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Aqueous Silica and Silica Polymerisation

Lucy Lunevich

Abstract

Dissolved silica (SiO_2) is supplied to the environment by chemical and bio-chemical weathering processes despite the fact that dissolved silica has many stable and unstable dissolved forms (silica species). The processes involve ion substitution and chelate forming reactions which remove mineral lattice cations. The concentration of dissolved silica in natural waters is determined by a buffering mechanism which is thought to require the sorption and desorption of dissolved silica by soil particles. For instance average concentration of silica in some groundwater like coal seam gas water ranges between 0.1 and 80.0 ml/L. The dissolution process of silica and silicates from rocks into water is mainly due to hydrolysis of silica-oxygen-silica bonds, resulting in the liberation of silicic acid ($\text{Si}(\text{OH})_4$) and silicates into aqueous phase. It is difficult to define precisely the term 'aqueous silica' as there is an array of silica species possible. Temperature, pH and ionic strength have a substantial influence on the solubility of amorphous silica and forms of silica present in a solution. This phenomenon of silica chemistry can be explained by presence of various silica species, which frequently define silica solubility and physicochemical reactions. It appears that some silica species behave as organics. For seawater the composition is relatively balanced; though, this might not explain low silica precipitation in seawater desalination.

Keywords: aqueous silica, silica speciation, silica polymerisation, silica chemistry, reverse osmosis desalination, brine treatment, coagulation

1. Introduction

In this chapter, the past and recent studies on various aqueous silica species and its impact are discussed. Behaviours of aqueous silica species were studied using reverse osmosis (RO) desalination systems and ^{29}Si NMR techniques and coagulation to gain better understanding of aqueous silica species polymerisation and practical implications of these techniques [1–6].

Practical silica solubility or the solubility defined empirically is a key for prevention of silica polymerisation in RO desalination systems [1–5, 7]. Soluble or dissolved (reactive) silica contains different forms of silica or silica species (**Figure 1**); monomer, dimers, trimers and other polymers of silicic acid in different solutions [5, 7, 8, 12]. These dissolved silica species ($\text{Q}^0 < \text{Q}^1 < \text{Q}^2 < \text{Q}^3$ aggregation) (**Figure 1**) can be presented in various ionisation states which depend on the pH of solutions and silica concentrations and presence of other anions and cations [1, 2, 5, 8, 10–16]. Chemical reactions between these silica species and cations and

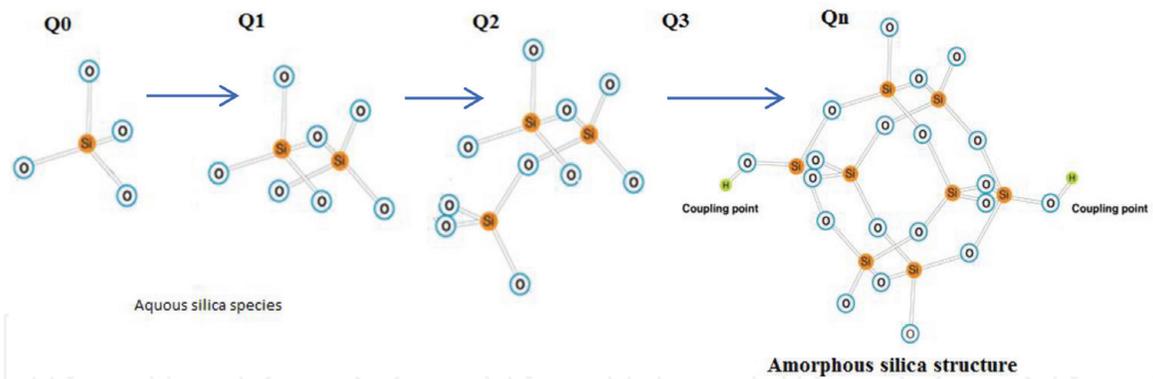


Figure 1. Dissolved silica species ($Q^0 < Q^1 < Q^2 < Q^3$ aggregation) polymerisation path into amorphous silica structure (mechanism proposed by Iler [14]).

anions often present in the Concentration Polarisation (CP) layer in super-saturation conditions during the reverse osmosis chemical separation of water molecules are commonly lead to irreversible silica scale formation on the membrane surface [17–20]. Contrarily, not all highly super-saturated silica streams lead to scaling of membrane surfaces as it was shown in the past research [1, 5, 9].

1.1 Summary

Let us start with summary of the set of conclusions which the author found in the past research [1–25]. Because aqueous silica polymerisation depends on number of oxygen atoms attached to the particular group of aqueous silica the term ‘Practical’ silica solubility was introduced in that research to be able more accurately define aqueous silica chemistry and polymerisation processes [5–9]. Dissolved silica species polymerisation path or aqueous silica solubility was originally described by Kiselev [10, 11] and then adopted by Iler [14] and then later developed by Bergna [12, 13] others [26, 27] (**Figure 1**).

The solubility limit for silica in various waters vary, it is estimated, however, at approximately 120 mg/L at 25°C [5, 28–30]. Practical means an experimental silica solubility to verify the silica solubility in specific conditions – physical and chemical [1, 2, 5, 31]. The solubility defined empirically is also a key for prevention of silica polymerisation and silica scale formation in RO desalination systems [5, 32–43].

According to Sjorberg, Lunevich, and others soluble or dissolved (reactive) silica contains different silica species; monomer, dimers, trimmers and other polymers of silicic acid in different solutions [43–51]. These dissolved silica species can be presented in various ionisation states which depend on the pH of solutions, silica concentrations, presence of other silica species and other cations and anions [3, 5, 43–51]. During the reverse osmosis chemical separation of water molecules (separation of salts) dissolved silica accumulate on the membrane surface which could lead to silica scale formation on the membrane surface.

Interesting that not all highly super-saturated silica streams lead to scaling of membrane surfaces [1, 3, 5]. According to Lunevich in high salinity waters sodium could prevent silica deposition on the membrane surface [1, 5]. The phenomenon of silica chemistry can be summarised as follow:

- i. Silica precipitation profiles (various silica concentrations and pH conditions) studied in deionised water showed that rapidly increasing silica concentrations in the recycled stream had little impact on flux decline likely as the result of reversible hydrolysis and condensation processes [5].

- ii. The results documented in the research [1–3, 5] shown that NaCl in relatively high concentrations (8–60 g/L) depress silica solubility limits showing silica fouling at 90–81 mg/L, but no silica deposition or single silica bonding to the membrane surface was found on the membrane surface suggesting that precipitated silica remained in the recycled stream, again the indication on various silica polymerisation processes via silica species which were formed during the specific conditions, silica concentrations, pH [1–6].
- iii. The maximum and stable residual silica concentration concepts were introduced to highlight potential theoretical silica solubility deviations in different water matrices and recorded pseudo-silica solubility [5] again leading to new research on silica species. Residual silica concentrations can increase above the silica solubility limit, to form super-saturated solutions, especially for low salinity and high flux conditions where silica concentrations increase rapidly in accordance with the RO concentration factor [19, 20, 52–54]. However, this result does not explain what silica species is present there. The kinetics of precipitation is slow due to the requirement for nucleation to occur and the relatively short time of the desalination experiments. It is understood that different experimental conditions could lead to formation of different silica species which are more or less resistant to precipitation and membrane scale formation.
- iv. The presence of minor (7–11 mg/L) to moderate (27.7 mg/L) concentrations of aluminium in CSG waters increased silica fouling and deposition as aluminium silicate on the membrane surface dramatically [2, 3, 5]. The deposit formed on the membrane surface was much harder to dissolve compare to other silica deposit found in the experiments [5].
- v. Silica precipitation occurred at pH 3 condition in both synthetic and natural CSG waters—the phenomenon which requires to further study [2, 3, 5]. The practical implications of the results of silica study obtained in the past study [5, 52] can be summarised as follows:
- vi. Silica present in medium concentrations (20–45 mg/L) in CSG waters increased scale formation on the membrane surface, and therefore residual aluminium concentrations need to be minimised in the RO pre-treatment stages [5, 52]. This remains as a significant problem for industries [5]

1.2 Key findings

The research was undertaking in three prolonged phases to study potential impacts of various silica species and their forms on silica solubility and silica scale formation [5, 23, 52–57]. Comparison of the results obtained by different techniques (reverse osmosis, ^{29}Si NMR spectroscopy and coagulation) on the effect of sodium, aluminium and pH on silica polymerisation and silica precipitation patterns the following conclusions can be drawn as follows, specifically from the ^{29}Si NMR study described in the study [5]:

- a. As a result of dilution with deionised water, dissolved silicate species gain (condensation process) and/or lose (hydrolysis process) monomeric silicic acid (Q^0 type surroundings). A gradual decrease of ^{29}Si NMR spectrum intensity, increased proportions of Q^0 and decreased Q^1 , Q^2 and Q^3 , indicates that hydrolysis or dissolution of monomeric silicic acid occurred immediately.

Overall, a consistent proportional decrease of ^{29}Si NMR spectrum for Q^1 , Q^2 , and Q^3 indicated that there was an equilibrium between species at the Si/M molar ratio 1.7 [2, 3, 5].

- b. Here it is shown that addition of sodium chloride slightly increased the release of monomeric silicic acid (Q^0) and decreased hydrolysis of more complex silicate species (Q^2 , Q^3) compared to similar dilutions with deionised waters. It suggests that sodium prevents an access of water molecule into more complex silica species structures like Q^2 , Q^3 [3, 5, 56–60].
- c. The effect of sodium ions on silicate species indicates that Q^0 type silica species Si-OH is the preferred attraction bond over Si-O-Na, while for Q^1 and Q^2 type surroundings Si-O-Na is preferred over Si-OH. For Q^3 type both reactions with Na^+ and OH^- may occur in combination and mix of bonds depending on the pH, and presence of stable and non-stable more complex silicate species [3–5, 31, 61]. The effect of sodium ions on silica species indicates a slowdown of the hydrolysis process.
- d. There was a clear indication of a structural shift of silicate species towards condensation (precipitation reaction) processes in presence of aluminium in concentrations higher than >7 mg/L [3–5]. The presence of aluminium on silicate species has the following effects: (a) aluminium ions connected to silicate, Al-O-Si-O, resulting in a loss of sensitivity of ^{29}Si NMR spectrum, (b) aluminium forced re-arrangement of species perhaps into polymerisation and precipitation, which are also lead to a loss sensitivity of ^{29}Si NMR spectrum, and (c) it is likely some silicate species Q^1 , Q^2 type precipitated as aluminium silicate.
- e. A significant impact of minor concentrations of aluminium (>7 mg/L) into relatively rich in silicon sodium silicate solutions is an indication that low aluminium concentrations have a significant impact on dissolved silicate species which assume to be present in the solution in non-stable forms [2–5, 52].
- f. The chemical shifts recorded at low pH 2 and 3 illustrate the presence of monomeric silicic acid, have not been found in other studies [23, 35, 66] probably due to rapid particle formation at these pH conditions and due to low interest in this experimental data from a practical application perspective [3, 5, 52].

Looking into silica behaviours as simultaneous charge neutralisation and sweep coagulation of silica is a more complex process than just incorporating the mechanisms of collision and particle growth [5]. The results demonstrated that the concentration of sodium chloride in solution inhibits the removal of silica by coagulation [2, 3, 5, 8]. In this study [5] the new hypothesis was introduced reflecting that aluminium (Al^{13+}) can substitute for sodium ions to neutralise and bridge silica sol [2, 3, 5, 12]. The relationships between $\text{Si}(\text{OH})_4$ and Al^{3+} and Na^+ seems to play a key role in effective silica removal by coagulation [5], the details described by Lunevich [2, 3, 5]. In summary, these fundamental knowledge suggest the practical implication for the operation of a full-scale coagulation pre-treatment process in a RO plant for various groundwater as follows [5]:

1. Reduction of dissolved silica by coagulation can be relatively effective treatment via precipitation and precipitation mechanisms of dissolved silica species if an effective coagulant is selected and coagulation process is optimised [2, 3, 5].

- It appears that pre-hydrolysed coagulant as ACH (PACI) is an effective coagulant in silica removal; however, residual aluminium concentrations could increase dramatically and required careful monitoring of the downstream concentrations and as mentioned the above optimisation of coagulation processes [3, 5, 61–70].

2. Silica chemistry and its effect on RO chemical separation

2.1 Aqueous silica (dissolved silica)

A major observation was made in the past by El-Manharawy [17–20], Gabelish [32, 33], about silica scale deposition in RO desalination for different water matrix Gabelish [17–20], El-Manharawy [32, 33]. In desalination of groundwater and coal seam waters [1–5], however, silica tends to precipitate on the membrane surface, but in desalination of seawater silica precipitates to a lesser extent El-Manharawy [18, 19]. Why? This phenomenon of silica chemistry can be explained by presence of various silica species, which we call aqueous silica or dissolved silica species we discussed the above. The silica chemistry for those waters as all groundwater is difficult to predict as composition could rapidly change [2, 3, 19, 20]. Those various silica species (**Figure 1**) are frequently define silica solubility and physicochemical reactions as it was verified by Kiselev and others [1–5, 7, 12]. Because silica in seawater consumed by various biological species or accumulated in seawater as the results of biological life the composition of silica species is relatively balanced and frequently in amorphous state (**Figure 2**); though, this might not explain low silica precipitation in seawater desalination [17, 18, 21, 22].

Dissolved silica is supplied to the environment by chemical and biochemical weathering processes which involve ion substitution, formation of various silica species and chelate forming reactions which remove mineral lattice cations. The concentration of dissolved silica in natural waters is controlled by a buffering mechanism (well known in biochemical science) which is thought to involve the sorption and desorption of dissolved silica by soil particles and sediment [22–26].

The dissolution process of silica and silicates from rocks into water is mainly due to hydrolysis of silica-oxygen-silica bonds, resulting in the liberation of silicic acid ($\text{Si}(\text{OH})_4$) and silicates into aqueous phase [27–32]. Many suggested that It

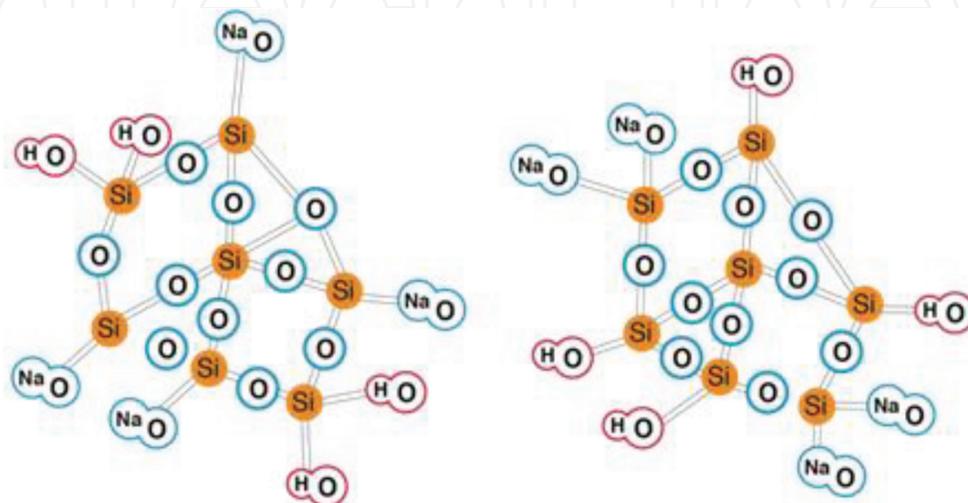


Figure 2.
Structure of two typical $\text{Si}_7\text{O}_{18}\text{H}_4\text{Na}_4$ molecules present in the concentrated sodium silicate which provides baseline for amorphous silica [1–3, 5].

is difficult to define precisely the term 'aqueous silica' as there is an array of silica species possible [8, 12, 13, 20, 21, 32, 33].

Temperature, pH and ionic strength have a substantial influence on the solubility of amorphous silica and forms of silica present in a solution [2, 8–13]. Silica may occur in natural waters in different forms linked to special terminology as follows:

- 'Soluble' or 'dissolved' silica [8, 12] containing monomers, dimers and polymers of silicic acid, again some silica species are always in transition depending on pH and concentration of other silica species [5].
- 'Insoluble' or 'colloidal' silica [8, 12, 57], which results from polymerisation of silicic acid forming particles and three dimensions gel networks (not discussed in great details in this chapter).
- 'Reactive' silica containing monomers and dimers forms that react with ammonium molybdate within 10 min and other forms are called as 'non-reactive' silica [21, 26].

Silica polymerisation is simple a structural growth process (**Figures 1 and 2**) [1–3, 8, 10, 12]. This process leads to the formation of 'colloidal silica', which is a complex and amorphous product [8, 12, 21]. When silicate ions polymerise (condensation process), they form rings of various sizes, cross-linked polymeric chains of different molecular weights, and oligomeric structures. The arrangements of $[\text{Si}(\text{O}_4)]^{4-}$ and $[\text{SiO}_6]^{8-}$ and the tendency of these units to form a three-dimensional framework structure are fundamental to silica crystal chemistry and are studied by Smolin, Kiselev in greater details [11, 12, 23, 25, 28].

Aqueous silica sols and silica species are of particular interest in colloidal silica science because their coagulation-dispersion behaviour is said to be 'anomalous', that is, their stability in terms of electrolyte—pH control does not follow the pattern followed by almost all other oxide and colloidal materials [37–40]. To date, there has been little agreement on what constitutes stability for aqueous silica [2, 3, 8, 12]. One of the unexpected properties of silica is that silica, unlike other oxides, will not regulate charge during the approach of two surfaces [23, 37]. An explanation for the 'anomalous' behaviour of silica sols as defined by Healy [37] can be related to steric stabilisation effects that require oligomeric or polymeric silica species be present at the silica-water surface and that steric repulsion results during overlap of such layers [8, 23, 37]. At high $\text{SiO}_2/\text{Na}_2\text{O}$ ratios, polymerisation leads to the formation of polysilicate species containing silica polymerised structures which includes 6–8 silicon atoms and consisting of predominately dissolved silica groups (Q^0 , Q^1 , Q^2 , Q^3 , Q^4 type surroundings). Very limited number of research on silica species have been conducted so far was to identify as many silica species as possible (Kiselev, Lunevich, Dietzel, Sjoberg, Marsmann, Silver).

2.2 Dissolved silica species

Aggregation (polymerisation) of dissolved silica species into more complex networks under various physical and chemical conditions leading to silica precipitation might be considered a key to understanding of silica scale deposition on the RO membrane surface when groundwater or coalseam gas water used as the feed water [1–5]. Past results from others on silica structural evolution obtained by ^{29}Si NMR show that structural control of silica polymerisation processes is complicated because many and diverse variables affect concurrent reactions differently [41–46]. Inductive and steric factors contribute to the reaction rates [34, 42, 43]. pH is

probably the single most important variable in these reactions. Lunevich [2, 3, 5] and Markides [46, 47] demonstrated by ^{29}Si NMR that for all pH values from 2.5 to 11.5. The smallest particles were of a similar size being only a few nanometers in diameter [2, 3, 5], and the rate of formation of such particles gradually increased with pH (from pH 2.5 to pH 11.5). This agrees with literature models of particle nucleation and growth by Iler [12] and Bergna [50]. The effect of pH, sodium chloride concentration and presence of other cations show a different connection between the rates of aggregation, precipitation and gelation have been summarised in this chapter previously [4, 5, 51]. None of these arguments are definitive due to the nature of silica species, although assignments to monomer, dimer, etc. have been made and speculations are put forward regarding other sub-species present by a number of studies [1–40].

Dissolved and amorphous silica species can be found in commercial sodium silicate solutions, which makes it very attractive to study various silica species (Figures 1 and 2). Moreover, sodium silicate solutions consist of two domain states of silica—the colloidal domain (amorphous SiO_2) (Figure 3) illustrates two silica conditions—the dissolved silica species (mononuclear domain) and colloidal (amorphous silica—insolubility domain) silica and also illustrated in Figure 1. Mononuclear sodium silicate solutions contain a network of $[\text{SiO}_4]^{4-}$ species, which exist in the sodium silicate solution in equilibrium with amorphous silica (Figure 2).

Figure 3 illustrates that the mononuclear domain or mononuclear wall follows the line characterising $[\text{Si}(\text{OH})_4]$ up to a pH of approximately 9, and then ionisation of dissolved silica species dramatically increases as soon as the pH 9 value is past. Within the interval between pH 9 and pH 11.5 the concentration of mononuclear silica and other silica species increase dramatically. This domain in particular is important for the study dissolved silica species (aqueous silica) by ^{29}Si NMR in particular: the monomeric domain where mononuclear Si species $[\text{Si}(\text{OH})_4]$, $[\text{Si}(\text{OH})_3^-]$ and $[\text{Si}_2(\text{OH})_2^{2-}]$ prevail thermodynamically.

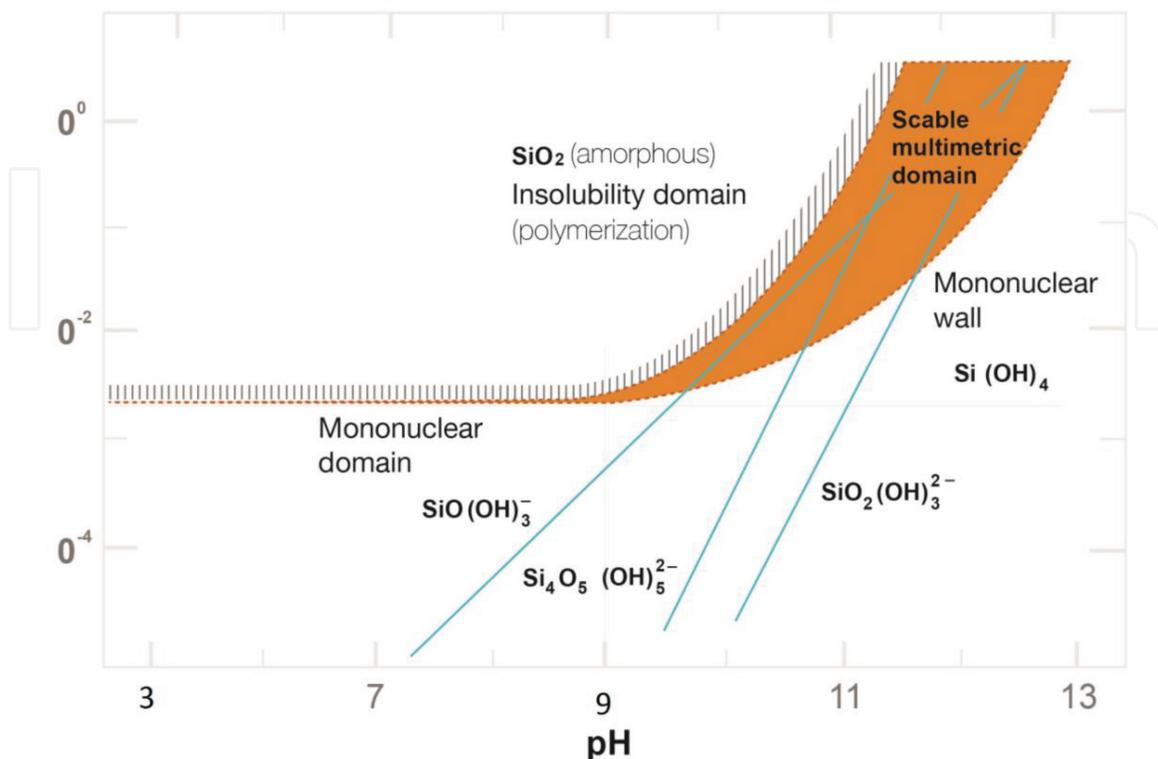


Figure 3. The Stumm and Morgan diagram where silica species present in equilibrium with amorphous silica depending on pH and silica concentrations [5, 25].

2.3 Colloidal silica and silica species

Colloidal silica is another phenomenon of formation of various silica species during hydrolysis and condensation processes. Silica is a primary cause of concern for fouling RO membranes in desalination systems [52–56]. In the presence of carbonic acid (H_2CO_3), silica has two acid–base characters that impacts the characteristics of the silica and its interaction with membrane surfaces. First, the complexation of silica with hydrated forms of heavy elements (calcium, aluminium, magnesium and iron) creates colloids that grow through polymerisation and bridge with organic and inorganic matter to form gel-like layers on membrane surfaces the data which have been well studied by others [52–56]. Second, reactive silica is known to consist of low ionised forms (such as monomeric silica acid) at pH of 6–9 and to form an essentially all-silica gel or cake structure [52]. These silica structures cause flux decline and higher TMPs. Research has shown that colloids can be composed of any number of different materials; the mostly commonly encountered inorganic colloid is silica (SiO_2) [56–60].

Colloidal silica results from the polymerisation of silicic acid containing particles and three-dimensional gel networks [2, 12, 23, 38]. Silica may also form amorphous silica deposits especially in the presence of calcium carbonate and calcium sulphate [5, 21, 28, 56]. Colloidal silica is the result of the silico-oxygen acid polymerisation process [12]. Colloidal silica can form in bulk solution or RO feed when dissolved silica solubility exceeds the silica solubility limit.

In CSG waters, silica exists as either colloids or as un-dissociated (ortho-) silicic acid (H_4SiO_4) when the pH is between 8.5 and 9.2. A second form of silica foulant is silicates, which are complex forms of silica in which hydroxides of other elements copolymerize with silicic acid [10–12, 57]. Therefore, silica fouling may be mitigated to some extent through pre-treatment of the raw water by coagulation [5, 37]. Ideally, coagulation should leave no aluminium, no silica, and no ferric ions in the pre-treated water for RO feed [5, 37].

2.4 Silica polymerisation

Silica polymerisation and deposition, on the RO membrane surface, has been researched experimentally [54–56] and more recently computational simulations have been performed [2–8, 17–20] where the molecular mechanism and rate of hydrolysis have been explored through calculation of the reaction barriers and pathways the main factors influencing silica polymerisation are pH, temperature, saturation, impurities present in the solution, and the autocatalysis effect of already precipitated silica that could accelerate further precipitation and scale formation [5, 8, 12, 23, 56]. As can be observed total silica surface area in solution is also a factor determining the rate of silica polymerisation [11, 12, 57].

Computational simulations found that the siloxane bond, often presented on silica surfaces, is difficult to hydrolyse because of the high reactivation energy barrier, especially with the aid of hydrolysis [11, 57, 79]. However, monomers of silicic acid condense to form larger oligomers, which link together to produce primary particles (nucleation) [5, 79]. Depending on process conditions, these particles can either grow by reaction with monomers or grow by aggregation [8, 9, 12]. Aggregation can lead to gelation of the colloidal suspension, but not necessarily to silica deposition on the membrane surface [5, 8, 9, 37].

2.5 Silica species: scaling phenomena

Flexibility in silica solubility limit makes it difficult to control the scale formation as exact limit is unknown due to many variables and in particular silica species

present. Membrane scaling phenomena are governed by the silica solubility limit prevailing in the CP layer on the membrane surface [54–56]. Semiat [54–56] suggest that the rate of change in the silica scale formation during the course of RO processing is dictated by two opposing trends: the concentration effect due to permeate withdrawal and increasing osmotic effects which acts as to decrease the rate of silica scale deposition. Permeability decline data provides a more accurate characterisation of the silica scaling process [5, 54–56]. What is not yet confirmed in the experimental silica studies by Semiat [54–56] is that the impact of dissolution (hydrolysis) on existing silica deposits. This study was in the detail discussion by others [2, 3, 5]. Will silica deposit on the membrane surface as a result of monomer silica groups form colloidal silica structure and concentrations exceeding the practical solubility limit or will it remain in dispersion because hydrolysis and condensation processes reversible.

Baoxia [61] and Elimelech [53] studied silica scaling reversibility in RO process by proposing three steps of both homogeneous and heterogeneous nucleation processes on the membrane surface. The mechanisms proposed by them of silica precipitation leading to two different nucleation processes are conflicting to what can be expected for homogeneous silica nucleation [5, 8, 57] and discussed by Bergna and Iler [10, 12]. The diagram (**Figure 3**) describes indicative silica species distribution in different silica solubility zones, for various pH and concentrations. These silica species ($Q^0 < Q^1 < Q^2 < Q^3$) arise from published light-scattering experiments and was well documented by Kiselev and others [8, 9].

Figure 4 illustrates a typical silica polymerisation path proposed by Iler—increasing dissolved silica concentration well above solubility limit in the CP layer will lead to silica precipitation likely firstly by aggregation of monomeric silica acid in bulk solution (colloidal state) before deposition on the membrane surface. Dietzel [21–25] also illustrated in his analytical study of dissolved silica polymerisation pathways that dissolved silica species in the polymerisation process follows as $Q^0 < Q^1 < Q^2 < Q^3$ aggregation path until they react with other impurities in the other words the silica polymerisation path distracted [2, 5]. It is possible, however, the presence of other potential coupling points on the membrane surface such as $-OH$, $-COOH$ groups and coupling points that are a function of the water chemistry from precipitates such as $Al(OH)_n$, $Fe(OH)_n$ leading to monomeric silicic acid coupling to the membrane surface [5, 37]. Therefore, the chemical processes of water desalination by RO (Dehydration Model) are discussed in greater details by El-Manharawy and Hafez [15–18].

2.6 Kinetics of silica polymerisation

According Lunevich, Bergna and others a considerable amount of study has been devoted to the polymerisation of silicic acid, but little work has been done

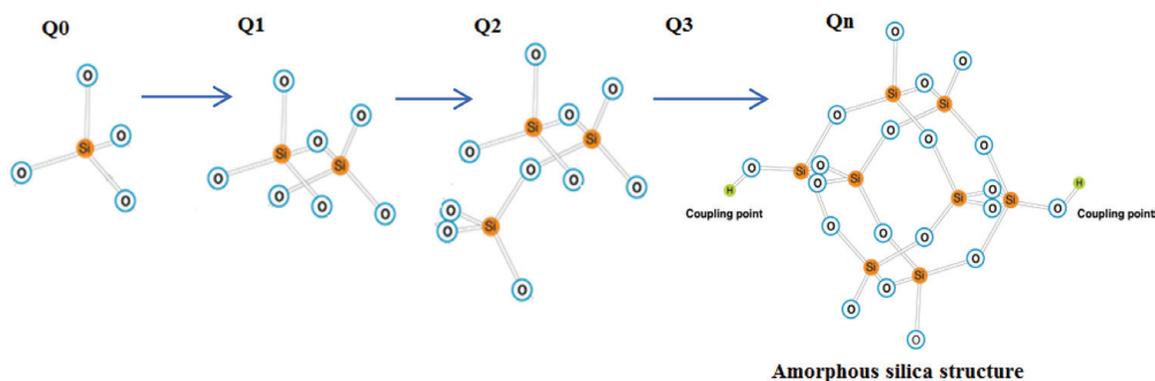


Figure 4. Dissolved silica species polymerisation ($Q^0 < Q^1 < Q^2 < Q^3$ aggregation) path (mechanism proposed by Iler and confirm by others [5, 8, 9, 12, 57]).

on the understanding of kinetics involved in the process of polymerisation of silica on RO membrane surface and colloidal silica layer formation [2, 3, 5]. Semiat [54–56] and Sheikholeslami [59] have studied RO feed solutions and precipitation of silica in concentrations approaching those found in synthetic and natural waters. In an examination of an aqueous solution of silicic acid in the pH range 7–10, the rate of disappearance of monomeric silicic acid was found to follow third order kinetics. Kiselev [8] and Zhuravlev [78] offer similar results. The third order kinetic behaviour of silica polymerisation has also been noted by Marshall [70–76], in acid solutions, but as the pH of the system is increased there was a noticeable change in mechanism. It appears, however, the mechanism of polymerisation of silica species or silica systems of low concentrations is not completely understood [15–17, 19, 54–56]. It seems in different silica concentration ranges, the silica polymerisation rate is quite different [5]. Again Kiselev [8] and Zhuravlev [78] offer similar results. For instance, the polymerisation reaction of monomeric silicic acid in the presence of base was found to follow second order kinetics. Iler [12] and Kiselev [8, 9] and Smolin [60] have reported that the polymerisation process follows second order kinetics in relatively low silica concentrations 1.8–3.0%. Semiat [54–56] and Ning [58–59] studied silica in the relatively lower concentration range 0.2–0.5% and reported that the reaction was first order with respect to SiO_2 and first order with respect to hydroxide and it was enough time for silica precipitation. It seems many agreed that the two species are necessary for the polymerisation reaction to take place are a silicic acid anion and a neutral silicic acid molecule [5, 8, 9, 12, 57, 78]. As the two reactants approach each other in the solution, it is possible the first reaction involves the formation of a hydrogen-bonded intermediate which leads to formation various silica species. The hydrogen bond formed would allow the reactants to be held in close proximity, so that the splitting out of a hydroxyl with subsequent formation of a silicon-oxygen bond can occur. However, it is unknown which silica species will be formed and how many stable and unstable silica species. This mechanism is controlled, as would be expected, by the ionisation of silicic acid which in turn depends on the pH of the system [5, 37]. Bishop [45] and Greenberg [8, 66] confirmed that the polymerisation occurs through one oxygen bridge and the system appears to form only in linear chains [8, 12, 57, 79].

The kinetics of silica polymerisation in dilute aqueous solutions was also studied by Weres, Smolin [60], Marshall [28–32], and Semiat [33]. They all found that the state of ionisation of the silica surface controls the rate of polymerisation. It has been confirmed that the rate of deposition of dissolved silica on the surface of amorphous silica is proportional to the surface density of ionised silanol groups [62, 65, 66, 79]. The extent of surface ionisation also determines the value of the surface tension, and this also the rate of homogeneous nucleation [79]. Applin [79], Lunevich [5] Zhuravlev [78] found that the ‘polymerisation rate’ increased rapidly with increasing dissolved silica concentration in solutions, and with increasing dissolved salt concentration at pH 3.

2.7 Impact on NaCl on silica species and silica polymerisation

The results recorded in the dilution with H_2O study illustrate that monomeric silicic acid may exist as isolated molecules, so called monosilicic acid Q^0 type surroundings or $(\text{Si}(\text{OH})_4)$ and Q^1 type or $\text{Si}_2\text{O}_3(\text{OH})_4^{2-}$, (and as linked molecules, called polysilicic acid) and as Q^2 , Q^3 types. Silica polymers consist of silicate tetrahedrons that are linked via silicon-oxygen-silicon bonds. Addition of H_2O to the solution immediately initiates hydrolysis of monosilicic acid groups and as a result adjustment of equilibrium between the rest of the silicate species [5].

The model of silica polymerisation in high salinity waters (10–30 g/L as NaCl) presented in **Figure 5** illustrates that the introduction sodium chloride into the mother sodium silicate solution impacts the sensitivity of ^{29}Si NMR spectrum for Q^1 , Q^2 , Q^3 types. The proportion of Q^3 type was significantly reduced immediately after the first addition of sodium chloride at Si/M molar ratio 1.41, presumably due to shielding effect of sodium ions. Further addition of sodium chloride into the studied solutions, Q^1 and Q^2 type surroundings disappeared, and Q^3 type also gradually decreased. This is consistent with the hypothesis that sodium ions tend to surround polymeric silica species (**Figure 5**) acting as a stabilising agent, protecting polymeric species from attack by water molecules [2–5].

The research with sodium dilution showed significant increased proportions of monomeric silicic acid (Q^0) compare to similar dilutions with H_2O , [2, 3, 5]. This is a result of sodium ions attracting water shells, which initiate separation of monomeric silicic acid from polymeric silica groups.

When concentrations of dissolved silicate species exceed its solubility limits the nucleation process will, in principle, be governed by interacting silanol groups that interact to form $-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}$ bonds [5, 8, 9, 12]. This is a fundamental reason why practical silica solubility is necessary to define for any specific process conditions as it was studied for RO systems by many discussed in this chapter. Under these conditions, the probability of interactions between neighbouring silanol groups to form $-\text{Si}-\text{O}-\text{Si}-$ bonds is higher, and therefore intramolecular nucleation would be favoured [5, 12, 52].

When silicate precipitation the monomer groups $[\text{SiO}_4]^{4-}$ and $[\text{SiO}_6]^{4-}$ randomly pack and rapid growth results in a non-periodic structures (**Figures 1** and **2**) [5, 8, 12, 54]. In medium to high salinity waters, however, dissolved and already polymerised silicate species will be surrounded by sodium ions as shown in **Figure 5**. Sodium ions attract to silicate and in particular silica monomers $[\text{SiO}_4]^{4-}$, but also can interact with $-\text{OH}$ groups present on the membrane surface in abundance according to the Dehydration Model by El-Manharawy. It appears, however, the $\text{Na}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}$ attractions is stronger than $-\text{O}-\text{H}-\text{O}-\text{Na}$ attractions [23, 42–46]. According to Lunevich then more silicon atoms present in silicate polymeric structure the stronger (equal) the sodium binding structure will be formed.

As can be seen from **Figures 1** and **2** polymeric silicate species will aggregate into colloidal silica in bulk solution. The polymerised silicate is unlikely to deposit

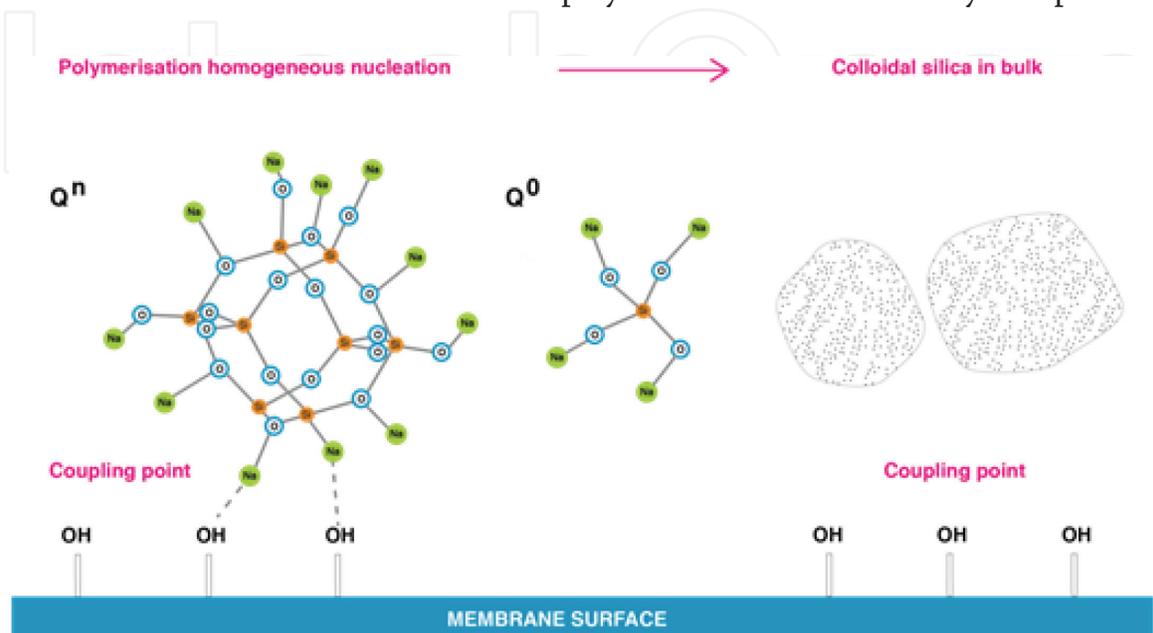


Figure 5.
Impact of sodium on silica polymerisation high salinity waters without presence of aluminium [5].

on the membrane surface due to sodium ions creating barriers between $-OH$ groups and silicate. Monomeric silicic acid can potentially deposit solely on the membrane surface, but the reverse of this process will be apparent as it is likely dissolution (hydrolysis) process will dominate for monomeric silicic acid (**Figures 1 and 2**) [2, 3, 5]. It is known that monomeric silicic acid can coat natural organic matters presented on membranes, in this case silicate deposition on membrane surfaces is possible [72, 73, 78]. Healy [64–69] suggests that sodium ions have a number of effects on silicate species. For instance Na^+ ions in small concentrations (<8 g/L) attract water molecules and sustain further dissolution (hydrolysis) of monosilicic acid increasing the concentration of Q^0 type and at the same time preventing access to polymeric silicate structures such as Q^2 , Q^3 types.

The effect of aluminium ions on silicate species, shown in **Figure 6**, is reduced ^{29}Si NMR spectra peak proportion due to silicate precipitation as aluminium silicates. It appears aluminium ions can over time disassemble polymeric silicate structures due to $(AlO_4)^{-5}$ having similar bonds to Si with oxygen $O=Al-O=Al-O-$, so Al can easily access polymeric silicate species leading to an irreversible process of scale formation on the membrane surface as shown in **Figure 6** [2, 3, 5].

Opposite to the effect of sodium ions on silicate species, aluminium ions force re-arrangement of silicate species leading potentially to precipitation (**Figure 6**). This is represented in **Figure 6**, when major peaks representing Q^1 , Q^2 , Q^3 types transformed into small, multiple peaks. It appears that in presence of aluminium ions, monomeric silicic acid and other dissolved silicate species can deposit on the membrane surface without following the classical polymerisation path ($Q^0 \rightarrow Q^1 \rightarrow Q^2 \rightarrow Q^3 \rightarrow Q^4$). Silica polymerisation does not occur in the order described by Iler and others [8, 12]. Instead it appears as silica polymerisation occurring via monomeric silicate species (**Figure 6**). It is likely occurs in water when a number of conditions are present for silicate to deposit as monomeric silicate, such as elevated residual aluminium [3, 5, 77–79].

As many recognise [8, 9, 12, 35, 57] silicate has a special relationship with sodium and aluminium. Sodium tends to surround silica species preventing it from polymerisation [2, 3, 5]. Aluminium seems to be able to break silica species [2, 3, 5, 8, 12] and change silica precipitation patterns as it was found in the recent study [5].

The effect of aluminium on dissolved silica species recorded in the research [5] showed that aluminium ions can interact with dissolved silicate species such as Q^2 , Q^3 types forcing re-arrangement of species (**Figure 6**). Aluminium ions can serve as coupling points for polymerised silicate to deposit on the membrane surface as shown in **Figure 6**, leading to heterogeneous silicate polymerisation [5, 8, 9, 12, 57]. Both sodium and aluminium are present in CSG waters as other groundwaters and

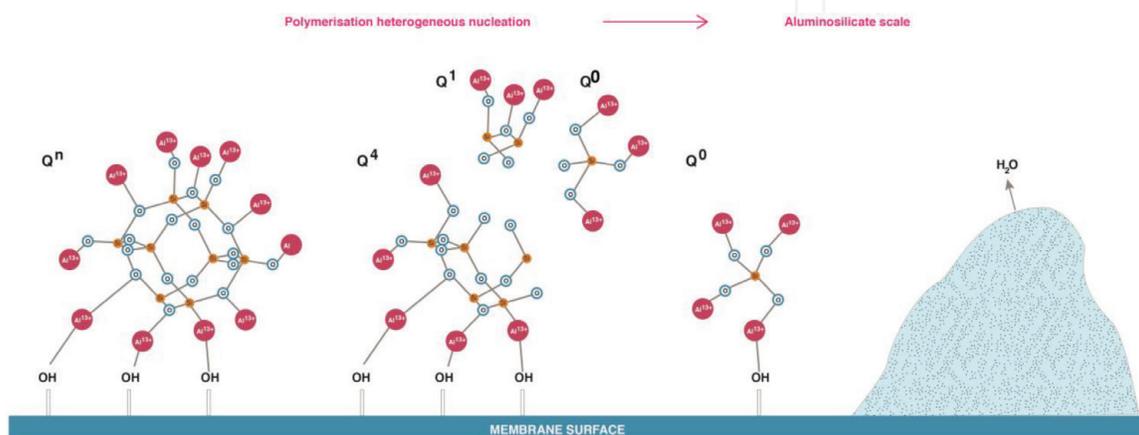


Figure 6.
Impact of aluminium ions presence on silica species polymerisation and deposition on RO surface.

affect the speciation of silicates and precipitation patterns as it can be concluded from the results recoded here [2, 3, 5]. The relative proportion of silicate species, such as Q^0 , Q^1 , Q^2 and Q^3 type surroundings, is strongly pH-dependent [79], and controlled by different processes such as hydrolysis (dissolution), condensation (precipitation) and complexation (aggregation) [70–72].

Structural bonding of the silicate species, or how many silicon atoms are bound to other silicon atoms via oxygen, is complex because diverse variables affect concurrent reactions in different ways [5, 8, 12, 57]. The silica system such as $-O-Si-O-Si-O-$ linkages, however, is often considered as the key reaction dominating many geochemical processes [8, 12, 57]. The bonds play a key role in many silicate transformations [8, 12, 56]. The hydrolysis of this siloxane bond in the absence of defects has been studied by Walsh and Wilson [12], Marshal [70–76] Cypryk [12] and Pelmenschikove [12, 65–76]. These studies indicate that the high activation energy barrier effectively makes this kind of hydrolysis unlikely at ambient conditions and requires confirmation of silica solubility in specific process conditions.

2.8 Conclusion

In this chapter, results the study various aqueous (dissolved) silicate species are discussed. For the first time a method was developed to evaluate the impact of sodium and aluminium cations on dissolved silicate species using three different research methods. The discussion highlights importance of silica species in light of understanding basic silica chemistry.

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Conflict of interest

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Thanks

To the creator, for providing for me with a life of fulfilment and so many wonderful opportunities to grow, discover, and learn from others and to be able to contribute body of knowledge on silica and the next century of research which will be defined by silica (SO_2).

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