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Discussion of silica speciation, fouling, control and maximum reduction

Robert Y. Ning

*King Lee Technologies, 8949 Kenamar Drive, Bldg. 107, San Diego, CA 92121, USA
Tel. +1 (858) 693-4062; Fax +1 (858) 693-4917; email: klt@kingleetechn.com*

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Abstracts

In the production of ultrapure water for the power and microelectronics industries, multiple pass reverse osmosis (RO) process is commonly the major step in the reduction of dissolved and suspended matter before polishing by ion exchange and other methods to attain the high purity requirements. With the diverse location of power plants and microelectronic manufacturing facilities around the world, silica concentrations in source waters can range between 1 and 60 ppm (mg/L) to even 300 ppm in some volcanic regions. High pressure steam generators and fine microelectronic structures now require water containing less than 1 ppb (ug/L) concentrations of silica. In designing purification processes, silica has presented issues not only as formidable challenges in many locations as RO membrane foulants, as well as a contaminant requiring efficient removal. Analyses of RO membrane foulants and correlation with water chemistry in the course of trouble-shooting numerous RO processes continues to offer us opportunities to understand silica chemistry, the patterns of silica fouling and methods by which we can chemically control the RO process. Such understanding is applicable to the operation of ion-exchange resin beds as well. In this paper we review the speciation of silica in feedwaters, and chemical approaches to controlling fouling and maximizing silica reduction. Silica and silicates are addressed in the three categories of reactive soluble, non-reactive soluble (colloidal, not filterable) and non-reactive insoluble (particulate, filterable) forms. A brief review of geochemistry, the chemical and biochemical dissolution and deposition of silica and silicates in nature is provided for insights and understanding of natural processes that can be applied to the task of process design and control in silica removal from water.

Keywords: Silica; Silicates; Silicic acid; SiO_2 ; Reactive; Non-reactive; Colloidal; Reverse osmosis; Ion-exchange; Fouling; Polymerization inhibitor; Dispersants; Coagulation; Fouling control; Rejection; Process design

1. Chemistry

High pressure steam generators [1] and fine microelectronic structures [2] now require water

containing less than ppb (1 ug/L) concentrations of silica. In designing purification processes, silica has presented issues not only as formidable challenges in many locations as foulants, as well

as a contaminant requiring efficient removal. Analyses of reverse osmosis (RO) membrane foulants and correlation with water chemistry in the course of troubleshooting numerous RO processes [3,4] continues to offer us opportunities to understand silica chemistry, the patterns of silica fouling and methods by which we can chemically control the process.

Silica [5–8] and silicates [8–11] are generic names given to the family of silicon dioxide related compounds derived from the dehydration-polymerization of silicic acid — $\text{Si}(\text{OH})_4$. Silicic acid, variously called orthosilicic acid, monosilicic acid or silicic acid monomer, is a weak tetravalent acid with pK_a values of 9.9, 11.8, and 12. Although silicic acid is prevalent in natural waters, and is readily available from acidification of commercial crystalline sodium silicate or metasilicate [12], it has a great propensity to polymerize by dehydration to form Si–O–Si anhydride bonds: $n \text{Si}(\text{OH})_4 \rightarrow (\text{OH})_3\text{Si–O–Si}(\text{OH})_3$ dimer \rightarrow oligomers \rightarrow colloidal polymers $\rightarrow (\text{SiO}_2)_n$.

Thus silicon dioxide (SiO_2 , silica) is the final and most stable product at normal conditions of silico-oxygen acid polymerization. The molecules of silica represented by the formula SiO_2 is polymeric, and is more accurately represented by the formula $(\text{SiO}_2)_n$, where n is unlimited in number, allowing for infinite extensions in amorphous and crystalline forms of silica.

The rate of silicic acid polymerization is strongly pH-dependent, and is influenced by polymerization reaction concentration. It is very fast in neutral and slightly alkaline solutions, and extremely slow at low pH values of 2–3. Dilute polysilicate solutions that are under saturated with respect to amorphous silica will depolymerize to monosilicic acid.

Silicates imply more complex forms of silica in which there is a copolymerization of silicic acid with hydroxides of other metal elements covering almost the entire Periodic Table. This gives rise to the immense variety of rocks found on earth, which are copolymers of silicic acid in the ultimate dehydrated forms. In solution, silicic acid would

readily react with alcohols and other hydroxyl group containing organic compounds to form anhydrides. This provides for great diversity of products and interactions in the biosphere.

2. Classification

Silica in natural waters is commonly classified as reactive or non-reactive. Reactivity refers to the staining with molybdate reagent in colorimetric assay of dissolved silica. The rate of this staining reaction is quantitatively reproducible only with low molecular weight polysilicic acids, and varies inversely with the degree of polymerization of silicic acid [13]. Monosilicic acid will react with molybdic acid under assay conditions within 2 min, while disilicic acid reacts completely in about 10 min. Higher polysilicic acids require much longer times for substantial but incomplete reactions. After removal of suspended insoluble silica by filtration with typically 0.45 filter, total dissolved silica (reactive plus colloidal non-reactive) can be measured with atomic emission or absorption spectroscopy. Colloidal silica value would be the difference between the total and reactive silica. Normal detection limits of reactive silica with 25 ml samples are 0.1 mg/L. Greater sensitivity of 0.001 mg/L is possible with 100 ml sample sizes [13].

Agglomerated silica and silicates can reach the size, in solution, where they are no longer ions, but are actually colloidal particles that can remain in visually clear suspension indefinitely, and are very difficult to remove by filtration. They range in size between 1 μ down to molecular sizes of 10 angstroms. In this particle size range, varied surface properties of these and a host of ubiquitous organic and inorganic colloidal particles found in natural and process waters result in complex interactions that are difficult to characterize and predict.

3. Geochemistry

In nature, silica (SiO_2) occurs not only in the crystalline forms of quartz, cristobalite, and tri-

dymite, but in the form of amorphous silica and glass as well. In terms of number of atoms as well as weight, silicon is exceeded only by oxygen in the Earth's crust. More than 95% of the volume of the Earth's crust is composed of quartz and a small number of other rock-forming silicates. Second only to carbon, silicon forms the largest number of compounds with other elements. The large number of carbon compounds is due to the fact that the bond energies of the C–C, C–O, and C–H bonds are of about equal magnitude, and they will therefore be formed with about the same probability. In contrast, the bond energy of the Si–O bond is considerably higher than that of the Si–H bond and more than twice that of the Si–Si bond. As a consequence, instead of the common C–C–C chains of carbon chemistry, chains of the type Si–O–Si–O are the skeletons of silicon chemistry [11].

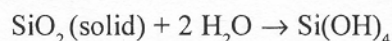
Typical concentrations of dissolved silica in natural waters are shown below in Table 1.

In river and seawater, silica is found not to be exclusively in the colloidal state, but also in a molecular solution, since its saturation concentrations are not attained. Despite the propensity for monosilicic acid to polymerize, it has been shown that silica in seawater is nearly exclusively in the monosilicic acid form in concentrations in the range of <0.006 ppm–10.1 ppm [14,15]. The concentration is low at the surface and increases with depth. Samples of lake and river water were found to contain only monosilicic acid, with no evidence of the presence of dimeric silicic acid [16]. Silica in ground waters also appear to be in the low molecular weight forms rather than the colloidal form [17]. The concentration of particulate

silica in seawaters of several oceans has been determined to be 0.0006–0.43 ppm SiO_2 [15]. It is thought to be mainly of biogenic origin. Colloidal silica is depolymerized by seawater, which is considered at least one order of magnitude undersaturated with respect to amorphous silica.

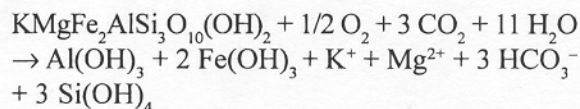
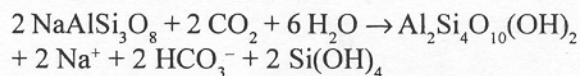
4. Dissolution of silicate rocks

Pure silica such as quartz is completely dehydrated silicic acid. Depolymerization by re-hydration as represented below would represent the dissolution to form soluble silicic acid:



The dissolution rate is temperature and pH dependent, being minimum at pH = 2–3, rising about 100-fold — pH = 11. Heat-accelerated hydrolysis would be expected in volcanic regions.

Silicic acid is also generated from the weathering of silicate rocks. Silicates are basically dehydrated forms of metal ion salts of silicic acid, which can be decomposed by carbonic acid. The following two reactions represent important dissolution processes of silicates [5]:



Field measurements of weathering rate on a m^2 catchment area basis from different geographic areas are remarkably similar: 10^{-2} – 10^{-1} moles $\text{m}^{-2}\text{y}^{-1}$. It is estimated that 10^6M^2 surface area of mineral grains active in weathering is available per M^2 of geographic area, and that only a few monolayers of rock silicates are dissolved per year [5]. The silica concentrations of the pore water increase continuously from the Earth's surface to a depth of 3 M. The silica concentration decreases slightly with depth either by precipitation or — under the influence of the ground water — by dilution. The

Table 1
Typical concentration of dissolved silica in natural waters

| Natural waters | ppm |
|----------------------------------|--------|
| Lakes | 1–3 |
| Major rivers | 3–15 |
| Seawater | 1–10 |
| Wells | 2–60 |
| Wells in volcanic and oil fields | 50–300 |

total annual chemical load delivered from the continents to the oceans is estimated to be 39.3×10^{14} g of which SiO_2 amounts to 4.26×10^{14} g [18].

5. Deposition of silica and silicates

While most natural waters are undersaturated with respect to amorphous silica and silicates, unusual conditions found in geothermal waters [19], and industrial concentration or utilizations of waters do lead to deposition of silica and silicates. Biochemical extraction and deposition of silica by living organisms (see below) constitute a major deposition pathway.

Up to pH values of approximately 9, the solubility of amorphous silica (SiO_2) is relatively constant. It has been reported by various investigators to be 100–150 ppm at 25°C, the dissolved species being in the form of $\text{Si}(\text{OH})_4$. Amorphous silica is metastable relative to quartz. The rate of crystallization of quartz is so slow at ordinary temperatures that the solubility of amorphous silica represents the upper limit of dissolved aqueous silica.

The precipitation of amorphous silica and silicates apparently proceed in a series of steps. Polymerization by dehydration accompanied by cross-linking reactions and aggregation (by van der Waal forces) leads to negatively charged silica colloids. Further aggregation eventually leads to soft then hard gels.

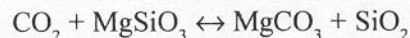
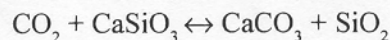
At suitably high pHs, if $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ are present, these hydroxides readily participate in the copolymerization resulting in the incorporation of Fe, Al, Ca and Mg into the complex anhydrous silicate structures. The strong tendency of magnesium hydroxide to react with silica, even in the monomeric state, is shown by the fact that the addition of 300 ppm of $\text{Mg}(\text{OH})_2$ to water will reduce the soluble silica content from 42–0.1 ppm. The order of precipitability starting with the most readily precipitated metal is copper, zinc, manganese, cadmium, lead, nickel, silver, magnesium, and calcium. Metals which react in acidic solutions with silicates are: Fe^{3+} , Co^{2+} , Zn^{2+}

and Cu^{2+} [8]. Aluminum seems to occupy a unique position in regards to its combination with silica. Aluminosilicate gels (zeolites) can be prepared with ion-exchange properties. A gel composition of $5\text{SiO}_2:\text{Al}_2\text{O}_3:\text{Na}_2\text{O}$ has an exchange capacity of 6% of its weight of CaO , while almost all of the sodium ions are exchangeable.

Colloidal silica and silicates are active as flocculants, and would precipitate with other natural colloidal matter in the rivers, lakes and the sea.

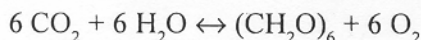
6. Geochemical silica cycle

Geologically, the Silica Cycle is intimately associated with the Carbonate Cycle. The atmospheric CO_2 concentration of about 0.04% on the time scale of millions of years is controlled mainly by a combination of degassing from the Earth's interior, balanced by the uptake of carbon dioxide via the weathering of calcium and magnesium silicate minerals [20,21]. The carbon dioxide in water as carbonic acid is converted to dissolved calcium and magnesium bicarbonate on land during weathering. This carbon form is stored in lakes and aquifers or carried to the sea by rivers, and precipitated there as calcium and magnesium carbonate minerals. The overall reactions shown here were first formulated by Urey [21] in 1952.



The reactions going from left to right represent carbon dioxide absorption via weathering. The reactions going from right to left represent degassing due to the thermal decarbonation of the carbonates after burial to sufficient depths in the Earth's crust. Added to the Urey reactions should also be the Organic Carbon Subcycle. It exerts an important additional control on atmospheric carbon dioxide level. This involves the removal of carbon dioxide from the atmosphere through photosynthesis by organisms, the burial of organic matter in sediments, and the weathering of organic matter (or its thermal decomposition) which returns the carbon

dioxide. The overall reaction is represented as:



Together these reactions regulate carbon dioxide and silica on a geologic time scale.

7. Biochemical aspects

The importance of silicon for life on Earth results primarily from the fact that the fertility of soil relies in large part on the ability of clay minerals to absorb and release water and several cations that are indispensable for plant nutrition. This process is fundamental to the life of plants, and based on these, to the life of those animals which in turn feed upon plants. Data on the physiology of silicon is limited, except that in a number of species, its presence is needed for normal growth.

Dissolved silica compounds play a substantial role in the cells of living organisms. Large amounts of silica are found in horsetail, rice, feather grass, reed and bamboo, where it contributes to the strength of the leaves and stems, and in the skeletons of diatoms which consist of very pure SiO_2 . Silicon compounds are vital components in the metabolism of many bacteria, especially those living in hot springs. The bacterium *proteus mirabilis* even substitutes silicon for phosphorous in phospholipids. Silicon is also present as a trace element in higher animals and in man, where it constitutes about 10 mg per 1 kg live weight. It is essential in the cells of connective tissue and is involved in the biosynthesis of collagen, the substance that forms hair and nails, and in the formation of bony tissue.

Spectacular is the enrichment of silicon in mineralized tissues of unicellular organisms, such as diatoms and radiolaria, and a few metazoa, such as sponges and gastropods [22]. The mineral phase is always amorphous silica in various stages of hydration as $\text{SiO}_2 \cdot n\text{H}_2\text{O}$. Individual diatom populations require a certain level of monosilicic acid, and that declining ambient silica concentrations in natural environments may influence the sequence of seasonal successions. Present-day ocean

contains a few ppm of dissolved silica; diatoms are often cited as being the primary agent of silica removal from the world's ocean, and keeping a low silicic acid level. Others favor inorganic extraction as the main regulating mechanism, since common silicates take up dissolved silica from silica-rich seawater. The data suggests that world ocean was low in silicon for most of its history.

8. Silica reduction processes

Typical efficiencies of silica reduction by different processes starting with 10 ppm in the raw water are given in Table 2. In high purity water production, high silica reduction is attained along with other solutes with an initial passage through RO membrane. Following this step, multiple treatments with ion-exchange beds along with a second passage through RO membrane in the polishing sequence can reduce the silica concentration to 0.1 ppb level [2,24,25].

Two aspects of silica chemistry pose difficulties to silica reduction processes. Firstly, due to polymerization of reactive silica along with cross-linking of the growing silica polymer with hydrated forms of iron, aluminum, magnesium and calcium even under the conditions of concentration in the RO system, the resulting colloidal silica and silicates either by themselves or after coagulating with organic polymeric pretreatment chemicals or colloidal organic matter such as bacterial slime, effectively foul RO membranes resulting in severely reduced flux, and in more advanced stages, increase in differential pressure across membrane elements

Table 2
Typical reduction of silica by different processes [23]

| Process | Residual silica, ppm |
|----------------------------|----------------------|
| Raw water | 10 |
| Partial cold lime | 9 |
| Hot lime–soda | 1 |
| Hot lime–zeolite | 1 |
| Ion-exchange | 0.05 |
| Reverse osmosis, at pH 7.5 | 0.3–1.3 |

[3,4]. Hydrated silica and silicates are known to be flocculants [26,27]. Secondly, reactive silica is essentially unionized at normal pH of natural waters of 6–9. The pK value of the first ionization of silicic acid is 9.9. This means that even at pH 8.9, approximately 90% of reactive silica is unionized and not optimally removed by RO or ion-exchange resins. Only strong-base ion-exchange resins in the hydroxide form exhibit any preference for silica [25].

Presence of reactive and non-reactive silica and silicates in RO feedwaters limits recovery rates. Without inhibitors or dispersants, fouling often occurs for waters containing in the RO concentrate 120–150 ppm of “silica” where typically silica is measured with colorimetric assay with molybdate reagent as reactive silica. Fouling by pre-existing colloidal silica is sometimes seen severely reducing the flux of only lead elements of RO systems. Autopsies would show only a barely visible film of silica on the fouled membrane surface [28]. The distribution of coagulated silica and silicate foulants formed within the RO system tends to prefer the tail elements.

We have introduced two lines of products [29] to address the two fouling mechanisms: a line of dispersant or anticoagulants to address colloidal foulants, and a line of antiscalants with silica polymerization inhibition activities. Separate or synergistic application of these products are steadily extending the limits of silica control, and will be the subject of forthcoming case studies. The introduction of silica-specific dispersants have been reported by others [30–32]. At dosages of less than 10 ppm to the feedwater, maximum levels of “silica” controllable in the brine appears to be 160–240 ppm for these products. Without a practical method of analyzing silica foulant species, maximum control limits cannot reliably be stated without reference to the numerous parameters that contribute to silica fouling. Likewise in the application of antiscalant/silica polymerization inhibitors, parameters such as reactive silica, iron, aluminum, magnesium, calcium, total dissolved solids, non-reactive silica and other colloidal particulate concentrations as well

as pH can be expected as important in controlling fouling.

Avoidance of silica fouling by operating RO systems at high pH of 10–11 with alkali injection has been reported [33,34]. Total silica reached 400–450 ppm in the RO concentrate in these systems. Much higher solubilities of hydrated silica species due to some ionization at elevated pHs is expected. To attain such high pHs in the first pass through the RO however requires control of the severe scaling potential of calcium carbonate and hydroxides of aluminum, iron, magnesium and calcium among other multivalent cations. One approach is to remove all hardness and alkalinity in the feedwater by a sequence of treatment with cation-exchange resins in the acid form followed by acidification and degasification to remove carbon dioxide [33] or completely remove hardness in the feedwater with cation-exchange resin in the sodium form [34]. An alternative approach proposed is to use high efficiency antiscalants to permit high pH operation [35]. By operating at high pH, silica rejection in the first pass RO of 99.8–99.9% was substantially higher than conventional RO operations [33]. One study of rejection of silica in the second pass in the pH range of 5.5–10.5 showed insignificant differences possibly due to the extremely low levels (1–2 ppb) of silica being measured [36].

9. Conclusions

Speciation of silica and silicate under natural and process conditions is an important consideration for fouling control and maximizing removal. The propensity of reactive silica and hydroxide forms of various common di- and trivalent cations in water to polymerize and flocculate in nature and under the conditions of the operation of RO systems limits the degree of concentration of the brine, hence the recovery, in order to avoid fouling of the membrane elements. Further, the weakly acidic nature of silicic acid monomer and its reactive homo and heteropolymers

require pH of 10–12 to ionize to improve rejection and increase solubility to prevent fouling.

To understand the starting and transition species of silica and silicates, we have briefly reviewed the chemistry and geochemistry of silica. This serves as the foundational information on which the design, operation and improvement of silica removal processes can proceed. We presented our current understandings and progress in these regards.

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