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Reactive silica in natural waters —A review

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ABSTRACT

Polymeric (colloidal) silica formed from reactive silica in water deposits on equipments and membranes used in the desalination and treatment of water and wastewater. Fouling of the equipment used has caused problems leading to numerous investigations into silica removal processes and fouling prevention methodologies. This review of literature from a wide scientific field is undertaken seeking insight on the known chemistry of reactive silica, and how it can be investigated and managed. Due to the wide field covered, the review is necessarily not exhaustive. However, key points of reactive silica chemistry are presented. Keywords and references can be used for deeper searches of the literature. This review defines reactive silica as primarily monomeric silicic acid – $Si(OH)_4$, which spontaneously polymerizes by dehydration reaction to form a dimer, oligomers and ultimately high silica and silicate polymers. It is primarily the only molecule that reacts with molybdic acid colorimetric reagent that we use to quantitate silica. The condensed silicic acid does not react sufficiently with molybdic acid to give the yellow to blue color in standard assay method, hence as a group is called non-reactive silica. When the non-reactive silica molecules grow to nanometer-sized range they take on colloidal silica properties. In ultimate highly dehydrated states, it can be represented as silica $(SiO_2)_n$, where n is a very large number. Copolymerization with hydroxides of aluminum, iron, magnesium and other metals give rise to the clays, silt and rocks as mixed silicates. As designed by nature, the condensation reactions are reversible. For this reason, the review is presented under the headings of characterization of reactive silica, hydrolysis of rocks, polymerization reactions and silicification of plants and animals as models of fouling mechanisms in desalination and water treatment. The key point noted as they apply to desalination and water treatment is that reactive silica undergoes reversible dehydration polymerization with itself and commonly with hydroxide molecules of iron, aluminum, magnesium and calcium to form silica and silicates, respectively. When water is highly concentrated during desalination, it is a complex reaction mixture of monomer, oligomer and polymer of silicic acid that lead to silica fouling. The deposition of silica and silicate on surfaces of membranes and equipment arise from the surface properties of unstable colloidal particles of sizes and shapes not yet understood.

Keywords: Silicic acid; Reactive silica; Non-reactive silica; Colloidal silica; Hydrolysis of rocks; Silicates; Polymerization; Silicification; Oligomeric silicic acid; Biosilification; Biomineralization; Fouling mechanisms

$$\mathrm{Si(OH)_4} + \mathrm{Si(OH)_4} \rightarrow {}_3\mathrm{(HO)\text{-}Si\text{-}O\text{-}Si\text{-}(OH)_3} \rightarrow \text{Oligomers} \rightarrow \mathrm{(SiO_2)_n}\ \text{(silica polymer)}$$

$$+\ \mathrm{Al(OH)_3} \rightarrow {}_3\mathrm{(HO)\text{-}Si\text{-}O\text{-}Al\ (OH)_2} \rightarrow {}_3\mathrm{(HO)\text{-}Si\text{-}Al(OH)\text{-}O\text{-}Si(OH)_3} \rightarrow \rightarrow \text{(Al silicate)}$$

$$+\ \mathrm{Fe(OH)_3} \rightarrow {}_3\mathrm{(HO)\text{-}Si\text{-}O\text{-}Fe(OH)_2} \rightarrow {}_3\mathrm{(HO)\text{-}Si\text{-}O\text{-}Fe(OH)\text{-}O\text{-}Si\text{-}(OH)_3} \rightarrow \rightarrow \text{(Fe silicate)}$$

$$+\ \mathrm{Mg(OH)_2} \rightarrow {}_3\mathrm{(HO)\text{-}Si\text{-}O\text{-}Mg\text{-}OH} \rightarrow {}_3\mathrm{(HO)\text{-}Si\text{-}O\text{-}Mg\text{-}O\text{-}Si(OH)_3} \rightarrow \rightarrow \text{(Mg silicate)}$$

$$+\ \mathrm{Ca(OH)_2} \rightarrow {}_3\mathrm{(HO)\text{-}Si\text{-}O\text{-}Ca\text{-}OH} \rightarrow {}_3\mathrm{(HO)\text{-}Si\text{-}O\text{-}Ca\text{-}O\text{-}Si(OH)_3} \rightarrow \rightarrow \text{(Ca silicate)}$$

Fig. 1. Formation of silica and silicates by spontaneous dehydration polymerization.

1. Introduction

All natural waters contain levels of dissolved and suspended forms of silica that end up on the surfaces of boilers, reverse osmosis (RO) membranes and cooling towers as solids ranging from layers of glass, gels, powders, and invisible nanometer-sized particles seen only with scanning electron microscope. Silica fouling of water treatment equipment has been dealt with since the earliest development of industrial water chemistry [1–3]. Severe flux reductions in the operation of RO membranes due to polymeric silica deposition leading to restricted water recoveries has led to much recent investigations of silica chemistry in natural waters [4–16]. Reactive and non-reactive silica in water covers a large spectrum of molecular sizes ranging from the monomeric silicic acid [$\mathrm{Si(OH)_4}$], to dissolved oligomeric forms, to polymeric colloidal suspensions, and ultimately as silica [$\mathrm{(SiO_2)}_n$] or silicate particles in which n represents huge numbers [8]. Metal silicates of the composition of rocks are formed by the incorporation of metal hydroxides such as of aluminum, iron, magnesium and calcium during dehydration polymerization reactions illustrated in Figure 1 [6,8,9]. An understanding of the chemical and physical properties of all these species is necessary for the control of silica fouling on membranes. This review of literature from a broad range of science is motivated by such a need.

2. Characterization of reactive silica

Molybdate colorimetric assay for silica in water developed in the 1920s has remained till now the standard assay. Ammonium molybdate at pH approximately 1.2 reacts with reactive silica and any phosphate present to produce yellow heteropolyacids of uncertain structures. Oxalic acid is added to destroy the molybdophosphoric acid but not the molybdosilicic acid. The intensity of the yellow color is proportional to the concentration of molybdate-reactive silica. Addition of a reducing agent changes the yellow color to an intense blue color offering enhanced sensitivity to the colorimetric assay [17]. Total silica in water is measured with inductively coupled plasma method. The difference between total silica and reactive silica is non-reactive or colloidal silica. It is known that molybdate-unreactive silica can be converted to the molybdate-reactive form by heating or fusing with alkali [17].

Weitz et al. [18] discovered that silica in the monomeric state will react with molybdic acid completely within 75 s at 20°C while disilicic acid [$_3\mathrm{(HO)\text{-}Si\text{-}O\text{-}Si\text{-}(OH)_3}$] reacts completely in about 10 min, and higher polysilicic acid requires even longer. They determined molecular weights by freezing point depression method. It seems likely as shown by literature cited below on hydrolysis of rocks (silica and silicates) that disilicic acid and higher polysilicic acid analytes undergo acid catalyzed hydrolysis to silicic acid under assay conditions for color development. Alexander [19,20] prepared monosilicic acid from addition of sodium orthosilicate solution in a thin stream to an excess of violently stirred dilute sulfuric acid so that the resulting pH was 2.5, and silicic acid concentration was about 0.1%. Under these conditions, the resulting monomeric silicic acid was seen to not polymerize. Alternatively, methyl orthosilicate was hydrolyzed to silicic acid in dilute sulfuric acid and stabilized in acid. The disilicic acid was prepared from hydrolysis of hexaethyl disilicate (712 mg) in 500 ml of 0.002 M sulfuric acid for 2 h at 25°C. Alternatively, the disilicic acid was prepared by the dimerization of monosilicic acid using cryoscopic method for determining the dimerization end-point. By assaying freshly prepared solutions obtained in this manner, Alexander confirmed that under the short times in which standard molybdate colorimetric assays are completed, the color formation is primarily derived from monosilicic acid.

Silicomolybdic acid formed in the colorimetric assay has been characterized in two isomorphic forms which when reduced showed further complexity [21]. Salts of silicomolybdic acid with organic bases have been useful for the gravimetric determination of small amounts of silica [22]. The precise structures of this class of heteropoly silicomolybdic acids are not known.

The studies of the relative reactivities of monosilicic acid and disilicic acid with molybdic acid and their preparations and stabilization from spontaneous polymerization as described above have shed much light on the nature of monosilicic acid and its tendencies to spontaneously polymerize. Despite such reactivity, it is interesting to realize that monomeric silicic acid is the predominant dissolved silica species found in natural waters, varying from a concentration of about 1–3 mg/L in mountain lakes to 50–300 mg/L in well waters in volcanic and oil production fields [8]. It apparently exists in equilibrium and does not polymerize under those conditions of pH, concentration, other dissolved salts and suspended solids. In geothermal aquifers at 200–350°C, silicic acid concentration is reported in 300–700 mg/L range. When such hot waters cool, silicic acid polymerized, and coat the surfaces of pipes and heat exchangers. It was found that the rate of silica scale formation can be reduced by aging superheated water to allow silicic acid to polymerize to an amorphous precipitated polymeric form before use. Rapid heat extraction with capillary heat exchangers before aging also minimized silica scaling [23]. Laboratory studies [12] on the precipitation of silica from solutions of silicic acid in the range of 200–700 mg/L prepared from sodium silicate, at pH 7 and 25°C was reported. Reactive silica concentrations in these solutions decreased over 10 h or more asymptotically to a remaining pseudo-equilibrium concentration of about 180 mg/L. The addition of ferric ions effectively removed silicic acid as ferric silicate.

The relative absence of non-reactive, polymeric forms of dissolved silica in natural waters has been noted [24,25]. Non-reactive silica at low concentrations formed from freeze-thawing of river water samples [26] or partially allowed to form from silicic acid in the laboratory [24,25] was shown to revert to the reactive silicic acid form over several days in natural waters and even in distilled water although much slower. Concentration of total dissolved solids in the water such as in seawater catalyzes the hydrolysis of the non-reactive silica. In the reactive form, silica can be reversibly adsorbed on strong anion-exchange resins in the hydroxyl form [27]. The pK_a values of the four sequential ionizable hydrogens in silicic acid are 9.9, 11.8, 12 and 12 [28]. Silicic acid is a very weak acid and is essentially not ionized in the neutral pHs of natural waters. Activated alumina was found to be a suitable adsorbent for the removal of silica from brackish and geothermal waters [29]. A maximum of 90% reactive silica removal could be achieved at pH 8.0–8.5, the optimal pH range. The advantage over removal by ion-exchange process is that there is no competition by other anions.

The application of fast atom bombardment mass spectrometry (FAB-MS) (negative ion mode; Xe, 1 mA emission) to reactive silica in water [30,31] has led to a series of papers on the identification of silica oligomers ranging from monomer to heptamer in molecular weights, by themselves as well as complexes with single to multiple monovalent and divalent cations. The typical analysis condition is as follows. About 0.03 ml of the sample solution was loaded onto the sample holder in the FAB-MS spectrometer and the sample solution was overlaid with an equal or lesser amount of glycerine. The sample solution and glycerine were ascertained to be in the liquid state on the sample holder after each measurement. The negative ion mass spectra in the 0–1000 *m/z* mass range were compared with the mass spectra of the reference solutions without silica to identify silicon-containing peaks. The difference between the calculated mass of silicate complex and the detected *m/z* ratio was within ±0.1. Dilute (<0.6 mM) solution of silica in 0.1 M NaCl solution afforded the following observed peaks: $Si(OH)_2O_2Na^-$, $Si_2(OH)_5O2^-$, $Si_2(OH)_4O_3Na^-$, $Si_2(OH)_3O_4Na_2^-$, $Si_2(OH)_2O_5Na_3^-$, $Si_4(OH)_7O_5^-$, $Si_4(OH)_6O_6Na^-$ and $Si_4(OH)_5Na_2^-$. When silica gel was aged for a day in solutions of NaCl and $CaCl_2$, comparison of FAB-MS spectra showed cyclic tetramer, cyclic and linear heptamer preferentially formed in $CaCl_2$ solutions [32]. The pattern of reactive silica species in seawater as observed with FAB-MS to characterize regional differences in the ocean has been proposed [33]. Considering the facile reversible dehydration polymerization reactions of silicic acid, the highly complex matrix effects and energetic sample volatilization conditions of FAB-MS are of concern. Control experiments appear to be needed to show that the observed patterns of mass spectral particles are not an artifact of the analytical methodology.

3. Hydrolysis of rocks

The crust of the earth ranges between 10 km beneath the oceans to 45 km on land in thickness [34]. Amazingly it is composed of almost entirely of silica and silicate rocks [35]. The estimated elemental concentrations by weight in the crust are oxygen – 45.6%, silicon – 27.3%, aluminum – 8.4%. iron – 6.2%, calcium – 4.7%, magnesium – 2.8% in this order of the most abundant elements [35]. After physical breakdown on the surfaces by weathering and erosion, soil is generated composed of sand (50–2000 microns), silt (2–50 microns) and colloids (<2 microns) [36]. This breakdown greatly increases the surfaces of rocks to the chemical actions of water that come into contact with it. Colloidal particles do not settle out of water, are invisible to the eye, and have large surface areas per unit weight compared to visible particles. A 1-mm sand particle has a surface area/mass ratio of about 0.002 m^2g^{-1}; a 1 um clay particle, 2 m^2g^{-1}; and a 1 nm particle, 2000 m^2g^{-1} [36]. The soil is an O–Si–Al–Fe matrix containing relatively small amounts of essential elements for biotic life. The elemental content by weight in soil is estimated to be oxygen – 49%, silicon – 33%, aluminum – 7% and iron – 4% [36]. The presence of silicic acid monomer in water and uptake in plants and animals clearly indicate that rocks, silica and silicates, are hydrolysable into the ultimate monomeric species of silicic acid, aluminum hydroxide and ferric hydroxide, and utilized in nature as building blocks. The rates of hydrolysis of silica and silicates and the repolymerization of silicic acid hence are of interest in the chemistry of geology, soils, biology, paleontology, ceramics, nanotechnology and water purification among many others.

Chemical weathering rate of silicate minerals has been reviewed [37]. In the water environment, the Si–O–Si bonds are so easily formed reversibly that given sufficient contact, heat, pH and catalytic effects of solutes in water, hydrolysis will proceed. It is observed that in the crystalline state, the Si–O bond in the silicates is intermediate between purely ionic and purely covalent bonding [36]. Various silicate minerals in aqueous sulfuric acid at pH 3 dissolves initially to polysilic acids which ultimately hydrolyze to monomeric species [38]. A fluorescence probe technique was used to show that aluminum silicate complexes account for up to 95% of the total inorganic mononuclear aluminum in natural waters [39].

Factors affecting the rates of hydrolysis have been studied in the laboratory. Two sources of pure amorphous silica (fused purified quartz and pyrolyzed $SiCl_4$) were suspended in deionized water and NaCl solutions. Rates of dissolution in forming molybdate reactive silica were measured at 40 to 250°C [40]. Absolute rates of amorphous silica dissolution in deionized water exhibit an experimental activation energy, $E_{a,exp}$, of 81.9 $\pm$ 3.0 and 76 $\pm$ 6.6 kJ/mol for the fused quartz and pyrolyzed silica respectively. Amorphous silica dissolution rates are significantly enhanced with the introduction of NaCl to near neutral pH solutions such that 0.05 molal (1150 mg/L; approx. seawater) sodium ion concentration enhances rates by 21× compared to deionized water [40]. Measurements using single-salt solutions show that the rate-enhancing effects increase in the order: $Mg^{2+} < Ca^{2+} \sim Na^{+} < Ba^{2+}$. Barium ion increases dissolution rates by 114× compared to deionized water. In solution mixtures of two salts, dissolution rates are a non-linear combination of the bulk concentrations of cations in solution. The data suggest a physical model whereby rates in salt mixtures are determined by the intrinsic ability of each type of cation to promote the nucleophilic attack of Si–O surface structures and their ability to compete for interactions at the mineral surface [41]. Rates of hydrolysis of 100 mesh silica gel in LiCl, NaCl, $MgCl_2$, $CaCl_2$ and $SrCl_2$ solutions to low molecular weight species detected with fast atom bombardment-mass spectrometry (FAB-MS) showed that Na^+, Ca^{2+} and Sr^{2+} accelerate the dissolution/hydrolysis of silica gel, while Li^+ and Mg^{2+} do not [42]. In a survey of reactive silica in a number of surface waters in the arid Northwestern China, silicic acid concentration ranging from 2 to 28 mg/L correlated with increasing sodium ion concentration and not with increasing calcium ion concentration. Evidence by FAB-MS is offered as an explanation that Ca^{2+} preferentially binds bicarbonate anion more than with silica-silicate sites [43].

Silicon atom in silicic acid bonds with neighboring silicon atoms through the oxygen atom bridge. Bonds around the silicon atom spatially is tetrahedral – each connected oxygen atom occupying the apex of a tetrahedron. The more highly polymerized, the greater the fraction of Si–O bonds in silica and silicate particles is shielded from catalysis and nucleophilic attack during hydrolysis. The rates of silicate dissolution are a function of the state of polymerization [44]. The state of polymerization is the average number of bridging oxygen atoms per tetrahedron, designated as $Q^{\#}$ of a Si^{4+} atom, also known as connectedness. Silicate anions detected by ^{29}Si nuclear magnetic resonance (NMR) spectroscopy in aqueous alkaline silicate solutions typically have Q^0, Q^1, Q^2 or Q^3 centers [45]. Silicate minerals are characterized by the degree of connectedness between one silicon atom and another. Measured dissolution rates drop linearly with rising connectedness. Calculations have shown that the rate-limiting step in silicate dissolution is not the hydrolysis of Q^3 Si–O bonds but rather Q^2 or Q^1 Si–O bonds [46].

4. Polymerization reactions

In the perfect state of nature, reactive silica – the monomeric silicic acid – should be slowly released from the rocks by facile controlled hydrolysis to sustain biotic life. Silicic acid can return to some rock forms as diagenetic derivatives, or be utilized and regenerated in a biotic cycle, simply by the reversible hydration-dehydration/hydrolysis-polymerization reactions. Diagenesis is the physical and chemical changes occurring in sediments during and after the period of deposition in water up until the time of consolidation. Quartz (SiO2) is formed from silicic acid polymerization under high temperature and pressure [47]. Opal ($SiO_2{\cdot}nH_2O$) is formed more commonly under the milder conditions around geysers and hot springs [48,49]. Quartz cement is the most abundant form of diagenetic cement in sandstones and other sedimentary rocks [50].

Polymerization of silicic acid requires that it be present in the non-ionized state: $Si(OH)_4$. Since its pK_{a1} value is 9.9, it is substantially ionized at pH 11. The pH of a solution of sodium silicate is above 12. It has been long recognized that between pH 11 and 12, a solution of sodium silicate does not gel, but below pH 11, sodium silicate solutions, of a wide range of concentrations, become gradually more viscous and become gels due to polymerization [51]. The observed maximum stability of silicic acid is about pH 1.5 [52]. Above this pH, polymerization and gelling is catalyzed by hydroxyl ion, rising almost linearly with higher pH until pH 11 [52,53]. Below the pH of 1.5, polymerization is catalyzed by trace concentrations of fluoride ion. The reaction rate at low pH is proportional to the concentration of hydrogen as well as fluoride ions, inhibited by metal ions such as iron, aluminum, thorium and beryllium that complex free fluoride ions [52].

Kinetic studies of silicic acid polymerization using three different analytical methods of molybdic acid assay, trimethylsilylation-gas-liquid chromatography, and gel permeation chromatography allowed for distinguishing between the reaction rates of monomer-monomer, monomer-polymer and polymer-polymer reactions at different pH and temperatures [54]. Differences in the effects of temperature, pH and catalysis by ions are compared.

Polymerization of reactive silica results in oligomeric or polymeric forms reaching colloidal particulate sizes [4–16]. When amorphous particles reach large enough sizes to stick to membranes and evaporator or boiler tube surfaces, gel, fine powder or glass-like coatings are formed. Reactive silicic acid monomer can continue to form oligomers or react with deposited coatings adding to its thickness. The nature of colloidal particles is that colloidal silica, iron and natural organic colloids of humic acids and polysaccharides readily coagulate to form complex membrane foulants [15,16]. Silica polymerization inhibitors have been developed to retard silica and silicate fouling [8,55,56] or to control deposition as a colloidal foulant [57]. The adsorption of Mg^{2+} at elevated pH by amorphous silica and subsequent precipitation as magnesium silicate has been studied [58].

5. Silification of plants and animals – models of silica fouling in membranes during water treatment

Silicification (absorption followed by internal ordered polymerization) is widespread in the biological world and occurs in bacteria, single-celled protists, plants and invertibrates, imparting strength and resistance to diseases [59–61]. Silicic acid concentrations in the sea ranges between 1 and 10 mg/L [8]. In soil water (soil solution), silicic acid concentrations in the range of 10–60 mg/L is considered normal [62–64]. Soluble silica saturates the soil sorption sites so little is removed from solutions flowing through the soil. The course of soil weathering can be viewed as the slow release of soluble silica to the soil solution [36].

Silicic acid is unregulated in municipal drinking water and is normally found in human blood plasma with no discernable toxicity [65,66]. One recognized beneficial function is that at physiological pH, silicic acid is profoundly involved in aluminum homeostasis by reacting with aluminum in the intestines to restrict absorption while enhancing renal excretion of accumulated aluminum.

Plants absorb silicic acid and deposit it at different concentration in different parts of the same plant in ordered polymerized form. Silicon content of dry plant matter can vary from 0.1% to 10% by weight [61,67]. When deposited within the plants, ordered polymerization of silicic acid results in phytoliths. These are silica bodies which infill the cell walls and lumina of certain plant cells, however the nature of its association with cell-wall components including polysaccharides, lignins and proteins is not fully understood [68]. Phytoliths thus are microscopic opal silica particles produced in and between the cells of many plants. They are resilient often preserved type of microfossil. Today phytolith analysis is widely used in palaeoenvironmental studies, botany, geology and archaeology [69].

An outstanding user of silicic acid in oceans, seas, lakes, streams and soils, wherever there is water, are diatoms. There are more than 200 genera of living diatoms, and it is estimated there are approximately 100,000 existing species [70,71]. All of them are encased within silica cell walls with exquisite variety of patterns and shapes. Planktonic diatoms in freshwater and seawater typically exhibit a ‘‘bloom and bust’’ lifestyle. In the open sea, the condition that typically causes diatom spring blooms to end is a lack of silicic acid. The secret of the ability of diatoms to assemble silicic acid into colloidal oligomers that will solidify in defined shapes and infinite patterns has inspired the development of silica nanotechnology for industrial applications [72–75].

The mechanisms of biomineralization (biosilification) involving silicic acid is an active field of investigation. Selected papers referenced serve as lead articles and keywords for fuller searches for publications in the expanding field. Protein filaments (silicateins) and their constituent subunits comprising the axial cores of silica spicules in a marine sponge. They chemically and spacially direct the polymerization of silicic acid and its oligomers [76,77]. Silaffin – a silica morphogenic protein [78–82] and the genome of a diatom [83–85] are being studied. Amines of different chain lengths are reported to increase the rate of condensation of silicic acids and the rate and length of particle aggregation according their molecular lengths [86–90]. There is increasing evidence that clusters, nanoscale particles and other more complex precursors in the aqueous phase may play an important role in the solidification of silica structures [91–93].

A most visible form of silicification is petrified wood–wood that ''turned to stone''. Petrified wood found in the Petrified Forest National Park and the surrounding areas in the US is made up of almost solid quartz. The rainbow of colors is produced by impurities in the quartz such as iron, carbon and manganese. It is thought that over 200 million years ago, the logs washed into an ancient river system and were buried quickly enough and deeply enough with water and massive sediments to retard decay while allowing reactive silica to infiltrate the wood [94]. Silification of 10 nm thick dried biofilm exopolymers produced by bacteria have been identified around hot-springs [95]. In dentistry, induced silicification on dentin surfaces as a decay preventative and treatment strategy is being pursued [96].

This review of silification process in nature provides ample evidence that reactive silica is indeed reactive under the conditions we find in natural waters, and can occur as well in water treatment equipments. In seawater, due to very low concentration of 1–10 mg/l reactive silica [8], and likely hydrolysis of non-reactive silica and silicates, membrane fouling by hydrated silica gels is seldom seen. Elemental silica found in membrane foulants measured by X-ray emission or atomic absorption spectroscopies usually belong to colloidal silica and silicates coagulated with planktonic debris and extracellular polysaccharides [15]. In contrast, brackish waters containing 20–300 mg/l of reactive silica, membranes and equipments can be severely fouled. In RO systems, depending on the antiscalants used, reactive silica levels of 200–320 mg/l in the concentrate usually determine the limits of recovery. In such RO concentrates with growing silica polymer chains and a wide range of molecular weights and surface characteristics, hydrated silica gel is first laid down on the surface, with the thickening of the foulant layer caused by reaction or adhesion with reactive and non-reactive silica. Analyses of high silica RO concentrate often show a decline in reactive silica concentration (molybdate colorimetric assay) over time with corresponding rise in non-reactive silica concentration (calculated from total silica concentration by spectroscopy).

6. Conclusions

The ubiquitous reactive silica in water appears to affect all life, and chemistry on land and in the sea, and desalination and water treatment processes. This review necessarily is not exhaustive. Some keywords, concepts and data gleaned however, can serve as starting points of research, and for deeper searches in the literature of a wide range of scientific disciplines. It is amazing that the chemistry of one simple molecule, silicic acid – $Si(OH)_4$, digested from the rocks by water, can command such wide interest and applications in science and technology.

The key points to be noted as they apply to desalination and water treatment is that reactive silica as measured by molybdate colorimetric assay involves silicic acid monomer alone. It undergoes reversible dehydration polymerization with itself and commonly with hydroxide molecules of iron, aluminum, magnesium and calcium to form silica and silicate polymers respectively. When water is highly concentrated during desalination, it is a complex reaction mixture of monomer, oligomers and polymers of silicic acid that lead to silica fouling. The deposition of silica and silicate polymers on surfaces of membranes and equipment arise from the surface properties of unstable colloidal particles of sizes and shapes not yet understood.

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