Designing Ion Exchange Systems

Part II: Selecting A Resin

By C.F. Michaud

Solving a water problem with ion exchange is like any other problem solution. You have to ask yourself three questions

1. *Where am I?*
2. *Where do I wish to go?*
3. *How am I going to get there?*

In Part I of this series, we answered the first question by instructing the reader on the proper interpretation and handling of a water analysis. Now we must look at where we wish to go in order to assess the type of equipment we will need.

Softening

Low pressure boilers, canneries, laundries, residences, restaurants and a host of chemical manufacturers must remove scale forming elements from their process water before heating it. In addition, iron and manganese salts may adversely affect the taste of canned foods and beverages. These scale formers are primarily calcium and magnesium salts that we refer to as hardness. Removing them is called softening.

There are two types of hardness: 1) temporary and 2) permanent. Temporary hardness is caused by calcium and magnesium bicarbonate. It can be precipitated by heating the water to decompose the bicarbonate (soluble) to carbonate (insoluble). Permanent hardness is primarily calcium and magnesium sulfate and chloride. Although $CaCl_2$, $MgSO_4$ and $MgCl_2$ are soluble, they can react with soap to cause "scum" and with other chemicals to form precipitates. Therefore, for most water processes, softening is desirable.

This is readily accomplished by the use of sodium cycle ion exchange using a strong acid cation (SAC) resin in the sodium form.

Assume a water of the following composition:

Table 1

Ion	ppm as $CaCO_3$	Ion	ppm as $CaCO_3$
Ca^{++}	150	HCO_3^-	150
Mg^{++}	50	SO_4^{--}	50
Na^+	200	Cl^-	200
Cations	400		400
		Silica	35
		Anions	435

We can illustrate the composition on a bar graph:

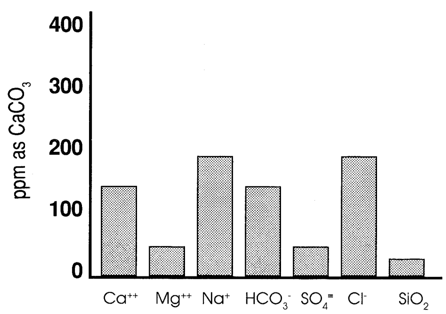
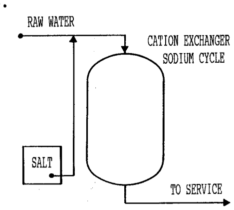


Figure 1

The softener system can be represented as:



And the softened water as:

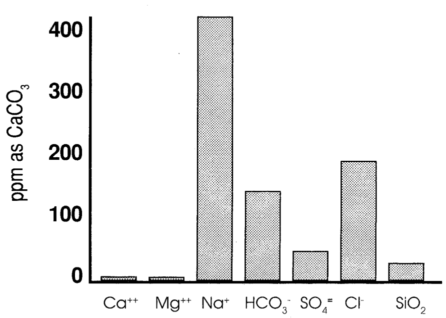
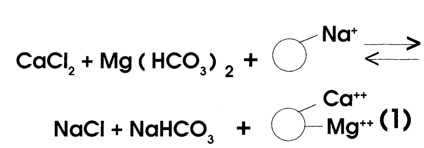


Figure 2



Regeneration is accomplished by introducing a strong brine (sodium) solution to reverse the exchange. Anions, of course, are unaffected by softening. Also, note that the TDS (as $CaCO_3$) is not reduced by sodium cycle softening.

Dealkalizing

When a salt is formed from the neutralization of a strong base (sodium, calcium or magnesium hydroxide) and a weak acid (bicarbonate, carbonate, silicate, borate), a high pH can result. This is called alkalinity. For the purpose of this discussion, we will deal only with bicarbonate which is the one ion most responsible.

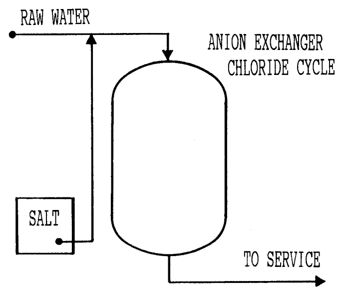
When heated, bicarbonate decomposes into carbonate, carbon dioxide and water. The CO_2 is carried with the steam to reform carbonic acid with water. This is very corrosive to iron and steel.

$$2\,NaHCO_3 \xrightarrow[\text{heat}]{\Delta} Na_2CO_3 + H_2O + CO_2 \qquad (2)$$

Bicarbonate can also cause ice to cloud and the alkalinity can adversely affect the taste of food and beverages. Removing alkalinity is called dealkalizing and there are a number of ion exchange approaches.

One method uses a strong base anion resin (SBA) in the chloride cycle. Using our prior example and assuming we have already softened the water, the system and the product water can be represented as:

$$NaHCO_3 + \bigcirc\!-Cl^- \rightleftharpoons NaCl + \bigcirc\!-HCO_3^- \qquad (3)$$



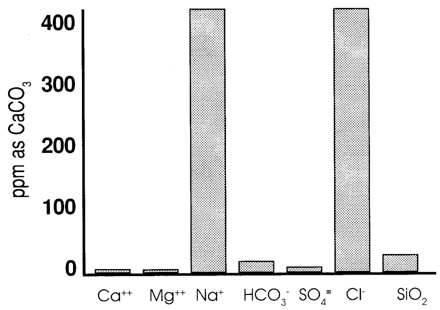


Figure 3B

Once again, regeneration is done with brine and TDS is not reduced. For many applications, raw waters as high as 1000 ppm or more can economically and effectively be treated in this manner. In cases involving fairly high hardness, it is strongly recommended that the water be softened first. Anion regeneration is more efficient when a small amount of caustic (NaOH) is used with the brine. Precipitation of hardness and resin fouling can occur unless soft water is used.

It is possible to soften, dealkalize AND reduce TDS all at once using only a single ion exchange vessel by taking advantage of the water chemistry. One such method utilizes a weak acid cation (WAC) in the hydrogen cycle.

$$Ca(HCO_3)_2 + 2\,\bigcirc\!-H^+ \rightleftharpoons \bigcirc\!-Ca^{++} + 2H_2CO_3 \rightleftharpoons 2H_2O + 2\,CO_2 \uparrow \qquad (4) \text{ or}$$

$$NaHCO_3 + \bigcirc\!-H^+ \rightleftharpoons \bigcirc\!-Na^+ + H_2CO_3 \rightleftharpoons H_2O + CO_2 \uparrow \qquad (5)$$

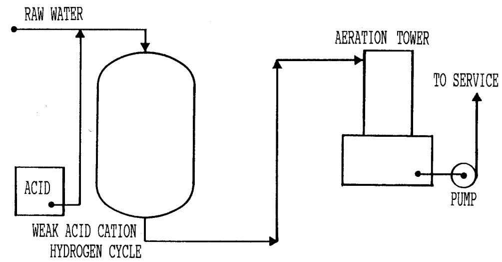


Figure 4A

WAC resins are effective at exchanging cations for H^+ ions on the resin. However, they are limited in this exchange by the amount of alkalinity (HCO_3^-) present. (Figs. 4A & 4B)

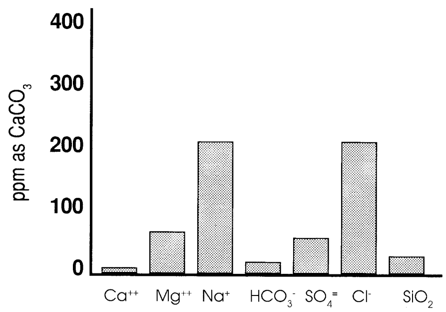


Figure 4B

Exchanging cations for H^+ reduces the pH of the water which effectively converts bicarbonate salts to carbonic acid ($CO_2 + H_2O$). Simple aeration removes most of the CO_2.

Note that in this example, the water is only partially softened and some CO_2 remains. However, TDS is reduced by approximately 150 ppm (the limit of the bicarbonate alkalinity). Since the resin is more selective for calcium than magnesium, we may assume that the hardness residual is primarily Mg^{++}.

This method of hardness, alkalinity and TDS reduction is very good for low to medium pressure boilers and food and beverage uses. If the alkalinity level had exceeded the total hardness (200 ppm), this system would have completely softened the water. On low alkalinity waters with high hardness, it is not recommended.

In such instances, a SAC resin can be used in H^+ cycle. (Figs. 5A & 5 B)

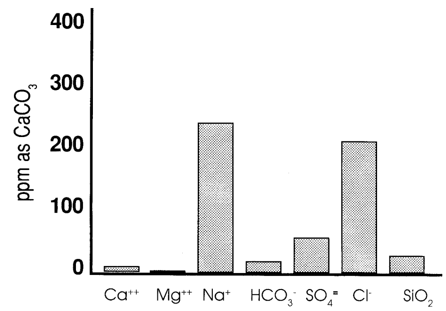


Figure 5B

$$Ca(HCO_3)_2 + NaCl + 3\,\bigcirc\!\!-H^+ \rightleftarrows \bigcirc\!\!<^{Ca^{++}}_{Na^+} + H_2CO_3 + HCl \quad (6)$$

Such water would be quite acidic and would require neutralization. If the free mineral acidity (sulfate and chloride content) - also called FMA is quite low, this water could be neutralized effectively by the addition of caustic following the aeration unit. The remaining CO_2 would reform the bicarbonate salt when neutralized. However, the level would be low - in the order of 10 - 15 ppm. High FMA water would require a high amount of caustic for neutralization.

The use of softened raw water is above an effective means of neutralizing SAC effluent providing moderate alkalinity is present. This technique essentially blends the water in Figure 2 and Figure 5 as shown in Fig. 6A and 6B.

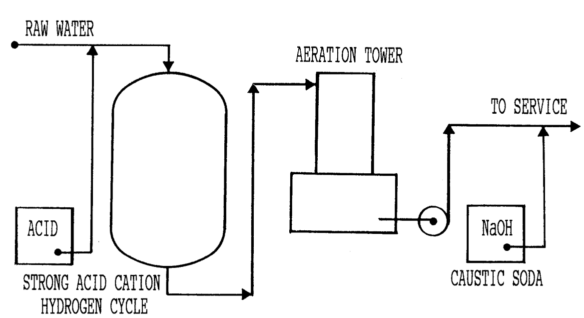


Figure 5A

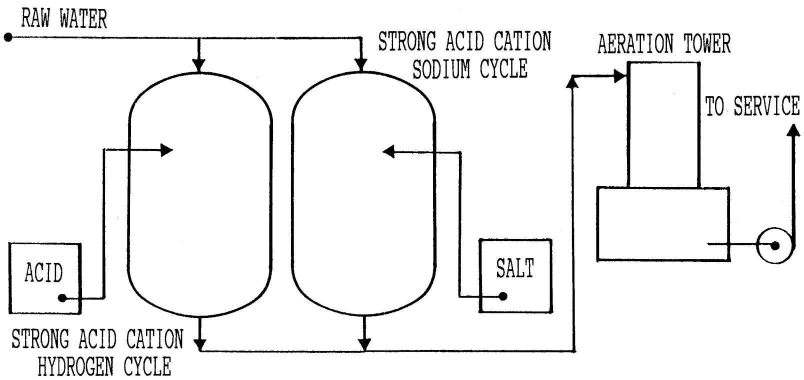


Figure 6A

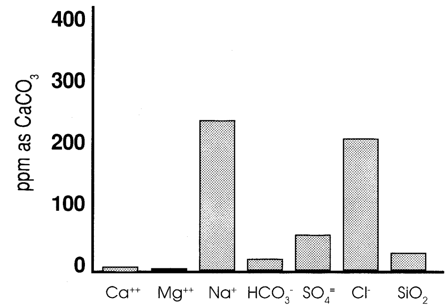
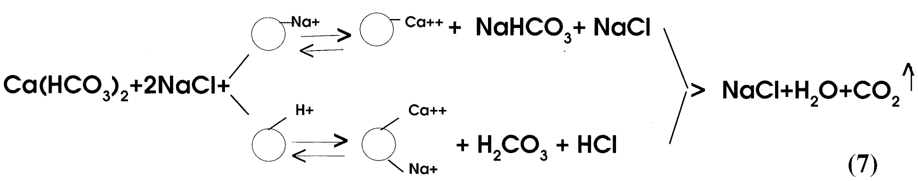


Figure 6B

Note that the hardness and alkalinity are almost completely eliminated and that the TDS is reduced by approximately 150 ppm. In this case, the softened water is fed in a ratio of 4:3 with decationized water to supply enough alkalinity to neutralize the acid. This system is also known as a "split stream" dealkalizer and can be used to reduce alkalinity to any level and have completely softened water regardless of influent water composition.

Table 2 below gives a guideline for the concentrations of various contaminants that can be tolerated in boiler water. As the concentration increases to the limit, some of the water must be removed (blowdown) and replaced with the higher quality make up water. The higher the quality of the make up water, the lower the amount of blowdown required - thus conserving more heat and energy.

Since desirable blowdown may run only in the range of 5 - 10% or less, the quality of the make up water must run 10 to 20 times or more better than the boiler water guidelines.



(7)

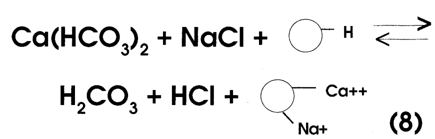
Table 2
Boiler Water Guidelines

Drum Pressure (psig)	Silica (ppm SiO_2)	Total Alkalinity* (ppm $CaCO_3$)	Conductance (micromho/cm)	TDS (ppm)
0 - 300	150	700	7000	3500
301 - 450	90	600	6000	3000
451 - 600	40	500	5000	2500
601 - 750	30	400	4000	2000
751 - 900	20	300	3000	1500
901 - 1000	8	200	2000	1000
1001 - 1500	2	0**	150	25
1501 - 2000	1	0**	100	10

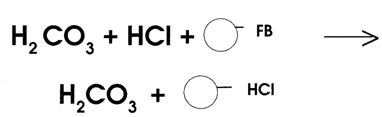
* Alkalinity not to exceed 10% of specific conductance.
** Minimum level of OH alkalinity in boilers below 1000 psi must be individually specified with regard to silica solubility and other components of internal treatment. (From American Boiler Manufacturers Assoc., Industry Standards and Engineering Information Manual).

FMA REDUCTION

For certain applications such as car washes and metal plating rinse water it may be desirable to eliminate cations and all FMA while there may be no objection to CO_2 or silica. This can be accomplished by using a H^+ cycle SAC followed by a weak base anion (WBA) which is regenerated very economically with low amounts of caustic or soda ash (Na_2CO_3). The resulting water is slightly acidic but very low in residue (only the silica remains after evaporation). The process can also incorporate an aeration tower to remove CO_2 if it is objectionable: (Figs. 7A and 7B)

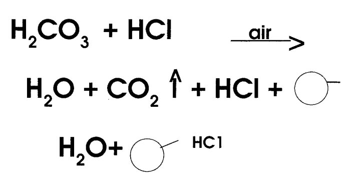


(8)



(9)

or



(9a)

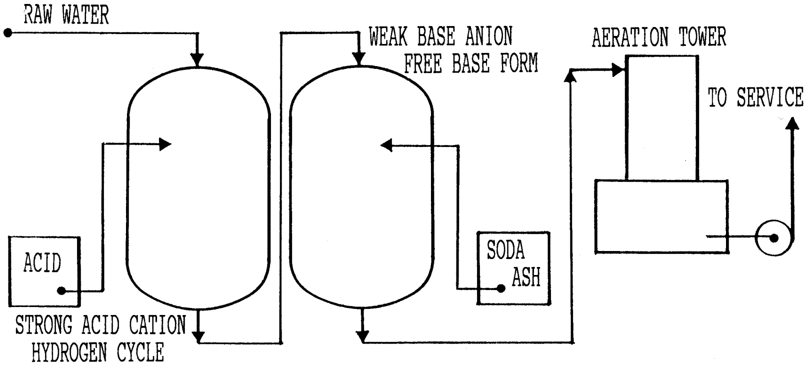


Figure 7A

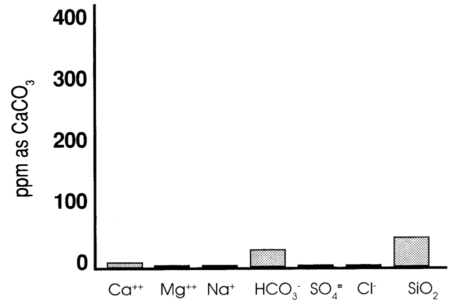


Figure 7B

SILICA REDUCTION

On low TDS waters or when electric boilers are utilized, some TDS can be tolerated (or in the case of electric boilers, necessary). However, hardness and silica may have to be removed. This can be done very economically using a SAC sodium cycle softener followed by a SBA regenerated with caustic. The effluent is dilute caustic (NaOH) and is usually partially neutralized with sulfuric acid:

$$CaCl_2 + Na_2SiO_4 + \bigcirc\!-Na^+ \rightleftarrows$$

$$NaCl + Na_2SiO_4 + \bigcirc\!-Ca^{++} \quad (10)$$

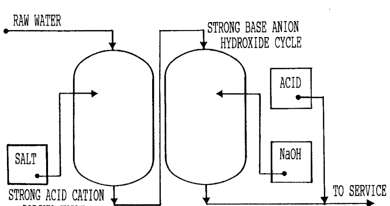


Figure 8A

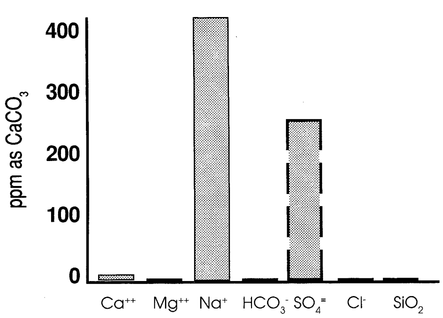


Figure 8B

$$NaCl + Na_2SiO_4 + \bigcirc\!-OH^- \longrightarrow$$

$$3NaOH + \bigcirc\!<^{Cl^-}_{SiO_4} \quad (11)$$

$$2\ NaOH + H_2SO_4 \longrightarrow$$

$$Na_2SO_4 + 2\ H_2O \quad (12)$$

Note that mild steel can be used throughout.

Water can essentially be completely demineralized by substituting a SBA resin in place of the WBA. SBA resins, unlike WBA's, will remove weakly ionized components such as CO_2 and silica. Typically, the FMA, CO_2 and hardness are reduced to zero while the silica is dropped to less than 0.1 ppm. Sodium, which usually leaks from the SAC at about .5 to 1% of total cation content, is the major component of the effluent. If the influent water has moderate alkalinity, an aerator will greatly reduce the size of the SBA unit and the cost of the caustic. With high FMA, a WBA can be incorporated and economically regenerated using spent caustic from the SBA. In either event, the resulting water has the same composition:

$$NaCl + \bigcirc\!-H^+ \rightleftharpoons \bigcirc\!-Na^+ + HCl \qquad (13)$$

$$HCl + \bigcirc\!-OH^- \rightleftharpoons \bigcirc\!-Cl^- + H_2O \qquad (14)$$

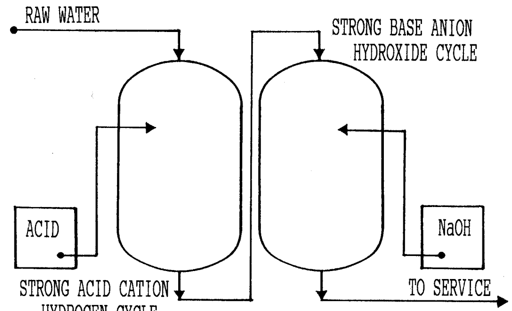


Figure 9A

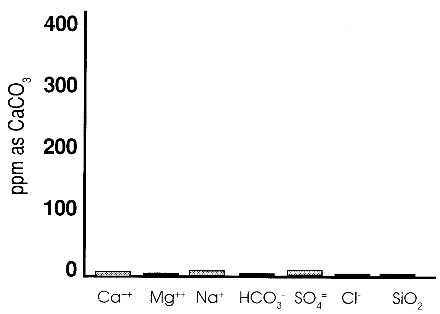
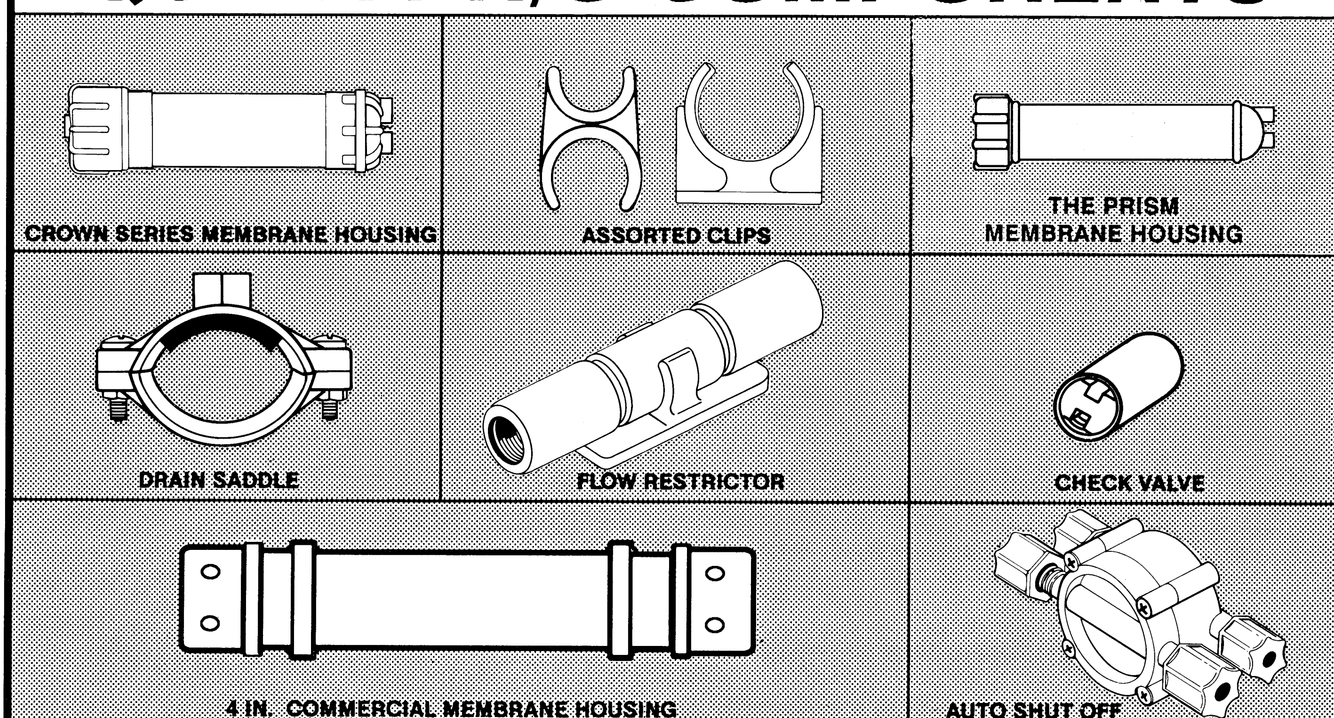


Figure 9B

Such water is suitable for moderate pressure boilers and many chemical applications requiring "pure" water with very low TDS. Because of the sodium residual, the pH is elevated to 9.0 plus and as the water evaporates, the pH will increase (the effluent is essentially dilute caustic). Some caution is needed and neutralization may be advised. This can be accomplished with an acid feeder or the sodium residual can be completely removed with a WAC polisher regenerated off the spent acid from the SAC unit. The quality of this water would be exceeded only by the incorporation of mixed bed (MB) polishers and could be suitable for even some high pressure boiler applications.



ULTRA PURE WATER

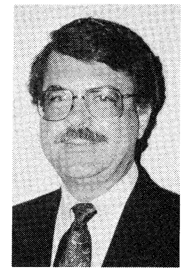
The ultimate in ionically pure water is obtained through the use of mixed bed polishers. Since ion exchange is an equilibrium reaction, extremely high purity can be obtained by repeating the SAC, SBA steps over and over. This is done, in effect, by utilizing a mixture of SAC and SBA in the same vessel. Water produced in this manner can have ppb levels of remaining TDS. Regeneration is done by first backwashing the bed to separate the anion from the cation which are then individually regenerated.

Ultra pure water is not only demineralized, it is also free of organics, particulates, pyrogens and gases. It represents everything we currently know about water filtration.

CONCLUSION

We now know where we are and, hopefully, where we're going. Having made the choice of system design based on the end use of our water source, we can now set out to design a working demineralizer. Part III of this series will deal with the actual rating of the resins and designing for neutral effluent.

About the Author



Chubb Michaud is a chemical engineering graduate of the University of Maine and has been involved in ion exchange water treatment for over 10 years. He is founder of Systematix Co. of Brea, CA and represents Purolite Co. in the Western states.

Correction

In Part I of "Designing Ion Exchange Systems," under the paragraph, "Rating Ion Exchange Systems" on page 25 in the August issue, the sentence should read: "To demineralize 10,000 gallons per day of a feed water such as that in Table 2 would require 10 ft.^{3} of cation (rated at 25.6 kg/ft.^{3}) and 21 ft.^{3} of anion (rated at 13.1 kg/ft.^{3})."

The author and WC & P regret any confusion this error may have caused our readers.