

FACTORS IN HIGH PURITY MIXED-BED DEMINERALIZERS

The operation of high purity mixed-bed demineralizers has become routine, but not without a growing need for maintaining and solving operating problems. We foresee increasingly stringent effluent specifications for specific ionic species to a range even lower than parts per billion. This article focuses on the equilibrium and kinetics of ion exchangers as related to mixed beds. Its purpose is to lay a foundation for future discussions of specific operating environments and for understanding of important relationships among the inorganic ions in mixed beds operating in the range of 18 megohm-cm resistivity.

For this discussion, it is assumed that the ion exchange resin is in excellent working order, and free of organics or any other form of fouling. Therefore, any leakage would be due to incompletely regenerated resin and would pass through the mixed bed as inorganic salts, acids, or bases.

Mixed-Bed Operations

A mixed bed is normally used as a condensate polisher, a polishing mixed bed, or a working mixed bed.

Condensate Polishers

In a condensate polisher, the influent water is based on corrosion products, mostly metallic oxides; leakage from the condenser cooling water; and chemical additives such as ammonia and filming amines. The ammonia or amines dominate the composition of the condensate returns. The pH is usually buffered because of the amines in the area of 9 to 10 pH.

In such a buffered system, the water chemistry can be easily defined on a

case-by-case basis, and pH can be considered as a constant value, which simplifies the mathematics. This approach, using assumed pH values to define H⁺ and OH⁻ concentrations before calculating other equilibrium values, has been done many times with good results. In applications dealing with total ion levels of a few ppb or less, however, this approach can lead to relatively large errors.

Mixed-Bed Polishers

Mixed-bed polishers encounter mostly sodium and silica (which leak from the two-bed or working mixed-

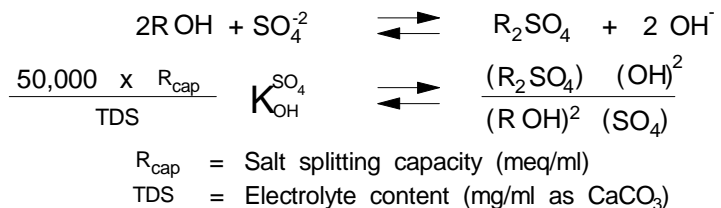
bed demineralizer) until they exhaust. Then traces of bicarbonate and carbonate are also present.

When a polishing mixed bed follows a two-bed primary demineralizer that uses a strongly basic anion resin, the influent is usually sodium hydroxide and a slight amount of silica.

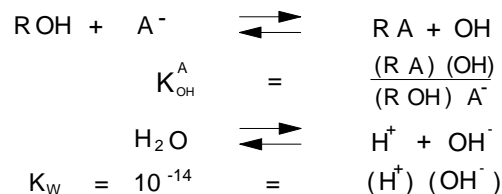
The presence of the hydroxide ion affects the performance of the polishing mixed bed by lowering the capacity for other anions. Initially, the hydrogen generated by the cation portion of the mixed bed neu-

TABLE A
Equilibrium Relationships and Material Balance

Divalent Ions (Sulfate)



Monovalent Ions (General)



Material Balance for Equilibrium Calculations

| Substance | Start | Change | Equilibrium |
|--|-------------------|--------|---|
| R _{OH} - Fraction in OH ⁻ form | S _{OH} | X | S _{OH} + (X/T _c) |
| R _A - Fraction in "A" form | 1-S _{OH} | -X | 1 - S _{OH} + (X/T _c) |
| (H ⁺) - Hydrogen ion concentration | 10 ⁻⁷ | -X+Y | 10 ⁻⁷ -(X/.3 + Y/.3) |
| (OH ⁻) - Hydroxide ion concentration | 10 ⁻⁷ | Y | 10 ⁻⁷ + Y/.3 |
| (OH ⁻) - OH ⁻ from hydrolysis | 0 | Y | Y/.3 |
| (A ⁻) - Anion "A" leakage | 0 | X | Y/.3 |

TABLE B

Approximate Selectivity Coefficients of Common Ions for Type 1 Porous Anion Exchangers

| "A" | K_{OH}^A |
|-------------|------------|
| SO_4^{-2} | 2.25 |
| Cl^- | 15 |
| HCO_3^- | 7.5 |
| HSO_4^- | 24 |
| NO_3^{-2} | 60 |
| F^- | 1.5 |

$R_{cap} = 1.2 \text{ to } 1.3 \text{ meq/ml}$

TABLE C

Position of ions in exhausted SBG1P

| |
|-------------------------------|
| SO_4^{-2} + HSO_4^- |
| Cl^- |
| CO_3^{-2} + HCO_3^- |
| SiO_2 |

constructed a curve of regenerant level versus the fraction of the resin converted to the hydrogen form when starting with 100% sodium-form resin. This is shown in **Figure 1A**. We then created a mathematical model to calculate the equilibrium sodium leakage as a function of the ratio of sodium to hydrogen sites on the resin in a pure water environment. This information was used to calculate conductivity and pH values. We then repeated the process using the anion resin performance to limit the effluent quality (anion limited).

Table A shows the mathematics we used to describe the equilibrium relationships for the cation and anion resins. The calculations assume that only four ions-sodium, hydrogen, one predefined anion species, and hydroxide contribute to conductivity; that sodium or one anion species are the only influent impurities appearing in the effluent; and that cation resin leakage is the sole sodium source, and anion leakage is the sole source of the anion species. This reduced the scope of our cation discussion to sodium and hydrogen. Anions, however, are more complex because more than one ionic species besides silica can cause leakage from anion resins. This makes it necessary to consider several cases. In order to avoid the complexity of calculating equilibrium values for several anions simultaneously, we examined the individual anions separately, by assuming influent waters containing as the counter ion only one anion species at a time. In each case, it was assumed that only three ions are present in the effluent of an anion limited mixed bed-hydrogen and hydroxide ions plus the specified counter ion-and that anion resin leakage was the only source of anions in the effluent.

Silica is a slightly soluble, very weak acid. In fact, silica is less dissociated than water and therefore does not contribute to the conductivity, nor does its presence normally affect the resistivity. As we are dealing with equilibrium relationships and their effect on the resistivity of

tralyzes the hydroxide ion. As the exchange zone moves downward, the incoming hydroxide is able to displace some of the other anions from the anion resin in the exhausted zone, which lowers the loading capacity (operating capacity) of the anion resin. The equilibrium for hydroxide against other anions is unfavorable, however, and this effect is usually small. For example, a standard Type I gel anion resin has a selectivity coefficient of 25 for chloride over hydroxides. If the influent water contained a 25:1 ratio of hydroxide to chlorides, it would only reduce the chloride loading capacity of a Type I gel anion resin by 50%.

On the other hand, the selectivity coefficient for sodium over hydrogen is 1.5 to 2 in 8% to 10% of cross-linked cation resins. Therefore, the sodium associated with the hydroxide leakage from a preceding two-bed demineralizer would have a far greater reductive effect on the capacity of the cation resin in the mixed bed. In such a case, the cation resin would limit the capacity and overall performance. It is interesting to note that, as ion loading is reduced due to capacity losses, so is the equilibrium ionic leakage. Any reduction in operating capacity has the effect of lowering the fraction of ions loaded onto the resin, which in turn results in lower leakage because of the lower loading and the increased ratio of regenerant dose

to ionic loading.

Working Mixed Beds

Working mixed beds encounter softened water with a full complement of anions, including silica. The polishing mixed bed is usually a safety net for stray ions, and needs to be regenerated only periodically to keep silica polymerization and bacterial growth under control. Sometimes the mixed beds are arranged in series and are rotated so that the working mixed bed becomes the polishing mixed bed after regeneration. In all cases, the regeneration and calculated leakage curves described in this article can be used to estimate minimum attainable resistivities for specific regeneration dosages.

Due to the intimate mixture of cation and anion resins in mixed beds, there are multiple cation-anion stages; and little or no significant levels of ionic leakage exist when both resins are performing well. Because of the extremely low concentrations involved, the hydrogen and hydroxide ions from the dissociation of water must be taken into account when calculating equilibrium leakages.

The Mathematical Approach

In order to investigate equilibrium relationships we took a two-stage approach. First, we assumed that cation resin performance limits the effluent quality (cation limited). We

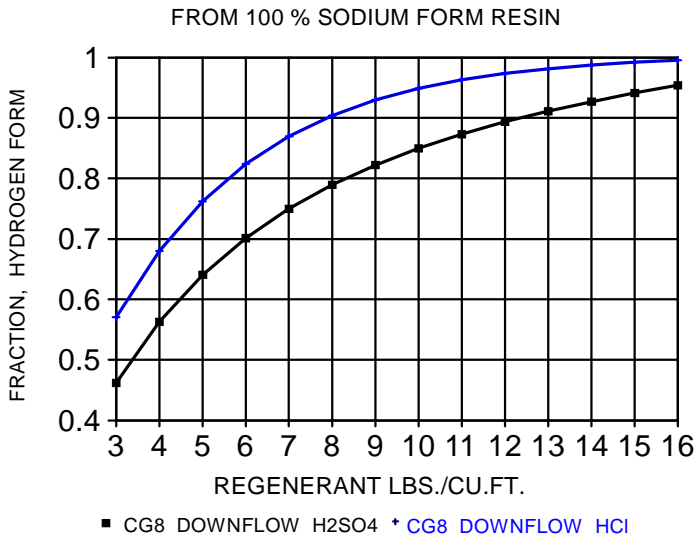


Fig. 1A CONVERSION TO HYDROGEN FORM

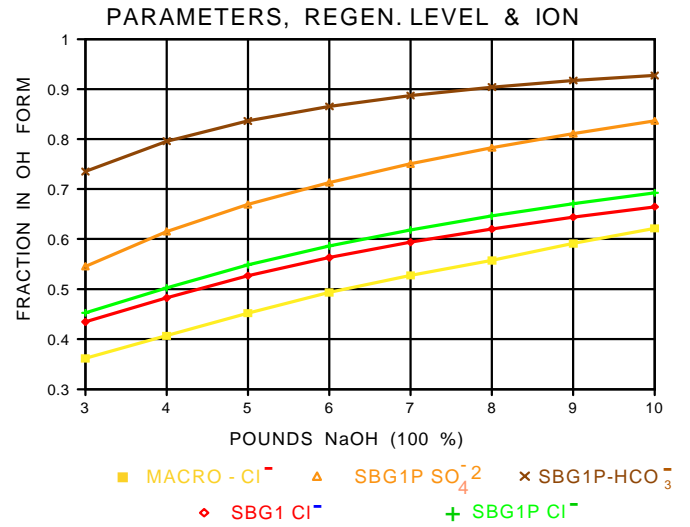


Fig. 1B FRACTION CONVERTED TO OH FORM

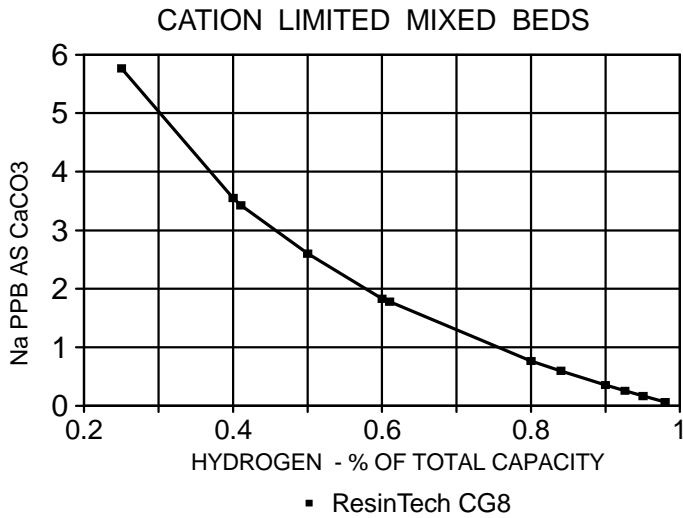


Fig. 2A FRACTION H VS Na LKG

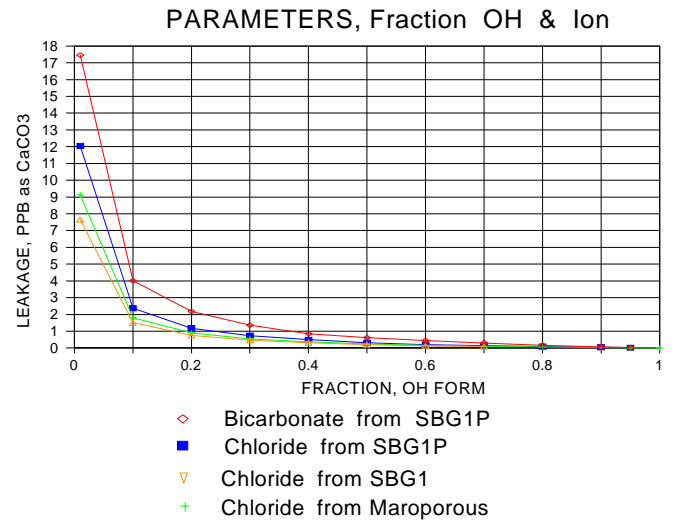


Fig. 2B Leakage from ResinTech SBG1P

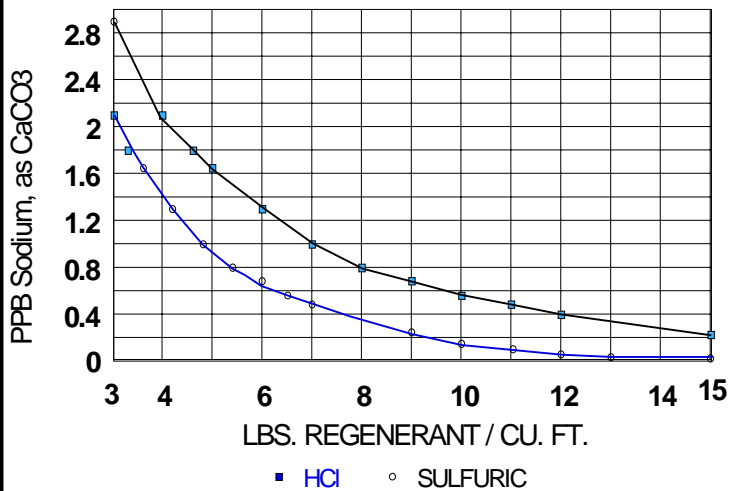


Fig. 3A Sodium leakage versus regenerant dose

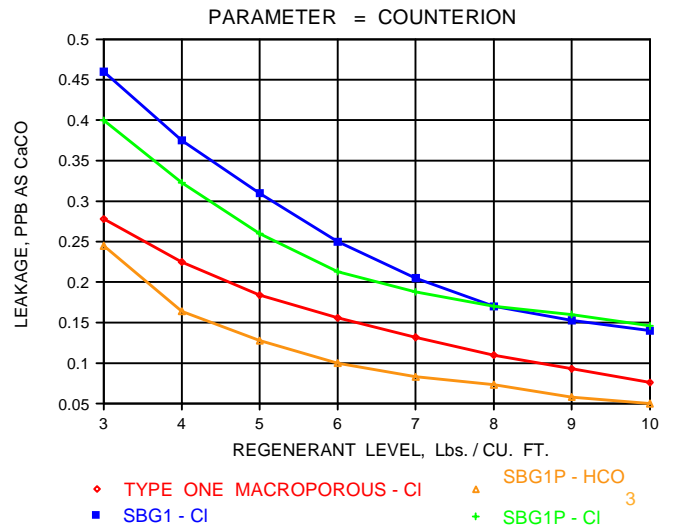


Fig. 3B Regenerant level versus ionic leakage

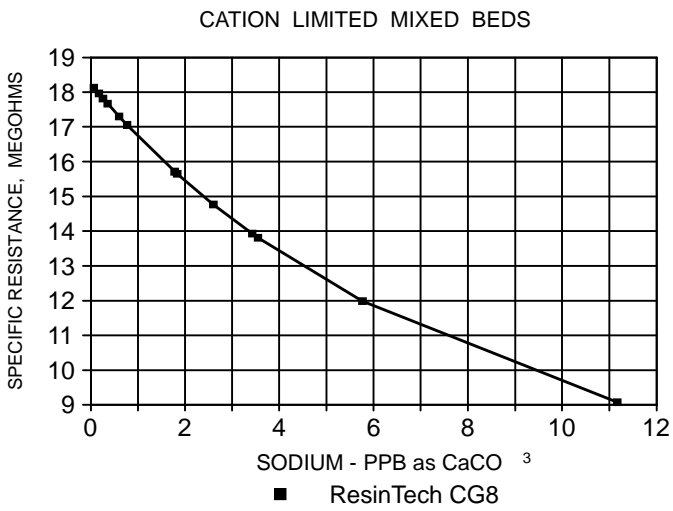


Fig. 4A RESISTIVITY versus Na LEAKAGE

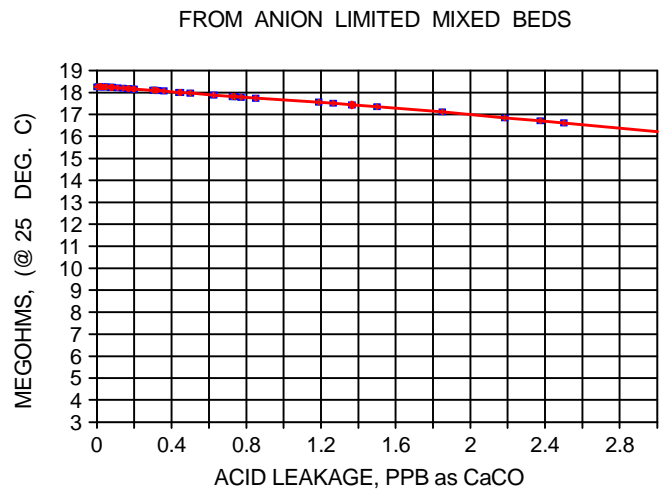


Fig. 4B RESISTIVITY versus LEAKAGE

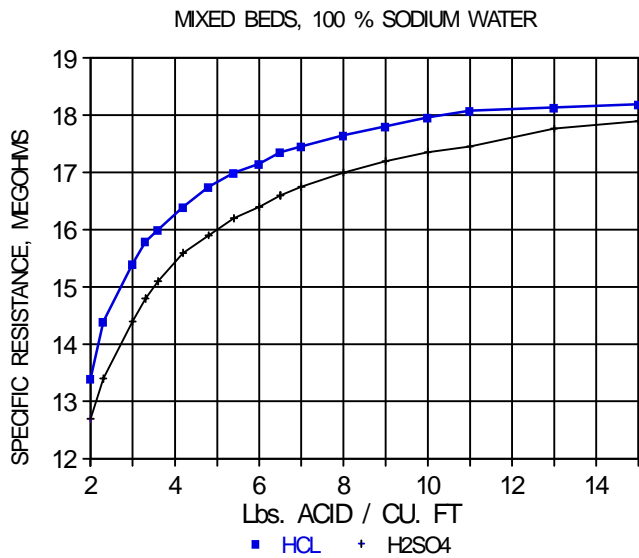


Fig. 5A Regeneration level versus resistivity

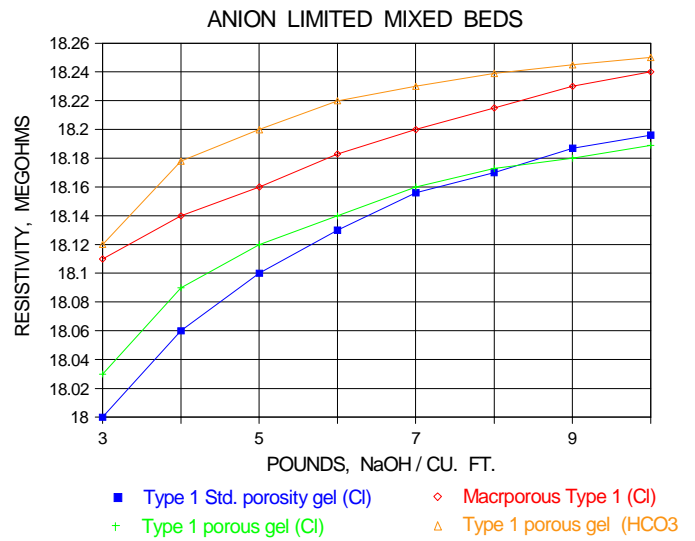


Fig. 5B Resistivity versus regeneration level

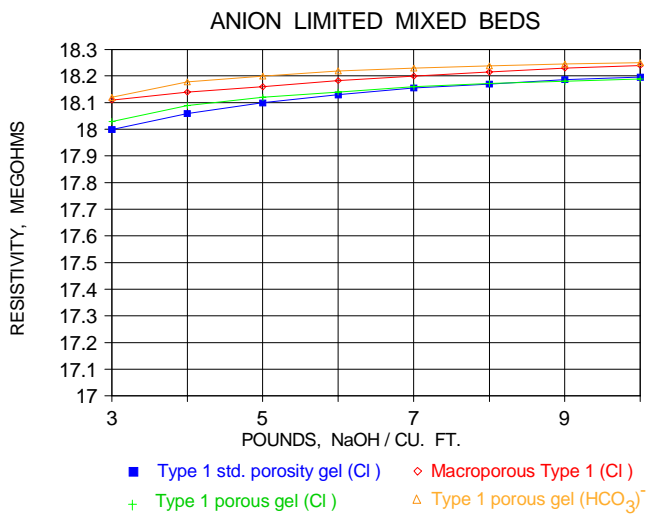


Fig. 5C Resistivity versus regeneration level

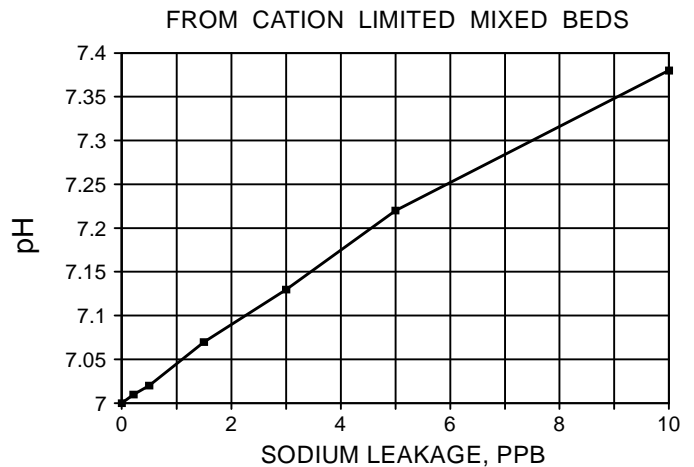


Fig. 6A Sodium leakage versus pH

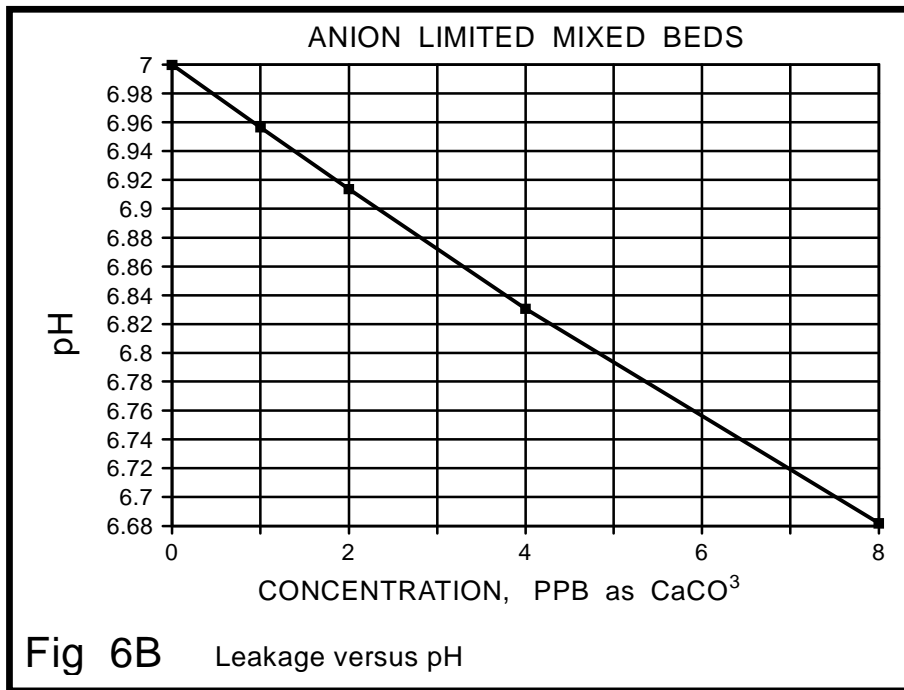


Fig 6B Leakage versus pH

demineralized water, silica is ignored in this discussion, except to explain why temperature is an important factor in anion regeneration and silica leakage.

The material balance of the exchange between the resin and water phases requires a mass relationship between phases. This was done by assuming a 30% void volume, filled with water in equilibrium with the resin. The assumed void volume relationship affects the leakage calculation. Lower void volumes give greater leakage concentrations. The increase depends not only on the void volume relationship, but also on the relative ratio of ions in the resins. At near 100% sodium loading levels on the cation resin, calculated leakages increase by 100% when void volumes are changed from 30% to 10%. However, at 10% sodium loading, calculated leakage is increased by only about 20%. Void volumes have no effect when the resin is fully regenerated. The higher the selectivity of the exchanging ion or the regeneration level of the resin, the lower the effect of changing the void volume in the calculation of equilibrium leakages. Most anions have relatively high selectivity values, so void volume changes are even less effect on anion resins. **Table B** shows the selectivity coefficients for some common anions against hy-

droxides on a Type I porous gel anion resin like ResinTech SBGLP. Mixed beds are usually operated at high regeneration levels; at these levels, the effect of changing the void volume fraction is minimal.

Most technical papers dealing with mixed-bed ion exchange equilibrium assume effluent pH values. This presents no problems in applications like condensate polishing where pH is a controlled variable through addition of chemicals such as filming amines, but it is not a valid assumption in very high resistivity waters.

When the pH is assumed 7.0, the concentration of the hydrogen and the hydroxyl ion are both defined as 5 ppb as CaCO₃ in the water phase. High purity deionized water has no buffering ability. Therefore, its pH will, in fact, rise from 7.0 to 8.0 with only 50 ppb of sodium hydroxide (as CaCO₃). From this it is seen that in high purity mixed bed applications, pH and ionic leakage values are related. Thus, pH 7.0 means either that the mixed bed is producing very low leakage or that leakages cations and anions are equal and self-neutralizing. In order to accurately estimate pH, sodium, and anion species values, the mathematical relationship between pH and ionic leakage was included in our model. In exchange for the extra work, we

gain one more measurement tool to use in monitoring and control functions, and the precision needed to make accurate estimates in high purity applications.

pH Relationships

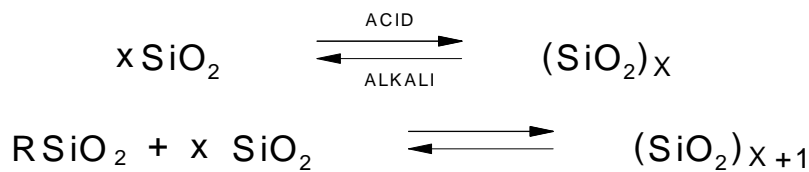
Generally speaking, anions can be held on the anion resin as salts, as acid salts (multivalent anions like sulfate), or as acids, depending on the pH of the resin. In most cases, the polishing mixed bed encounters resin as HCO₃⁻. The HCO₃⁻ is pushed down the column in a chromatographic fashion by incoming chlorides and sulfates. In "working" mixed beds on alkaline waters, CO₂ is present as a HCO₃⁻ or CO₃⁻², depending on pH. Since CO₃⁻² is divalent, it can compete effectively and displace chlorides. At pH above 10.6, CO₂ is present only as CO₃⁻². Below pH 8.3, the CO₂ on the resin is present only as the monovalent HCO₃⁻.

The chloride ion is monovalent. Its affinity and ionic form are unaffected by pH. Only the groups containing carbon dioxide are significantly affected by pH. The normal arrangement of the exhausted resin bed therefore usually looks as shown in **Table C**.

Divalent Ion Leakage

The equilibrium expression for divalent ions is shown, using sulfate exchange on an anion resin, in **Table A**. The relationship between the resin and water phases for divalent ions changes with the concentration of ions in solution. The "apparent selectivity" coefficient for divalent ions at any concentration is approximately 60,000 divided by the total dissolved solids (TDS) for Type I porous anion resins. During the regeneration, the TDS is approximately 60,000 ppm as CaCO₃. During the service cycle, however, it can be less than 0.01 ppm. Divalent ions like sulfate or carbonate have very low apparent selectivities during regeneration. Thus, they are easily eluted from the resin bed, leaving less of them than for an equivalent loading of monovalent ions. During the service cycle, however, they exhibit tremendously high

TABLE D
Polymerization of Silica



apparent selectivities, so that equilibrium works to prevent appreciable quantities of leakage.

Figure 1A shows the relationship of regenerant quantity to the percentage of conversion to the hydrogen form for sulfuric and hydrochloric acids on 8% DVB cation resins like ResinTech CG8; and **Figure 1B** shows hydroxide conversion for Type I porous gel anion resins like ResinTech SBGIP for several different anions. **Figures 2A** and **2B** show the amount of leakage as a function of the degree of conversion to the regenerated form for various ions. **Figures 2A** and **2B** were constructed from values calculated with the model described above.

The information in **Figures 1** and **2** were combined to form **Figures 3**. **Figures 3A** and **3B** show the ionic leakage as a function of regenerant dose for the same ions and resin combinations used in **Figures 1** and **2**. By inspecting the difference in the leakage behavior for the various ions and resins in **Figure 3B**, it is easy to see that there is little difference in actual leakage at the same regeneration level for ions with similar selectivities. The difference is slight even among resins with somewhat different regeneration efficiency curves for the same ions, such as is the case between macroporous Type I and porous Type I gel anion resins for chlorides.

Resistivity and pH

The equilibrium relationships described in **Figures 2** and **3** were used to construct pH and resistivity curves for cation and anion limited mixed beds. This was done by assuming that all sodium leakage appears as NaOH in cation limited mixed beds; and conversely, that all

anions appear as their corresponding acids in anion-limited mixed beds. **Figures 4** and **5** show the resistivity relationships. **Figure 6** shows the pH relationships.

At very low concentrations, even weak acids and bases are 100% dissociated. Therefore, only a single curve is needed in **Figure 6B** to represent pH relationships for leakages of carbonic acid, sulfuric acid, and hydrochloric acid at the range covered. At higher concentration levels, the curves separate. In the high purity range, however, the hydrogen and hydroxyl ions from water dominate, so that the pH values agree to the third and fourth decimal points.

The curves in **Figures 1A** and **1B** are based on resins that were 100% in the counter ion form before being regenerated. In practice, the resins in high purity mixed-bed demineralizers are rarely fully exhausted. In most instances, the cation resin is still 30% to 50% in the hydrogen form at the termination of the exhaustion cycle, while the anion resin can be as much as 90% in the hydroxide form. The actual value depends on the specific installation. For example, the resistivity, end point, and type of demineralizer preceding the mixed bed are important factors. Normally high purity mixed beds are run to an end point of 10 to 15 million ohms of resistivity. This could leave 30% to 50% of the ion exchange sites still in the regenerated form at the end of the service cycle.

The specific resistivity versus the regeneration level for cation-limited and anion-limited mixed beds is shown in **Figures 5A**, **5B**, and **5C**. The Y-axis range in each of these figures is different. **Figure 5A** de-

picts the cation-limited mixed bed and covers the widest range. This is because the sodium ion has the lowest selectivity and is most likely to give lower resistivity values. The scale size in **Figure 5C** that illustrates anion limited mixed beds is enlarged by a factor of 10 so that anion resins at the same degree of regeneration can be compared with the cation resin performance. The scale size of **Figure 5B** is expanded by a factor of 5 compared with **Figure 5C** in order to amplify the difference in performance between different kinds of anion. There are several kinds of anion resins in the chloride/hydroxide cycle; and SBG1P. A Type I porous anion resin, in the bicarbonate/hydroxide cycle.

Figures 5A and **5B** can be used to determine the minimum regenerant level required to reach a specific resistivity. For example, **Figure 5B** shows that with a Type I porous resin, a regenerant level of 3 pounds of sodium hydroxide per cubic foot is required to make 18-megohm-cm resistivity water from an RO effluent with a high bicarbonate content. **Figure 5A** shows that over 15 pounds of H₂SO₄ or 10.5 pounds of HCl are required for a standard gel cation resin like ResinTech CG8 operating on a 100% sodium water.

The information in these graphs and tables can be used to analyze or avoid operating problems, and to predict results. For example, **Figures 1** and **5** can be used to estimate minimum regenerant levels for resins known to be only partially exhausted at the end of the service cycle. First, determine the remaining percentage of hydrogen sites, and use that information to determine the equivalent regenerant level from **Figure 1**. Next determine from **Figure 5** the regenerant level needed to reach the quality goal, and then subtract the "equivalent regenerant level." The result is the regenerant level needed to make the required quality during the next cycle. For example, a bed with an equivalent 3-pound regenerant condition at exhaustion when regenerated with 6 pounds of HCl can perform at the 9-pound equivalent re-

regenerant level. However, any brine treatment of the bed would eliminate the leftover hydrogen sites, forcing a return to using the full 9pound regeneration until stability is reached. It is easy to see why mixed beds that perform well sometimes have problems returning to high resistivity values after brine treatments. This effect is much more pronounced in the cation resins.

Silica

During exhaustion, silica remains unionized until it reaches the hydroxyl form of the anion resin at the bottom of the exchange front, where it dissociates and is removed. A silica band moving downward toward the bottom of the bed typifies the exhaustion front of the resin. At low pH, silica polymerizes so that a portion of its removal occurs by combining with SiO₂ already on the resin to form polymeric SiO₂. Silica breakthrough normally indicates the end of the exhaustion or service cycle of the anion resin. Low pH favors polymerization while high pH favors de-polymerization, as shown in **Table D**.

Temperature is an important factor during anion resin regeneration for silica-laden resins because silica must be de-polymerized and re-dissolved. These reactions are much slower than the metastasis reactions of ion exchange. They are also sensitive to temperature. Regenerant temperature has a significant effect on the silica operating capacity and on the resulting silica leakage. This is why regenerant time and temperature are so important during anion resin regeneration. Except for silica, these would have little effect.

Causes of Poor Effluent Quality

Some common causes of poor effluent quality from high purity mixed beds are the following:

- Poor regeneration
- Improper location of regenerant

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- Incorrect resin volume ratios
- Organic fouling of the anion
- Polymer fouling of the cation
- Silica fouling
- Magnesium leakage from the preceding cation bed
- Oxidation degradation of the strong base anion weakly basic sites
- Poor mixing
- Poor separation due to heavy or fouled anion resin

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