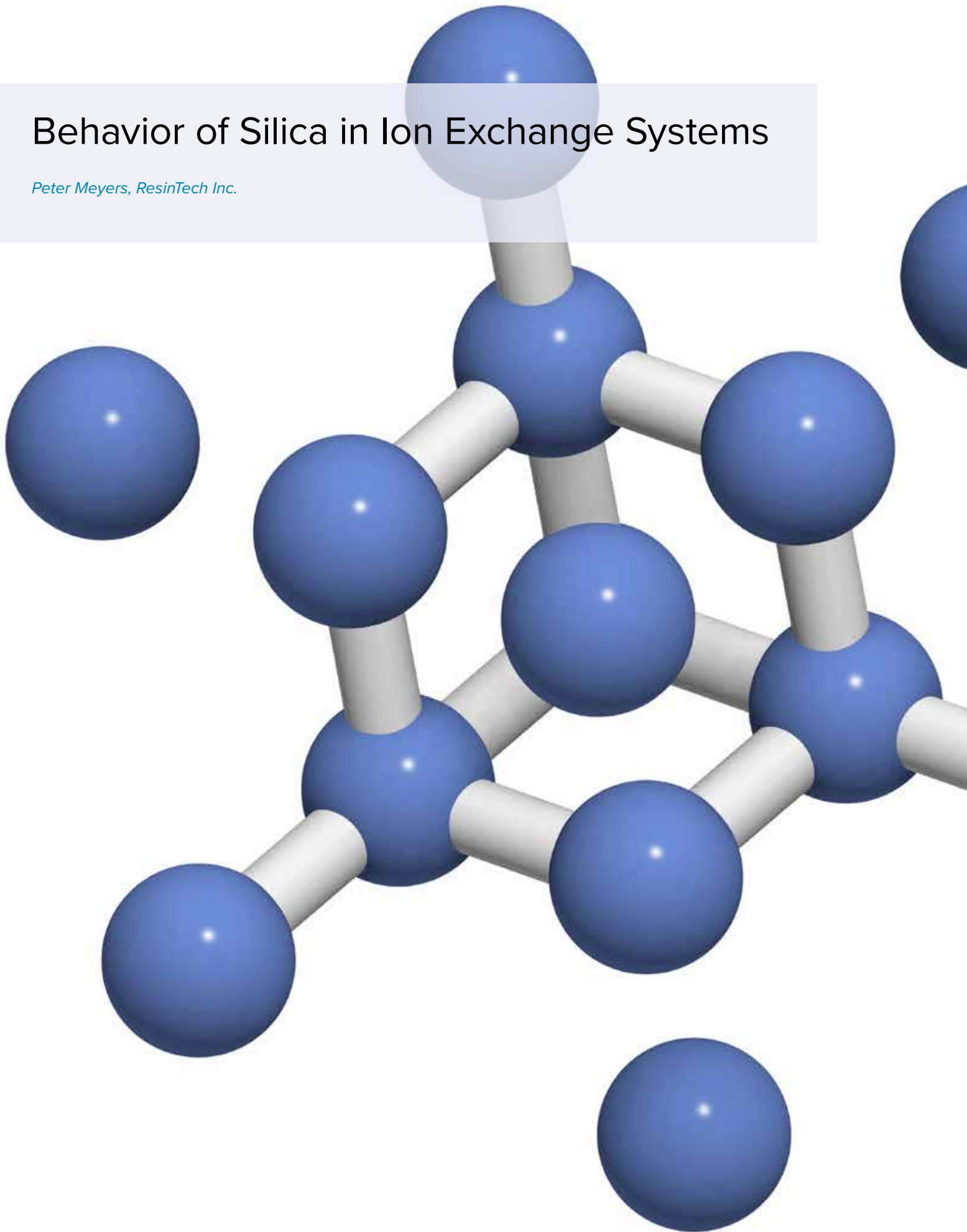


Behavior of Silica in Ion Exchange Systems

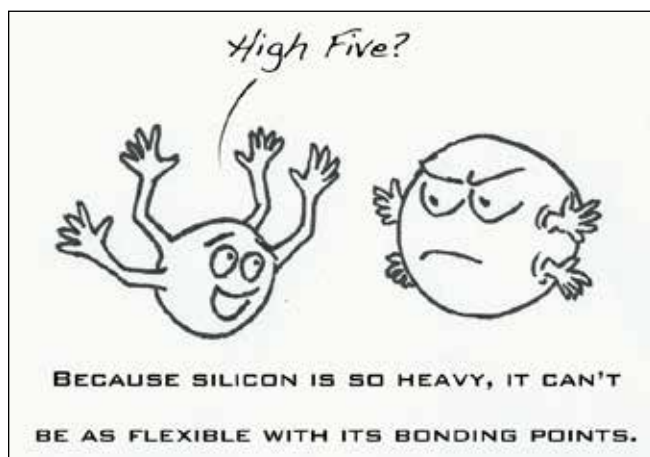
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Part One: Chemistry of Silica

Silicon is the second most abundant element found on earth. Although silicon itself (Si) is a glassy, insoluble solid, its various oxides (primarily "SiO₂") are somewhat soluble in water. Indeed, all natural water supplies contain some dissolved "silica." Many supplies also contain suspended or colloidal silica.

Silicon is directly underneath carbon on the periodic chart. Silicon, like its sister element carbon, has four covalent bonding sites and can, therefore, form a very large number of potential molecules. Silica chemistry is quite complex, second only to the chemistry of carbon compounds. Because the silicon nucleus is larger than the carbon nucleus, silicon does not easily form double or triple bonds, and silicon does not readily form chains more than six silicon atoms long. Silicon readily forms covalent bonds with oxygen and other elements, less readily with itself. In fact, since the bond energy is lower for silicon than for carbon, it does this rather easily.



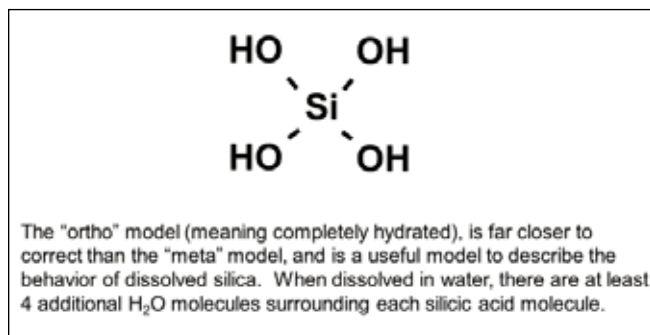
In water treatment, we are concerned with silica because of its tendency to form deposits (scale) on surfaces it comes in contact with. In boiler and turbine systems, the deposition is often associated with temperature, pressure, and phase state changes that occur. In microelectronics, the concern is deposition and/or changes to the surface properties of the "silicon" wafers.

The classic formula of "dissolved silica," as used by water treatment engineers, has traditionally been written as SiO₂. This is because amorphous silica and solid silica

deposits typically contain a ratio of two moles of oxygen per mole of silicon. We use the formula "SiO₂" because it is convenient, even though it does not apply to the actual silica species found dissolved in water.

As dissolved in water, silica is fully hydrated and generally present as orthosilicic acid H₄SiO₄ (also written as Si(OH)₄). Its formula and tetrahedral shape predicts the very weak acidity and also explains why silica is highly soluble at high pH (surrounded by OH⁻ ions).

Figure 1. Ortho-Silicic Acid Model



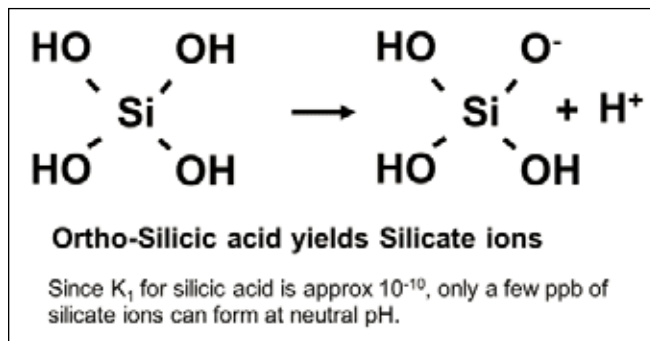
Silicic acid is considerably weaker than carbonic acid. The ionization constant for silicic acid is considerably smaller than for carbonic acid.

$$\text{Carbonic Acid } K_1 = 4.3 \times 10^{-7}$$

$$\text{Silicic acid } K_1 = 2 \times 10^{-10}$$

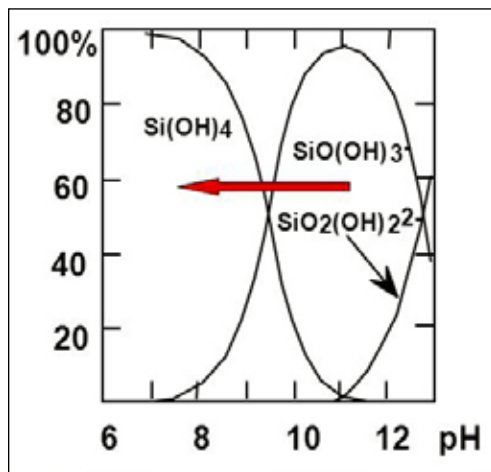
At pH greater than 10, silica is present as silicate ions and is quite soluble. At neutral pH, the ionization of silicic acid depends on the concentration of hydrogen ions. Since K₁ for silicic acid is very small, not much silicic acid can ionize when H⁺ is present.

Figure 2. Ionization of Ortho-Silicic Acid (under neutral conditions)



At very high pH, silicate becomes divalent. However, divalent silicate only exists when the pH is well up over 11.

Figure 3. Divalent Silicate



Silica readily polymerizes when there is insufficient alkalinity present to prevent this.

Published silica solubility leaves out a number of factors, not the least of which is the importance of alkalinity, which stabilizes silica and helps keep it in solution, sometimes at concentrations well beyond published data. Divalent and trivalent metal precipitants, notably aluminum, magnesium, and calcium, decrease silica solubility, or at least cause silica to coprecipitate in solutions where it otherwise would supersaturate or polymerize.

Figure 4. Published Silica Solubility

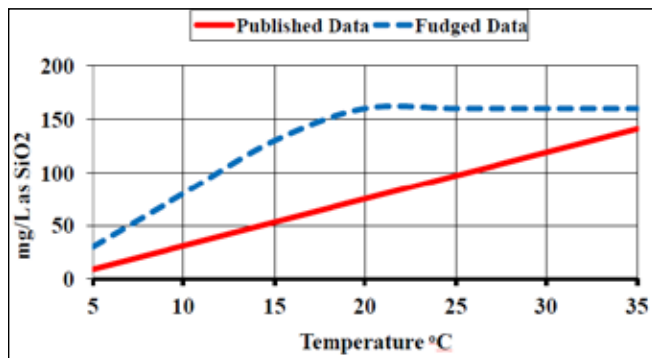
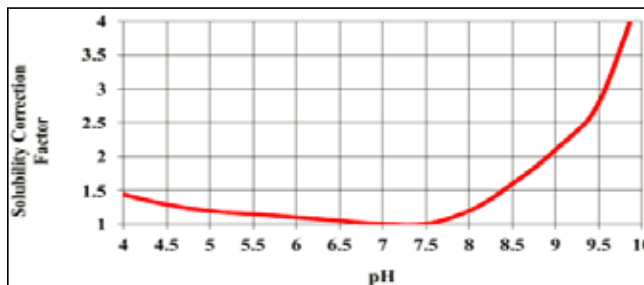


Figure 5. Effect of pH on Silica Solubility



Part Two: Silica Removal Methods

There are four basic ways to remove silica from water. These include chemical precipitation, membrane processes, evaporative processes, and ion exchange. Since this paper is primarily about ion exchange, the other methods are discussed only briefly.

Silica forms insoluble precipitants with various metals, notably magnesium, but also iron, aluminum, calcium, and others. By adding magnesium (if not already present) and raising the pH, silica can be precipitated out of solution. The precipitation process is enhanced at elevated temperatures. As with other solids separation methods, silica precipitation is messy and can be difficult to control if inlet conditions are not stable.

Reverse osmosis and other membrane processes are able to separate silica (and other salts) from water by creating a membrane barrier. The concentrate side of the barrier is susceptible to fouling when silica solubility is exceeded. Silica precipitation in membranes is almost always associated with a metal cation, although there are examples of pure silica gel formation in membrane concentrates. Silica solubility increases at elevated pH, and membrane systems designed to take advantage of this

are able to operate at higher silica concentrations and with lower silica in the product stream.

Evaporative processes work by evaporating and then re-condensing water, leaving silica and other salts behind in a concentrate stream. Evaporative processes are susceptible to the same solubility concerns and constraints as membrane processes.

Silica removal by ion exchange is primarily limited to strong base anion resins. All strongly basic ion exchange resins have the ability to split salts. This means that

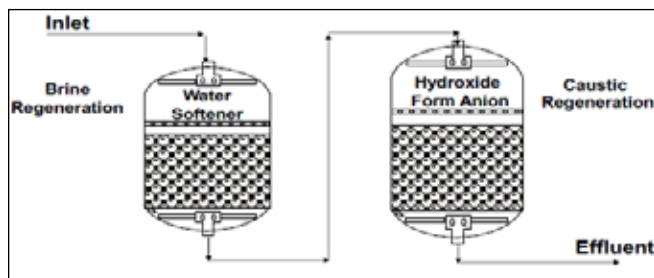
they can remove weakly ionized species, such as carbon dioxide and silica, by forcing them to become ions. Although the hydroxide-form strong base anion resin preference for silicate is much lower than for sulfates and chlorides, it is significantly greater than for hydroxide. Hydroxide-form strong base anion resin preference for silicate and alkalinity are similar (at least we know that silica break generally occurs at about the same percentage exhaustion as alkalinity break).

In the chloride form, or any other salt form, strong base anion resin has essentially zero preference for silica. Silica is non-ionized at typical raw water pH and can't enter the resin beads by means of the ion exchange pathways. The simple explanation for why hydroxide-form anion resin removes silica and chloride-form anion resin doesn't is that the release of hydroxide raises the pH and causes silica to become ionized (silicate). Ionized silica, or silicate, is then removed, along with other anions.

Ion exchange methods to remove silica all involve a hydroxide-form strong base anion resin. However, there are a number of variations on the theme, including desilicizers, two beds, mixed beds, and weak base/strong base pairs.

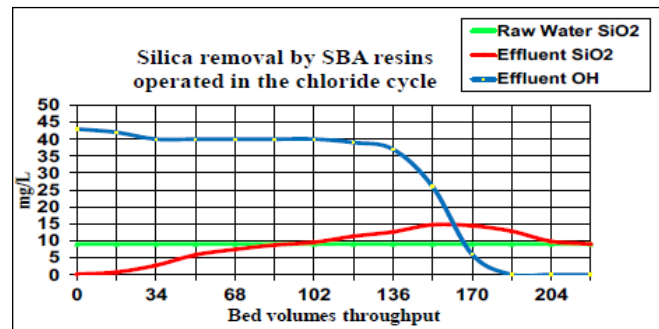
The anion desilicizer is a "poor man's" demineralizer, consisting of a strong cation exchanger in the sodium form (a water softener) followed by a strong base anion exchanger in the hydroxide form. Thank goodness there are not too many of these critters around anymore. They have most of the disadvantages of a demineralizer and few of the advantages. However, they do remove silica along with the other anions.

Figure 6. Desilicizer (poor man's demineralizer)



Over the years, more than one engineer has wondered if it might be possible to operate a desilicizer at a real small caustic dose (or perhaps with brine plus caustic) and use the anion resin as a dealkalizer while still removing some silica. This would avoid the excess causticity created by the complete anion exchange for hydroxides. ResinTech tried this in our lab with a Type II strong base anion resin.

Figure 7. Silica Removal by Dealkalizer Experiment



Influent was 250 ppm as CaCO_3

Regeneration was 20 lbs/cu.ft. NaCl & 2 lbs/cu.ft. NaOH

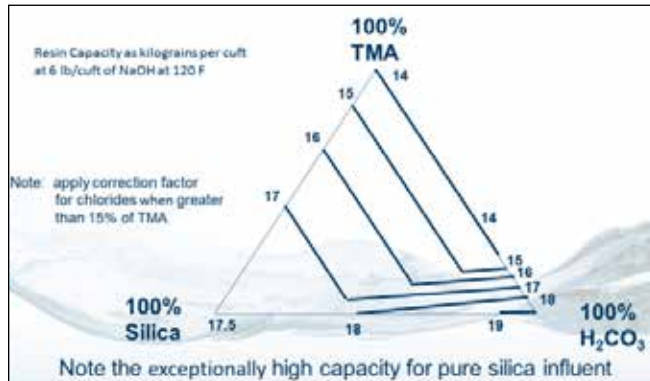
The results were quite interesting. As long as the resin had enough hydroxide exchange sites to remove all the anions, silica was well removed. As soon as the hydroxide sites were depleted, the resin dumped the silica. By the time the hydroxide concentration was substantially reduced in the product water, all the silica had dumped. There was no net removal.

The same dumping phenomenon seen in the previous "desilicizer" experiment can also occur in demineralizers but is less likely because the anion exchanger is seldom operated until every hydroxide exchange site is exhausted. Although silica dumping can and does occur, a substantial concentration of silica is frequently found on exhausted anion resins, even when no hydroxide form capacity is left. This might be due to the concentration of alkalinity on the resin along with the silica, or perhaps because the low pH after the cation exchanger restricts the ability of silica to leave the anion resin and re-enter the water stream.

Perhaps the most widely published and easy-to-use hard copy capacity curves for rating co-flow exchangers are the engineering notes developed by the Rohm & Haas Company. These notes depict the capacity of Type 1 porous anion resin as a function of caustic dose related to FMA, CO_2 and SiO_2 . The triangle charts for IRA-402

show extraordinary capacity for silica, in some cases approaching the total capacity of the resin.

Figure 8. Old Triangle Charts for Hydroxide-Form Type 1 Porous Anion Resin Capacity



I remember being told that the probable reason for the high silica capacity was that R&H used synthetic water with "unnatural" and monomeric silica. Therefore, this part of the curve was unreliable. For simple two beds, the fraction of silica to total anions seldom exceeds 50%, and the "inaccurate" part of the curve doesn't matter.

Part 3: Case Studies of Silica Fouling

Many years ago, at L*A Water Treatment, we hoped to determine the relative affinity of strong base anion resin for "pure silica." To avoid the potential "mistakes" caused by using "synthetic" silica, we went out into the California desert and collected some natural volcanic water that contained about 65 ppm of reactive SiO_2 . We ran it through cation and weak base ion exchangers, then air sparged to remove carbon dioxide. The solution, when freshly prepared, contained 65 ppm of reactive silica but almost nothing else. About a week later, we re-tested the solution and found the reactive silica to be less than 10 ppm!

Where did all the silica go? At first we thought it must have precipitated, but the water was crystal clear. We then "digested" the sample by adding sodium carbonate and heating. A re-test showed 65 ppm of silica.

We took that pure silica water and passed it through a lab column containing hydroxide-form strong base anion resin. We ran, and ran, and ran, and never got any silica leakage. Eventually, the resin bed plugged up with silica gel. We digested the various effluent samples to expose the original silica and subtracted this from the total. The

amount of silica loaded on the resin was several times the resin's capacity.

We gave up. The experiment was declared a "complete success." I now fully believe the Rohm & Haas notes, but also believe it isn't safe to operate a demineralizer in this fashion.

The problem of rating anion resins with very high fractions of silica comes up mainly in multiple bed demineralizer designs with degasifiers, or lime softeners, and with weak base anion exchangers. In these cases, the silica percentage of load on the strong base anion resin can approach 100% of the total anions.

There is another potential problem with high silica loading on an anion resin, which is the concern about silica fouling during the regeneration cycle.

Two cases crossed my desk in the last year that are worth sharing.

The Tale of a Weak Base/Strong Base Pair

A large petrochemical plant in the Houston area reported silica fouling of their weak base anion exchanger. The goo gummed up the resin and caused the water to channel (flow unevenly through the resin), leading to very poor results. Silica in the raw water is a modest 6 mg/L, but the system does have a degasser, so the silica load on the strong base resin is a large percentage of the total anions. We performed an elution study as a way to evaluate what happened.

A proper elution study on a demineralizer system involves more than specific gravity, as is common for water softeners. Specific gravity only confirms if the distribution system is working properly; it doesn't provide any information about how effectively the chemical is being used. To evaluate chemical efficiency, it is necessary to titrate samples for acidity or basicity. In this case, we also analyzed for silica.

There is a fair amount of work involved in taking the samples and then analyzing them, but it can yield valuable information about how best to operate.

Figure 9. Taking Samples

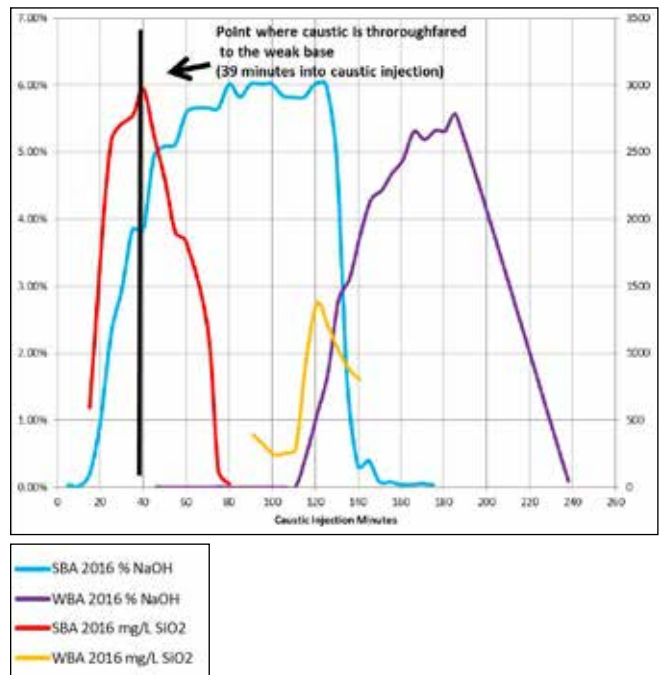


Figure 10. Additional Samples



Most strong base/weak base pairs thoroughfare caustic, using it first in the strong base unit and then a second time in the weak base unit. It is common practice to send the first part of the caustic leaving the strong base anion unit to waste. This plant followed that practice. However, it never checked to see where the silica eluted. The elution study showed that the spent caustic was thoroughfared just at the time the silica was reaching its peak concentration.

Figure 11. WBA and SBA elution



Later in the year, another similar issue came up at a refinery on the West Coast. This system also has a degassifier and a weak base/strong base pair with thoroughfare caustic, but this plant does not divert to waste any of its caustic from the strong base anion unit. All the spent caustic from the strong base unit goes through the weak base unit. A similar issue with short throughput through the weak base/strong base pair occurred. The refinery elected to do an elution study but only to check specific gravity.

This caused some problems and resulted in a wonderful photo opportunity to showcase what silica gel looks like.

Figure 12. Silica Gel



This sample is one of the weak base effluent samples taken toward the end of the caustic injection. As a good guess, they didn't get a valid specific gravity reading from that sample!

At L*A, we arbitrarily chose 6 kilograins/cu.ft. maximum safe silica loading, even if the resin wouldn't be "exhausted" with other anions. The concept that silica capacity is relatively independent of a strong base anion resin's capacity for other anions has been proposed by George Crits as well as others. No one should seriously consider trying to operate a strong base anion resin without limiting silica loading.

Figure 13. Various Rules to Limit Silica Loading on Strong Base Resin

Crits Rule	10 kgms/cuft max (all ions including silica)
L*AWT Rule	6 kgms/cuft max (silica loading only)
German Data	(reported in gm/L as SiO ₂)
• at 25 °C	3.0 gm/L @ 0.1 mg/L inlet 6.0 gm/L @ 0.3 mg/L inlet
• at 50 °C	0.9 gm/L @ 0.1 mg/L inlet 2.0 gm/L @ 0.3 mg/L inlet
Note: gm/L capacity (as CaCO ₃) x 0.436 = kgms/cuft German Data is for mixed beds	

Figure 14. Limiting Risk of Silica Fouling in WBA/SBA Pairs

Importance of alkalinity
All known cases of silica fouling in weak base anion resins have been associated with reduced alkalinity, either by chemical precipitation or by degassification
Dump initial portion of SBA spent caustic to waste
• Allow for displacement volume in SBA vessel
• Add additional time equal to the theoretical amount of caustic absorbed by the SBA resin
• Total is the time before caustic is thoroughfared from the SBA to the WBA
Perform elution study to verify silica elution pattern from the SBA unit

Part 4: Silica Removal by Chloride-Form Strong Base Anion Resins

Conventional ion exchange wisdom teaches that silica is only removed by hydroxide-form strong base anion resins. This "wisdom" has, for more than 70 years, prevented system designers from practicing silica removal by ion exchange, except as part of a demineralizer system that removes all the ions or with a hydroxide-form anion unit sometimes referred to as a "desilicizer." This brute force approach was for many years the best available technology (BAT) for boiler water and other systems that require deionization for other

reasons. However, now that ion exchange is increasing used as pretreatment to other treatment processes that have supplanted demineralizers for bulk ion removal, the need to selectively remove silica without removing everything else has gained importance. A closer look at silica exchange suggests that the problem is that silica is not well ionized at neutral pH, and that chloride-form strong base anion resins, in certain instances, have useful capacities for silicate.

Silicic acid is very poorly ionized. At neutral pH, almost all silica present in water is molecular rather than ionic. Even though strong base resins are capable of splitting salts, molecular silica cannot enter the ion exchange beads by means of the ion exchange pathways and is limited by the rate at which it diffuses into the beads. Chloride form anion resins remove less than 5% of inlet silica, partly due to diffusion limitations and partly due to unfavorable ionization of silica at neutral pH. Diffusion limitations are also a primary reason why the silica selective hybrids and adsorbents have slow and incomplete removal of silica. It simply takes a very long time for silica to reach an adsorption site, much longer than the water is typically in contact with the media.

Figure 15. Silica Removal by Type II Strong Base Anion Resin (other people's data)

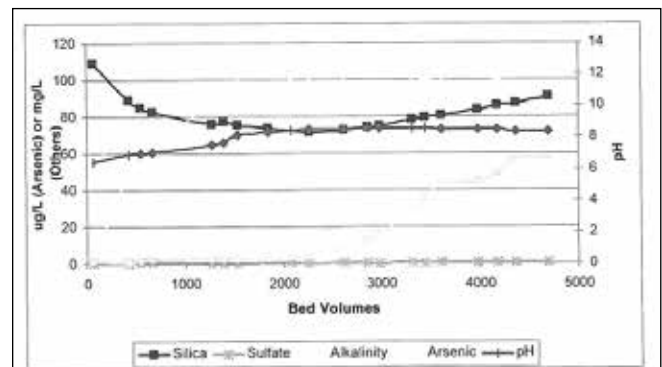
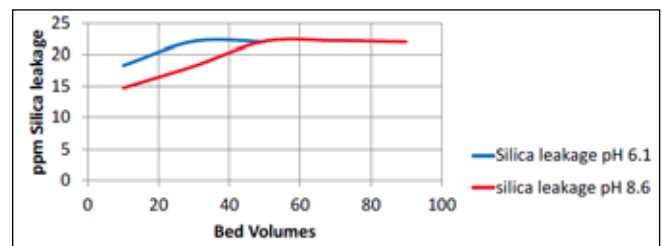


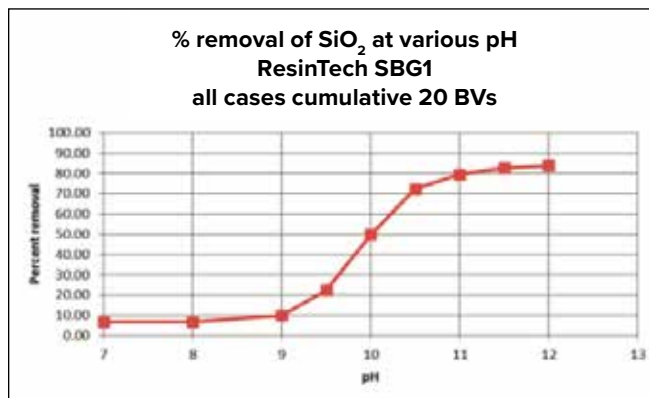
Figure 16. Silica Removal by Type 1 Anion Resin in the Chloride Form (Resin Tech data)



Inlet was 100 ppm CaCl₂ plus 100 ppm NaHCO₃ plus 22 ppm SiO₂, flow rate 0.5 BV/min.

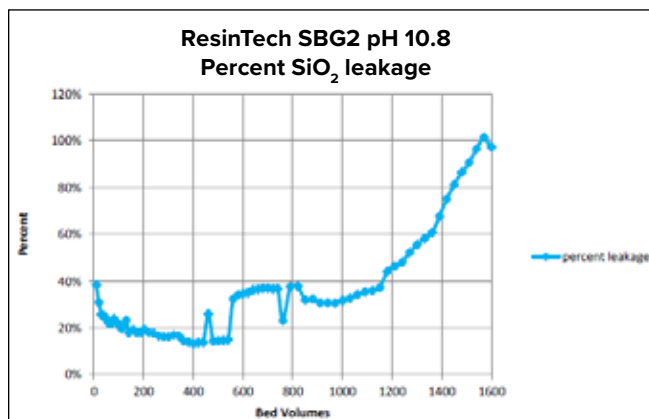
By raising the pH of the inlet water, molecular silica turns into ionized silicate. Once ionized, strong base resins in the chloride or other salt form are better able to exchange for silica. This is the reason that dealkalizers that are regenerated with brine plus caustic are able to remove modest amounts of silica. The high pH inside the resin bed converts silica to silicate and improves the removal efficiency. It should be understood, however, that in almost all cases, silicate is not the most preferred ion and that the exchange is somewhat unfavorable. Salt-form anion exchanges for silica are never complete, and dumping can occur if the system is operated past silica breakthrough.

Figure 17. Silica Removal by Chloride Form SBA Resin as a Function of pH



Inlet was 100 mg/L NaCl (as CaCO₃) plus 26 mg/L silica (as SiO₂), plus caustic to raise the pH as indicated.

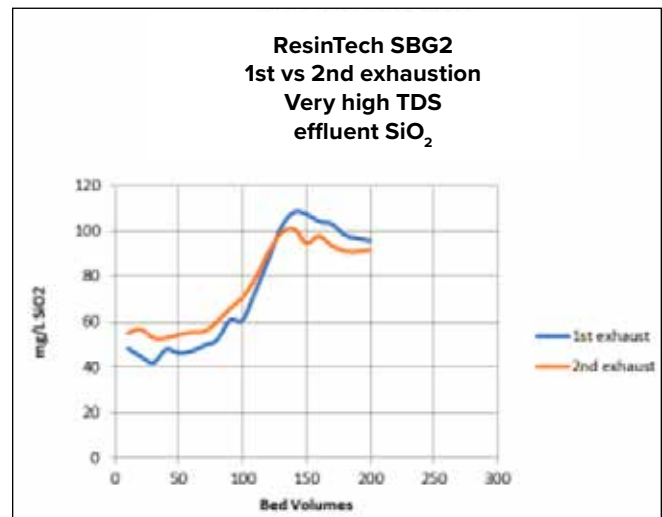
Figure 18. Silica Removal by Chloride Form SBA Resin, Influent pH Raised to Approx. 11 (no alkalinity present)



Inlet was 100 mg/L NaCl (as CaCO₃) plus 26 mg/L silica (as SiO₂), plus caustic to raise the pH as indicated.

As seen in these examples, silica removal, even at elevated pH, is by no means complete, and since silicate is one of the least preferred species, the presence of other anions and of high TDS reduces efficiency.

Figure 19. Silica Removal by Resin Tech SBG2, Very High TDS (pH 10.7)



Inlet was 100 mg/L NaCl (as CaCO₃) plus 100 mg/L NaHCO₃ (as CaCO₃) plus 100 mg/L of Na₂SO₄ (as CaCO₃) plus 100 mg/L silica (as SiO₂), plus caustic to raise the pH as indicated (conductivity 1700 uS/cm).

Although the removal of silica is not complete, in some cases, useful throughputs and substantial silica reduction can be obtained from brine regenerated anion exchangers. This technique could be used following softening to remove divalent cations, in front of RO or other membrane processes, or as a standalone method of reducing silica along with alkalinity as pretreatment to low pressure boilers.

Conclusion

Silica is poorly ionized at neutral pH and has limited solubility. Membrane and precipitation processes can be quite effective at elevated pH but are either ineffective or less than wonderful at neutral pH. Demineralizers, with hydroxide-form anion resin, remain one of the best methods for removing silica, especially when TDS removal is also required.

Removal of silica without also removing all the other ions is far more problematic, and there are no wonderful methods in the water treatment engineer's toolbox. Of the less than wonderful ways, ion exchange remains one of the available treatment methods, directly applicable as pretreatment to other unit processes or as a standalone method of removing silica along with other ions.

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