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New insights into silica scaling on RO-membranes

Andreas Kempter[a,*], Torben Gaedt[b], Volodymyr Boyko[a], Stephan Nied[a], Keith Hirsch[c]

[a]*BASF SE, 67056 Ludwigshafen, Germany*
Tel. +49 621 60 95272; Fax: +49 621 60 972336; email: andreas.kempter@basf.com
[b]*BASF Construction Chemicals GmbH, 83308 Trostberg, Germany*
[c]*BASF Corporation, Wyandotte, MI, USA*

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ABSTRACT

The polymerization of silica in hard water was investigated by using different supersaturation levels of silica at pH 7 and 8. The results indicate a kinetically stable range up to ~400 ppm [SiO_2] under the chosen conditions at pH 7, whereas no such range is present at pH 8. Additionally, polyvinylpyrrolidone and polyethers were tested for their silica inhibition capabilities. It was found that the performance is depending on molecular weight as well as dosage of the polymers, respectively. From these results, a mechanism for inhibition at pH 7 and 8 was suggested.

Keywords: Silica polymerization; RO membranes; Silica scale; Antiscalants; Polymers; Scaling process

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1. Introduction

In water treatment applications, membrane technologies like reverse osmosis (RO) became more and more crucial in the desalination industry since the beginning of the 1980s. This is due to the low-energy consumption, simple flow sheet and ease of scale-up of those technologies. However, all the membrane separation processes suffer from a common problem: fouling. Fouling or scaling generally relates to the deposition of material (inorganic and/or organic) from solution or suspension onto the membrane surface, leading to a decrease in membrane flux with time. Reduced RO efficiencies (due to high-pressure drops) with increasing energy losses and higher costs for water production are the result. Additionally, larger maintenance costs (due to the increased need for cleaning equipment and plant shutdowns for cleaning), material costs (if antiscalants are used) as well as costly membrane replacements make the prevention of fouling essential in water treatment applications. Besides mineral salts like carbonate, phosphate, or sulfate of especially calcium, silica and/or magnesium silicate has been described as the most challenging ones, where portable water is produced from seawater or brackish water via RO.

Silica or silicon dioxide (SiO_2) is one of the most abundant elements on earth and has many crystalline and amorphous forms. The formation of silica is a complex interplay of hydrolysis and condensation in aqueous solutions. Depending on pH, temperature, and water composition (i.e. the presence of salts in the solution), a plethora of different structures (spheres, gels …) and structural motifs like rings of various sizes, crosslinked polymeric chains of different molecular weights or oligomeric structures are formed

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*Corresponding author.

Presented at the International Conference on Desalination for the Environment, Clean Water and Energy, European Desalination Society, 23–26 April 2012, Barcelona, Spain when silicate polymerize [1]. Additionally, in waters with high Mg^{2+} levels and at $pH > 8.5$, magnesium silicates are formed which prevents operators from using high pH to increase silica solubility. However, the exact mechanism and influence of the different parameters on silica polymerization remain not fully understood. The solubility of crystalline SiO_2 is only 6 mg/l, whereas amorphous silica is in the range of 150–180 ppm depending on the water specifications. In natural waters, silica level range from 20 to 60 ppm, in some places (i.e. Mexico) reaching 100 ppm and can increase upto more than 1,000 ppm in brackish waters [2]. These high amounts of silica often lead to the formation of undesired, mostly amorphous silica deposits on the membrane surface. These deposits, once they are formed, are particularly difficult to remove and normally require harsh and potentially hazardous chemical (based on hydrofluoric acid) or mechanical cleaning. Thus, prevention of silica-scale formation is greatly preferred by the desalination industry. Attempts to control silica scaling include inhibition of silica polymerization, increasing solubility of formed silica as well as dispersing of precipitated silica by polymeric additives, as schematically shown in Scheme 1. Up to now, however, little is known about the mechanisms of polymers influencing the precipitation of silica in solution as well as the scaling process on membranes itself.

In this paper, we want to shed light into the formation of silica under supersaturated and hard water conditions (28° German hardness, i.e. 1 mmol/l Mg^{2+}, 4 mmol/l Ca^{2+}), which reflect the conditions on the retentate side of a RO unit. Therefore, different supersaturation levels of silica were used and the polymerization of silica was studied in hard water solutions at different pH. Additionally, we investigated the formation of silica in presence of a RO membrane surface under selected conditions and the results of adsorption onto the membrane by atomic force microscopy (AFM). Finally, the influence of selected nonionic polymers (polyethers and polyvinylpyrrolidones [PVPs]) on the polymerization of silica and their inhibitor capabilities are investigated. From these results, we conclude a mechanism for inhibition for those polymers.

2. Experimental

2.1. Reagents and instruments

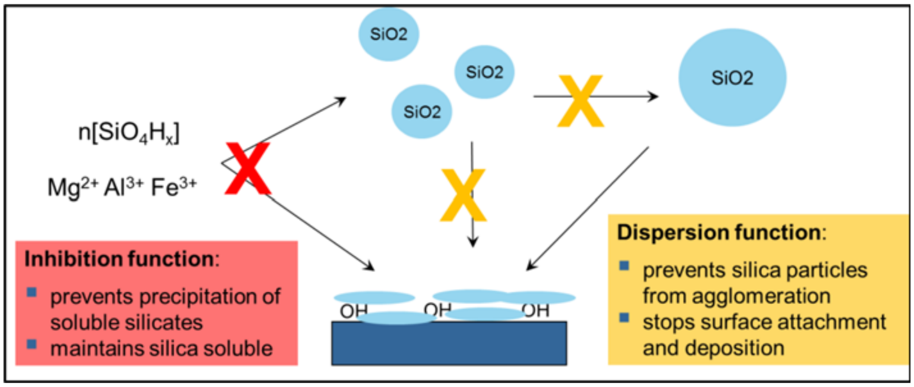
All chemical reagents used were analytical grade and used without further purification. Sodium meta silicate (Na_2SiO_3. $9H_2O$, 98%) was purchased from Sigma-Aldrich, magnesium chloride hexahydrate ($MgCl_2$. $6H_2O$) and calcium chloride dihydrat ($CaCl_2$. $2H_2O$) came from Merck. Sodium hydroxide (NaOH) and hydrochloric (HCl) acids were purchased from Fluka.

Polyethers of various molecular weigths were commercial available, whereas PVP homopolymers and copolymers of various molecular weights are commercially available from BASF SE under the brand names Kollidon® or Luvitec®. Materials and reagents for the silica analytical test were from Sigma-Aldrich (Aquanal Professional). The membrane used was a commercial Toray TMC 820 C RO membrane. The UV spectra for the determination of soluble silica was a HP 8452A Diode Array Spectrophotometer. Particle size determination was carried out with a Malvern Zetasizer nano.

2.2. Silica polymerization inhibition test method

The silica inhibition tests were done as followed:

Batch tests were carried out to determine the precipitation characteristics at different saturation levels of



Scheme 1. Different attempts to control silica scale in water treatment applications.

silica (1.4–4.1-fold supersaturation, i.e. 250 ppm to 750 ppm) under hard water conditions (1 mmol/l Mg^{2+}, 4 mmol/l Ca^{2+}, 28° german hardness). All experiments were performed in plastic containers to prevent silica leeching from glassware. The supersaturated solutions were prepared by adding known volumes of sodium silicate stock solution to distilled water. After adjustment of the pH with diluted hydrochloric acid and/or sodium hydroxide solution, known volumes of a Ca^{2+}/Mg^{2+} stock solution (consisting of a mixture of Ca^{2+} and Mg^{2+}:in a ratio of 4:1) were added and the pH again adjusted to the desired value. In case of an inhibitor used, a stock solution of the inhibitor polymer was added to reach the desired inhibitor concentration. The resulting solution was then tempered and kept constant at 40 °C under moderate stirring for 24 h. After filtration of the reaction solution through a 0.22 µm filter, the filtrate was analyzed with the silico-molybdate test (see below).

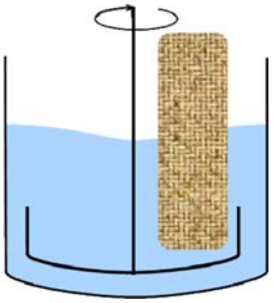
2.3. Determination of soluble (reactive) silica

To determine the soluble silica content, the silicomolybdato spectrophotometric method was used. This method is based on the principle that ammonium molybdate forms yellow heteropoly acids with reactive silica and any phosphate present in the solution at low pH (~1.2). To prevent color interferences caused by molybdophosphoric acid, oxalic acid is added leaving only the silicomolybdate intact. This method is able to determine soluble silica in the range of 1–100 ppm, thus dilution of the test solutions (with silica contents of 200–750 ppm) is necessary. It should also be mentioned, that this method is only able to measure soluble (reactive) silica, which includes not only monomer silicate but also dimers, trimers, and small oligomers of which the exact number is not known.

The chemicals used for this test are commercial available in prepared mixtures (reagents A, B and C) from Sigma-Aldrich. The determination of soluble silica was done according to the standard method. Briefly, some ml of the test solution was filtered through a 20 nm syringe filter. 1 ml of the filtered solution was diluted with 9 ml of distilled water and the molybdate containing reagent A was added. After complete dissolution, Reagent B (containing amidosulfonic acid) was added and kept for 12 min. Finally, reagent C (contains citric acid) was added to the solution and stored for 2 min up to a maximum of 20 min. From the measured UV/Vis extinction, the respective amount of soluble silica in the test solution was determined.

2.4. Adsorption tests on membrane surfaces

Adsorption tests on membrane surfaces were performed using the same silica-solution than for the inhibition tests. For the experiment, a piece of the membrane was put into the stirred solution for variable amounts of time and kept constant at 40 °C. The membrane was then removed, carefully washed with distilled water and analyzed using AFM.



3. Results and discussion

3.1. Silica polymerization with various supersaturation levels and pH

There have been several reports on the influence of ions on the polymerization behavior of silica in aqueous solutions. For example, Koo et al. [3] found, that an increase in calcium and magnesium also increases the polymerization rate of silica at pH 6.5, or more general, that an increase in total hardness also increases the silica polymerization. They also report, that up to 300 ppm of soluble silica, the solution is metastable (at pH 6.5) and no catalytic polymerization occurs. Sheikholeslami et al. [4] also reported, that the Ca/Mg ratio did not affect the solubility limit of the silica but influences the rate of polymerization.

Table 1
Soluble silica after 24 h of condensation at 40 °C at pH 7 and 8

	Soluble silica (ppm)	
Initial SiO_2 value (ppm)	24 h pH 7	24 h pH 8
200		196
250	212	230
300	245	228
350		178
400	313	182
450		191
510	185	169
750	180	172

Therefore, we conducted experiments with 4 mmol/l Ca2+(160 ppm) and 1 mmol/l Mg2+(24 ppm) (28° german hardness) at 40℃ at two different pH levels (pH 7 and pH 8) to examine the effect of pH and silicate supersaturation on the silicate polymerization. The silicate content was varied from 250 to 750 ppm (1.4–4.1-fold supersaturation) at pH 7 and pH 8 and the remaining solution was analyzed after 24 h reaction time at 40℃ for soluble silicate with the silicomolybdate test. The results are summarized in Table 1 and Fig. 1.

It was found that supersaturation levels of ~400 ppm (i.e. 2.2-fold supersaturation) SiO_2 in hard water at pH 7 are kinetically stable, i.e. little polymerization occurs up to 400 ppm initial silica for prolonged times up to 24 h without any additive present. Above this supersaturation level (>400 ppm SiO_2, e.g. at 510 or 750 ppm soluble silica), an immediate precipitation occurs. The remaining amount after 24 h of soluble silica is ~180 ppm (thermodynamic equilibrium solubility). It can therefore be concluded, that silica polymerization under the given conditions proceeds either via a metastable region up to ~400 ppm which is in agreement to the findings of Koo and Amjad [5] or that the rate of polymerization is reasonably slow at this silica. It should be noted, that test conditions without hardness ions (test results not shown here) result in a prolonged observation of the metastable region up to 48 h.

At pH 8, however, no such kinetic stabilization could be observed. Here, a drop of soluble silica to the thermodynamic equilibrium solubility limit of ~180 ppm within 24 h is inevitable. Fig. 2 summarizes these findings. Additional experiments with a variety

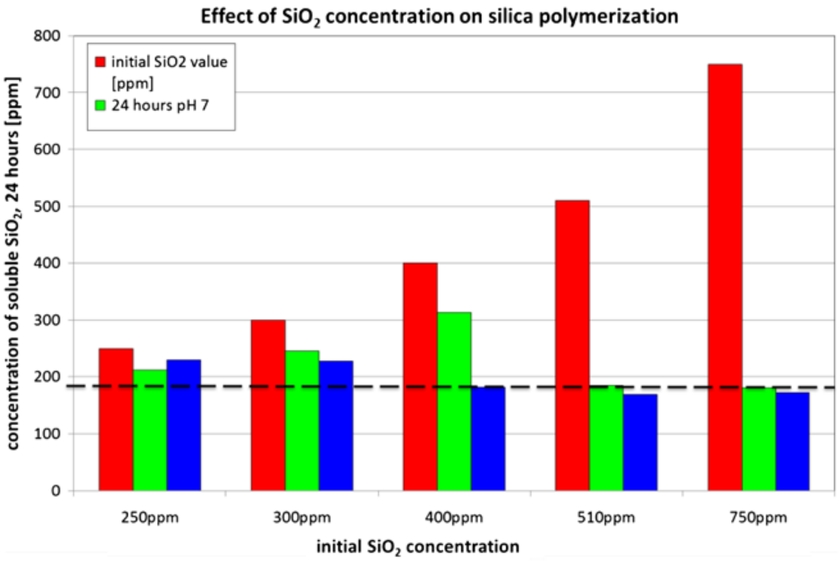


Fig. 1. Resulting soluble silica levels after 24 h of polymerization at different initial silica levels at pH 7 and 8 at 40℃. The dotted line indicates a thermodynamic solubility level of silica.

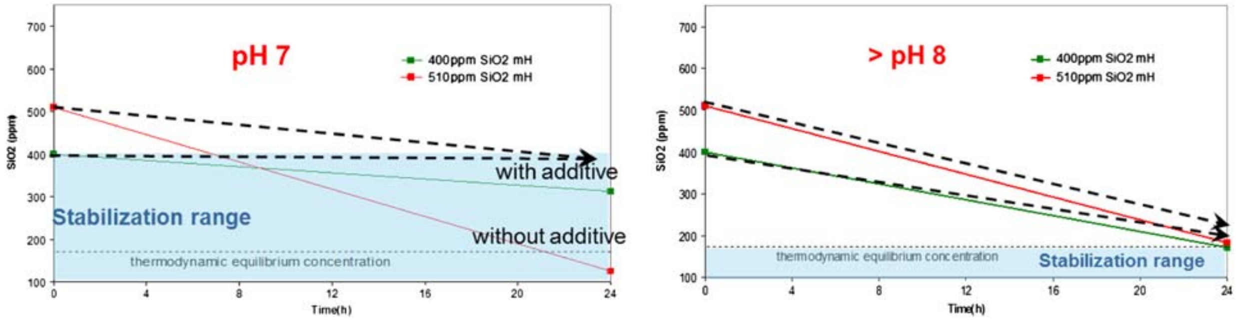


Fig. 2. Different stable regions at pH 7 and 8 for initial silica levels. At pH 7, a kinetically stabilized region was found up to ~400 ppm of initial silica level, whereas at pH 8 no such range exists.

of commercial available inhibitor polymers (results not shown here) have shown, that at pH 7 silica can be stabilized up to around 400 ppm from an initial silica level of 510 ppm, whereas at pH 8 commercially available antiscalant polymers do not show inhibition.

3.2. Membrane fouling

During the RO process, the silica level in water is continuously increased until it reaches oversaturation. This oversaturation consequently first occurs on or close to the surface of the membrane. Thus, if silica polymerization occurs, there is most likely a membrane surface in close proximity allowing the silica to settle down and block the membrane pores. The result is reduced membrane flux or an increase in pressure (if operated at constant flux). Whereas fouled membranes were studied by several research groups using scanning electron microscopy or transmission electron microscopy [2,6], there were, to the best of our knowledge, no time resolved studies performed so far. We therefore examined the polymerization of silica in the presence of a membrane surface by a simple procedure: a standard silicate solution (also used for the inhibition tests) was placed in a beaker and a piece of membrane was put into the beaker in such a way, that the membrane dips into the solution. The whole setup is schematically described in the experimental section. After distinguished times (1, 4, and 9 h), the membrane was removed from the solution and gently washed with deionized water to remove loosely adsorbed material. AFM measurements were performed to visualize the surface of the membrane as well as the morphology of silica present on the membrane.

As seen in Fig. 3, the membrane surface prior to the experiment is rough with a “mountain and valley”-like structure. However, no particles can be found on the membrane surface. After 1 h of exposure to the silicate solution, the first few silica particles can be observed, indicated by the arrows in Fig. 3. They are sphere-like particles with a diameter of 20–30 nm. After 4 h, a larger number and also clustering of the particles on the membrane surface was observed, which is in good agreement with the results of the determination of soluble silica, indicating that after 4 h more than 50% of the initial silica has already polymerized (results not shown here). After 9 h (Fig. 3, right), the surface of the membrane is densely covered with silica particles of the same size (20–30 nm). However, a certain assembly of the particles in the “valleys” of the membrane can be observed. These results indicate that the polymerization of silica at pH 7 proceeds via a spontaneous polymerization of silica giving a large amount of silica particles, comparable to spontaneous nucleation in inorganic crystallization. These particles then grow simultaneously up to a size of 20–30 nm, whereas no further growth could be observed afterwards. This fact can be explained by depletion of silica in the solution at the early stages of

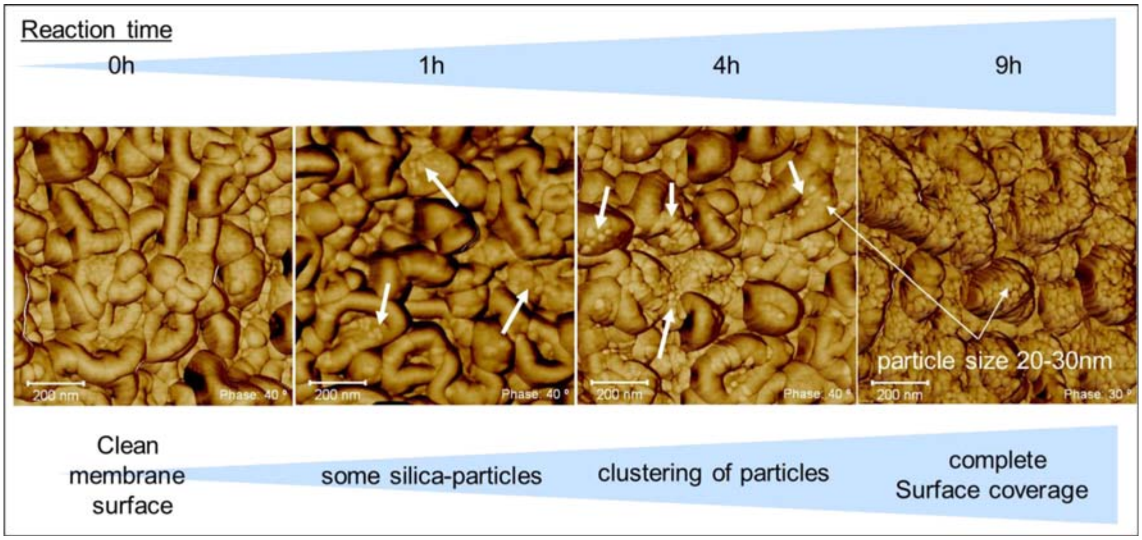


Fig. 3. Time-resolved AFM studies of the adsorption of silica onto membrane surface under hard water conditions. After 1 h, few small silica particles are observed, whereas their number increased after 4 h. Additionally, cluster formation occurs. After 9 h, the surface is densely covered with silica particles of the same size as seen at 1 h and 4 h, indicating no further growth of particles formed in solution.

polymerization thus allowing no further growth. We currently are investigating this phenomenon with time-resolved light scattering experiments to further elaborate on this hypothesis.

3.3. Polymeric inhibitors

Polymeric scale inhibitors are commonly used in water treatment applications to prevent scaling of inorganic materials. Effective silica polymerization inhibitors are reported to be cationic-based polymers and copolymers [5], also under geothermal conditions [7]. Demadis and Neofotistou evaluated the performance of polyaminoamide-based dentrimers as well as polyoxazoline polymers as inhibitors for cooling water applications [8]. They found that inhibitor performance strongly depends on the branching of the dentrimer. For RO, Amjad et al. investigated the performance of a number of polymers for scale inhibition [5]. They found, that commonly used polymeric inhibitors with different functional groups (homopolymers, copolymers, and terpolymers with carboxylic acid, sulfonic acid, ester, and nonionic functional groups) of variable molecular weight are usually poor silica inhibitors. Enhanced adsorption onto amorphous silica of a multipolymer with balanced hydrophilic/hydrophobic functional groups was reported by Hann et al. [9] The sulfonate and carboxylate groups of this polymer are thought to increase the dispersancy, whereas the hydrophobic groups prevent silica particles, once adsorbed, from agglomeration by steric repulsion. Under a different topic, Belyakova et al. recently investigated the adsorption and binding of the non-ionic polymer PVP onto the surface of dispersed silica particles. They found, that PVP is not only reversibly grafted (via hydrogen bonding between the surface of hydroxylated silica and electron-donor centers of PVP), but partly also irreversibly grafted (about ¼ of monolayer) [10]. Additionally, Spinde et al. [11] investigated the polymerization of silica in presence of PVP. Their ^{29}Si-NMR results indicate that PVP is able to stabilize monomeric as well as dimeric and disilicic acids through short-lived C=O – HOSi hydrogen bond complexes. These results indicate that non-ionic polymers with electron donors can possibly work as silica inhibitors in water treatment applications.

We therefore decided to study nonionic polymers like PVP and polyethers with proton acceptor functionality as potential inhibitors under hard water conditions at pH 7 and 8. According to our results (Fig. 4), there is an optimum dose rate for polyethers at pH 7 in the range of 25 ppm, leading to an inhibition of silica polymerization and keeping about 434 ppm of silica soluble. At higher dose rates (50 ppm), the inhibition slightly decreases to 342 ppm. This adverse effect on inhibition activity has also been observed for polyethyleneimine (PEI) polymers. It was suggested that at pH 7, the amines are protonated, thus rendering the polymer positively charged which then allow the polymer to interact with negatively charged silica particles and leading to PEI-Silica precipitates [12]. In the case of polyethers, we also observe precipitation in the form of colorless flocks in all our experiments. As evident from elemental analysis, the precipitate mostly consists of silica, however, a significant amount of organic material (as evident

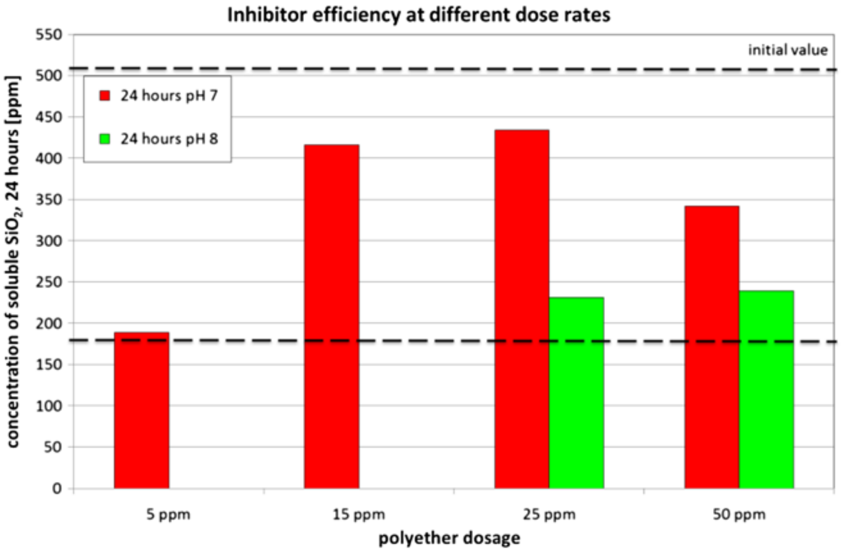


Fig. 4. Inhibitor performance of a polyether used at different dosing levels.

from carbon detection via elemental analysis in the precipitate) being incooperated. Since the used polyethers do not contain amines, the mechanism for inhibition and stabilizing of silica as well as flock formation must be different to those suggested for PEI (see below). Nevertheless, it can be concluded, that the formation of precipitate leads to a decrease of inhibitor in the solution thus lowering its inhibition activity when overdosed.

At pH 8, however, almost no inhibition activity after 24 h is observed for polyethers independent on the dose rate (Fig. 4). This finding can be explained by assuming a change in the mechanism of silica polymerization between pH 7 and 8 or additional effects as explained later.

We further studied the impact of molecular weight on the inhibition activity of the polyether polymers. According to our soluble silica tests after 24 h of polymerization, the inhibitor activity increases with increasing molecular weight of the polymer (Fig. 5). However, there seems to be a critical molecular weight (between 1,000 and 6,000) below which no inhibition function (at the dose rate of 50 ppm) of polyethers is observed. It should be noted that in all experiments with polyethers flock formation and precipitation of silica is observed after ~3 h of experiments.

The same trend regarding inhibitor activity and molecular weight is also observed for different PVP homopolymers and copolymers at 50 ppm inhibitor dosage. For the homopolymers, however, a minimum in inhibitor performance was observed for a molecular weight of ~50 kDa, giving 354 ppm soluble silica after 24 h (Fig. 6). Interestingly, not only the polymers with higher molecular weight (reaching a maximum of 427 ppm at 1,400 kDa) but also low-molecular PVP inhibits silica polymerization at a soluble silica level of ~400 ppm. The PVP-copolymers also show a good inhibitor performance which is slightly better in inhibition than the homopolymers. However, also in the case of PVP polymers, we always observed the formation of flocks throughout the experiments and precipitation of these flocks after several hours, respectively.

3.4. Inhibition mechanism

A possible mechanism for stabilizing silica with PVP polymers was recently presented by Spinde et al. [11]. They found, that at pH 5 and pH 4 mainly monosilicid and disilicid acids are stabilized by PVP via relatively strong C=O···H–OSi bonds, as also suggested by Gun'Ko et al. [13,14] It was further suggested, that for PVP the silicid acid condensation is slowed with the silica oligomers immobilized on the PVP polymer chain. Referring to those results, it is most likely that the proton acceptor functionalities in the polyethers interact with the hydrogen atoms of the silica species in solution, thus stabilizing small silicid acid monomers or oligomers in solution, respectively (Fig. 7). In addition, already formed silica nanoparticles are stabilized by the polyethers thus preventing these particles from nucleating further polymerization of silica. This "trapping" mechanism might also contribute to their inhibition capabilities.

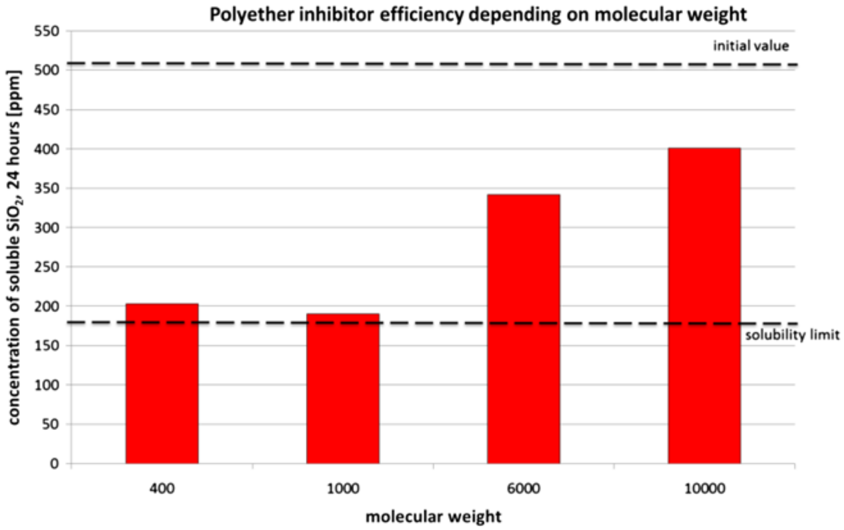


Fig. 5. Inhibitor performance of polyethers with different molecular weights at pH 7.

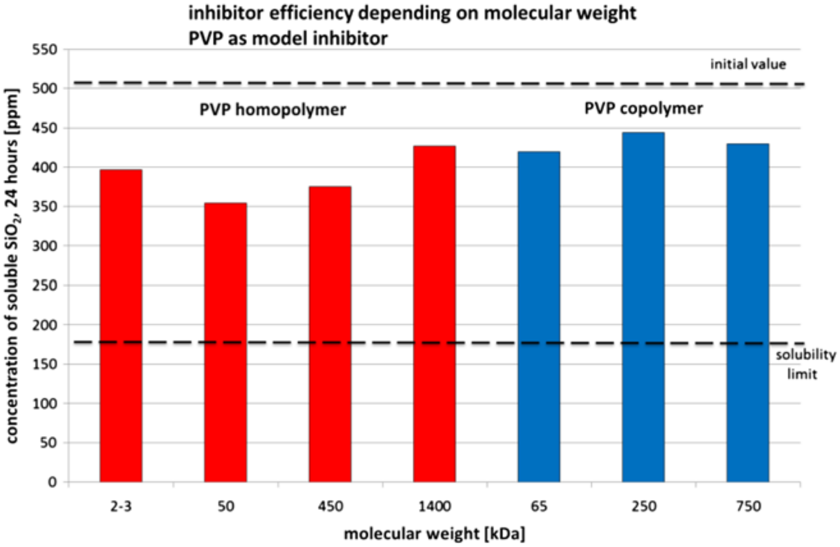


Fig. 6. Inhibitor performance of various PVP-type polymers at pH 7.

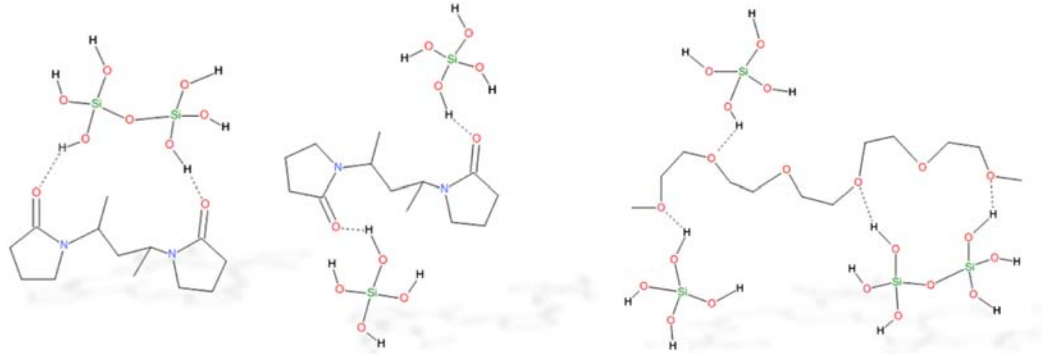


Fig. 7. Possible binding mechanisms for monomeric and dimeric silicid acids on polymers.

Taking these considerations as well as our results for inhibition at pH 7 and 8 into account, the question arises, if a polymeric silica inhibitor like PVP or polyethers showing inhibition at silica levels of 500 ppm and above really “inhibits” the formation of silica. It seems also likely to occur, that at pH 7 the “reactive” silica level is reduced (e.g. by binding of silicate ions and/or monosilicic and disilicic acids) to a level, where the kinetically stable conditions (soluble silica level ~400 ppm at the given hardness) apply. Since at pH 8 no such kinetically stable region exists, those polymers cannot reduce the silica level to a suitable level and silica polymerization and a drop of soluble silica occurs. Furthermore, it is also possible, that the total hardness in the solution is reduced due to the polymer addition leading to a slower polymerization rate of silica mimicking inhibition after 24 h. This complex question, however, is currently part of ongoing research and cannot be answered yet.

4. Conclusion

We have studied the influence of silica supersaturation on the polymerization of silica in hard water. It was found that supersaturation levels of ~400 ppm (i.e. 2.2-fold supersaturation) SiO_2 in water are kinetically stable, i.e. no precipitate is formed for prolonged times up to 24 h without any additive present. Above this supersaturation level (>400 ppm SiO_2) an immediate precipitation occurs keeping only ~180 ppm silica (thermodynamic equilibrium solubility) soluble. At pH 8, no such kinetic stabilization could be observed.

Additionally, silica polymerization inhibition tests were performed using PVP and polyethers. From these results, it appears that the mechanism of inhibition is the stabilization of monosilicid or disilicid acid on the proton acceptor functionalities of the polymers, therefore reducing the amount of silica to a level whereas kinetic stabilization occurs. Furthermore, already formed silica nanopraticles might be "trapped" by the polymers and their further growth is prevented.

We also investigated the adsorption as well as formation of silica scale on RO-membrane surfaces, for example by means of time-resolved AFM studies. According to our results, the first step of silica precipitation without additives is the formation of colloidal particles in the range of 20–30 nm in the bulk solution which deposit onto the membrane surface. Over time, the surface is densely covered with SiO_2 particles.

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