Background
Silica scaling becomes a problem when any hot water system becomes over-saturated with dissolved and colloidal silica. Silica scaling can then become a problem for the efficient use of high-temperature heat exchangers.

Natural Occurrence of Silicon
The greatest silica values are typically found in well water supplies, with wells in the California Central Valley being the most notorious in the United States, showing levels in the range of 20 to 60 milligrams per liter (mg/L).

Since most of the silica found in well waters is a result of dissolving silica-containing rock, well water will contain mostly reactive silica. Surface waters, on the other hand, will tend to contain more colloidal forms of silica, although the typical surface water will still contain more reactive than colloidal forms of silica.

The chemistry of silica in surface water supplies is very complex since biological activity tends to come into play. Diatoms, a species of algae, assimilate reactive silica in the dissolved form, using this material to create a protective shell made of silicon dioxide crystals. As these algal cells decompose, the silica is once again released into the environment as reactive silica, creating a complex ecological balance between dissolved silica and silicon dioxide structures. Interaction with biological matter will also create the colloidal silica that is inherent to most surface waters.

Basic Chemistry
Silicon is one of the most common elements. It has a rather low solubility and tends to have quite a bit of interaction with water molecules when dissolved in water. Silica is generally found in water supplies in three different forms: reactive, colloidal and suspended particles (e.g., sand), with the reactive being that portion of the total dissolved silica that is readily reacted in the standard molybdate colorimetric test, and the colloidal being that which is not.

The reactive form is silicon dioxide dissolved in water, creating the compound monosilicic acid (H4SiO4), as shown in Equation 1:

$$ \text{SiO}_2 + 2\text{H}_2\text{O} \leftrightarrow \text{H}_4\text{SiO}_4 \quad \text{Eq. 1} $$

In this form, silica is relatively un-ionized at most natural pH levels. At a pH of 8.5, only 10% of the monosilicic acid is ionized; and as the pH reaches 9 to 10, it still is only 50% ionized (Equation 2).

$$ \text{PKa} = \frac{[\text{H}_3\text{SiO}_4][\text{H}^+]}{[\text{H}_4\text{SiO}_4]} = 9-10* \quad \text{Eq. 2} $$

*concentration dependent
The colloidal species is generally thought to be either silicon that has polymerized with multiple units of silicon dioxide, or silicon that has formed loose bonds with organic compounds or with other complex inorganic compounds -- usually aluminum and calcium oxide structures.

Monosilicic acid attracts four additional water molecules beyond the two that make up part of the molecular structure in the hydrated state. Thus, the overall hydrated structure contains a total of six water molecules that probably play a significant role in its behavior in the RO process. The structure exists as shown in Figure 1.

![Figure 1. Monosilicic acid structure](image)

Silicate also plays a role in alkalinity measurements since it is titratable with acid through the reaction seen in Equation 3:

\[
\text{H}_3\text{SiO}_4^- + \text{H}^+ \rightleftharpoons \text{H}_4\text{SiO}_4^- \quad \text{Eq. 3}
\]

For example, at pH 9.7, for every 100 milliequivalents (meq) of silicate, 58 meq of alkalinity are contributed to the total alkalinity. Thus, for high pH water supplies that contain appreciable amounts of silica, this equation must be included in the alkalinity calculations in order to create a properly balanced water analysis.

**Deionized Water and Silica Removal**

Silica has historically created problems for water treatment because of its stability as an un-ionized compound, making it difficult to remove using ion-exchange processes, and is in fact one of the least preferred anions.

Because silica is found at the lower end of a selectivity chart for strong base anion resins (and not on the chart for weak base anions), silica is one of the first anions to breakthrough. As a result, silica can be effectively removed only if the ion-exchange resins are completely and properly regenerated with hot water over a sufficient time period. Further, since silica is a relatively poor electrolyte, a silica breakthrough or “Silica Dump” is difficult to detect in deionized water, and therefore difficult to prevent, using standard conductivity instrumentation.

**RO Pretreatment Option For Colloidal Silica Removal**

Using RO as a pretreatment process, colloidal silica can be removed very effectively simply by the filtration capabilities of an RO membrane. An RO would also help the ion-exchange process by alleviating the overall silica loading on the resin.

The downside of silica pretreatment by RO is the effect that the relative insolubility of silica can have on RO membranes as the feed water becomes more concentrated.
Silica Scale Prevention
Silica scaling in a hot water system, is affected by 1), the silica content of the input water, 2), the evaporation rate from the system, and 3), the blow-down policy of the system operators.

Input Silica Content
The input silica content can be controlled by a properly operated deionizer system. Reducing the silica load greatly reduces the probability of silica scaling.

But because silica is such a poor electrolyte, when silica is an issue in deionized water, the conductivity (resistivity) starting cut-off point for a deionizer system should be set for an artificially high quality. Because the silica breakthrough point is difficult to predict, the high quality cut-off point will assist the user in heading off an initial silica breakthrough.

The high quality cut-off point can be maintained, or through experimentation and testing, a new cut-off point can be established, that will assure that the deionizer system is always regenerated prior to a silica breakthrough.

Evaporation Rate
While a deionizer greatly reduces the silica load of the input water, whatever load there is will eventually become concentrated though evaporation. See Table A, Silica Solubility, below.

<table>
<thead>
<tr>
<th>pH</th>
<th>Mg/L SiO2 at STP</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 to 8</td>
<td>120</td>
</tr>
<tr>
<td>9</td>
<td>138</td>
</tr>
<tr>
<td>9.5</td>
<td>180</td>
</tr>
<tr>
<td>10</td>
<td>310</td>
</tr>
<tr>
<td>10.6</td>
<td>876</td>
</tr>
</tbody>
</table>

The evaporation rate can be determined by subtracting the blow down rate (if any) from the makeup rate.

The principle of determining cycles of concentration applies here. For Deionized water with an assumed content of 1 ppm at a pH of 7.5, the cycles of concentration can exceed 100 before precipitation will occur.

If city water is being used with an assumed silica concentration of 25 ppm, the allowable cycles of concentration can only be 4.

Again, through experimentation and testing, the correct cycles of concentration can be determined.

Blow Down Policy
Once the allowable number of cycles of concentration is determined, a blow down procedure can be established. NOTE: The purer the makeup water, the less water needs to be blown down.
Blow down can take two forms:

- Continuous
- Periodic

A continuous blow down allows a specified amount of water to go down the drain for whatever amount is recirculated. For example, if a hot water system were recirculating at the rate of 100 gpm, 16 hours per day with 500 gallons in the system, and 0.25 gpm were going down the drain, the blow down rate would be:

\[
0.25 \times 100 \times 60 \times 16 = 18.8 \text{ %/day} \quad \text{Eq. 3}
\]

A periodic blow down requires that an operator allow a specified amount of water to go down the drain during his shift. For example, if a hot water system were operated 16 hours per day (2 shifts) with 500 gallons in the system, and each operator drained the system at 5 GPM for 2 minutes a total of 20 GPD would go down the drain. With this scenario the blow down rate would be:

\[
\frac{20}{500} = 10 \%/\text{day} \quad \text{Eq. 4}
\]

Blow down frequency and quantities are dependent on evaporation rate and incoming water silica content.

**Remediation**

Removing silica scaling or “glassing” from pipes is a tricky business and must be done with care because of the chemicals required to accomplish the task.

The two most effective solvents for the removal of “glassed-on” silica are hydrofluoric acid (HF) and hot caustic soda (NaOH). Both substances are hazardous materials and should be handled with great care. MSDS sheets on whichever substance is selected should be first reviewed by management, then, in a meeting, reviewed by the personnel assigned the task of remediation. The selection of solvent is affected by the nature of the material to be de-fouled.

**Hydrofluoric Acid** - Dilute HF solutions can be used effectively in plastic piping systems, such as PVC, PVDF, polypropylene, polycarbonate, etc. Because HF is a weakly ionized acid, a concentration of a percent or more is needed for a cleaning reaction to take place with any speed. Also HF is corrosive to many metals.

**Caustic Soda** - Since most heating systems involve wetted metal parts, usually dilute hot caustic soda is a better selection than is HF.

Caustic soda is strongly ionized base, requiring ppm concentrations instead of percentage concentrations as with HF. It is compatible with most metals in its dilute form, and because it is highly ionized, the reaction can be closer to calculated stochiometric amounts.
As can be seen from Figure 1, the solubility of silica increases dramatically above a pH 10.

From Figure 2 it is readily apparent that an increase in temperature substantially increases silica solubility.

**Remediation Conditions**
Silica scaling will have taken place at 1), points of heat, and 2), points of low velocity. It is important for any cleaning solvent to be used as close to normal service conditions as is practical.

**Flow Rate** - The flow rate of a remedial solution should be approximately that of the normal recirculation service flow rate. Higher flow rates may have a tendency to omit affected areas of piping, as could lower flow rates.
**Heating Surfaces** – Heating surfaces should be operating normally during cleaning. The hot surfaces will have caused silica precipitation there and at adjacent surfaces, and during cleaning can help reverse the scaling process.

**Silica Scale Flaking During Remediation** – Flaking can take place during the remediation process, partially plugging certain pieces of equipment. Unless the flow stops entirely, the selected remediation solution will dissolve these flakes, at which point the proper flow rate will be restored, and the cleaning process will continue. The net effect on remediation process should be negligible.

**Example Remediation protocol:**
From the above information, a remediation protocol can be established:

**EXAMPLE:**
A heating system contains approximately 500 gallons of water. From surface area calculations, the piping and heat exchanger have a total surface of approximately 1,000 In\(^2\) with a uniform silica scale thickness of 3 mils.

Solution of NaOH needed: 500 gallons of a 0.5% (1/2 %) caustic soda solution at a temperature of 120 °F – 140 °F (48 °C – 60 °C) continuously recirculated at the normal recirculation flow rate can be used effectively to remove the calculated silica scaling from pipes, given sufficient contact time (4 to 8 hours).

**Summary**
In any Silica precipitation situation causing an operational problem, the first step is to implement the necessary steps as outlined for the prevention of silica scaling.

After the cause of the silica problem is eliminated, remediation can then take place with the confidence that it will be a one-time operation.

**References**


