

BEHAVIOR OF SILICA IN ION EXCHANGE AND OTHER SYSTEMS

By Peter Meyers / ResinTech Inc.

IWC-99-64

INTRODUCTION

Silica is the second most abundant element found on earth. Although silicon itself (Si) is a glassy insoluble solid, the 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.

Silica, 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 silica nucleus is larger than the carbon nucleus, silica does not easily form double or triple bonds, and silica does not readily form chains more than 6 silica atoms long.

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.

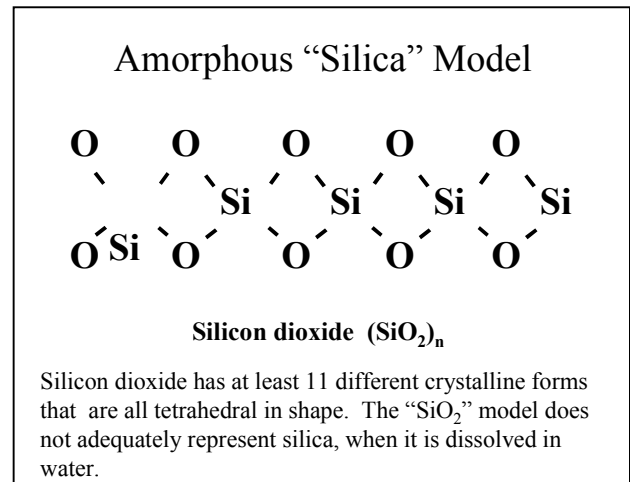
In this paper, we take up the task of describing the behavior of aqueous silica and of the various water treatment processes used for its removal.

PART I CHEMISTRY OF SILICA

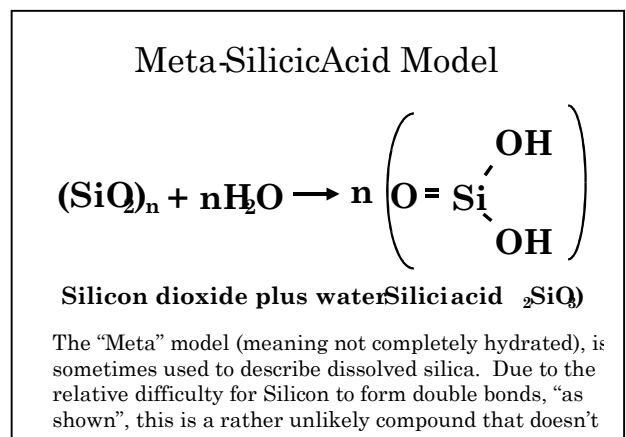
The classic formula of "dissolved silica" as used by water treatment engineers has traditionally been written as SiO₂.

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. When "silica" is dissolved in water, the (SiO₂)_n model is rather improbable.

The (SiO₂)_n model of amorphous silica is not applicable to water treatment because "SiO₂" depolymerizes in water, then hydrolyzes to form silicic acid.



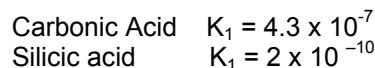
A popular but inaccurate model is that of silicic acid (H₂SiO₃).



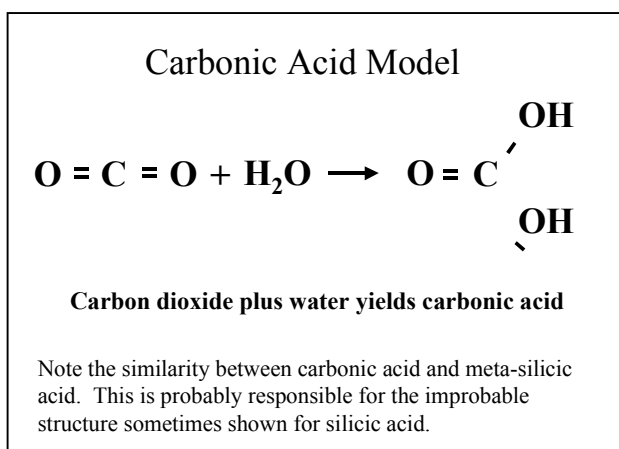
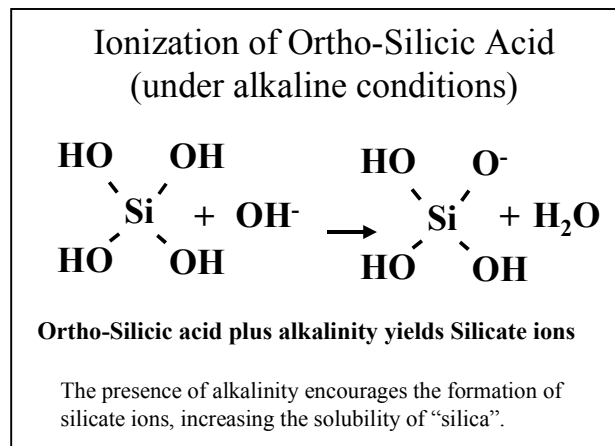
Since silicon atoms don't form double bonds (except under some very unusual conditions), the "meta" model doesn't actually exist.

Note the similarity to carbonic acid (H₂CO₃). This is probably the reason for the common error in the structure of silicic acid.

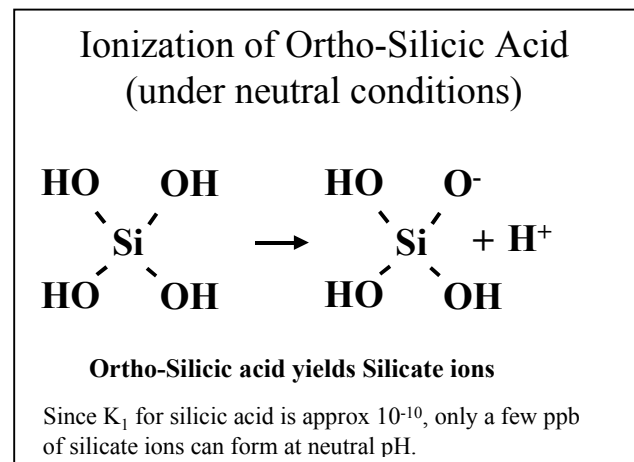
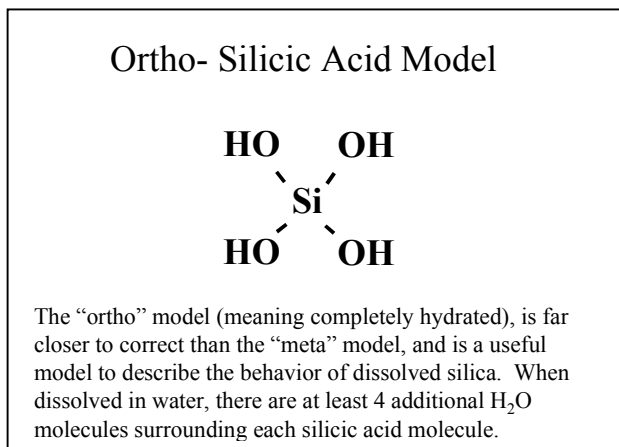
A better formula for silicic acid is H₄SiO₄. Some texts refer to this as "mono" silicic acid (meaning not polymerized), others as "ortho" silicic acid (meaning fully hydrated). This model satisfies the tetrahedral preference and predicts the very weak acidity. It also readily explains why silica is highly soluble at high pH (surrounded by OH⁻ ions).



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.



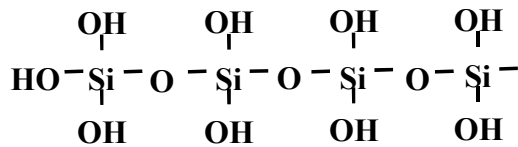
In addition to the water molecules that become part of the silicic acid molecule, other "waters of hydration" make the hydrated radius of dissolved silica almost as large as that of sulfate ions.

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

POLYMERIC SILICA

Silica, like carbon, 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. The H₄SiO₄ model is fine for monomeric silica and can be expanded to readily explain polymeric silica.

Polymeric "Silica" (H₂SiO₃)_n



Silicic acid molecules readily polymerize, in the absence of alkalinity or other "stabilizing ions".

THE MOLYBDATE TEST FOR SILICA

The molybdate reactive silica test will only expose one, or possibly two, of the Si atoms in a chain of polymerized silica. This means that the molybdate reactive silica test will only measure part of the total silica that may be in solution. This phenomenon gives rise to the term "giant silica" and also to what many people consider colloidal silica. Since polymerized silica molecules can approach the size of a true colloid, "Giant" silica can still be (at least partially) removed by ion exchange as well as by relatively large pore size micro filters.

SILICA SOLUBILITY

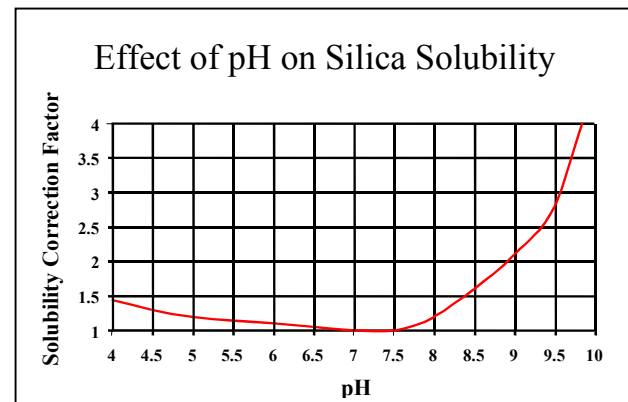
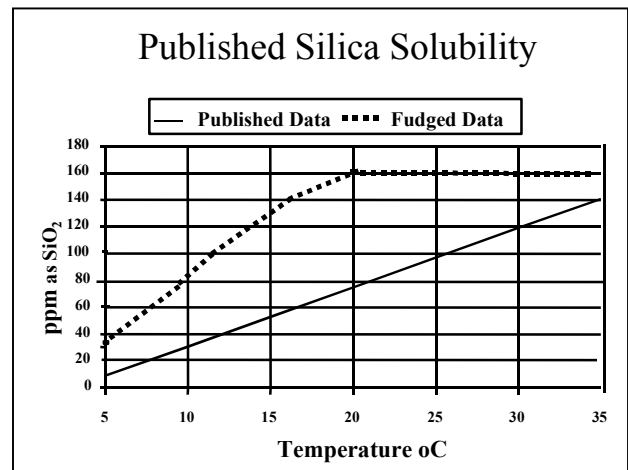
Many years ago at L*A Water, we hoped to determine the relative affinity of strong base anion resin for "pure silica". Instead, we performed a simple experiment in silica polymerization. We went out into the California desert and collected some natural volcanic water that contained about 65 ppm of reactive SiO₂. 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.

Note: Stay tuned for more details of the mysterious silica later.

So, what is the solubility of silica? The classic silica solubility graph relates silica solubility to pH and temperature.

This graph has been published in many places and almost always with a dotted line to indicate probable higher solubility. Certainly, in the L*AWT experiment, silica was not stable anywhere close to the published curve.



The "classic data" leaves a lot to be desired. There are numerous well-documented examples of silica concentrations much higher than the limits shown on the classic graph. The most famous are, perhaps, certain volcanic waters and oil field produced waters where reactive silica is fully soluble and stable at ambient temperatures and at neutral pH at concentrations exceeding 300 ppm! At L*A, we encountered a wastewater sample from a demineralizer in Hawaii where the silica concentration in the neutralized wastewater was close to 1000 ppm. Although the silica polymerized over time, it remained happily in solution.

Observed Silica Concentrations (all at approx. neutral pH)

Location	SiO ₂ PPM	HCO ₃ PPM
Midway, Ca	220	600
Placerita, Ca	320	900
Hilo, Hi	960*	Very high

* This sample gradually polymerized over several weeks.

Looking for common threads, the high alkalinity present in all these examples correlates very well with observed high silica concentrations in solution. As we shall see later in this discussion, the lack of alkalinity also has a strong correlation with silica precipitation.

COLLOIDAL SILICA

Before leaving the discussion on silica chemistry, the question of colloidal silica must be explored. Since colloids are generally smaller than 0.5 micron, a simple filtration test can be performed with a standard 0.45-micron filter such as those used to determine silt density indexes (SDI¹⁵) ahead of RO systems. Anything smaller than 0.01 micron is probably dissolved. The difference in silica, after digestion, reflects the concentration of colloidal silica.

The test work needed to quantitatively determine colloidal silica is hardly ever worth the effort and often fails to provide any truly useful data. A major problem is with accuracy. Inaccuracy is a consequence of the digestion. Sodium carbonate and other chemicals used to increase pH and dissolve or depolymerize silica always contain a significant silica concentration themselves. The manipulation of the "blank" prevents any serious accuracy at the ppb levels of colloidal silica typically found.

Size vs Type of Silica

Size vs type of silica	Size Microns
Filterable	>0.45
Colloidal	0.01-0.45
Polymeric ("giant")	<0.01
Monomeric	<0.0001

The bottom line is that most examples of so called colloidal silica are really filterable and are readily removed by careful coagulation/filtration techniques and/or by membrane processes.

PART II SILICA REMOVAL PROCESSES

In a water purification system, the treatment objective may include reducing silica concentration to permit increased cycles of concentration without scale.

Although conventional coagulation and filtration is effective to remove most (if not all) colloidal silica, this is usually a small fraction of the total silica in natural water supplies. Conventional precipitation technologies are reasonably cost efficient to achieve partial removal of silica. Drawbacks to precipitation are numerous. Precipitation of silica is a messy, time consuming process and can be difficult to accomplish without upsets.

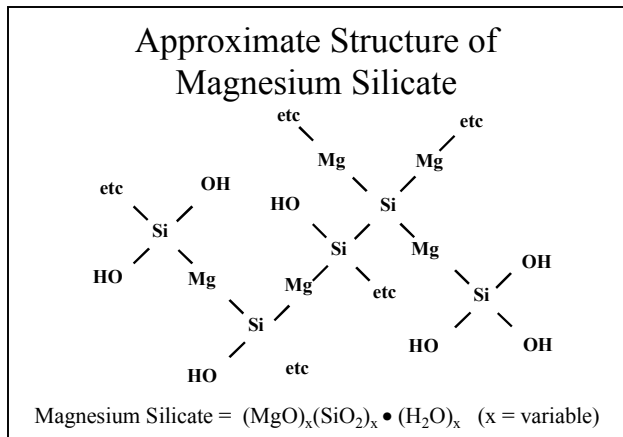
Silica Removal Processes

- Filtration
- Chemical Precipitation
- Reverse Osmosis
- ED & "E" cells
- Strong Base Ion Exchange

Where "complete" removal of silica is required, various combinations of RO and/or ion exchange processes are used. The current state of the art technology includes both multiple membrane and multiple ion exchange steps and can produce "reactive silica" concentrations in the neighborhood of 0.1 ppb.

CHEMICAL PRECIPITATION

Silica almost never precipitates as "SiO₂". Silica scale almost always contains a divalent (or trivalent) cation. Although calcium silicate is quite insoluble, this compound does not form rapidly except at very high temperatures. Although aluminum salts can be used to precipitate silica, the consequences of leaving a substantial aluminum residual in the product water makes this process undesirable. The conventional method of precipitating silica has always been co-precipitation with magnesium.



Since silica becomes part of the magnesium precipitant, some means of adding already precipitated magnesium (magnesium oxide) or of precipitating magnesium "in situ" (as Mg(OH)₂) is used. In situ precipitation works much better than already precipitated magnesium, probably due to surface area of the precipitant and proximity to a silica molecule.

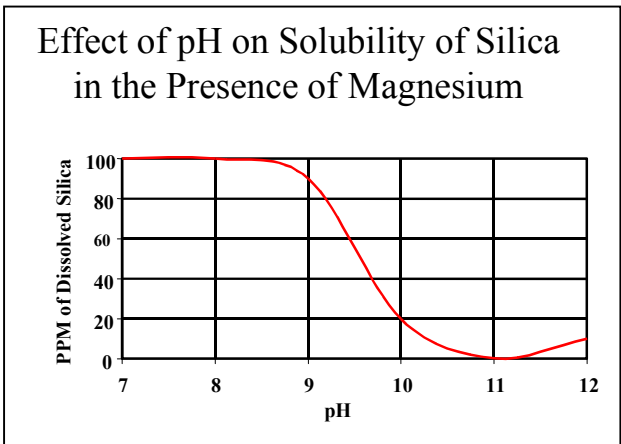
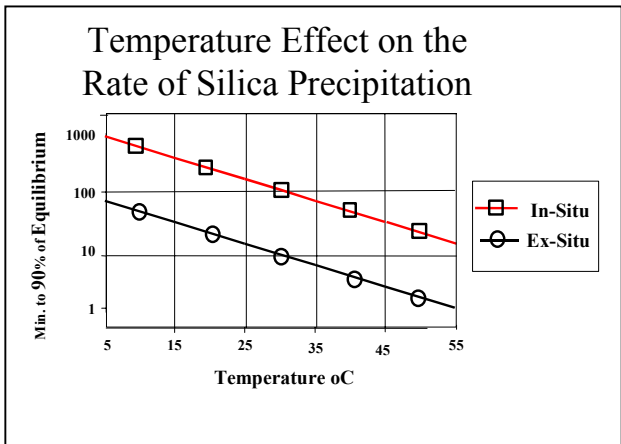
The addition of soluble magnesium salts (such as MgCl₂) is often undesirable due to an increase of T.D.S. MgO although much less effective, is more often used. The advantage of MgO is that it adds little or no dissolved solid to the water.

pH and temperature also have important effects on silica removal by precipitation. The precipitation mechanism occurs faster and more completely at high temperatures. pH must be high enough to

cause magnesium to precipitate but not so high as to make the precipitant resolvable.

Relative Efficiency of Magnesium to precipitate Silica

- "In-Situ" (by precipitation of ionic Mg)
 - Avg. 1 mg/l/L of SiO₂ per 1 mg/L of Mg (as Mg)
 - Better at higher temp and higher concentrations
- "Ex-Situ" (by addition of solid MgO)
 - Avg. 1 mg/L of SiO₂ per 10 mg/L of MgO (as MgO)
 - Better with finer mesh powder



REVERSE OSMOSIS SYSTEMS

RO systems can also be used to reduce silica concentration. Although "cellulose acetate" and early "thin film" composite materials only provided

moderate silica rejection, newer materials reject silica quite well. The mechanism of removal is probably by "hyper" filtration but is also related to degree of ionization since silica is more completely removed at a high pH. Since silica is concentrated by the membrane in the reject stream, silica solubility can be an important consideration. RO systems are currently unable to achieve as complete removal of "reactive silica" as ion exchange, but are far better at removing various forms of "non-reactive silica".

E CELLS

E Cells are electro dialysis stacks where the water flow channels are filled with ion exchange resin. The mechanism of removal probably is that the resin first exchanges for various ions (including silica), slowing them down, then allowing them to be pulled through the membranes. Since silica is weakly ionized, a higher current density is needed for a high percentage of silica removal. The "E Cell" process is currently more expensive than RO for bulk removal of ions and suffers the same inability as ion exchange to remove "non-reactive" silica. However, it is competitive with RO and IX for polishing and offers a perceived advantage over IX, in that its use does not involve handling of strong mineral acids and bases. Still, the lowest silica residuals currently achievable are produced by ion exchange resins.

Relative Selectivity based on Ionic Form (Type I SBA)

Relative Selectivity for	Chloride Form	Hydroxide Form
Bicarbonate (HCO ₃)	0.25	6
Chloride (Cl)	1	20
Silica (SiO ₂)	None	5

ION EXCHANGE TECHNOLOGY

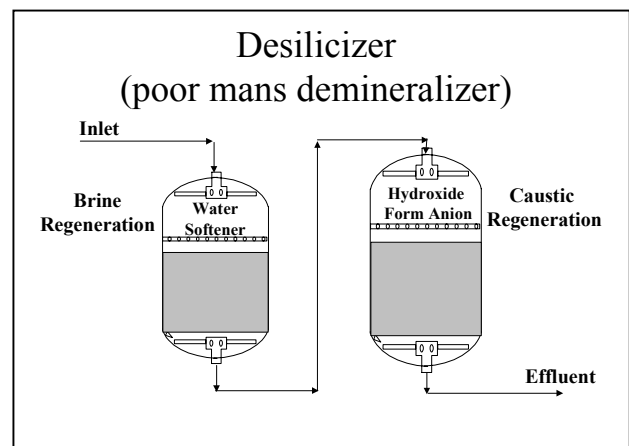
All strongly basic ion exchange resins have the ability to split salts. This means that they can remove weakly ionized species such as carbon dioxide and silica. Although hydroxide form strong base anion resins, preference for silica is much lower than for sulfates and chlorides; it is significantly greater than for hydroxide. There is

pretty good evidence that only when in the hydroxide form, does strong base anion resin exhibit any preference for silica. When in the hydroxide form, (SBA resin) preference for silica and for 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 zero preference for silica (probably because silica is non-ionized at typical raw water pH), although it still can be used for alkalinity removal.

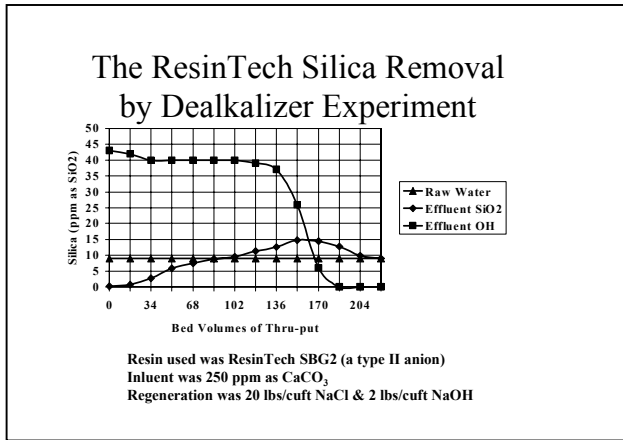
This suggests that silica is not exchanged in the same way as other anions.

DESILICIZERS

An anion desilicizer is a "poor mans" 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.



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 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 anion resin (SBG2).



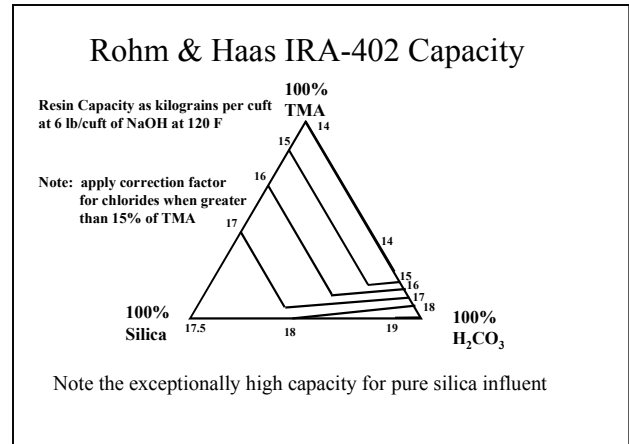
The results were quite interesting. As long as the resin had enough hydroxide exchange sites to remove all the anions, silica was well removed. As soon as the hydroxide sites were depleted, the resin dumped the silica. By the time the hydroxide concentration was substantially reduced in the product water,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

DEMINERALIZER SYSTEMS

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 is probably 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, CO₂ and SiO₂. The triangle curves for IRA-402 show extraordinary capacity for silica, in some cases approaching the total capacity of the resin. Modern curves (by ResinTech and others), are in various software formats.

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. 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 total anions.

Various Rules to Limit Silica Loading on Strong Base Resin

- Crits Rule 10 kgms/cuft max
- L*AWT Rule 6 kgms/cuft max
- German Data reported in gm/L as SiO₂
 - at 25 °C 3 gm/L @ 0.1 mg/L inlet
 - 6 gm/L @ 0.3 mg/L inlet
 - at 50 °C 0.9 gm/L @ 0.1 mg/L inlet
 - 2 gm/L @ 0.3 mg/L inlet

Note: gm/L capacity (as CaCO₃) x 0.436 = kgms/cuft
German Data is for mixed beds

THE REST OF THE GREAT SILICA EXPERIMENT

If you recall the earlier example of the mysterious disappearing silica, the point of the experiment was to try to determine a strong base anion resin’s ultimate capacity for pure silica.

We took that 65 ppm silica (and nothing else) 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. Even after 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 resins' capacity.

We gave up. The experiment was declared a "complete success". At L*A, we arbitrarily chose six (6) kilograins/cu.ft. maximum safe silica loading.

Actually 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. Rohm & Haas data may or may not be correct, but no one should seriously consider trying to operate a strong base anion resin without limiting silica loading.

SILICA REMOVAL BY STRONG BASE ANION RESIN

The conventional theory of silica removal by strong base anion resins doesn't fit the observed behavior of silica very well at all. What is needed is a model that does a better job of explaining observed behavior.

Suppose that silicic acid is neutralized by hydroxide form anion resin and is not exchanged for another anions. Silicic acid remains ionized, only so long as there are sufficient hydroxide exchange sites available to keep it ionized. Since ion exchange resins do not have selectivity for un-ionized substances, when the pH drops in the resin phase, silica falls off the resin.

Silica Exchange by Strong Base Anion Resin

Hydroxide form resin



Note that this is a neutralization reaction, rather than an exchange of one ion for another.

Chloride form resin



This exchange is extremely unlikely, due to the very poor ionization of silica at neutral pH

This neutralization reaction requires the exchange site to be in the hydroxide form in order to capture silica and does not require hydroxide ions to be exchanged by the resin in the way that exchange for other anions occur.

This model, although somewhat different than the conventional theory, explains why silica is not removed by salt form anion resins.

Silica, once exchanged onto the resin, is still able to polymerize. pH drops in the resin as it exhausts, encouraging polymerization or dumping. Polymerized silica probably stays on the resin, while monomeric silica dumps. In the desilicizer example, the high pH prevented silica polymerization and allowed dumping to occur. Two bed demineralizers do not dump silica as easily as mixed beds due to the lower pH at the inlet to the anion exchanger.

Silica is removed from strong base resin at high pH in an exchange of silicate ions for hydroxide ions. It probably is possible to remove some silica by washing an exhausted anion resin with water or with salt but since silica solubility is quite low, this would not ordinarily be practical. Also, at neutral pH, polymerized silica would be trapped inside the resin beads.

THEORY OF NET EXCESS CAUSTIC

Many water treatment engineers believe that Type I anion resins are inherently better for silica removal than Type II anion resins. The facts, including various resin manufacturers' charts and graphs, do not support this belief! Under equivalent operating conditions, all strong base anion resins behave similarly toward silica. Differences in silica leakage are caused by differences in regeneration conditions. Although the regeneration of a Type I resin at 4 lb./cu.ft. caustic dose may appear to be identical to a Type II resin at 4 lb./cu.ft. dose, the Type II resin is regenerated more efficiently than the Type I resin leaving less net excess caustic to remove silica.

Various Rules to Limit Silica Loading on Strong Base Resin

- Crits Rule 10 kgrns/cuft max
- L*AWT Rule 6 kgrns/cuft max
- German Data reported in gm/L as SiO₂
 - at 25 °C 3 gm/L @ 0.1 mg/L inlet
 - 6 gm/L @ 0.3 mg/L inlet
 - at 50 °C 0.9 gm/L @ 0.1 mg/L inlet
 - 2 gm/L @ 0.3 mg/L inlet

Note: gm/L capacity (as CaCO₃) x 0.436 = kgrns/cuft
German Data is for mixed beds

The theory of net excess caustic has been proposed by John Farrar, formerly of the Permutit-Boby (UK) Group, and by Michael Gottlieb of Resintech as well as others.

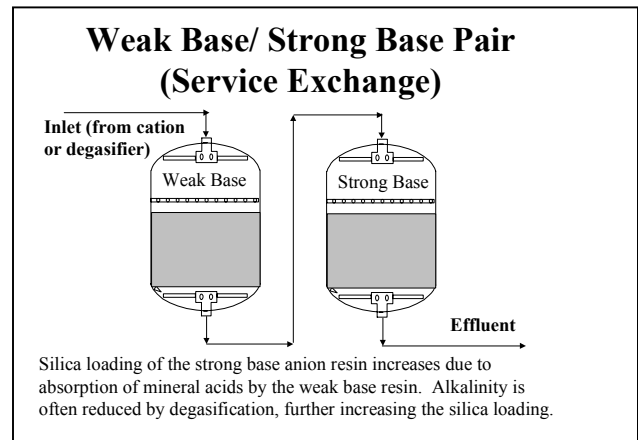
Excess caustic is needed to reverse the neutralization reaction of silica with hydroxide form anion resin. Excess caustic is also needed to depolymerize silica. Depolymerization must occur before silica can reconvert to silicic acid and be removed from the resin.

Since this type of reaction is sensitive to the laws of thermodynamics, time and temperature are significant factors in the removal of polymerized silica.

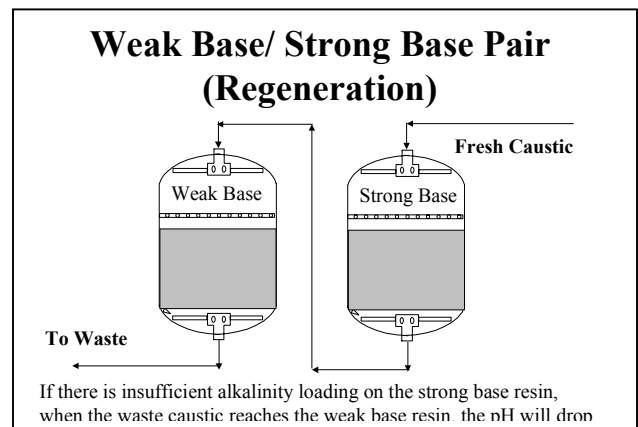
One last comment with respect to silica removal from strong base anion resins is the theory of "long on - long off". The longer silica remains on an anion resin, the more it polymerizes and the longer it takes to get it off.

SILICA PRECIPITATION IN ION EXCHANGE SYSTEMS

Most ion exchange systems in the USA operate pretty inefficiently. Plenty of net excess caustic is present in the spent regenerant. The wastewater pH stays high and silica stays in solution. This is not the case when a weak base anion and strong base anion pair is used. Caustic efficiency can, in some cases, approach 100%. Conventional wisdom says to dump the first 30% of the caustic to avoid silica precipitation in the weak base anion.



It is somewhat ironic that many of these systems dump the first 30% of the water flowing through the strong base anion resin and begin thoroughfaring through the weak base resin just about at the point when the caustic finally reaches the bottom of the strong base resin.



Although there are only a few documented cases of silica precipitation in anion resins, they all are in systems with low alkalinity either following degasification or lime softening. Again, the correlation between the presence of alkalinity and high silica solubility is quite strong.

Rules to Avoid Silica Fouling of Strong Base Resins

- Permutit Boby Data (Type I or Type II)
 - 7 gm/L of SiO₂ -amb. NaOH
min dose = 15 x Silica load
 - 14 gm/L of SiO₂ -35 °C NaOH
min dose = 9 x Silica load
 - 20 gm/L of SiO₂ -60 °C NaOH (type I only)
min dose = 5 x Silica load

For example, if the silica load is 7 gm/L (3 kgrens/cuft) with ambient regeneration, then a minimum of 105 gm/L of NaOH (6.6 lb/cuft) should be used to avoid silica fouling.

Rules for lowest possible leakage of Silica from Strong Base Resin

- Use plenty of excess caustic
- Allow for a long contact time
- Use highest practical caustic temperature
- Use highest practical caustic concentration
- Limit inlet sodium to less than 1 mg/L
- Limit silica loading on the resin

Silica Solubility

- Increases with
 - increasing temperature
 - increasing pH
 - increasing sodium alkalinity
- Decreases with
 - Increasing divalent ion concentration
 - particularly when the divalent cation is associated with carbonate or hydroxide alkalinity
 - increasing precipitation of any salt

7. Micheletti, W.C., "Silica Removal In Lime-Soda Softeners, presented at the 46th IWC Conference 1985.
8. Michael C. Gottlieb, George P. Simon, "Type II Strongly Basic Anion Exchange Resins for Two Bed Demineralizers," 13th Liberty Bell Corrosion Conference, Philadelphia, PA (Sept., 1975)

CLOSURE

There is much more to the tale but it will be left to future discussions. If anyone has support for (or against) the theories presented in this paper, please feel free to express them. If there is sufficient response, another paper will be created. We may be reached at: ResinTech, Inc. – 160 Cooper Rd. West Berlin, NJ 08091 – Phone: (856) 768-9600, Fax:(856)768-9601, E-mail:pmeyers@resintech.com

REFERENCES

1. Venderbosch, H.W., Snel, A., Overman, L.J., Kema, N.V., Concerning The Capacity Of Ion Exchange Resins When Removing Trace Impurities From Water, presented at VGB Feed Water Conference 1971.
2. Dupont Company Technical Bulletin No. 421, "Silica Solubility".
3. Lerman, S.I., Scheerer, C.C., "Instrumentation – The Chemical Behavior Of Silica", Ultrapure Water 24, December 1988.
4. Wibowo, J., Shadman, F., Blackford, D., The Measurement And Removal Of Dissolved And Colloidal Silica In Ultrapure Water.
5. Hann, W.M., Robertson, S.T., Bardsley, J.H., "Recent Experience In Controlling Silica And Magnesium Silicate Deposits With Polymeric Dispersants", presented at the 54th IWC Conference 1993.
6. Comb, L.F., "Silica – Silica Chemistry and Reverse Osmosis", Ultrapure Water 41, January/February 1996.