RESIN FOULING.** A normal decrease in exchange capacity due to resin fouling is about 5% per year. Any decrease greater than this should be investigated and the reason determined.

**2.5.1.4.2 FOULING DUE TO IRON.** A common cause of loss of capacity is resin fouling by iron salts. Soluble iron will exchange for sodium during the service cycle, but sodium will only be incompletely exchanged for iron during the regeneration cycle. There is a simple test to determine iron fouling: a pinch of iron-fouled ion exchange material added to a 10% hydrochloric acid solution in a test tube will cause the hydrochloric acid to turn yellow, indicating the presence of iron. Iron-fouled resin can be returned to design capacity by cleaning with dilute hydrochloric acid, sodium bisulfite, or special resin cleaners. Specific procedures are required.

*NOTE: The softener manufacturer's recommendations should be consulted before using this acid cleaning procedure, including those prohibiting acid procedures with a galvanized or unlined steel tank. To use acid procedures, the tank must be constructed of reinforced plastic or rubber, or must be plastic-lined with no breaks in the lining.*

**2.5.1.4.3 IMPROPER BACKWASH.** Improper backwash is another common problem. A backwash rate that is too high can result in the ion exchange material being washed out of the unit. The bed depth can be measured by carefully probing to the underdrain support bed. Normal bed depth is usually 0.75 to 1 meter (30 to 36 inches). The bed volume in cubic meters (cubic feet) can be calculated by the following formula:

$$\text{Volume, m}^3 = (\text{Radius, m})^2 \times (\text{Depth, m}) \times 3.14$$

Check the bed depth at 10 points and use the average value. If there is much difference (15% or more) in the thickness of different points, channeling may be occurring. Channeling can be caused by too low a backwash rate. If the calculated bed volume is less than the volume given by the manufacturer, material has been lost during the backwash step. The lost material should be replaced and the backwash rate carefully controlled to ensure material is not being washed out. If the cause of the unit's performance problem or deficiency cannot be determined, the manufacturer's service representative should be consulted.

**2.5.1.4.4 RESIN REPLACEMENT.** The resin in the ion exchanger should be replaced when either the resin capacity or the softening efficiency has decreased by 25% and cannot be restored by cleaning and by following the specific procedures recommended by the manufacturer. Based on a normal decrease of 1 to 5% per year, the typical ion exchange resin should last from 5 to 25 years. With good operation, the average service life is 8 to 10 years.

**2.5.2 HYDROGEN ION EXCHANGE.** The hydrogen ion exchange process is essentially the same as the sodium ion exchange process except that the regenerant chemical is an acid (sulfuric or hydrochloric) rather than a salt. The hydrogen ion exchange process will reduce both the amount of the total dissolved solids and the alkalinity of the treated water. During operation of the hydrogen cycle softener, it is necessary to check the outlet (softened) water at regular intervals. The hardness of the outlet water should always be

less than 1 ppm. The ion exchange resin must be regenerated if the hardness exceeds 1 ppm. This check can be performed daily, once per shift, or as required depending on unit capacity.

**2.5.2.1 EXCHANGE PROCESS.** Resins exchange calcium, magnesium, sodium and all cations with hydrogen ions.



The hydrogen salts are acidic and will react with alkalinity to produce carbon dioxide and water. To provide for effective operation, the carbon dioxide must be removed after leaving the vessel by other means.

**2.5.2.2 REGENERATION METHOD.** The spent ion exchange material is regenerated by contact with dilute acid, such as sulfuric acid or hydrochloric acid.



Adding sulfuric acid in several steps of increasing strength, such as 2, 4, 6 percent, is required for sulfonated styrene resins if fouling of the exchange resin with calcium sulfate is to be avoided.

**2.5.2.3 EQUIPMENT REQUIREMENTS.** The hydrogen ion exchanger is much the same as the sodium ion exchanger, except that all equipment must be made of, or lined with, acid-resistant material.

**2.5.2.4 REGENERATION CYCLE.** The regeneration cycle is much the same as that for the sodium ion exchanger, except that sulfuric acid is used instead of salt. To improve efficiency, regeneration of hydrogen ion exchangers is commonly done counter-currently. During operation of the hydrogen cycle softener, it is necessary to check the outlet

(softened) water at regular intervals. The hardness of the outlet water should always be less than 1 ppm. The ion exchange resin must be regenerated if the hardness exceeds 1 ppm. This check can be performed daily, once per shift, or as required depending on unit capacity. Available information on safety and first aid should be reviewed before using sulfuric acid. Chemical handling and safety instructions should be posted near sulfuric acid equipment. Sulfuric acid is corrosive to skin, eyes, clothing, and other materials. Hydrochloric acid should be used with the same precautions.

**2.5.2.5 TROUBLESHOOTING.** Troubleshooting is much the same as for sodium ion exchange, although iron fouling does not occur in hydrogen ion exchangers since the acid removes iron from the resin.

**2.5.2.6 EFFLUENT WATER PROPERTIES.** The hydrogen ion exchange effluent water is acidic and cannot be used directly. The water can be mixed with the outlet of a sodium ion exchanger with the result that the acid in the hydrogen ion exchange water will be neutralized to some degree and, at the same time, the degree of alkalinity in the sodium ion exchange water will be lessened. The proportion of the effluent waters to be mixed is dependent upon the analysis of the water being treated, but typically the proportion is approximately one-to-one (half-and-half). The testing of blended water should be done prior to blending to assure that the blended water is satisfactory for use in the boiler or cooling water system. If neutral (pH 7) water is required, a chemical (such as sodium hydroxide) must be added.

**2.5.2.7 CARBON DIOXIDE PRODUCTION.** Carbon dioxide is produced during the hydrogen ion exchange process and is also produced when the effluent water from hydrogen and sodium ion exchange is mixed. It is removed from the water in a decarbonator (degasifier or deaerator).

**2.5.3 DEMINERALIZATION.** Sodium and hydrogen ion exchangers remove only the positively charged ions (cation exchange - i.e., calcium, magnesium, and sodium). Other ion exchange materials have been developed to remove negatively charged ions (anion

exchange - i.e., sulfates, chlorides, and alkalinity). The process of demineralization uses both cation and anion exchange resins to remove all ions from the water, thus producing mineral-free water. A typical deionization (demineralizer) process is illustrated in Figure 4. During operation of the demineralizer, it is necessary to check the outlet water at regular intervals. The TDS of the outlet water should always be less than 1 ppm. The ion exchange resin must be regenerated if the TDS exceeds 1 ppm. This check can be performed daily, once per shift, or as required depending on unit capacity.

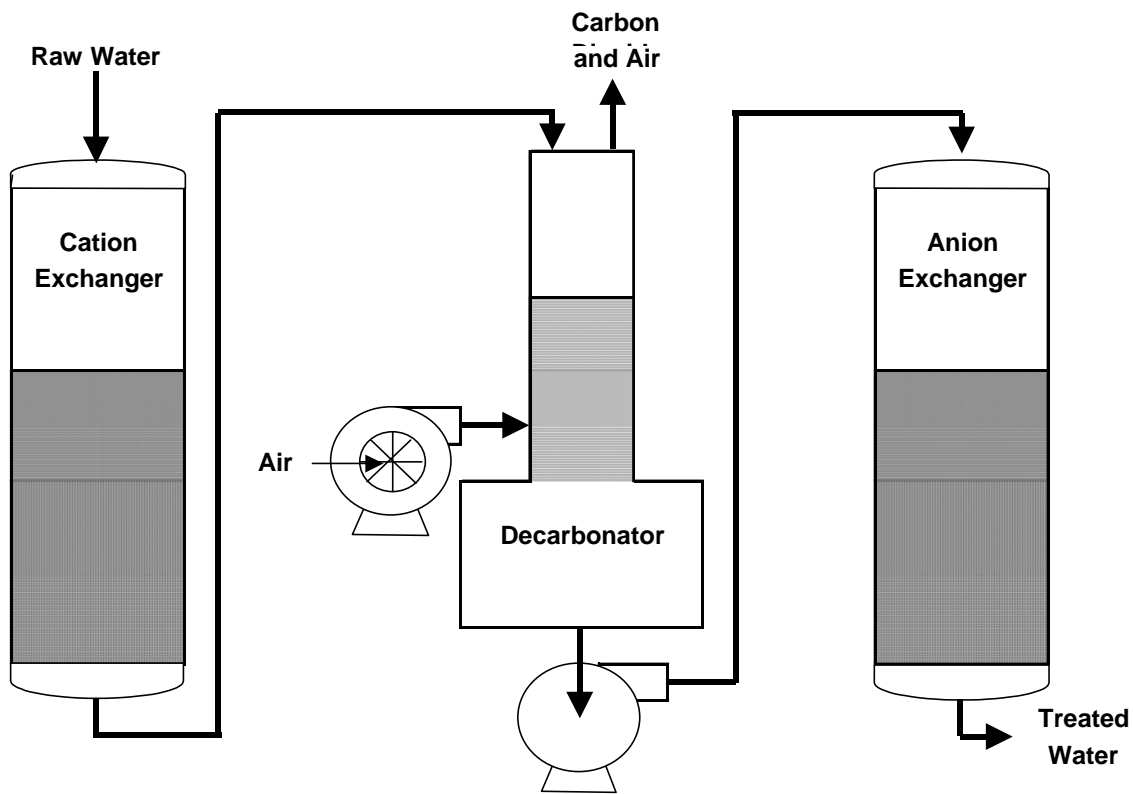
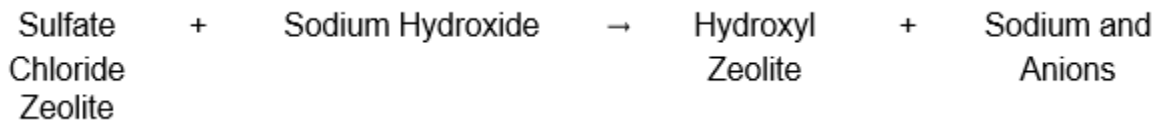


Figure 4  
Demineralization Process

**2.5.3.1 ANION EXCHANGE PROCESS.** The hydrogen ion cation exchange process is described in paragraph 2.5.2. The anion exchange process involves reactions of hydroxyl-regenerated zeolite with the effluent from the hydrogen ion exchanger:



**2.5.3.2 ANION ION EXCHANGE REGENERATION METHOD.** The spent anion ion exchange material containing chlorides, sulfates, and other anions is regenerated with sodium hydroxide (caustic).



**2.5.3.3 EXCHANGE PROCESS RESULT.** When the anion exchange process is combined with the hydrogen exchange process, the resulting final water will contain no minerals. It has become deionized (also referred to as demineralized) by exchanging all minerals to hydrogen hydroxide, HOH, commonly referred to as water and written as H<sub>2</sub>O.

**2.5.3.4 EXCHANGE METHOD.** The two reactions can take place in separate vessels (a “two-bed” deionizer), or the two ion exchange materials can be combined in a single vessel (a “mixed-bed” deionizer).

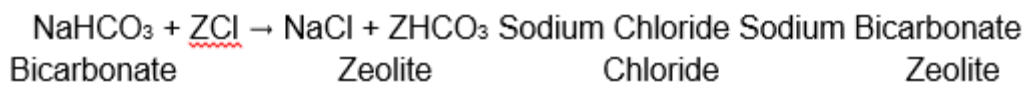
**2.5.3.5 HIGH SILICA WATERS.** Removal of silica and magnesium beyond what most demineralizers will provide is accomplished through pre-heating of caustic solution used for regeneration. Optimum temperature is 49 °C (120 °F) and should not exceed 60 °C (140 °F), as that temperature can damage the resin; however, few demineralizers are designed for this application.

**2.5.3.6 DEIONIZATION PROCESS USE.** The deionization process is not used at Owner installations. It is required mainly for high-pressure boilers or high-purity water use. The deionization process may also be used by the Navy for shore plants providing steam or boiler feedwater to ships.



## 2.5.4 DEALKALIZATION

**2.5.4.1 ANION DEALKALIZATION.** It may be necessary to treat water having low hardness and high alkalinity to reduce the alkalinity (bicarbonate and carbonate). The anion exchange process called “anion dealkalization” will remove alkalinity and other anions (i.e., sulfates and nitrates). In most cases, the anion dealkalizer is used following a hardness softener (i.e., it is located downline from the softener) because hardness, if not previously removed, can precipitate in the anion resin bed and cause plugging. Bicarbonate and carbonate (anions) are exchanged for chloride (anion) as illustrated by the following reaction, where “Z” is the zeolite resin material:



**2.5.4.1.1 SYSTEM REGENERATION.** The system is regenerated with sodium chloride (salt) as shown below. The regeneration will be more efficient and effective if the brine used contains about 10% of the salt as caustic.



**2.5.4.1.2 EQUIPMENT AND OPERATION.** The equipment and operation of such a system is much the same as for a sodium ion exchange material system described in Paragraph 2.5.1. This process is illustrated in Figure 5.

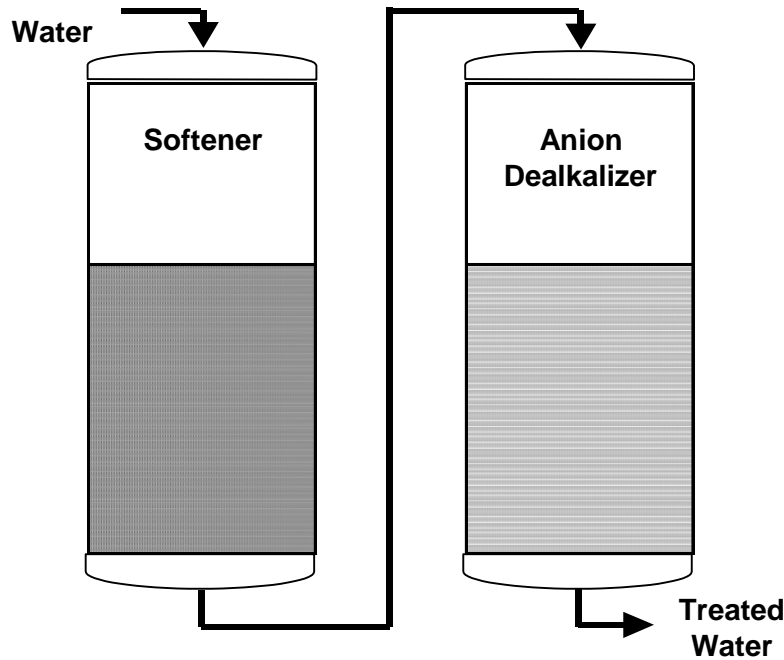
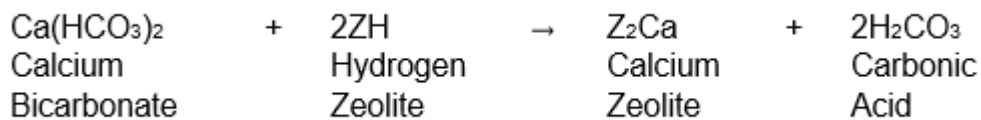


Figure 5

Anion Dealkalization Process

**2.5.4.2 SPLIT-STREAM DEALKALIZATION.** In a split-stream dealkalization process, the water is split into two parallel streams with one stream passing through a strong acid cation exchanger (dealkalizer) and the other through a sodium zeolite softener. Blending of the two product streams produces a soft water that is low in alkalinity. The alkalinity reduction is described by the following equation, where “Z” is the zeolite resin material:



The carbonic acid dissociates into carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O). The water is then passed into a decarbonator (degasifier or deaerator) to remove the CO<sub>2</sub>.

**2.5.4.2.1 FREE MINERAL ACID PRODUCTION.** The strong acid cation exchange resin replaces the sodium, calcium, and magnesium ions with hydrogen ions. Thus, due to the presence of chlorides, sulfates, nitrates, and other anions, free mineral acids (FMA) (i.e., hydrochloric, sulfuric) are produced. Adjustment of the pH level is necessary to balance alkalinity with acidity (FMA) and form neutral water.

**2.5.4.2.2 SYSTEM REGENERATION.** The strong acid cation system is regenerated with sulfuric acid as described in Paragraph 2.5.2.

**2.5.4.2.3 EQUIPMENT REQUIREMENTS.** The acid exchanger tank must be made of, or lined with, an acid-resistant material.

**2.5.4.2.4 DECARBONATOR USE.** Since blending the two split streams of finished water also produces CO<sub>2</sub>, a decarbonator (degasifier or deaerator) is normally used to reduce the CO<sub>2</sub> concentration to 5 to 10 ppm or less. A typical split-stream process is shown in Figure 6.

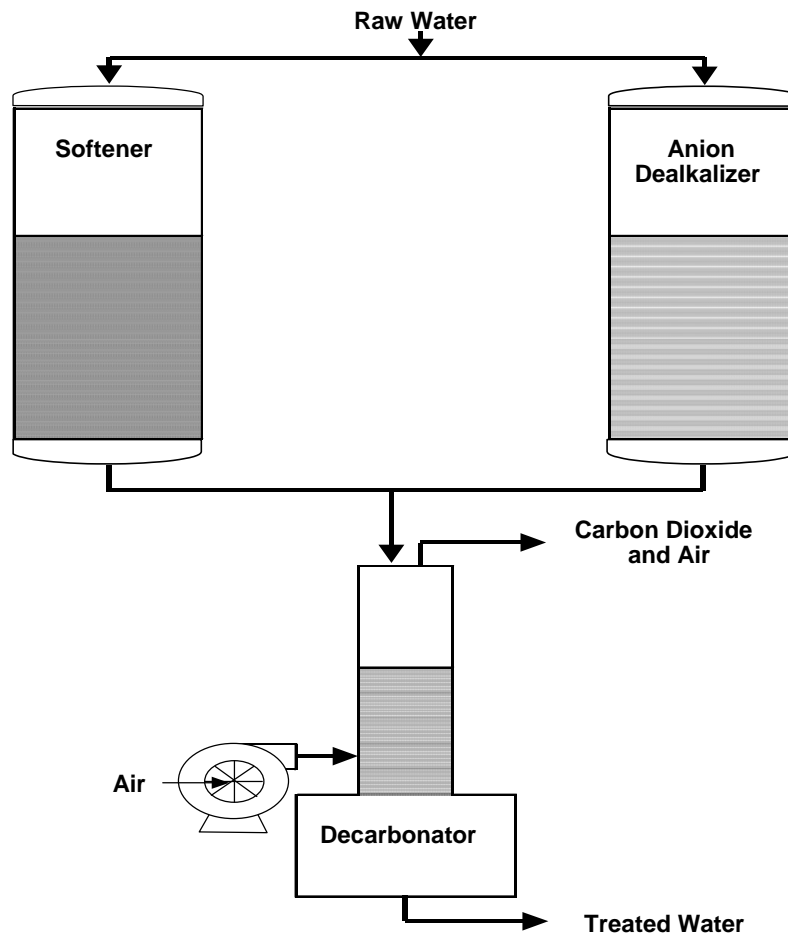


Figure 6  
Split-Stream Dealkalizer

**2.5.5 DECARBONATION.** Carbon dioxide is produced during hydrogen ion exchange and when the effluent waters from strong acid cation ion exchange and the sodium ion exchange are mixed. Carbon dioxide dissolved in water can cause corrosion in water lines, pump impellers, and vessels. As described in Chapter 3, the carbon dioxide concentration must be kept as low as possible in the boiler feed water and in the water entering steam condensate lines.

**2.5.5.1 METHODS OF DECARBONATION.** Free carbon dioxide is commonly removed in a degasifier or aerator (see Paragraph 2.2). In steam systems and in high temperature water systems, removal of CO<sub>2</sub> is usually achieved in the deaerator rather than with a separate degasifier unit, although steam systems can have degasifiers.

**2.5.5.2 ANALYSIS OF CARBON DIOXIDE CONTENT.** By analyzing the water for the hydrogen ion concentration (pH) and the total (M) alkalinity, the free carbon dioxide content can be calculated (see Table 4).

pH	CO <sub>2</sub>	pH	CO <sub>2</sub>	pH	CO <sub>2</sub>
5.4	4.4 M	6.6	0.45 M	7.3	0.099 M
6.0	1.9 M	6.7	0.38 M	7.4	0.079 M
6.1	1.5 M	6.8	0.31 M	7.5	0.062 M
6.2	1.23 M	6.9	0.24 M	7.6	0.050 M
6.3	0.92 M	7.0	0.19 M	7.7	0.040 M
6.4	0.75 M	7.1	0.15 M	7.8	0.033 M
6.5	0.62 M	7.2	0.12 M	7.9	0.026 M

Table 4  
Carbon Dioxide Content of Water vs. pH

**NOTES:**

1. At pH levels of 8.0 or higher, the free CO<sub>2</sub> content is negligible.
2. "M" is total alkalinity (as calcium carbonate [CaCO<sub>3</sub>]).

EXAMPLE:

- a) Total alkalinity (M) of an inlet water to a degasifier is 100 ppm and the pH is 6.8.

$$\text{CO}_2 \text{ content} = \text{Value} \times M = 0.31 \times 100 = 31 \text{ ppm}$$

- b) The outlet pH is 7.9, so the CO<sub>2</sub> content will be (let M = 80, since some alkalinity was removed as CO<sub>2</sub>):

$$\text{CO}_2 \text{ content} = 0.026 \times 80 = 2.1 \text{ ppm}$$

- c) The carbon dioxide removal is:  $31 - 2.1 = 28.9$  ppm

**2.6 EVAPORATORS.** In the evaporation process used in evaporators, water is heated to produce relatively pure water vapor that is then condensed to liquid water and used for boiler feed. Evaporators are of several different types. The simplest is a tank of water through which steam coils are passed to heat the water to the boiling point. To increase efficiency, the vapor from the first tank may pass through coils in a second tank of water to produce additional heating. Another type of evaporator operates under a partial vacuum, lowering the boiling point of water and enabling evaporation at lower temperatures. Following its production in the evaporator, water vapor is cooled and becomes liquid water that is essentially pure water, without any dissolved solids. Using evaporators may be economical where inexpensive steam is readily available as the source of heat. Evaporators also have an advantage over deionization units when the dissolved solids in the raw water are very high, such as on ocean-going vessel.

**2.7 REVERSE OSMOSIS (RO).** This process is the opposite of osmosis. It produces very pure water by separating dissolved minerals from the water. Water pressure is used to push water through a membrane. The membrane allows only pure water to pass through. Water thus produced is known as RO product water. All dissolved solids, organics, and gases that do not pass through the membrane are removed in the waste stream of RO reject water. Sufficient care must be taken to protect the membrane from deposits, which

reduce efficiency or plug the membrane. This RO process is illustrated in Figure 7. An RO unit is shown in Figure 8.

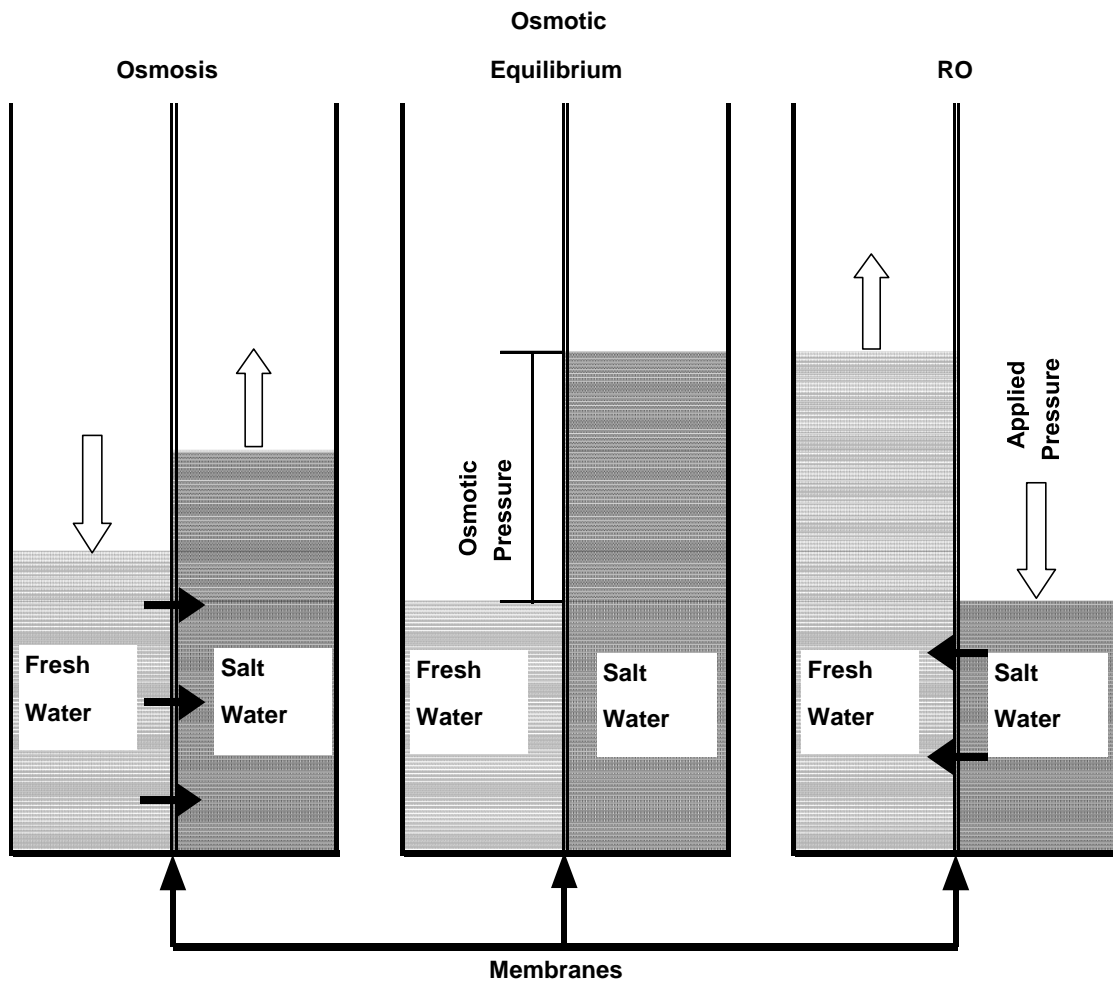


Figure 7

RO Schematic

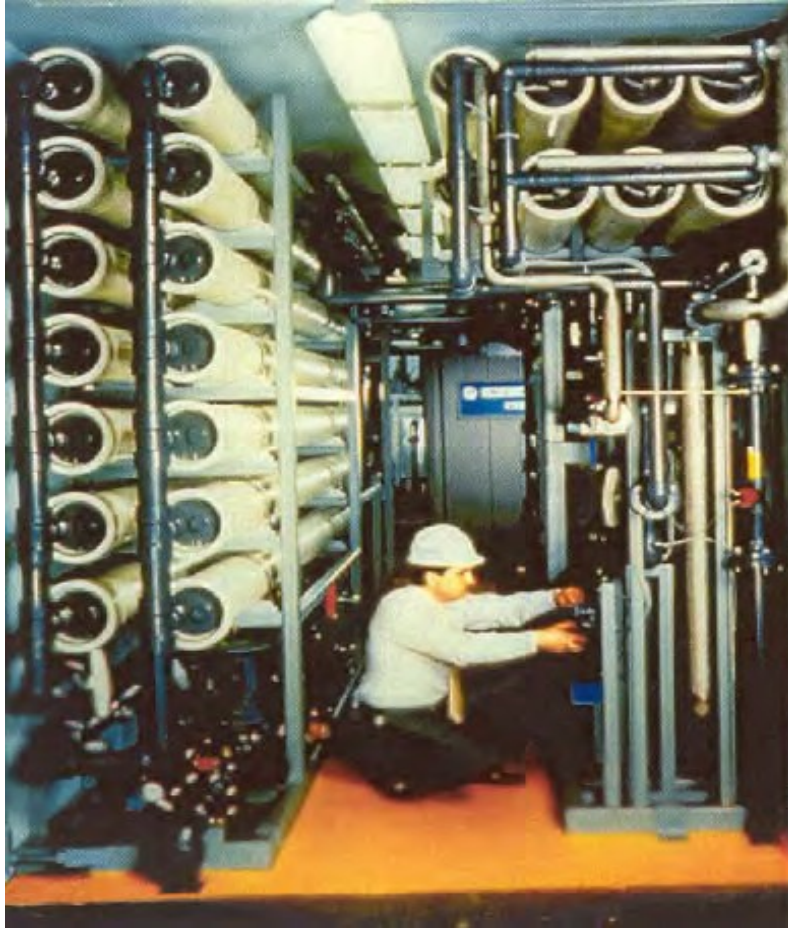


Figure 8

RO Unit

**2.7.1 RO PRETREATMENT.** Material that can potentially foul (or plug) the membrane will interfere with the RO process and must be removed before the water contacts the membrane. Foulants include suspended and colloidal solids, iron, metal oxides, scale, and biological materials. It is important to determine a Silt Density Index (SDI), a measurement of suspended materials in the water, prior to using the water in the RO unit. Only water determined to be within the manufacturer's acceptable SDI range should be used. Pretreatment may be required to achieve an acceptable SDI.

**2.7.1.1 SS REMOVAL.** SS can be removed by filtration, usually using a sand filter followed by a cartridge filter. The addition of filter aids may be necessary to achieve acceptable filtration. In certain instances, coagulation and clarification may be required before the filtration step.

**2.7.1.2 IRON OXIDE REMOVAL.** Iron oxides are the result of the oxidation of dissolved ferrous salts or corrosion of the equipment. The first process can be controlled by aerating the water prior to its being filtered, the second by threshold treatment with sodium hexametaphosphate before any aeration. For proper operation, these iron oxides must be removed prior to the water contacting the membrane.

**2.7.1.3 SCALE PREVENTION.** Scale-forming salts are concentrated as a result of the RO process just as they are during an evaporative process. To prevent scale, the water's pH is adjusted by adding either acid to produce a pH of between 5.0 and 6.5, or a scale inhibitor such as sodium hexametaphosphate or any of the phosphonates (PBTC [2-phosphonobutane-1,2,4-tricarboxylic acid], HEDP [1-hydroxyethylidene 1,1diphosphonic acid], or AMP [amino-tri (methylene) phosphonic acid]). The solubility of scale-forming salts controls the rejection rate of the water that cannot be processed through the RO unit (i.e., the amount of blowdown water produced). Specific guidelines should be obtained from the RO manufacturer.

**2.7.1.4 BIOLOGICAL FOULING.** Biological fouling is a condition that must be prevented. Potentially, the RO unit membrane may be damaged when chlorine or other oxidants are used. For proper operation, the water must be dechlorinated with a reducing agent or with activated carbon before it contacts the RO membrane.

**2.7.2 MEMBRANE CONFIGURATION.** There are three basic membrane configurations: tubular, spiral-wound or scroll, and hollow fiber.



**2.7.2.1 TUBULAR CONFIGURATION.** The tubular configuration is simply a porous tube supporting a membrane. Feedwater is introduced into the tube. Product water permeates the membrane going to the outside of the tube. The reject water exits from the far end of the tube.

**2.7.2.2 SPIRAL CONFIGURATION.** The spiral configuration is a sheet membrane that is supported on each side by a porous material that provides flow distribution and rolled into a spiral or "jelly roll" configuration. The membrane is put in a pressure vessel so pressure can be maintained on its surface. This pressure forces the water through the membrane, separating it from the impurities. The membrane is laminated between porous sheets and sealed on three sides. The laminate is then attached on the fourth side to a porous tube and rolled around the tube into an element. Feed solution is forced into the element at one end, and the permeate works its way through the spiral to the axis tube where it emerges as purified product.

**2.7.2.3 HOLLOW CONFIGURATION.** The hollow fiber configuration consists of small (85-millimeter [3.3-inch] diameter) tubes whose outside wall is semi-permeable. A large number of these tubes are placed in a shell, similar to a heat exchanger. Water, under pressure, on the exterior of the tubes permeates the tubes and is collected from the tube interiors.

**2.7.3 SEA WATER.** RO technology is particularly useful when feedwater is high in dissolved solids or when the source is brackish water or seawater. When used ahead of a deionizer, the chemical requirements for the deionizers are greatly reduced, resin life is extended, and a smaller quantity of chemical regenerants is required.

**2.8 ULTRAFILTRATION.** The term "ultrafiltration" describes a pressurized membrane process in which particulate, colloidal, and high-molecular-weight dissolved materials are filtered from the water. Ultrafiltration is a process that is similar to RO in that a semi-

permeable membrane is used to remove the filterable solids, except that the membrane is more porous, thus allowing some water-dissolved minerals to pass through with the product water. The feedwater flows through the inside of the fibers, permeates through the membrane, and is removed as product from the shell side. The filtered solids are continuously removed from the other end of the fiber in a reject stream that typically contains 5 to 10% of the feedwater dissolved solids.

**2.9 ELECTRODIALYSIS.** The term “electrodialysis” describes a process that separates all materials and minerals that are ionized from water by attracting the ions dissolved in the water through membranes that are oppositely charged. When the water is high in dissolved minerals, as in brackish water that contains more than 2500 ppm TDS, its use may be more economical than the ion exchange methods. Under some circumstances, it may remove enough minerals to make seawater usable in industrial water systems. This process does not remove un-ionized or poorly ionized materials such as some organics and soluble silica. As with RO, membranes must be kept clean.

**2.10 NANOFILTRATION.** This is a process that, in terms of the size of materials removed, is intermediate between ultrafiltration and RO. The molecular weight cut-off properties of nanofiltration membranes are in the range of  $< 1 \times 10^{-3}$  m (400 to 800 Daltons or 10 angstroms). Ionic rejections vary widely depending on the valence of the salts. Multivalent salts such as magnesium sulfate ( $\text{MgSO}_4$ ) are rejected as much as 99%, while monovalent salts such as sodium chloride ( $\text{NaCl}$ ) may have rejections as low as 20%.