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Revision Memo

12/03 Added a Reliability Checklist Appenbix B

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SCOPE

This section describes water treating processes which are commonly used to produce boiler feedwater for utility and waste heat boilers. This practice does not cover water treating processes associated with once-thru steam generation or dirty steam generation systems. These applications are very site and process specific and cannot be generalized. The EMRE STEAM SYSTEM SPECIALISTS are available for consultation on specific requirements. A method is presented to select the process which will produce boiler feedwater of the required quality from municipal water, well water, surface water or salt and brackish waters.

Included are design criteria for specific water treating units and considerations for selecting an optimum system.

REFERENCES

DESIGN PRACTICES

Section II	Design Temperature, Design Pressure and Flange Ratings
Section V	Drums
Section IX	Heat Exchange Equipment
Section X	Pumps
Section XII	Instrumentation
Section XIV	Fluid Flow
Section XXII	Storage Facilities

GLOBAL PRACTICES

GP 1-1-1	Drawings, Diagrams and Line Lists
GP 3-10-4	Plastic and Plastic-Lined Piping
GP-11-0-0	Water Treating Units

COMPANY REFERENCES

ExxonMobil, *Refinery Construction Materials Manual*, EMRE Manual No. EETD 028
Chemical And Mechanical Cleaning Guide
ExxonMobil, *Water and Wastewater Design Guide*, EMRE Manual No. TMEE 080

OTHER LITERATURE

1. *New Guide to Boiler Water Treatment*, ER&E Report No. EE.2E.86.
2. *Polyelectrolite Guide*, ER&E Report No. EE.20E.84.
3. Applebaum, Samuel B., *Demineralization by Ion Exchange*, New York and London, Academic Press, 1968.
4. Drew Chemical Corporation, *Principles of Industrial Water Treatment*, Boonton, NJ, Drew Chemical Corporation, 1977.
5. Betz Chemical Corporation, *Betz Handbook of Industrial Water Conditioning*, Philadelphia, PA, Betz Laboratories Inc., 1991.
6. Aqua-Chem Inc., *Process Selection Guide for Seawater Desalting*, Technical Presentation 750-3550.
7. Bechtel Group Inc., *Desalination Technology-Report on the State of the Art*, San Francisco, CA; Bechtel Inc., 1983.

BACKGROUND

The main objective of boiler water treatment is to eliminate or minimize problems caused by impurities in the water and steam. The problems include corrosion, scale, carryover, and caustic embrittlement.

Corrosion can affect deaerators, feedwater heaters, boilers, economizers, condensers, piping, etc. Scale reduces heat transfer and causes overheating of boiler tube metal. Foaming and priming cause boiler water carryover with the steam, which results in turbine mechanical problems, plus superheater and turbine deposits. Carryover may also foul catalysts in process units. Caustic embrittlement or intercrystalline cracking of metal occurs when the boiler water has embrittling characteristics and is capable of attacking boiler metal.

General principles are given for designing boiler feedwater treatment systems. However, these principles are presented as a guide only, since it is virtually impossible to provide a complete design covering every aspect of water treatment. It must be recognized that treatment requirements are contingent on raw water quality, boiler type and pressure, steam usage, etc.

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BACKGROUND (Cont)

Effective water quality control can involve several steps and require proper monitoring at all times.

The two general classes of boiler feedwater conditioning are external and internal to the boiler. Both treatments have an effect on each other and must be integrated to provide a uniform treatment program.

The **external** treatment process involves the following:

- Treatment of make-up water to reduce suspended solids, dissolved solids and organics to an acceptable level.
- Treatment of return condensate streams to reduce iron, dissolved solids and trace organics to an acceptable level, and to maintain the proper pH.
- Degasification and deaeration to reduce the amount of dissolved gases in the make-up water and condensate streams.

The **internal** treatment process controls boiler water quality via chemical addition and blowdown control. This is required to prevent corrosion of the boiler system and to avoid foaming, scaling and carryover into downstream equipment (e.g., steam turbines, letdown stations, heat exchangers, etc.).

DEFINITIONS

Alkalinity

Includes the total carbonate, bicarbonate, and hydroxide ion concentration in the water expressed as ppm calcium carbonate equivalent. Alkalinity is measured by double titration with acid and Phenolphthaline (P) and Methyl Orange (MO or M) indicators. The MO alkalinity includes all carbonate, bicarbonate and hydroxyl ions and the P alkalinity includes all hydroxyl and 1/2 of the carbonate ions.

Anions

Negatively charged ions in the water (e.g., sulfates, chlorides, nitrates, bicarbonates, etc.).

Anion Exchanger

A vessel containing insoluble resin which is capable of exchanging one anion, usually hydroxide ions, for other anions in the water (e.g., sulfates, chlorides, nitrates, etc.).

Backwash

The upward flow of water through a filter or fixed bed ion exchange unit to remove accumulated suspended solids and to reduce compaction of the bed.

Bed

The depth of ion exchange resin or other solid media in a vessel.

Blowdown

The removal of a portion of water from the boiler drum to control the concentration of dissolved and suspended impurities in the boiler water.

Brine

A solution of sodium chloride in water.

Calcium and Magnesium Hardness

The concentration of calcium and magnesium ions in the water, expressed as ppm calcium carbonate equivalent.

Cations

Positively charged ions in the water (e.g., calcium, magnesium, sodium, etc.).

Cation Exchanger

A vessel containing insoluble resin which is capable of exchanging one cation, usually hydrogen or sodium ions, for other cations in the water (e.g., calcium, magnesium, etc.).

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DEFINITIONS (Cont)

Caustic or Caustic Soda

The chemical compound sodium hydroxide (NaOH).

Coagulation

A process whereby suspended and colloidal particles, which cause turbidity and color in water, are combined by physical means into masses sufficiently large to be settled.

Colloid

A substance made up of very small, insoluble particles less than one micron in size. These particles are small enough so that they remain suspended in a liquid without settling to the bottom.

Concentrate

The waste (high dissolved solids) water stream from a membrane system (eg. Reverse Osmosis, Electrodialysis, etc.).

Conductivity

The ability of water to conduct electricity due to the presence of ionized material within the solution. Conductivity is expressed in micromhos (or micro Siemens), and is in direct proportion to the amount of dissolved matter in the water.

Degasification / Decarbonation

The process of removing dissolved gases other than air from water. Air from a blower comes into intimate counter-current contact with the water droplets and scrubs out the gases. Degasification in boiler water treatment usually has as its aim the removal of carbon dioxide.

Demineralization

The removal of dissolved ionic matter from water.

Dissolved Solids

Normally salt impurities which are present in the water in solution, usually as ionic material.

Dolomitic Lime

Lime containing 30 - 35 wt% magnesium oxide.

Filtration

The process of passing water containing suspended matter through a suitable porous material in such a manner as to effectively reduce the concentration of suspended matter in water. The suspended matter is normally reduced to less than one NTU of turbidity.

Free Mineral Acidity

The presence of acids such as sulfuric, nitric, and hydrochloric in the effluent of a cation exchanger, expressed as ppm calcium carbonate equivalent.

Hardness Alkalinity

The concentration of calcium and magnesium bicarbonate and carbonate salts in water, expressed as ppm calcium carbonate equivalent.

Hydrate Alkalinity

The free hydroxide ions in water, expressed as ppm calcium carbonate equivalent.

Ion

Electrically charged particle formed when a molecule dissociates into positive and negative particles in water (e.g., salt into sodium + and chloride - ions).

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DEFINITIONS (Cont)

Lime, Slaked

The chemical compound calcium hydroxide, $\text{Ca}(\text{OH})_2$. Slaked lime is also called hydrated lime.

Nephelometric Turbidity Unit (NTU)

Turbidity of a sample of water, measured by light reflection.

Osmosis

A natural process where pure water flows from a dilute saline solution, through a membrane, into a more concentrated solution.

Osmotic Pressure

The pressure (head) of a solution which is a function of its impurities (salt concentration).

Permeators

Membrane units which are used in the desalination of water. The most widely used permeators are either "spiral wound" or "hollow fiber" type units.

Permeate

The product (pure) water stream from a permeator or RO System.

Raw Water

Water which has not yet been processed by the water treating plant.

Regeneration

The process of replenishing the ion exchange capacity of an ion exchange resin.

Reverse Osmosis

A process which uses pressure energy to separate water from its contaminants. Pressure is applied externally to overcome the osmotic pressure of the fluid. This allows the passing of "pure" water (permeate) through a membrane while retaining the solids rich residual (concentrate).

Resin

A term referring to ion exchange material used in a water treating process.

Silica

An impurity present in water sources, expressed as reactive SiO_2 .

Softening

The process of removing calcium and magnesium ions from water.

Soda or Soda Ash

The chemical compound sodium carbonate (Na_2CO_3).

Sodium Zeolite

A cation resin capable of removing calcium and magnesium ions from water by exchanging the calcium and magnesium ions with sodium ions.

Suspended Solids

Finely divided insoluble matter present in water. The suspended solids are normally inorganic material, such as clay, rock, silt, etc.

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DEFINITIONS (Cont)**Total Hardness**

See Calcium and Magnesium Hardness.

Total Solids

The sum of the suspended and dissolved solids in water.

Train

Two or more vessels operating in series.

Treated Water

Water which has been processed by the water treating plant to reduce the level of suspended and dissolved impurities.

Turbidity

A term referring to the lack of clearness in a water due to the presence of suspended or colloidal matter and expressed in Nephelometric Turbidity Units (NTU).

BOILER WATER QUALITY REQUIREMENTS

The allowable concentration of impurities in boiler water determines the type of boiler feedwater treatment required. Operating experience with new boilers throughout the ExxonMobil circuit has shown that serious carryover problems have resulted when boiler water treatment is designed for the maximum total solids concentration that used to be permitted by the American Boiler Manufacturer's Association (ABMA). Wide fluctuations in steam load, high heat flux rate and small steam drums on modern boilers increase carryover, which result in loss of superheater tubes and excessive turbine blade deposits. To avoid these problems, ExxonMobil based its designs on limits which were about 50% lower than the ABMA limits.

In recent years, the American Society of Mechanical Engineers (ASME) developed a *Consensus on Operating Practices for the Control of Feedwater and Boiler Water Quality in Modern Industrial Boilers*. ER&E's *New Guide to Boiler Water Treatment* (Report No. EE.2E.86) incorporates these new standards. The following simplified tables are extracted from the EE Guide and can be used for planning purposes. Consult with the WATER TREATING DISCIPLINE SPECIALIST regarding specific design requirements.

[Tables 1A&B](#) lists the Boiler Drum Water limits for **Non-demineralized** and **Demineralized** Operations, respectively.

In general, boiler blowdown rates of less than 5% require demineralized water. In addition, boiler operating pressure ranges determine the type of make-up water treatment required for trouble free and economic operation.

BOILER PRESSURE RANGES psig (bar)	TYPE OF MAKE-UP WATER TREATMENT
< 500 (35)	Softening
500 - 1000 (35 - 69)	Demineralization or Softening
> 1000 (> 69)	Demineralization

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BOILER WATER QUALITY REQUIREMENTS (Cont)

Table 1
Boiler Drum Water Limits
Non-Demineralized Operation

Table 1A

PARAMETER	BOILER PRESSURE, psig (barg)					
	0 - 150 (0 - 10)	151 - 300 (10 - 21)	301 - 450 (21 - 31)	451 - 600 (31 - 41)	601 - 750 (41 - 52)	751 - 900 (52 - 62)
Conductivity at 25°C (77°F) (μS/cm)	< 1750	< 1500	< 1250	< 1000	< 750	< 625
Total (M) Alkalinity (ppm as CaCO ₃)	< 350	< 300	< 250	< 200	< 150	< 125
Free Hydroxyl Alkalinity (2P-M) (ppm as CaCO ₃)	< 175	< 150	< 125	< 100	< 75	< 60
Silica (ppm SiO ₂)	< 125	< 90	< 50	35	< 20	< 8
Chloride (ppm Cl)	< 250	< 225	< 200	< 175	< 150	< 50
Suspended Solids (ppm)	< 15	< 15	< 10	< 8	< 6	< 4

Table 1B
Boiler Drum Water Limits
Demineralized Operation

PARAMETER	BOILER PRESSURE, psig (barg)					
	450 - 600 (31 - 41)	601 - 750 (41 - 52)	751 - 900 (52 - 62)	901 - 1200 (62 - 83)	1201 - 1500 (83 - 103)	1501 - 2000 (103 - 138)
Conductivity at 25°C (77°F) (μS/cm)	< 300	< 200	< 175	< 150	< 100 ----- >	
Silica (ppm SiO ₂)	< 35	< 20	< 8	< 2.5	< 1.0	< 0.5
Chloride (ppm Cl)	< 50	< 10 ----- >			< 5	< 2
Suspended Solids (ppm)	< 8	< 6	< 4	< 2	< 1	—

Note: For planning purposes, multiply conductivity by 0.75 to obtain ppm TDS for raw water. For Demineralized water, divide conductivity by 2.25 to obtain ppm TDS.

EXTERNAL BOILER WATER TREATING PROCESSES

GENERAL

Selection of an appropriate water treating scheme depends primarily on the raw water source and the required treated water quality. However, there may be several parallel paths which could provide similar treatment and satisfy plant requirements. An optimum configuration typically requires some economic analysis reflecting both investment as well as operating costs. In the case of expansion projects, the existing BFW treating configuration may dictate the design. Some processes require mainly utilities (e.g., power or steam) while others are high chemicals consumers (e.g., acid or caustic). Periodic replacement of filter media or cartridges, membranes or ion exchange resin also have to be considered. Additionally, water losses, fuel consumption (a function of blowdown rate) and disposition of waste streams (e.g., sludges) can influence the selection of the most appropriate water treating scheme. [Table 2](#) shows a listing of several water treating processes and their ability to reduce water impurities.

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EXTERNAL BOILER WATER TREATING PROCESSES (Cont)

Raw water sources are either fresh water or salt water and within those categories there may be significant differences which require special treatment attention. Fresh water could be purchased municipal water; or it could be surface water from a lake or river; or it could be well water. Salt water could be pumped from a sea water intake station or from a sea water well located on land.

[Figure 1](#) - *Water Treatment Flow Plan with Fresh Water Supply*, shows the various treatment alternatives and resulting impurities reduction possibilities when the make-up water source is fresh water. The figure also shows typical steam condensate impurities and deaerator effluent qualities.

[Figure 2](#) - *Water Treatment Flow Plan with Salt Water Supply*, shows alternative treatment paths with salt water supply.

Table 2
Impurity Reduction for Various Water Treating Processes

WATER TREATING PROCESS	TOTAL HARDNESS	TOTAL DISSOLVED SOLIDS	SILICA	METHYL ORANGE ALKALINITY	TURBIDITY
Clarification					X
Cold Lime Softening	X	X		X	X
Hot Lime Softening	X	X	X	X	X
Filtration					X
Sodium Zeolite Treating	X				
Hydrogen/Sodium Zeolite Treating	X	X		X	
Demineralization	X	X	X	X	
Evaporation	X	X	X	X	
Reverse Osmosis (Membranes)	X	X	X	X	

Note: X - Indicates reduction of Listed Water Impurity by Water Treating Process

CLARIFICATION

Clarification reduces the colloidal and suspended matter found in many raw water sources. This is often the first step in a water treating process and is typically followed by filtration.

The clarification process incorporates coagulation, flocculation and sedimentation. Each is a distinct procedure which mandates certain requirements to insure the desired results.

Alum or iron salts have generally been used as primary coagulants. However, as sludge disposal becomes more stringent, other coagulants are often used. These include aluminate and organic polymers. Refer to Report No. EE.2E.86 (*New Guide to Boiler Water Treatment*) and Report No. EE.20E.84 (*Polyelectrolite Guide*) for more details.

The two most commonly used designs are sludge-contact clarifiers and tilted-plate (or parallel plate) clarifiers. Sludge-contact clarifiers are more forgiving to fluctuations in raw-water quality and flow rates than tilted-plate clarifiers and for this reason they are utilized in typical ExxonMobil designs. However, tilted-plate clarifiers require less space, are less costly, and function well enough for some applications.

Most ExxonMobil designs utilize the sludge-contact type clarifier to produce best possible effluent quality. The tilted plate unit may find application in retrofit designs where space is limited. A sludge-contact clarifier is shown in [Figure 3](#) and [Figure 4](#) depicts a parallel plate type clarifier unit.

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EXTERNAL BOILER WATER TREATING PROCESSES (Cont)

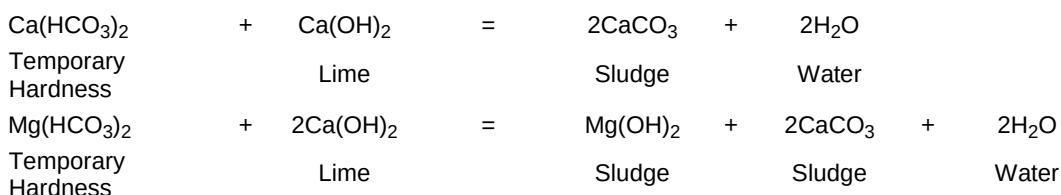
Clarifiers are available in a wide variety of shapes. They can be square or rectangular, circular or box type construction (e.g., parallel plate type units). The most common type is the circular unit and following are some considerations and design parameters:

- Clarifiers (and filters) are normally included upstream of demineralization plants with surface water sources. Municipal water is normally clarified water.
- Clarifiers are used when the turbidity in the raw water is > 50 NTU.
- Water retention time should be more than one hour.
- Clarifier effluent turbidity is in the 3 to 10 NTU range and normally requires filtration prior to use or subsequent treatment.
- Maximum rise rate should be limited to 1.0 gpm/ft² (0.7 L/s/m²).
- Sludge concentration should be in the 2 to 5 wt% range.
- Flow changes should be < 10% per hour.
- Flow rates should be kept in the 40 to 100% range to avoid excessive carryover.
- Installation is typically above ground for hydraulic considerations.
- For cold weather locations, winterization can be provided via housing enclosure or roof / dome.
- Sludge disposition may require special attention to meet local environmental regulations.

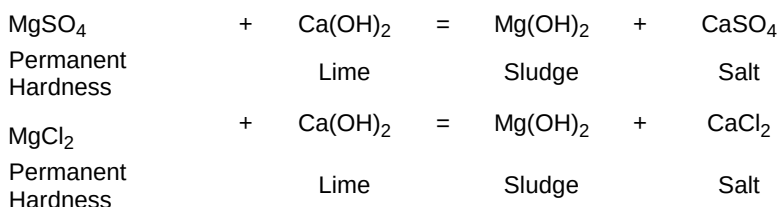
COLD PROCESS SOFTENERS

Cold process softening is one step beyond clarification because of the added benefit of total solids reduction. When lime or soda ash is added to the water at ambient conditions, the process is known as Cold Lime Softening. Most raw waters contain calcium and magnesium bicarbonate hardness which is often referred to as carbonate or temporary hardness. Hardness may also exist as sulfate or chloride salts and this is often called non-carbonate or permanent hardness.

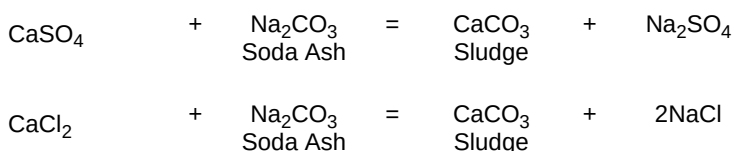
When hydrated lime is added to the water, the following reactions occur:



Hydrated lime may also react with magnesium salts associated with sulfates and chlorides. In these reactions, insoluble magnesium hydroxide sludge is produced. This precipitate is removed by sedimentation and filtration. However, the soluble by-products of calcium sulfate and calcium chloride are also formed and the result is that there is no reduction in dissolved salts as shown by the following equations:



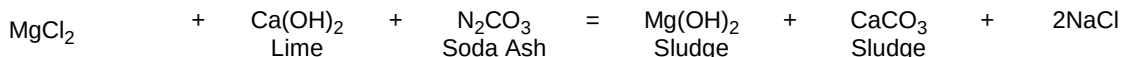
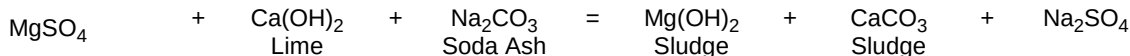
For improved hardness reduction, soda ash may be used. It reacts with the non-carbonate calcium hardness as follows:



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EXTERNAL BOILER WATER TREATING PROCESSES (Cont)

The non-carbonate magnesium hardness reduction requires added lime:



Therefore, the combined use of lime and soda ash effectively removes noncarbonate hardness but the total dissolved solids content of the water is not reduced due to the formation of soluble sodium salts.

Typically, the effluent from a cold lime softener will fall in the following range:

Hardness	10 - 100 ppm as CaCO ₃
Alkalinity	40 - 100 ppm as CaCO ₃
Turbidity	5 NTU
Free Carbon Dioxide	NIL
pH	10.2

The methodology for predicting the effluent quality from a cold lime softening unit is as follows:

1. Using a standard Water Analysis Sheet ([Table A-1](#)), list the concentrations of all known impurities in the raw water. With the exception of iron, free carbon dioxide and silica, all dissolved solids concentrations are to be reported as ppm calcium carbonate equivalent.
2. The sodium, sulfate, chloride, and silica values will be unchanged.
3. Lime will be added, in sufficient quantity to obtain a 5 ppm as CaCO₃ hydroxide ion residual in the treated water. Show pH at 10.2, turbidity at 5 NTU.
4. If the magnesium concentration in the raw water is greater than 70 ppm, enter 70 ppm magnesium in the treated water analysis. If magnesium concentration in raw water is less than 70 ppm, enter 90 percent of the actual value.
5. Use [Figure 5](#) to determine the concentration of calcium and carbonate (as CaCO₃ equivalent) in the lime treated water.

Example:

Total Hardness (TH) 270 ppm, Methyl Orange Alkalinity (MO) 150 ppm, Magnesium (Mg) 90 ppm.

From the Figure:

$$\text{TH} - \text{MO} + (70 - \text{Mg}) = 270 - 150 + (70 - 90) = 120$$

From the curve Ca = 75 ppm, CO₃ = 20 ppm

Hardness reduction can be maximized with a minimal increase in alkalinity by the continuous addition of 55 ppm of soda ash or caustic (both expressed as CaCO₃). The effect of this addition will be a reduction of calcium to 34 ppm, an increase in alkalinity to 34 ppm, and an increase of sodium by 55 ppm (all expressed as CaCO₃). All other impurities remain the same.

The cold lime softener is similar to the clarifier in terms of operation and controls (sludge blanket/recirculated sludge/chemical feeds) and physical appearance ([Figure 3](#)). However, the cold lime softener forms a heavier sludge from precipitating the hardness in the feed water; and therefore may be operated at higher flowrates than clarifiers with the same diameter.

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EXTERNAL BOILER WATER TREATING PROCESSES (Cont)

Cold process softeners accomplish clarification and softening in the same vessel. Design guidelines / parameters are as follows:

- Minimum water retention time should be one hour.
- Maximum rise rate should be limited to 1.25 gpm/ft² (0.85 L/s/m²).
- Underflow (Blowdown) slurry concentration should not exceed 5 wt%.
- An example of typical cold process softener performance for an assumed raw water analysis is shown in the following table.

PARAMETER	RAW WATER	COLD PROCESS SOFTENING	
		LIME ONLY	LIME AND SODA ASH
Total Hardness (as CaCO ₃), ppm	250	145	81
Calcium Hardness (as CaCO ₃), ppm	150	85	35
Magnesium Hardness (as CaCO ₃), ppm	100	60	46
"P" Alkalinity (as CaCO ₃), ppm	0	27	37
"M" Alkalinity (as CaCO ₃), ppm	150	44	55
Silica (as SiO ₂), ppm	20	19	18
pH	7.5	10.3	10.6

- Additional calculation procedures for cold lime softening units performance are covered in Report No. EE.2E.86. They include:
 - Effects of metal coagulants on raw water analysis.
 - Predicting effluent quality from cold lime softening units.
 - Calculation of chemicals requirements for cold lime units.
- Design of lime slurry feed systems requires special attention to avoid plugging of lines and equipment.
- Thickeners are typically an integral part of this system to concentrate the waste lime sludges from 5 to 25 wt%.

HOT PROCESS SOFTENERS

The hot process softener, also commonly called the hot lime softener, works on similar principles as the cold lime unit with regard to clarification and hardness removal.

The hot process softener also removes carbon dioxide and oxygen from the water. In addition, silica is reduced via adsorption on the magnesium hydroxide precipitate (sludge).

There are basically two types of units: the downflow type as shown in [Figure 6](#) and the upflow type as shown in [Figure 7](#). The upflow unit is more effective in reducing silica by passing the water through a large sludge blanket.

Hot process softeners are usually followed by pressure filters and hot sodium zeolite units. Since the filters require frequent backwash (at least once every 24 hours), adequate storage of filtered backwash water should be an integral part of the system. A typical hot process softening system is shown in [Figure 8](#).

A typical effluent from a hot process softener will have the following analysis:

Hardness	10 - 100 ppm as CaCO ₃
Alkalinity	20 - 50 ppm as CaCO ₃
Silica	1.0 ppm as SiO ₂
Turbidity	5 NTU
Free Carbon Dioxide	Nil
pH	> 10.2

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EXTERNAL BOILER WATER TREATING PROCESSES (Cont)

The methodology for predicting the effluent quality from a hot lime softening unit is as follows:

- Using a Standard Water Analysis Sheet, list the concentration of all known impurities in the raw water. With the exception of iron, free carbon dioxide and silica, all dissolved solids concentrations are reported as ppm calcium carbonate equivalent.
- From [Figure 9](#), determine the dilution factor resulting from the condensate forming from the steam required to heat the cold raw water.
- The sodium, sulfate, chloride, and chloride values in the lime softened water will be the amount shown in the Water Analysis Sheet multiplied by the dilution factor.
- Lime will be added, in sufficient quantity to obtain a 5 ppm as CaCO_3 hydroxide ion residual, a pH at 10.2, turbidity at 5 NTU and magnesium at 5 ppm as CaCO_3 in the lime treated water.
- Using [Figure 9](#), determine the concentration of calcium and carbonate (as CaCO_3 equivalent) in the lime treated water.

Example:

Lime Softener Operating Pressure - 10 psig

Raw Water Temperature - 60°F

From the Figure, the dilution factor equals 0.84. Sodium, sulfate, and chloride values shown in the raw water analysis are multiplied by the dilution factor 0.84.

Total Hardness - 300 ppm, Methyl Orange Alkalinity - 200 ppm.

Raw Water Total Hardness - Raw Water Alkalinity times a dilution factor (300 – 200) 0.84 = 84.

From the curve, using the value of 84, Ca^{++} (calcium) = 100 ppm, CO_3 – (carbonate) = 16 ppm.

- Additional procedures for hot lime softening units performance are covered in Report No. EE.2E.86. They include:
 - Determination of Soda-Ash or Caustic requirements for calcium non-carbonate hardness reduction.
 - Silica reduction with hot lime softening.
 - Predicting effluent silica content from hot lime softener units.
 - Calculation of chemicals requirements for hot lime units.
- As in the case for cold lime units, design of chemical feed and sludge disposal systems require special attention.

Design guidelines/parameters for hot process softeners are as follows:

- Vessel capacity shall provide a minimum of one hour holdup of makeup water.
- The maximum allowable water flowrate (rise rate) shall be 2.25 gpm/ft² (1.5 L/s/m²) at water temperatures above 200°F (90°C). This rate shall not be exceeded when backwashing filters or rinsing zeolite softeners.
This rate shall be reduced to 2.0 gpm/ft² (1.4 L/s/m²) for waters containing appreciable organic matter, turbidity, or magnesium to meet guaranteed effluent turbidity of less than 5 NTU for a throughput ranging from 10 to 100% of design rate.
- An example of hot process softener performance is shown in the table below. The assumed raw water analysis is the same as the one used for the cold lime softener example discussed previously. The table shows that silica reduction is greatly improved over the cold lime process and that lime-soda hot process softening yields a significant reduction in hardness over lime only hot process softening.

PARAMETER	RAW WATER	HOT PROCESS SOFTENING	
		LIME ONLY	LIME AND SODA ASH
Total Hardness (as CaCO_3), ppm	250	120	20
Calcium Hardness (as CaCO_3), ppm	150	115	15
Magnesium Hardness (as CaCO_3), ppm	100	5	5
"P" Alkalinity (as CaCO_3), ppm	0	18	23
"M" Alkalinity (as CaCO_3), ppm	150	28	40
Silica (as SiO_2), ppm	20	1 - 2	1 - 2
pH	7.5	10.4	10.5

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EXTERNAL BOILER WATER TREATING PROCESSES (Cont)

Removal of SiO_2 by the hot process, to the levels shown, may require the feed of supplemental magnesium oxide. Sludge recirculation is necessary. All raw water constituents will be diluted by the steam used for direct heating by approximately 15%.

- Steam requirements for hot lime units can be estimated as follows:

$$F_{\text{STM}} = \frac{F_{\text{HL}} h_{\text{HL}} - F_{\text{RW}} h_{\text{RW}}}{h_{\text{STM}}}$$

where:	F_{STM}	=	Steam Requirements, lb/h (kg/s)
	F_{HL}	=	Hot Lime Effluent Rate, lb/h (kg/s)
	F_{RW}	=	Raw Water Rate, lb/h (kg/s)
	h_{STM}	=	Enthalpy of Steam, Btu/lb (kJ/kg)
	h_{HL}	=	Enthalpy of Hot Line Unit effluent, Btu/lb (kJ/kg)
	h_{RW}	=	Enthalpy of Raw Water, Btu/lb (kJ/kg)

FILTRATION

Filtration removes suspended and colloidal solids as well as unsettled chemical precipitates from the water. Location and type of filter used depend on the various other steps of the water treating process.

Filter media typically consists of one or more layers of fine material (sand, anthracite, garnet) and an underdrain/collection system.

In-depth filtration utilizes at least two filter media of different densities for effective removal of coarse and small particles. Anthracite coal which is of lower density than sand is placed on top of the finer sand or garnet layer. The anthracite removes the coarser particles while the sand provides polishing action. This type of filter provides longer service runs and produces effluent water quality of less than 0.5 NTU.

The service cycle of the filter is terminated based on pressure rise through the bed(s), on a timed basis or high effluent turbidity. After the filter is taken out of service it is backwashed with water only or in combination with an air scour or subsurface wash cycle. Filters are spared to provide sufficient onstream capacity while one filter is backwashed. In addition, filtered water storage volume has to reflect backwash water requirements.

Valved Gravity Filters are usually employed on pretreated water with low turbidity. These filters can be rectangular concrete field erected units or round steel pre-fab units. The local economic factors will determine the optimum choice. These filters can be cleaned via air-scour and backwash water. This type of filter is shown in [Figure 10A](#).

Valveless Gravity Filters offer the attractiveness of automatic self-cleaning by means of a built-in backwash system. These filters look like cylindrical tanks and can contain several filter compartments. During the filtering cycle, the water level rises slowly in the backwash pipe as the pressure across the filter bed rises. At a preselected level, water overflows to waste and the water from the backwash storage section flows through the bed and out through the same pipe. Backwashing stops when the end of a siphon breaker is exposed to air. The unit thus automatically cycles through service and backwash periods. These operations are shown in [Figure 10B](#). These filters have the following disadvantages:

1. No valves. Therefore backwash frequency and cycle duration are not controllable.
2. The media cannot be air-scoured to assist in cleaning.

Pressure Filters contain filter media in closed vessels. These can be installed in piping systems without repumping, and permit operation at elevated temperature without loss of heat. Various types and sizes are available.

In the **downflow** type pressure filter, the water passes through two layers of filter material before it exits the vessel. Anthracite coal is usually the top layer followed by fine sand or garnet as shown in [Figure 11A](#). The anthracite is for high capacity filtration of coarse impurities and the sand or garnet provides the polishing filtration. Dual media filters have higher capacities and longer run lengths than single media filters. The filter is taken out of service and backwashed when the filter media becomes clogged as exhibited by increased pressure drop.

In an **upflow** type pressure filter, the direction of water flow is reversed so that the unfiltered water passes through layers of coarse material first and final filtration is via the finer sand layer. This allows removal of larger suspended solids in the bottom coarse layer while smaller particles are trapped in the finer sand layer. A retaining grid is used to prevent loss of sand during the normal (upflow) service cycle as shown in [Figure 11B](#). Filter cleaning is accomplished via flushing and air scouring in the reverse (downflow) mode.

Horizontal pressure filters may find application in cases where vertical space is limited. Filters as large as 10 ft (2.4 m) diameter and 25 ft (7.6 m) long are available. These filters can be compartmentalized in order to limit high backwash water requirements. A horizontal pressure filter is shown in [Figure 12A](#).

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EXTERNAL BOILER WATER TREATING PROCESSES (Cont)

Cartridge and Pre-Coat Filters are used for polishing action on particulates which elude media filtration (20 - 30 microns and smaller). **Cartridge** filters go down to the sub-micron range but they are most commonly rated at 5 or 10 microns. Effective operation depends on in-depth filtration rather than surface action. When cumulative removal results in excessive pressure drop, the filter medium is discarded. This type of filter may find application upstream of a Reverse Osmosis (RO) plant in order to prevent fouling of membranes. **Pre-Coat** filters target even finer particles and are often used in condensate polishing service. Filter coats are performed with powder slurries which are deposited on wire screen or porous cloth tubes. These tubes are inserted into a filter vessel housing and the unit is kept in service until the filter elements show increasing pressure drop or if effluent water quality shows signs of deterioration. Cleaning of filter elements (via air pressure and flushing) plus application of new pre-coat is required before the filter unit is placed back in service. Examples of Pre-Coat and Cartridge filters are shown in [Figure 12B](#).

Design guidelines / parameters for filters are as follows:

- Feed systems shall be designed to minimize pressure and flow surges.
- Normal and maximum hydraulic loadings for filters shall be (with one unit out of service for backwashing):

FILTER SYSTEM TYPE	MAXIMUM	
	gpm/ft ²	L/s/m ²
Downflow (cold) pressure filters [$< 150^{\circ}\text{F}$ (65°C)]	4.0	2.7
Downflow (hot) pressure filters [$> 150^{\circ}\text{F}$ (65°C)]	4.5	3.0
Downflow gravity filters	4.0	2.7
Upflow pressure filters	Vendor Standard	

Filter systems / units shall be designed so that maximum flowrates are not exceeded when a vessel is not in service due to backwash or maintenance requirements.

- Minimum design backwash flowrates shall be as follows:

TYPE	gpm/ft ²	L/s/m ²
Sand	15	10.2
Anthracite Coal	12	8.1
Garnet	25	17.0

- Minimum design air scour rate shall be as follows:

TYPE	scfm/ft ²	L/s/m ²
Downflow filters (Dual Media and Gravity)	5	25
Upflow, sand	4	20

- Bed depth in filters shall be 30 in. (750 mm) minimum.
- For "in-depth" filters at least two different density media, of different sizes, shall be provided. Typically an 18 in. (450 mm) layer of anthracite coal on top of a 12 in. (300 mm) layer of fine sand is used.
- Freeboard volume shall be provided to facilitate backwash and air scour operations without loss of filter media.

DEMINERALIZATION BY ION EXCHANGE

GENERAL

The ion exchange process utilizes vertical cylindrical vessels which contain ion exchange resin of various types. These resins remove dissolved salts from the water and replace them with Hydrogen (H^+) and Hydroxyl (OH^-) ions thus producing "pure" water.

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Resins which replace positively charged ions such as Calcium (Ca^{++}), Magnesium (Mg^{++}), Sodium (Na^+), etc., are called cation resins and they are regenerated with an acid (sulfuric or hydrochloric) to replace the hydrogen ions which were exchanged for the "cations". Sulfuric acid is used most often because it is cheaper than hydrochloric acid and requires less investment for vessel internals and related facilities. Construction material for hydrochloric acid is Hastelloy whereas stainless steel is acceptable for sulfuric acid. Hydrochloric acid is more efficient than sulfuric acid and there are no concerns with scaling and fouling. Hydrochloric acid has a high volatility thus producing vapors. The design may require using vent scrubbers to limit exposure to HCl fumes.

Resins which replace negatively charged ions such as Sulfate (SO_4^{-}), Chloride (Cl^-), Carbonate (CO_3^{-}), etc., are called anion resins and they are regenerated with caustic (NaOH) to replace the hydroxyl ions which were exchanged for the "anions." There are weak and strong cation as well as weak and strong anion resins. In general, the weak resins are more efficient in terms of chemicals (acid or caustic) consumption. However, these resins are also limited in their ability to remove ions. For example, cation removal with weak acid cation (WAC) resin is limited to the amount of Bicarbonate (HCO_3^-) Alkalinity in the water; and Anion removal is limited to Sulfides, Chlorides and Nitrates in the acidic form when using Weak Base Anion (WBA) resin.

Some cations and anions will slip through the ion exchange system and this is called "leakage." The amount of leakage is a function of many factors (e.g., influent water quality, regeneration chemicals dosage and specific resin type).

Multiple beds in series, or variation in regeneration procedures, and/or mixed bed polishing units can be used to reduce final leakage and to produce a very low solids effluent.

Ion exchange resin can also be employed in the water softening process by using cation resin in the sodium cycle. Resin regeneration is with a Salt (NaCl) solution and this process has the advantage of not producing a waste sludge stream as is the case with hot and cold lime softening.

Optimum plant configuration should be based on economics and the following factors should be considered:

- Investment for facilities (vessels, piping, regeneration system).
- Layout Optimization.
- Chemical costs.
- Power costs (for pumping, fans etc.).
- Resin cost, resin life.
- Disposition of waste streams (e.g., Environmental Factors).

The plant can include single bed units (cation or anion), layered beds (weak and strong resins of similar type in same vessel), or mixed bed units (polishing type containing strong cation and strong anion resins in the same vessel).

The plant may include degasifiers for efficient mechanical removal of bicarbonate alkalinity (instead of incremental anion exchange capacity and thus increased chemicals usage). A typical forced draft degasifier is shown in [Figure 13](#).

Historically, most plants were designed in the downflow mode with co-current regeneration systems where regenerant chemical flow is in the same direction as service flow. In those systems, the bottom resin layer is not regenerated as completely as the top most layer thus resulting in high ionic leakage.

Layered bed units (Stratabeds®) combining weak and strong cation or anion resins have been used to minimize chemicals consumption during regeneration.

More recent designs have used counter-current regeneration (CCR) techniques which improve effluent water quality significantly. With such a scheme, regenerant chemical flow is in the opposite direction of the service flow and this assures that during normal operation the water contacts the best regenerated resin layer last. Designs with counter-current regeneration systems have essentially negated the need for mixed bed polishing units in many locations.

Another development in CCR technology is "packed bed" units. These systems employ shorter vessels than those used in conventional co-current or counter-current units. The packed bed system essentially eliminates the need for the vessel "freeboard" space thus saving vessel volume and also reduces total regenerant volumes. A typical conventional ion exchange vessel is shown in [Figure 14](#). Examples of demineralization plant configurations which have been used in ExxonMobil plants are shown in [Figure 15](#).

Regeneration of the ion exchange units requires several steps and during that period, spare vessels and/or treated water storage capacity are needed to provide uninterrupted supply of treated water. Typical steps in the regen sequence include backwash, chemical injection, displacement of chemicals and rinse prior to returning the unit back to service. Regeneration time can vary significantly depending on the number of steps involved. [Figure 16](#) shows the sequence of steps required for mixed bed units.

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EXTERNAL BOILER WATER TREATING PROCESSES (Cont)

Design guidelines / parameters for fixed bed ion exchange (excluding packed beds) units and forced draft degasifiers are as follows:

- Influent water quality shall not exceed the limits listed in order to avoid plugging, fouling and deterioration of resins.

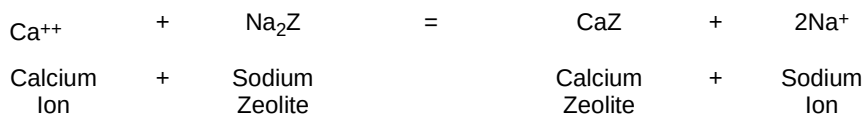
PARAMETER	CO-CURRENT	COUNTER CURRENT
Turbidity	1 NTU	0.1 NTU
Iron and manganese	0.3 ppm	0.3 ppm
Chlorine	0.1 ppm	0.1 ppm
Oil	0.3 ppm	0.3 ppm

- Flowrates for design of vessel diameter should be kept in the 2 - 15 gpm/ft² (18 gpm/ft² if uniform resin is used) (1.4 - 8.1 L/s/m²) range. The lower limit prevents channeling and the maximum rate allows higher service flows during those periods when other vessels are in regeneration. The maximum flowrate for mixed bed units in polishing service shall not exceed 24 gpm/ft² (16.3 L/s/m²).
- Maximum and minimum bed depths shall be 84 in. (2100 mm) and 30 in. (750 mm), respectively.
- The maximum practical vessel diameter is 15 ft (4.6 m).
- Freeboard (as measured from the top of the exhausted resin bed) shall be as follows:
Cation Units – 0.75 x resin bed depth + 42 in. (1050 mm)
Anion Units – 1.0 x resin bed depth + 48 in. (1200 mm)
Mixed Bed Units – 1.0 x resin bed depth + 48 in. (1200 mm)
- Units should be designed with a maximum of one regeneration per 24 hours.
- Parallel units and storage shall be provided to maintain design plant water requirements at all times.
- Forced draft degasifiers (also known as Decarbonators) typically reduce free carbon dioxide (CO₂) to 5 ppm and oxygen (O₂) to the 6 - 8 ppm range.
 - Maximum allowable water flowrate shall be 17.5 gpm/ft² (11.9 L/s/m²) of cross sectional tower area. Minimum tower height shall be 16 ft (4800 mm).
 - The minimum allowable air flowrate shall be 3 scfm per gpm (20 L/s per L/s) of design water flow.
 - Storage capacity shall not be less than 10 minutes of design throughput rate. Additional storage capacity may be needed for regeneration water requirements.

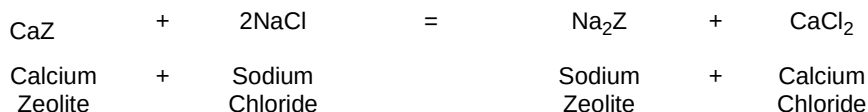
SODIUM ZEOLITE SOFTENING

This process removes scale-forming calcium and magnesium salts from the water by replacing them with an equivalent amount of sodium salts. This treatment does not change the total dissolved solids in the water and has no effect on other constituents such as silica and alkalinity. Effluent water hardness is reduced to 2 ppm expressed as Calcium Carbonate (CaCO₃). Lower leakage can be obtained by considering CCR.

Synthetic polystyrene resins (Z) are commonly used for sodium zeolite softening. The fundamental reaction with calcium in the sodium zeolite softening process is:



When the zeolite resin is exhausted and will not release any more sodium in exchange for calcium or magnesium, the bed must be regenerated. It is regenerated with a salt (NaCl) solution. The regeneration reaction for calcium may be written as follows:



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Zeolite softeners are also used in combination with hot process lime softener units (refer to [Figure 8](#)). Since the zeolite unit operates on the hot effluent from the softener, it is essential that it be maintained under pressure at all times. If the pressure inside the vessel is permitted to drop, the water temperature may be high enough to cause steam to form under the zeolite bed. If enough steam is formed, resin may be lost with the backwash water. To avoid flashing conditions, valves on the units must be carefully operated in the proper sequence. Water used for regenerating a zeolite softener should come from storage. Dirty backwash water, if recovered, should go to separate storage. Problems with hot lime/zeolite plants are caused by overloading the hot lime softener. Overloading results from using the lime softener as a source of backwash and regeneration water without having separate storage compartments.

The Sodium Zeolite regeneration procedure requires three steps:

1. Backwash for 15 minutes.
2. Inject 10% Salt (NaCl) solution based on the resin volume and the desired exchange capacity. The salt also has to meet minimum purity specifications to avoid resin fouling (see [Table 3](#)).
3. Rinse the resin until effluent quality is acceptable to return the vessel back to service. Use 50 gal/ft³ (6700 L/m³) of resin volume to establish rinse water requirements.

Table 3
Typical Cation Resin Capacities - Sodium Cycle
(Co-Current Regen)

REGENERANT DOSAGE VS. EXCHANGE CAPACITY	
Regenerant Dosage lb 100% NaCl/ft ³ Resin	Exchange Capacity kilograins as CaCO ₃ /ft ³ Resin
5	17.0
6	18.5
7	19.5
8	20.4
9	21.2
10	22.0
11	23.0
12	24.0
13	24.7
14	25.5

Notes:

- (1) 7 kilograins equals one pound.
- (2) Leakage is 2 ppm as CaCO₃.
- (3) Regeneration is with 10% salt solution.
- (4) For planning purposes only; use resin vendor data for design.

SALT (NaCl) SPECIFICATION	
Either rock or evaporated salt meeting the following purity requirements is acceptable:	
NaCl	- minimum 97 percent by weight
Fe ₂ O ₃	- less than 0.05 percent by weight
H ₂ O	- less than 0.5 percent by weight
CaSO ₄	- less than 0.2 percent by weight
CaCl ₂	- less than 0.05 percent by weight

HYDROGEN ZEOLITE SOFTENING

This process uses a weak acid cation resin in a hydrogen cycle to remove temporary hardness (all hardness associated with alkalinity). The permanent hardness (all hardness associated with sulfates, chlorides, etc.) will pass through the resin. The hydrogen ions combine with the bicarbonate ions (HCO₃⁻) to form carbonic acid (H₂CO₃) which dissociates into water (H₂O) and carbon dioxide (CO₂). The carbon dioxide can then be stripped out in a forced draft degasifier.

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The resin is regenerated with acid (sulfuric or hydrochloric).

Hydrogen zeolite and sodium zeolite can also be combined in series to accomplish total hardness reduction.

Both weak and strong cation resins can be layered in the same vessel (e.g., stratified with the weak resin on top). The top layer of weak cation resin is regenerated with acid while the bottom layer of strong cation resin is regenerated with salt. This process is also known as the "Starvation Process" since the amount of acid used is insufficient to regenerate the entire resin column.

The ion exchange vessels are typically followed by a forced draft degasifier to remove carbon dioxide. This treatment scheme removes hardness and lowers the total dissolved solids as well. The low pH effluent requires neutralization (with caustic) prior to direct use.

Exchange capacity of the weak cation resin varies considerably depending on the water analysis as shown in [Table 4](#).

The weak acid cation resin is very efficient in that regeneration acid consumption is only about 120% of theoretical (based on amount of impurity removed). In addition, the WAC resin exhibits a very high exchange capacity. For sulfuric acid, a highly diluted solution (0.8 wt% acid) is used in order to prevent Calcium Sulfate precipitation on the resin.

Specification for acid purity requirements is given in [Table 5](#).

Table 4
Typical Weak Acid Cation Resin Capacities

RATIO OF HARDNESS TO ALKALINITY IN RAW WATER	TOTAL FREE MINERAL ACIDITY AS CaCO ₃ , ppm ⁽¹⁾	CAPACITY, KILOGRAINS AS CaCO ₃ OF ALKALINITY REMOVED PER ft ³ OF RESIN
0	5	8
	65	10
	130	10
	280	14
0.5	5	9
	65	11
	130	13
	280	17
0.9	5	10
	65	12
	130	16
	280	19
1.0 or more	5 to 280	40

Notes:

- (1) Total free mineral acidity as CaCO₃ equals the chlorides and sulfates and nitrates expressed as CaCO₃ in the raw water to the demin plant.
- (2) 7 kilograins equals one pound.
- (3) Resin is regenerated with 120% of theoretical using dilute acid solution.
- (4) For Planning purposes only; use resin vendor data for design.

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EXTERNAL BOILER WATER TREATING PROCESSES (Cont)

Table 5
Acids Specification for Cation Regeneration

SULFURIC ACID (H₂SO₄)

Virgin technical grade 66° Be' sulfuric acid, free of suspended matter and light in color (water white to light brown) with a minimum concentration of 93 percent H₂SO₄, shall not form any precipitate when mixed in any proportion with water. Acid containing inhibitors shall not be accepted. The following impurities shall not exceed the amounts given:

Iron (Fe) maximum	= 50 ppm
Nitrogen compounds maximum	= 20 ppm
Arsenic maximum	= 0.2 ppm
Organic contaminants	= 0.01 percent by weight
Copper	< 0.5 ppm
Chlorides	< 10 ppm
Sulfur Dioxide	< 100 ppm

The freezing point shall be -24°F and the acid shall weight 15.2 lb per gallon at 60°F.

HYDROCHLORIC ACID (HCl)

Technical grade 18°Be' virgin hydrochloric acid, free of suspended matter and light in color (water white to light yellow) with a minimum concentration of 28 percent HCl, shall not form any precipitate when mixed in any proportion with water. Acid containing inhibitors shall not be accepted.

The following impurities shall not exceed the amounts given:

Sulfuric acid as SO ₃	= 0.4 percent by weight
Iron (Fe)	= 0.01 percent by weight
Organic contaminants	= 0.01 percent by weight

The freezing point shall be -40°F and the acid shall weight 9.5 lb per gallon at 60°F.

Hydrochloric acid obtained by the salt-acid process or by the hydrogen chlorine process is acceptable provided it meets the above specifications; Hydrochloric acid obtained as a by-product from the hydrolysis of chlorinated organic chemicals is not acceptable.

DEMINERALIZATION PLANT (CO-CURRENT REGENERATION)

Demineralization via ion exchange requires cation and anion resin beds in series. Cations such as calcium, magnesium and sodium are removed by the cation resin which is operated in the hydrogen cycle. Anions such as chlorides and sulfates are removed by the anion resin which is operated in the hydroxide cycle. The treated water produced in this process is basically pure water except that there is some leakage (primarily sodium from the cation bed which picks up hydroxide alkalinity in the anion bed).

A typical treated water analysis which can be obtained from such a primary demineralization process is as follows:

- Sodium 0 - 1 ppm as CaCO₃
- Alkalinity 0 - 1 ppm as CaCO₃
- Silica less than 0.1 ppm as SiO₂
- CO₂ 0.01 ppm as CO₂
- Dissolved Salts less than 2 ppm
- Conductivity less than 5 micromhos (< 5 µS/cm)

The basic two bed strong acid cation/strong base anion unit configuration can be optimized based on economics. The trade-offs are resin and vessel volumes against regenerant chemicals consumptions. Additionally, mechanical removal of carbon dioxide with a forced draft degasifier may be justified in order to reduce strong base anion operating cost.

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EXTERNAL BOILER WATER TREATING PROCESSES (Cont)

General guidelines are as follows:

- Weak acid cation (WAC) resin is more efficient than strong acid cation resin but cation removal is limited to cations associated with alkalinity. Typical exchange capacities for weak cation resins are shown in [Table 4](#).
- Weak base anion (WBA) resin is more efficient than strong base anion resin but anion removal is limited to sulfates, chlorides and nitrates in the mineral acid form. Additionally, this resin can also be used to remove surface water organics which could foul downstream resin and/or cause boiler problems. Exchange capacities for weak base anion resins range between 16 and 24 kgr as $\text{CaCO}_3/\text{ft}^3$ depending on regenerant dosages and particular resin types.
- Strong acid cation (SAC) resin is capable of removing all types of cations and typical exchange capacities as well as leakage rates are shown in [Table 6](#).
- Strong base anion (SBA) resin is capable of removing all types of anions and exchange capacities vary widely depending on regenerant dosages and particular resin types. Sample performance data from one manufacturer is shown in [Table 7](#). These resins are prone to organic fouling which can lead to reduced capacity and deterioration of treated water quality.
- The minimum configuration normally includes SAC resin followed by SBA resin to achieve acceptable treated water quality. In cases where raw water TDS is low and/or for low flowrate requirements, the SAC and SBA resins may be contained in a working mixed bed unit.
- Caustic specification for anion regeneration is shown in [Table 8](#).
- Forced draft degasifiers are typically justified if the raw water bicarbonate alkalinity is greater than 100 ppm. Use of a degasifier requires pumps to serve downstream ion exchange units.
- Vacuum degasifiers shall be considered if the treated water, downstream of the Water Treating Plant, has to be transported for long distances in CS piping systems. (See section covering Deaeration)
- Layered resin beds (Stratabeds®) can be used to minimize the total number of vessels in the plant. WAC/SAC resins are contained in the cation vessels and WBA/SBA resins are contained in the anion vessels. Application requires that the raw water impurities are in the right ratios to allow correct amounts of resins in the vessels.
- Regeneration is typically done on a "train" basis. This means that cation and corresponding anion units are taken out of service simultaneously. Cation and anion regenerations proceed independently and simultaneously except those steps where the cation is required to feed the anion. De-cationized water can be made available for anion regeneration. Regeneration steps include the following:
 - Backwash of resin beds.
 - Injection of dilute chemicals.
 - Displacement of chemicals (slow rinse).
 - Fast rinse to produce effluent water which is adequate for service cycle.
- The waste regenerants (acid and caustic) have to be collected and neutralized. Design should strive to produce a "balanced" waste stream so that chemicals usage for final pH control can be minimized. Such a system saves time in the neutralization cycle and allows more efficient use of neutralization tankage volume.
- Regeneration is done on a timed cycle or controlled volume of water treated. ExxonMobil practice is not to let the resin beds run to exhaustion. Experience has shown that double dosages of chemicals are required to return resins to base operating conditions. Monitoring of silica and conductivity in the effluent water is also provided to assure no premature deterioration of water quality.

MIXED BED UNITS

Mixed bed units containing a mixture of strong acid cation and strong base anion resins can be used as a stand-alone system if the dissolved solids concentration of the untreated water is very low (below 100 ppm) and the units can be designed with reasonable service run lengths. Mixed bed units may also find application in cases where very low flowrates are required. More commonly, mixed bed units are used downstream of primary demineralization systems to serve as polishing units or high pressure steam condensate systems. It is desirable to obtain long run lengths [7 days maximum for polishing units, 24 hours maximum for working mixed bed(s)] in order to avoid too many long regeneration cycles. Steps involved in mixed bed unit regeneration are shown in [Figure 16](#) and total elapsed time required can fall in the 3 to 4 hour range.

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EXTERNAL BOILER WATER TREATING PROCESSES (Cont)

Typical effluent water quality from mixed bed units is as follows:

- Sodium 0.05 ppm as NaCO_3
- Alkalinity 0.05 ppm as CaCO_3
- Silica 0.02 ppm as SiO_2
- CO_2 Nil
- Conductivity less than 0.5 micromho ($< 0.5 \mu\text{S/cm}$)

DEMINERALIZATION PLANT (COUNTER-CURRENT REGENERATION)

Counter-current regeneration (CCR) has revolutionized demineralization plant performance. Chemicals used during regeneration flow in the opposite direction to the service flow. During normal operation, the water will contact the best regenerated resin last and this will result in reduced ionic leakage. Counter-current regeneration also reduces regeneration chemicals consumption and waste effluent production. [Figure 17A](#) shows exhaustion patterns (as well as relative effluent qualities and chemicals dosage requirements) of co-current, counter-current and mixed bed units.

[Figure 17B](#) shows the effect of acid (HCl) regenerant dosage on sodium leakage from a cation unit for both the co-current and counter-current operations.

The challenge in counter-current regeneration is to maintain the integrity of the resin column at all times. This is done by adding a regenerant collection system at the top of the resin bed and introducing a blocking water or air flow as shown in [Figure 18](#). ExxonMobil prefers air blocking to reduce water consumption and to achieve reliable blocking action.

In co-current units, the beds are backwashed during every regeneration cycle. For counter-current designs, frequent backwash is avoided to maintain the integrity of the resin bed column. Typically, the beds are backwashed once every 20 regeneration cycles and this results in time as well as water savings. Low turbidity (less than 0.1 NTU) raw water is required for the cation units.

Typical effluent water quality from counter-current designed units is as follows:

- Sodium 0.1 ppm as NaCO_3
- Alkalinity 0.1 ppm as CaCO_3
- Silica 0.02 ppm as SiO_2
- CO_2 Nil
- Conductivity less than 1.0 micromho ($< 1.0 \mu\text{S/cm}$)

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Table 6
Typical Strong Acid Cation Resin Capacities
(100% Sulfuric Acid)

Alkalinity, %	Na, %	2.5 lb/ft ³ (Acid/Resin)		5.0 lb/ft ³ (Acid/Resin)		7.5 lb/ft ³ (Acid/Resin)	
		Exchange Capacity kgr/ft ³	Cation Leakage %	Exchange Capacity kgr/ft ³	Cation Leakage %	Exchange Capacity kgr/ft ³	Cation Leakage %
0	0	6.3	2	9.0	1	10.9	0
	25	6.2	4	9.0	2	10.9	1
	50	6.3	7	9.0	3	10.9	2
	75	6.3	16	9.2	6	11.0	4
	100	8.1	49	14.4	28	16.6	18
50	0	7.2	0	9.9	0	11.7	0
	25	7.2	2	9.9	1	11.7	0
	50	7.2	4	9.9	2	11.7	1
	75	7.2	9	9.9	5	11.7	4
	100	11.7	28	17.1	15	18.9	10
100	0	7.7	0	10.4	0	12.2	0
	25	8.6	0	10.8	0	12.6	0
	50	9.0	0	11.7	0	13.5	0
	75	10.3	1	13.0	0	15.3	0
	100	13.5	2	18.5	1	21.5	0

Notes:

- (1) Cation leakage for co-current regeneration. For counter-current regeneration, maximum leakage will be 0.1 ppm as CaCO₃.
- (2) 7 kilograins equal one pound.
- (3) For planning purposes only; use resin vendor data for design.

Table 7
Typical Performance of Strong Base Anion Resin
Exchange Capacities and Silica Leakage as a
Function of Regenerant Level (100% Caustic)

REGEN LEVEL lb/ft ³	CAPACITY, kgr/ft ³ % WEAK ACID ⁽¹⁾			AVERAGE SILICA LEAKAGE, ppm % SILICA ⁽²⁾				
	25	50	75	10	30	50	70	90
4	10.8	11.8	12.6	0.05	0.19	0.30	0.41	0.53
5	11.7	12.7	13.5	0.04	0.12	0.19	0.27	0.34
6	12.2	13.4	14.2	0.02	0.05	0.08	0.12	0.14
8	13.4	14.2	15.0	0.01	0.03	0.05	0.07	0.09

Notes:

- (1) Percentage of (SiO₂ + CO₂) as CaCO₃ in Total Exchangeable Anions (TEA).
- (2) Percentage of SiO₂ as CaCO₃ in TEA.
- (3) 7 kilograins equal one pound.
- (4) For planning purposes only; use resin vendor data for design.

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Table 8
Caustic Specification For Anion Regeneration

Anion exchange resins are normally regenerated using diluted 50 percent sodium hydroxide. The following specification should be included in the purchase requisition.

50% CAUSTIC	
COMPONENT	CHEMICAL PROPERTIES SPECIFICATION LIMITS % BY WEIGHT
NaOH	50 - 52
Na ₂ CO ₃	0.06 max.
NaCl	0.003 max.
Fe	0.0002 max.
Na ₂ SO ₄	0.002 max.
SiO ₂	0.002 max.
Al ₂ O ₃	0.0006 max.
CaO	0.002 max.
MgO	0.0002 max.
Mn	0.00004 max.
Ni	0.00003 max.
Cu	0.00005 max.
NaClO ₃	0.0003 max.

The appearance shall be water white - a density of 12.6 lb per gallon at 100°F and a freezing point of 55°F. Important - iron content is very critical as to fouling of the anion resin.

DEMINERALIZATION PLANT (PACKED BED DESIGN)

Packed bed design demineralization plants have been installed in several European affiliate locations (i.e., Augusta and Port Jerome). This design offers all of the advantages of counter-current designed units and in addition reduces vessel sizes and simplifies regeneration procedures.

In the packed bed design, freeboard space is essentially eliminated. The vessels contain compartments which are entirely filled with resin (except for a small space to accommodate resin swelling and shrinkage resulting from exhaustion and regeneration cycles). Bed movement is therefore eliminated and counter-current regeneration becomes quite simple. Some vendors offer upflow designs with downflow regeneration while others prefer downflow designs with upflow regeneration.

Packed bed units can have one compartment or multiple compartments. Multiple compartments can be used to house different resins in a single vessel or split the same resin into two or more compartments to avoid a very deep bed (minimize single bed compaction and resin movement).

In general, packed bed unit internals are simple when compared to conventional counter-current designed units. Vendor know-how is critical to achieve a reliable design. Support plates with large number of strainers assure good water and chemicals distribution and keep the resin beds fixed.

As is the case for plants, packed bed units do not require regular backwashing. Experience has shown that Packed Bed units can be kept in service without backwashing for up to 6 months to a year. This can result in reduced water consumption even when compared to CCR plants. Fines generation is minimized selecting only uniform particle size resin and by following recommended procedures during resin loading steps. Some vendor designs can facilitate in-situ backwash by providing a two compartment vessel where one of the compartments is only partially filled with resin. A method for resin transfer between compartments is also provided so that the packed layer can be moved for backwashing. Nevertheless, for ExxonMobil Designs, external backwash facilities are highly recommended. These facilities are also extremely useful for resin fines removal during initial start-up and periodic resin replacement steps.

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Design guidelines / considerations for Packed Bed systems are as follows:

- Maximum resin bed delta P should not exceed 25 psi
- Maximum vessel diameter should be limited to 15 ft (4.6 m)
- Maximum resin bed depth should not exceed 108 in. (2,740 mm)
- Maximum service velocity should be limited to 18 gpm/ft² (12.2 L/s/m²)
- An external backwash tank shall be provided to facilitate backwashing the entire resin contained in the largest ion exchange vessel.
- Upflow designs shall be critically reviewed for required turndown (Is recycle needed to keep resin bed suspended during low flow?)
- Only uniform particle size resin shall be used

A schematic representation of packed bed ion exchange vessels and an external backwash tank are shown in [Figure 19](#).

Some non-ExxonMobil facilities have retrofitted co-currently regenerated demin plants for packed bed operation in order to gain water quality improvements and to reduce regeneration costs. Such conversions are difficult and the EMRE WATER TREATING SPECIALISTS should be consulted in order to maintain reliable water treating plant operation.

REVERSE OSMOSIS

Reverse Osmosis (RO) is a well-established process which has been used extensively to produce potable water from brackish water and seawater. More recently, this process has found wider application in the production of "pure" water in many industrial uses. This process uses pressure energy to overcome the osmotic pressure in a solution, thus reversing the natural osmosis process.

RO is typically considered when raw water TDS is greater than 300 ppm and in places where electric power costs are low. The RO process requires pretreated water in order to avoid membrane fouling and the final effluent may need to be "polished" prior to use as BFW. [Figure 20](#) shows a simple RO Module and a typical Pretreatment Scheme.

Membranes used in the RO process vary from one manufacturer to another. However, the most common types are "spiral wound" or "hollow fiber" as shown in [Figure 21](#).

There are many factors which influence membrane performance and it is recommended that specifics of the raw water source and treated water quality requirements be communicated to the EMRE WATER TREATING SPECIALISTS and/or the RO system supplier.

Some general membrane performance characteristics are shown in [Figure 22](#). The graphs show that both feed pressure and % conversion (e.g., recovery) have an effect on treated water quality (salt passage) and flowrate. The relationships were developed for the specific basis as noted in the graphs and using a single stage membrane system.

Designs of RO systems can vary from one application to another based on specific flowrate and water quality needs. Most systems require more than one permeator and the most common arrangements are as follows. Combinations of these systems are also used.

1. Parallel Single-staged RO System

The arrangement shown in [Figure 23](#) is typically used for seawater designs. Individual permeators vessels are connected to common feed, permeate and concentrate headers. Flow and pressure balancing are needed to avoid differences in individual permeator performance. Recovery of a single stage system is limited to about 40%.

2. Brine Staged RO System

The arrangement shown in [Figure 24A](#) may be used for brackish waters to improve overall recovery of the system and to minimize waste production. It is not normally used for seawater since the TDS level of the first stage brine may be too high to make the second stage practical. A two stage system will boost recovery to the 70 to 75% range. Adding a third stage can increase recovery to the 90% level.

3. Product Staged System

The arrangement shown in [Figure 24B](#) is used when a single-pass RO system does not yield the desired product water quality. The product water from the first system becomes the feedwater for the second system. Each system is in effect a separate RO plant requiring its own high pressure pumps. Since the brine from the second system has a lower TDS than the raw water feed to the first unit, it can be recycled and added to the feedwater of the first system. If salt rejection of each stage is 90%, a series two stage configuration will result in 99% salt rejection.

Simplified schematics of seawater and brackish water RO systems are shown in [Figures 25 and 26](#). These sketches illustrate the use of different types of RO modules as well as recycle and blending options. A listing of electric power requirements is also given for the two examples.

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Design guidelines / considerations for RO systems are as follows:

- Due to small pore size, membranes are vulnerable to fouling. Therefore, design of pretreatment facilities is critical for a reliable system and for long membrane life.
- Dissolved gases such as carbon dioxide will pass through the membranes into the permeate. Removal via degasification or ion exchange may be required.
- Feed streams have to be treated and/or adjusted to meet the limits of the membranes.
 - Suspended colloidal solids must be < 5 SDI (Silt Density Index) for spiral wound and < 3 SDI for hollow fiber.
 - Guidelines for pH and free residual chlorine are:

PARAMETER	ACETATE MEMBRANES	POLYAMID MEMBRANES
pH	≤ 6.3	2 - 10
ppm Cl ₂	≤ 0.5	≤ 0.1

- Ideal operating temperature for membranes is 77°F (25°C). Upper temperature limits are in the 86 to 122°F (30 to 50°C) range depending on the membrane type.
- Pilot testing of the RO feed stream is highly recommended in order to determine the necessary pre-treatment (e.g. filtration) system and optimum chemicals dosing requirements (e.g. de-chlorination, pH adjustment, anit-sealant addition).
- RO systems operate at fixed flowrates and total capacity is achieved by providing multiple trains. Maintaining fixed flowrates will cause the treated water inventory to fluctuate. A spare train is recommended to enable maintenance and cleaning of RO facilities. Sizing of trains will depend on total water demand as well as standard modules or skid sizes available from the RO suppliers.
- Raw water source facilities should include a pressure control system to minimize the impact on the RO system flows.
- The operating philosophy of the RO plant (e.g. manual, semi-automatic, fully automatic) should be determined early in the planning stage of the project. This will impact control system and water storage requirements.
- Membrane cleaning facilities are required to facilitate in-situ cleaning of the spare train.
- System design shall consider 4 in. (102 mm) and 8 in. (203 mm) spiral wound and 4 in. (102 mm), 8 in. (203 mm) and 10 in. (254 mm) hollow fiber membranes.
- Spiral wound pressure vessels (permeator housings) shall be sized to contain 6 or 7 permeators.
- Derating of membrane performance should be considered in order to maintain continuity of design throughput as the membranes age (e.g. reduced performance).
- Vendor offerings and designs should be carefully reviewed to assure plant reliability and ease of performing the required routine maintenance. For example:
 - Individual Cartridge Filter for each RO train vs. common/spared filters.
 - Individual RO Feed pump for each RO train vs. common/spared pumps.
 - Number and capacity of individual RO trains in light of plant turndown, flushing operations, etc.
 - Layout, access for membrane removal.
 - Membrane cleaning operations.
- Typical energy consumption is as follows:
 - For brackish water 6 to 8 kWh/1000 gal (1.6 to 2.1 kWh/m³).
 - For seawater 35 to 40 kWh/1000 gal (9.2 to 10.6 kWh/m³).
 - Energy recovered via hydraulic turbines on the high pressure brine reject has been utilized in some seawater RO installations.

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FLASH EVAPORATION

Evaporation involves the application of heat to a liquid and thereby producing a vapor. Condensation of this vapor will yield a distilled liquid product which is virtually free of dissolved and suspended solids which are present in the feed liquid stream. Wire mesh or other devices are used to prevent liquid droplets containing solids to carry-over into the vapor phase. The mechanical or thermal vapor compression units work on a similar principle except that the evaporative heat is imparted from thermal or mechanical compression energy. [Figure 27A](#) shows a schematic of the thermal distillation process and [Figure 27B](#) pictures the mechanical vapor compression (MVC) process.

Evaporation processes have been used successfully for many years to produce drinking water and other low solids water streams from seawater and brackish water sources. An advantage of the flash evaporation process is that the composition of the feedwater to the plant has an almost negligible effect on the energy consumption per unit of product water produced. This contrasts with the performance of other desalination processes (e.g., Reverse Osmosis) in which energy consumed is a direct function of feed composition.

Multi-stage Flash (MSF) desalination is the most commonly used process for desalting seawater feed. The principles involved are shown in [Figure 28](#).

Seawater is heated and discharged into a chamber maintained slightly below the saturation vapor pressure of the water, a fraction of its water content flashes into steam. The flashed steam is stripped of suspended brine droplets as it passes through a mist eliminator and condenses on the exterior surface of heat transfer tubing. The condensed liquid drips into trays as hot product water.

The unflashed brine enters a second chamber, or stage, where it flashes to steam at a lower temperature, producing a further quantity of product water. Simultaneously, the distillate from the first stage passes to the distillate tray in the second stage, at a lower pressure giving up some of its heat and thereby lowering its temperature. The flashing-cooling process is repeated from stage to stage until both the cooled brine and the cooled distillate are finally discharged from the plant as blowdown brine and product water, respectively.

It is common practice to recycle a fraction of the blowdown water, combined with feedwater, through the entire circuit in order to extract an additional fraction of its water content. The recirculating stream, flowing through the interior of the tubes that condense the vapor in each stage, serves to remove the latent heat of condensation. In so doing, the circulating brine is preheated to almost the maximum operating temperature of the process, simultaneously recovering the energy of the condensing vapor. This portion of the MSF plant is called the "heat recovery" section. The preheated brine is finally brought up to maximum operating temperature in a brine heater supplied with steam from an external source.

At the cool end of the plant, a separate set of tubes is installed in several of the stages in a "heat rejection" section to remove the waste heat. The coolant there is generally not recycled brine, but the feedwater (e.g., seawater), of which the greater portion is discharged to waste. A small fraction of this coolant becomes preheated makeup water.

In principle, MSF is the simplest of the desalination techniques. Once the interstage orifices are adjusted, the plant can operate for long periods without resetting of flows.

High efficiency can be obtained by incorporating many stages and a large heat transfer area into the design. Steps aimed at reducing the capital cost of MSF plants have included the substitution of lower cost materials and by using the compact vertical/stacked designs.

Multi-Effect Distillation (MED) is the oldest evaporative process. The principles involved are shown in [Figure 29](#).

In the vertical tube evaporator the feed descends as a thin film on the inside of vertical tubes. The partially concentrated brine is delivered to a second chamber (effect), maintained at a slightly lower pressure than the first effect. Likewise, the vapor liberated from the first effect feed is sent to the second effect. There it condenses on the heat transfer tubes, giving up its latent heat to evaporate an additional fraction of water from the brine flowing on the opposite wall of the tube. The process of evaporation plus condensation is repeated from effect to effect, each at successively lower pressure and temperature. The combined condensed vapor constitutes the product water.

Several design alternatives exist. For example, the feed may flow counter-currently to the vapor, thereby subjecting the most concentrated brine to the maximum evaporative driving force. Conversely, the brine, partially preheated by a fraction of the vapor, may flow co-currently with the steam. The latter flow pattern has the advantage of minimizing scale formation, since the most concentrated brine is exposed to the lowest temperature. Another design variation uses horizontal rather than vertical heat-exchange tubes. This configuration requires more plot space.

MED plants can be made more energy efficient by increasing the number of effects and the heat transfer area or by increasing the maximum operating temperature. On the other hand, when low-cost heat is available, it is preferable to sacrifice some of the energy efficiency by operating at a lower temperature because of the resultant decrease in the rate of corrosion and scale formation. The low corrosion and scaling tendencies of the low-temperature multi-effect (LTME) process not only improve reliability and decrease operating costs but permit the construction of the plant from lower cost materials.

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One design variation reverses the common procedure of passing the brine through the heat-exchange tubing. Instead, the brine is sprayed on the outside of the tubing while the hot vapor flows inside. Thus, in the unlikely event of a leaky tube wall, the vapor (which is at a higher pressure than the brine) would leak into the brine chamber, thereby avoiding contamination of the product water.

Design guidelines/considerations for flash evaporation systems are as follows:

- Selection of the optimum seawater desalination system normally requires an economic analysis. Vendor supplied hardware requires evaluation based on investment and operating cost considerations.
- Effluent water (distillate) quality is < 10 ppm (< 10 mg/L).
- Mechanical Vapor Compression (MVC) should be considered if:
 - Demands can be met with relatively small units. Maximum sizes are available up to 1200 TPD (317,000 GPD).
 - An economic heat source (e.g., steam) is not available.
- In general, low temperature operation appears to have major advantages in the area of scale and corrosion control, which in turn should lead to higher service factor. On the negative side, operating at lower temperature requires a larger unit and usually a higher capital cost. Higher temperature operation saves significant capital, but introduces a higher potential for scaling and corrosion, and places more importance on operator control (especially for plants using acid). Newly developed chemical dispersants can also be considered for minimizing scale. An exception to this trade-off between high and low temperatures is the low temperature multi-effect which operates at 160°F (70°C) [versus 190°F (90°C) for other low temperature processes]. At this low temperature there is little scaling concern, and use of lower cost materials may offset the investment required for a larger unit.
- The major factor influencing unit reliability and service life, as well as capital cost, is choosing the correct materials for the specific operating conditions present in each portion of the desalination unit. The duty specification should specify acceptable materials for given operating conditions (temperature, O₂ content, TDS concentrations, etc.).
- Thermal units are provided with either long tube (full length or height of unit) or cross-tube configurations. The major advantage of long tube units is lower cost. Cross-tube units are generally easier to maintain (short tubes to pull), and if leaks occur, plugging of a tube does not significantly impact heat transfer capacity.
- The MSF system is the standard of the industry and the long operating history has led to steady improvements in reliability. On the negative side, MSF plants are difficult to operate under changing feed conditions and turndown is limited to about 70%.
- Multi-effect (ME) plants can be designed for higher efficiencies, and generally have an advantage over MSF when energy costs are high. In addition ME plants are easier to operate under changing feed conditions and have a greater turndown capability (to about 50%).
- A qualitative comparison of MSF and ME evaporation system parameters is shown in [Table 9](#).