Boiler Feed Water

Reducing Scale and Corrosion,

Part 2 of 2

By C.F. "Chubb" Michaud, CWS-VI

Summary: *In Part 1 of this series last month, we discussed salt regenerated ion exchange systems for softening and dealkalizing. Part 2 will deal with the more advanced chemical regeneration systems and silica removal, beginning with weak acid softening.*

Since softener leakages increase with increasing total dissolved solids (TDS), the upper limits of strong acid systems is generally taken at 5,000 parts per million (ppm). With feed water above 5,000 ppm TDS, a weak acid cation (WAC) resin can be substituted for the strong acid cation (SAC) polisher in a series softener to produce very low leakages (<1 ppm). WACs are very selective for divalent ions such as calcium (Ca^{++}) and manganese (Mg^{++}) and regenerate quite efficiently with almost no excess acid. WACs, although operated in the sodium form, cannot be regenerated with salt. It's necessary to first regenerate with acid (preferably HCl) and then neutralize with caustic (preferably in up-flow mode). There's no advantage to counter-current acid flow.

Regeneration of WAC

Reaction 14*: O^{Ca++}** + HCl à O^{H+} + $CaCl_2$

Reaction 15: O^{H+} + NaOH à O^{Na+} + HOH

* For previous reactions, see Part 1 of this article in *WC&P's* March 2001 issue.
** For purposes here, O represents an ion exchange resin with Na, Ca, HCO_3 or Cl attached.

There are numerous combinations of ion exchange for the simultaneous reduction of hardness and alkalinity. These typically use cation exchange to first reduce the pH of the feed stream by removing cations in exchange for hydrogen (H^+).

Reaction 16: $Ca(HCO_3)_2$ + O^{H+} à O^{Ca++} + H_2CO_3

Reaction 17: H_2CO_3 à CO_2 + H_2O

Since the resulting pH is usually low enough to convert all alkalinity to free CO_2 and water as in Reaction 17, the resulting CO_2 can be removed mechanically by aeration (also known as degasification or decarbonation). The ratio of total hardness to alkalinity will determine the resin scheme to be used. These ratios are calculated by converting all components to ppm as $CaCO_3$—calcium carbonate. A 1:1 ratio means the total hardness is approximately equal to the alkalinity.

Weak acid dealkalizer

When a weak acid resin operates in the hydrogen form, it will only exchange with cations (hardness and sodium) up to the level of the feed water alkalinity. Therefore, if complete hardness removal is required, the hardness:alkalinity ratio must be less than 1. In other words, alkalinity must equal or exceed hardness. Table 1 offers an example of the before and after.

The setup is illustrated in Figure 5.***

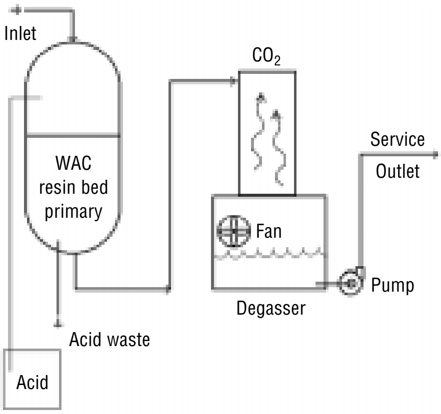
This water may be slightly acidic at this point but typically doesn't require neutralization. This process has

Table 1. Transformation of water through WAC and degasification

Raw Water Before				**After WAC & Degas**			
Ca	80	HCO_3	110	Ca	0	HCO_3	10*
Mg	20	SO_4	30	Mg	0	SO_4	30
Na	100	Cl	60	Na	90	Cl	60
	200		200		90		100

* Note: Degassing will not remove 100% of the free CO_2.

Figure 5.



*** For Figures 1-4, see Part 1 of this article in *WC&P's* March 2001 issue.

been effectively used for pre-treatment of water for both beverage and ice production. There's a reduction of TDS as well as removal of hardness and alkalinity. WAC resins can produce very low pH effluent at the beginning of their runs. To avoid this, use only 100 percent of the stoichiometric quantity of acid. Stoichiometric refers to proportions in which chemicals combine to form compounds and the weight relations in chemical reactions. WAC resins may produce a slight hardness leakage when operated in the H^+ form. If absolute soft water is required, the WAC must be followed by a regular SAC softener.

Strong acid plus degas

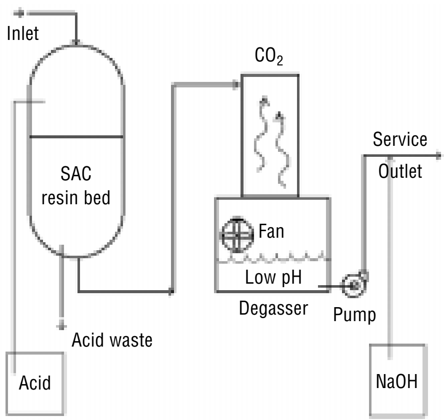
If the hardness:alkalinity ratio is equal to or greater than 1, a WAC cannot be used. The effluent water will still contain hardness. Instead, an SAC can be used (see *Figure 6*).

Since our effluent will still contain considerable acid even after degassing (see *Table 2*), it will be necessary to neutralize the acid with approximately 160 ppm of NaOH.

Combination SAC/WAC

It seems a shame to remove all that cation, only to have to add some back for neutralization. There is, however, a method of dealkalizing and softening without the use of caustic. This method uses the WAC in H^+ form to remove some of the hardness (up to the level of alkalinity) and a SAC in Na form to remove the rest. A degassifier is still used and the resulting water analysis is the same as in Table 3. Although the best design control is achieved by placing the WAC and SAC in separate vessels, they can

Figure 6.



be combined. When combined, the WAC is layered on top of the SAC (special resin choices and sizes required). The system is first regenerated with acid in a down-flow design. This converts the WAC and some of the SAC to H^+ form. Next, a brine solution is then passed down through the bed. Since the WAC doesn't react, the brine converts the SAC to Na^+ form and the desired result is obtained. Care must be taken not to upset the layers. For this reason, the dual resin bed cation is rarely used.

Split stream dealkalizer

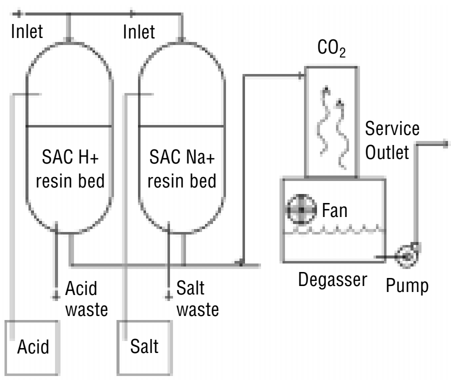
If seasonal fluctuation in feed water composition or variable sources (surface, city, well) makes the hardness to alkalinity ratios highly variable, there's a scheme that can operate with great flexibility—the split stream dealkalizer.

A split stream dealkalizer uses two SAC beds. One operates in the H^+ form and one in the Na^+ form. Both share the same water supply (see *Figure 7*).

The effluent stream from the H^+ cycle system will contain essentially no cations and will have an acid content equal to the TDS (including its original alkalinity). The effluent stream from the Na^+ cycle system will contain no hardness but will contain all of its original alkalinity. By juggling the ratios of the two streams, it's possible to "match" effluent acid to the combined alkalinity and then degas. The total flow is always the same—only the ratios change.

For example, let's assume you have to design a 60 gallon per minute (gpm) system for a low-pressure boiler feed. From Table 3 (see page 42), we see the need to essentially

Figure 7.



remove hardness, alkalinity and TDS. Using the water analysis in Table 4, we can follow the progression:

Desilicizers

The removal of silica with ion exchange requires the anion resin to be operated in the hydroxide (OH) form—similar to deionization (DI)—and that water first be thoroughly softened. Four to six pounds of NaOH per cubic foot are required to regener-

Table 2. Effects of SAC and degassing on water

Raw Water Before				After SAC & Degas				Neutralized			
Ca	8	HCO_3	50	Ca	0	HCO_3	10*	Ca	0	HCO_3	10
Mg	20	SO_4	30	Mg	0	SO_4	30	Mg	0	SO_4	30
Na	100	Cl	120	Na	0	Cl	120	Na	160	Cl	120
	200		200		0		160		160		160

* Note: Degassing will not remove 100% of the free CO_2.

Table 3. Boiler water guidelines (conditions in boiler)

Drum pressure (psig)	Silica (ppm as SiO_2)	Total alkalinity* (ppm as $CaCO_3$)	Hardness (ppm as $CaCO_3$)	Conductance (micromhos/cm)
0-300	150	700	0	7000
301-450	90	600	0	6000
451-600	40	500	0	5000
601-750	30	400	0	4000
751-900	20	300	0	3000
901-1000	8	200	0	2000
1001-1500	2	0**	0	150
1501-2000	1	0**	0	100

* Alkalinity not to exceed 10% of specific conductance

** Minimum level of OH alkalinity in boilers below 1,000 psi must be individually specified with regard to silica solubility.

SOURCE: www.abma.com

ate the desilicizer resin, which is a Type I strong base anion (SBA) resin. This must also be done with softened water.

Table 4. Proper analysis for a 60-gpm system

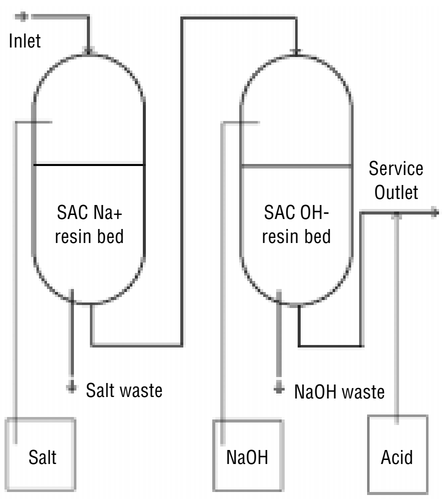
Raw Water Before				After SAC H+ Cycle				Softened Raw Water				Blended & Degassed			
Ca	80	HCO_3	100	Ca	0	HCO_3	100	Ca	0	HCO_3	100	Ca	0	HCO_3	100
Mg	20	SO_4	30	Mg	0	SO_4	30	Mg	0	SO_4	30	Mg	0	SO_4	30
Na	100	Cl	70	Na	0	Cl	70	Na	200	Cl	70	Na	100	Cl	70
	200		200		0		200		200		200		100		110

A desilicizer will remove all anions—alkalinity, chlorides and sulfates as well as silica. Since the effluent will be essentially dilute NaOH with a pH of about 12, acid will have to be added to reduce the pH. This makes the economics questionable if the TDS of the feed water is fairly high.

Desilicizers are intended for use with groundwater sources that are fairly low (under 200 ppm) in solids and where silica makes up 10-to-20 ppm of the anion load. Many natural well waters, from areas where quartz predominates in the soil, fit this description. Often economics can be improved by first dealkalizing the water by one of the degassing techniques to reduce the load on the anion unit. Such a schematic is represented in Figure 8.

To further minimize operating costs, the NaOH regenerant should first be heated to 120°F and the second half of the caustic is saved for recycle in the next regeneration. Since no acid is used in this part of the process, unlined steel may be used in the tank, pipes and valves. Boiler blow down can be reduced by a factor of 10 times or more.

Figure 8.



Conclusion

The supply of equipment for softening and dealkalizing for low and medium pressure boiler feed treatment presents a tremendous opportunity for commercial / industrial system manufacturers. The simplest systems regenerate with salt and can be put together with off the shelf components. The specific needs for completeness of removal may dictate that more conservative guidelines be used for hydraulic design—<3-to-4 gpm / ft³ and <10 gpm / ft². The use of acid and caustic as regenerants requires some attention with respect to the materials of construction and safety. Here are a few tips. Use Schedule 80 pipe and fittings. Provide check valves on all chemical lines. Separate acid and caustic storage tanks and containers. Finally, always provide an operating and maintenance manual so the end-user can do the same. q

References

1. *The Nalco Water Handbook*, second edition, McGraw-Hill, New York, 1988.

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4. *Boiler Feed Guidelines*, American Boiler Manufacturers Association, Arlington, Va.: http: / / www.abma.com

About the author

S *C.F. "Chubb" Michaud, CWS-VI, holds bachelor's and master's degrees in chemical engineering from the University of Maine and has more than 30 years of professional experience in water and fluid treatment processes. Michaud is CEO and technical director for Systematix Co., of Buena Park, Calif. He's also chairman of the Water Quality Association's Ion Exchange Task Force, as well as a founding member of the WC&P Technical Review Committee. Michaud can be reached at (714) 522-5453, (714) 522-5443 (fax) or email: chubb@ systematixUSA. com*

Water Factoid

Canadians are the trustees of almost 25% of all the world's wetlands, currently covering 16% of the land area of Canada.