



SILICA REDUCTION IN REVERSE OSMOSIS DESALTING PLANTS

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ABSTRACT

The chemical pretreatment in the reverse osmosis desalting plants is considered the major part of the whole process. It generally includes lime-soda softening, flocculation, coagulation and acidification. The objective of the softening process is to prevent scaling of membranes in the reverse osmosis units.

Lime softening process affects the deposition of the insoluble silica. Silica will be reduced with the precipitation of magnesium hydroxide in the lime softening. Silica is removed by adsorption on the magnesium precipitates. The addition of sodium aluminate is an effective process to reduce silica content. However, it was observed that the elevation of the pH above 10.2 in the precipitators helps in lowering silica content to a limit that makes the addition of sodium aluminate not necessary.

This paper aims at better understanding of the silica fouling and hence improving silica scale control in reverse osmosis systems. It covers the chemistry of silica removal by lime and soda ash and estimates lime and soda ash requirements for silica removal. The effect of lime dosing on silica removal both in laboratory experiments and field experiments were investigated. The effects of lime dosing and pH in the precipitator will be studied.

Keywords: *Silica Fouling, Silica Scale, Silica Removal, Lime and soda Softening, Pretreatment in Revers Osmosis, Water Treatment Plant.*

1. INTRODUCTION

Silica exists in various forms. The soluble form of silica is initially monomeric, as it contains only one silicon atom. In this form it is often called monosilicic acid. Monosilicic acid is generally deionized at most natural pH levels. At a pH of 8.5 only 10% of the monosilicic acid is ionized and, as the pH reaches 10, 50% is ionized. Polymerization of mono-silicic acid is initiated in the presence of hydroxyl groups when only fractional ionization exists. High degrees of ionization prevent polymerization.

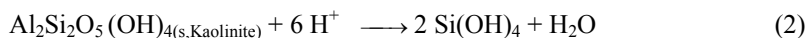
Monosilicic acid remains in the monomeric state for long periods in water at 25 °C, as long as the concentration remains less than about 2×10^{-3} M [Iler, 1979]. At higher concentrations the monosilicic acid polymerizes, usually rapidly, initially to form polysilicic acids of low molecular weight and then larger polymeric species which are in colloidal forms. The colloidal species can also be formed by silicon bonding loosely with organic compounds or with other complex inorganic compounds, usually aluminum and calcium oxide [Comb, 1996].

Amorphous silica is classified in terms of its reactivity. It can be in the form of “dissolved silica” (also referred to as “reactive silica”) or in the form of a colloid (also referred to as “unreactive silica”), or as particulate (also known as “suspended silica”).

Dissolved silica in water exists in hydrated forms as orthosilicic acid ($\text{Si}(\text{OH})_4$) and metasilicic acid (H_2SiO_3). The existence of orthosilicic acid in natural water can be due to the dissolution of siliceous rocks and minerals such as Albite [Werland, 1997] as shown in Eq. (1).



Kaolinite produced in the above reaction may further react with hydrogen and generate more orthosilicic acid:



Another means of orthosilicic acid generation and its presence in water is by dissolution of quartz and amorphous silica:



Silica fouling occurs in reverse osmosis systems when the dissolved silica exceeds its solubility limit and precipitates with other compounds. Any polysilicic acid formed will form silicates in the presence of metals and at suitable pH. The silicate gets more viscous as it sits on the membrane surface and as it dehydrates becomes hard like cement. This formation of silica scale in reverse osmosis systems leads to limited recovery in many installations and unnecessary increase in costs. For this reason, the polymerization of silica, presence and effect of cations and operating conditions on polymerization, and pretreatment are important aspects of mitigating fouling in silica bearing waters.

To reduce the extent of silica fouling in reverse osmosis membranes, the feed water is pretreated for removal of silica. The most common method of silica removal from raw water is by precipitation with polyvalent metal hydroxides; Fe(OH)_3 , Al(OH)_3 , and Mg(OH)_2 are effective in removing both soluble and colloidal silica. Addition of salts lowers amorphous silica solubility but in addition the alkaline environment favours the formation of silicate ion reacting with the metal ions and forming insoluble metal silicates. However, the exact mechanism by which silica is removed by these hydroxides is not sufficiently clear. The amount of hydroxide required for removing silica increases with the silica concentration, but not in direct proportion. Adsorption [Betz et al, 1941 and Foust and Aly, 1983], chemical reaction [Knudsen, 1978] or a combination of both [Mujeriego, 1976] can be responsible for silica removal.

This paper is focused on understanding of the silica fouling to improve silica scale control in reverse osmosis systems. The chemistry of silica removal by lime and soda ash will be reviewed. The effect of lime dosing and pH on silica removal both in laboratory experiments and field tests will be discussed.

2. SILICA REMOVAL BY PRETREATMENT

Silica removal is usually part of a lime-soda softening process where calcium, magnesium and alkalinity concentrations are reduced. Lime softening is considered an effective method to reduce dissolved silica, although its primary purpose is to control water hardness [Bradley, 1993 and Henley, 1992]. Lime-softening reactions [Eqs. (5)–(11)] are listed in Table 1. In the lime softening process, silica will be reduced with the precipitation of magnesium hydroxide. The precipitation of magnesium hydroxide and calcium carbonate is pH-dependent as shown by Powell [Powell, 1954]. The solubility of magnesium hydroxide drops steeply as the pH rises above 9.5 and approaches zero a little below 10.5 [Powell, 1954]. Although the solubility of silica increases with pH, the solubility of the alkaline silicates decreases with increasing pH. Silica is removed by adsorption on the magnesium precipitates. The precipitation and adsorption of silica by magnesium hydroxide is widely used in water treatment technique for silica removal [Hamer et al, 1961 and Semiat et al, 1996]. However, very little attention has

been paid to the increases of absorption of OH^- ions on the silica surface with high pH values [Chan et al, 1993]. The optimal pH for silica adsorption onto $\text{Mg}(\text{OH})_2$ is around 10–11, which coincides nicely with the conditions created during lime softening [Roque, 1996]. Soluble silica can also be removed by magnesium bicarbonate [Eq. (13)].

Table 1 Lime-soda softening and silica reactions

Process	Chemical reactions involved
a) Removal of CO_2	$\text{CO}_2 + \text{Ca}(\text{OH})_2 \longrightarrow \text{CaCO}_3\downarrow + \text{H}_2\text{O}$ (4)
b) Removal of carbonate hardness by lime	$\text{Ca}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 \longrightarrow 2\text{CaCO}_3\downarrow + 2\text{H}_2\text{O}$ (5)
	$\text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 \longrightarrow \text{CaCO}_3\downarrow + \text{MgCO}_3 + 2\text{H}_2\text{O}$ (6)
	$\text{MgCO}_3 + \text{Ca}(\text{OH})_2 \longrightarrow \text{CaCO}_3\downarrow + \text{Mg}(\text{OH})_2\downarrow$ (7)
c) Removal of calcium non-carbonate hardness	$\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3\downarrow + 2\text{NaCl}$ (8)
	$\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3\downarrow + \text{Na}_2\text{SO}_4$ (9)
d) Removal of magnesium non-carbonate hardness	$\text{MgCl}_2 + \text{Ca}(\text{OH})_2 \longrightarrow \text{Mg}(\text{OH})_2\downarrow + \text{CaCl}_2$ (10)
	$\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3\downarrow + \text{Na}_2\text{SO}_4$ (11)
e) Sodium aluminate dissociation	$\text{Al}_2\text{O}_4^{--} + 2\text{H}_2\text{O} \longrightarrow \text{Al}(\text{OH})_3\downarrow + 2\text{OH}^-$ (12)
f) Soluble silica with Mg hardness	$\text{Mg}(\text{HCO}_3)_2 + 2\text{H}_4\text{SiO}_4 \longrightarrow \text{MgSi}_3\text{O}_6(\text{OH})_2 + 6\text{H}_2\text{O} + 2\text{CO}_2$ (13)
g) Hardness removal by sodium aluminate	$\text{Na}_2\text{Al}_2\text{O}_4 + \text{Mg}(\text{HCO}_3)_2 + 4\text{H}_2\text{O} \longrightarrow 2\text{NaHCO}_3 + \text{Mg}(\text{OH})_2\downarrow + 2\text{Al}(\text{OH})_3\downarrow$ (14)
	$\text{Na}_2\text{Al}_2\text{O}_4 + \text{Ca}(\text{HCO}_3)_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{Na}_2\text{CO}_3 + \text{CaCO}_3\downarrow + 2\text{Al}(\text{OH})_3\downarrow$ (15)
	$\text{Na}_2\text{Al}_2\text{O}_4 + 2\text{Ca}(\text{HCO}_3)_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{NaHCO}_3 + 2\text{CaCO}_3\downarrow + 2\text{Al}(\text{OH})_3\downarrow$ (16)
	$\text{Na}_2\text{Al}_2\text{O}_4 + 2\text{CO}_2 + 4\text{H}_2\text{O} \longrightarrow 2\text{NaHCO}_3 + \text{Al}(\text{OH})_3\downarrow$ (17)
h) Removal of silica as aluminosilicate	$\text{Na}^+ + \text{Al}^{3+} + 3\text{H}_4\text{SiO}_4 \longrightarrow \text{NaAlSi}_3\text{O}_8 + 4\text{H}_2\text{O} + 4\text{H}^+$ (18)

Sodium aluminate is a combination of sodium oxide (Na_2O) and aluminum oxide (Al_2O_3 , alumina) and is soluble in distilled water. Alumina, Al_2O_3 , is an excellent adsorbent for dissolved silica. Best result can be obtained if alumina is produced in the solution. Alumina salts (chloride or sulfate) can be dosed into the water where silica content has to be reduced. The formation of fresh alumina in the presence of dissolved silica leads to hydrolysis, formation of Al_2O_3 precipitate and SiO_4 adsorption onto the precipitate. It is suggested to use 4 mol of Al per mole of dissolved silica to be removed [Roque, 1996] and optimum pH of between 8 and 9. In addition, reaction of sodium aluminate with water according to Eq. (12) produces OH^- ions that further promotes precipitation of magnesium hydroxide and hence enhancement in silica reduction. Sodium aluminate also reduces hardness according to Eqs. (14)–(17).

In the presence of colloidal silica (uncreative silica), alumina acts as a catalyst. Much smaller quantities of Al^{3+} will be needed to remove colloidal silica (around 1 mole Al^{3+} per 40 mole of colloidal SiO_2) than to remove the same amount of dissolved silica [Roque, 1996]. The optimum pH range in this case is around 4.1–4.7 [Okamoto et al, 1996].

Aluminum atoms can substitute for silicon in the crystal structure [Okamoto et al, 1996]. The difference in valence (+3 vs. +4) creates negatively charged groups. The negative charge of this microanions, created by the different valences of Al and Si, must be compensated by hydrogen ion or other cations; this will produce aluminosilicate compounds. Not all cations are suited for assuring the electroneutrality of the crystal structure. The charge can be compensated either by monovalent ions such as Na^+ , K^+ , Li^+ or by 8-coordinate divalent cations (e.g. Ca^{++} or Ba^{++}) which supply 2/8 of valence [Okamoto et al, 1996]. The solubility of the Si-O-Si bond in the mineral solution depends on the kind of metallic ions adjacent in the silicate lattice. The solubility increases in the order $\text{K} < \text{Na} < \text{Ca} < \text{Mg}$ [Matthess, 1982]. In lime softening, sodium, calcium and magnesium ions are in abundance and can react with soluble silica in presence of aluminum ions. The formation of albite ($\text{NaAlSi}_3\text{O}_8$) is an example of this reaction [Eq. (18)].

Lime can be used for removal of carbonate hardness while soda ash is required for removal of any non-carbonate hardness. Lime is used in conjunction with soda ash if non-carbonated magnesium hardness is present. So in general when non-carbonate hardness is present, both lime and soda ash are used together and for only carbonate hardness, lime by itself is employed. Values of hardness and total alkalinity are used to obtain the criteria for approximating the type of hardness present and the results are summarized in Table 2 indicating that when total hardness is greater than total alkalinity, simultaneous usage of both lime and soda ash are required. The conventional method for calculating lime and soda ash dosages uses the total hardness, calcium, magnesium, bicarbonate alkalinity, total alkalinity and free carbon dioxide concentrations obtained from laboratory test results and is summarized in Table 3 and the weight conversions obtained from American Water Work

Association, AWWA [AWWA, 1980]. The actual dosages of chemicals are estimated from the stoichiometric ratios required for reaction of lime and soda ash to neutralize all the hardness as discussed above. An excess amount is included in each dosage to insure complete reaction and softening of the feed required.

Table 2 Lime and Soda Ash Requirements Criteria

Criteria		Chemical Required
If Tot. Hard. \leq Tot. Alk	All hardness due to carbonate hardness	Lime
If Tot. Hard. $>$ Tot. Alk	Both carbonate and non-carbonate hardness	Lime and Soda Ash

Table 3 Calculations Method for Lime and Soda Ash

Criteria	Dosage
Tot. Hard. \leq Tot. Alk	Lime = $[\text{CO}_2] + [\text{Total Hardness}] + [\text{Mg}] + [\text{Excess}]$
Tot. Hard. $>$ Tot. Alk	Lime = $[\text{CO}_2] + [\text{HCO}_3^-] + [\text{Mg}] + [\text{Excess}]$ Soda = $[\text{Total Hardness}] - [\text{HCO}_3^-] + [\text{Excess}]$
When non-carb. hardness given	Soda = $[\text{Non-carb. Hardness}] + [\text{Excess}]$

3. EXPERIMENTAL

The experiments were performed both in the laboratory and in the field. The field tests were carried out on the Salbukh water treatment plant and assessed the effectiveness of lime softening and sodium aluminate additions in silica removal. The water treatment plant receives raw water from wells at 50–60°C and the water is cooled down and divided to two streams of “A” and “B”. The main stream “A” undergoes several stages of chemical pretreatment (lime-soda softening, silica reduction by sodium aluminate or pH increase, flocculation and acidification) and filtration before it is being sent to RO modules. The objective of the softening process is to prevent scaling of membranes in the RO units. Coagulation takes place by the addition of ferric chloride or polyelectrolyte anionic polyacrylamid. Sodium aluminate ($\text{Na}_2\text{Al}_2\text{O}_4$) was added to reduce the silica content. Sodium aluminate is also suitable for flocculation of waters rich in carbonate and with high magnesium hardness [Babcok Water Manual, 1982] according to Eqs. (14)–(16). The permeate from the RO modules is being mixed with the stream “B” to produce the product water. The characteristics of the plant water before and after pretreatment are summarized in Table 4.

Table 4 Chemical Analysis of Water in Salbukh Water Treatment Plant

Parameter	Raw Water	RO Feed
pH	8.13	6.19
Temp, °C	60	33
T.Hardness, (mg/l)	718	272
Ca Hard., (mg/l)	426	149
Mg Hard., (mg/l)	292	123
T.Alklinity (mg/l)	143	6
Conductivity, (μS/cm)	2016	2015
TDS, (mg Ion/l)	1450	1450
Sulphate (mg Ion/l)	400	450
Chloride, (mg Ion/l)	294	288
Iron, (mg Ion/l)	0.445	0.022
Silica, SiO ₂ (mg /l)	26.8	7.6
CO ₂ mg/l	9	-
Turbidity, NTU	1.86	0.154

The membranes used in the plant are B-9 hollow fine fiber, HFF, membrane made of aromatic polyamide (PA) with 80 micron outside diameter and a 40-micron inside diameter. These membranes are assembled in Permasep modules of model type 0840-150 and manufactured by DuPont with specifications summarized in Table 5. The chemical treatment utilized in these plants as well as the operating conditions are most important in bringing the silica content down within the RO membrane specifications. Lime softening and high pH levels affect the deposition of the insoluble and colloidal silica. Table 6 shows the pH and silica content of three different samples at different locations in the plant.

Table 5 Specifications of membrane modules used in the plant

Average recovery	85%
Salt rejection	87–92%
Operating pressure range	2415–2760 kPa (340–400 psig)
Operating temperature	25–40°C
pH range	4–11
Average cleaning interval	1.5 years
Module arrangement	4:2:1

Table 6 Variation of pH and Silica in Salbukh Water Treatment Plant

Sample Location	pH values			Silica Content, mg/L		
	s1	s2	s3	s1	s2	s3
raw water before cooling	7.03	6.97	6.97	25.8	26.0	26.0
raw water after cooling	8.01	8.02	8.01	27.1	27.3	27.2
after precipitator	10.25	10.23	10.3	6.95	6.95	7.0
after pri. acidification	6.58	6.48	6.14	6.60	6.70	6.60
Net	8.15	8.08	8.08	5.30	5.30	5.40

4. RESULTS AND DISCUSSION

4.1 Effect of pH in Lime-Soda Softening

Silica concentrations of raw water and softened water were monitored during the softening process. The silica concentration of raw water was about 28ppm. Measurements of silica content of softened water were performed at different pH levels in the precipitator. Eq. (19) was used to calculate the total soluble silica concentration from the data on pH.

$$\frac{S_1 - S_o}{S_2 - S_o} = 10^{pH_1 - pH_2} \tag{19}$$

Where, S1 and S2 are respectively the concentration of total soluble silica at pH1, and pH2. So is the concentration of Si(OH)₄ which is the solubility of silica in neutral water. Fig. 1 illustrates the variation of the silica content with the pH values in the precipitator effluent. Fig.2 shows the percentage removal of silica at different pH values in the precipitator effluent.

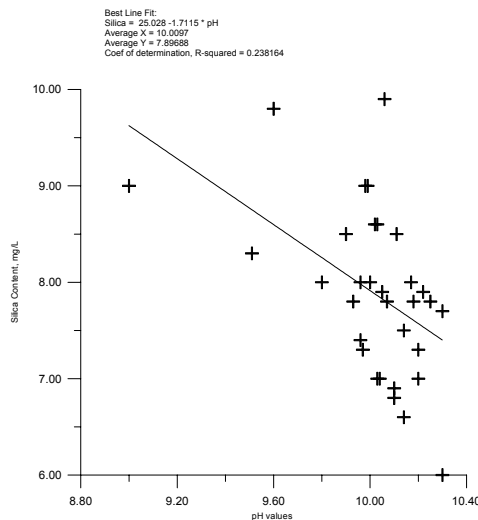


Fig 1 Variation of Silica Concentration with pH values in the Precipitator.

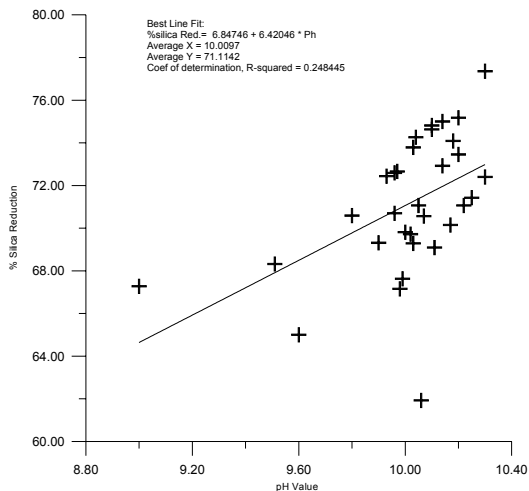


Fig 2 Variation of % Silica Reduction with pH values in the Precipitator.

4.2 Effect of Sodium Aluminate Addition in the Plant

Silica concentrations in the precipitators in the water treatment plant were collected and are plotted in Fig. 3 as a function of sodium aluminate dosing. Silica concentrations of treated water reached a value of 14 mg/l at sodium aluminate dosing of 20 to 21.7mg/l which represented a silica removal of about 50% (raw water had approximately 28ppm of silica). Comparing Figs. 1 and 2, it is evident that the elevation of the pH above 10.2 in the precipitators helped in reducing silica content to a limit which would make the addition of sodium aluminate not necessary. For that reason sodium aluminate addition was stopped.

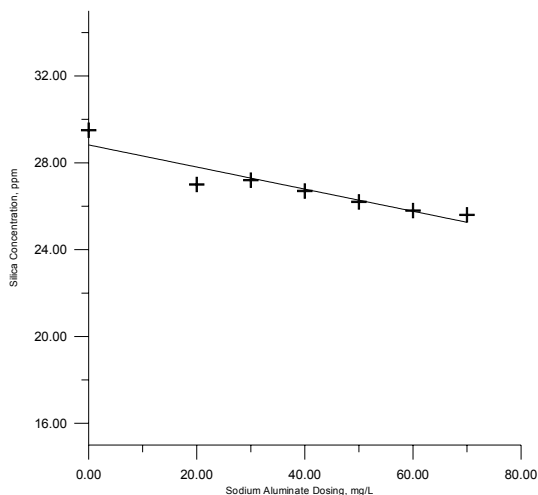


Fig 3 Silica Concentration at various Sodium Aluminate Dosing

4.3 Effect of Lime Addition in the Plant

Silica concentrations in the precipitators in the water treatment plant were obtained during January to April 1999 where both lime and soda ash were added to the plant. The raw water silica concentration was on the average about 28–30 ppm and pH on the average was about 7.9. The lime and ash treatment raised the pH of treated water to an average of 9.9 and silica reductions are plotted as a function of lime and also lime/soda ash in Figs. 4 and 5, respectively. As the lime dosing increases silica concentration in the precipitator decreases. The minimum lime dosing was 102 mg/l where silica concentration in the precipitators are 16.0, 15.6 and 17.0 mg/l corresponding to a reduction in silica as 46.1%, 42.2% and 40.8%, respectively. The maximum lime dosing was 150 mg/l. The silica concentration in the precipitator was reduced to 9.1 mg/l with a reduction of 67.0%. Fig. 4 shows the percentage reduction in silica vs. the lime dosing. Again at higher lime dosing the silica reduction reaches the maximum value of 69.93%. The minimum reduction in silica concentration was 40.77% at lime dosing of 102 mg/l. The ratio of lime to soda dosing shows a scattering effect (Fig. 5) and therefore no particular conclusions could be made.

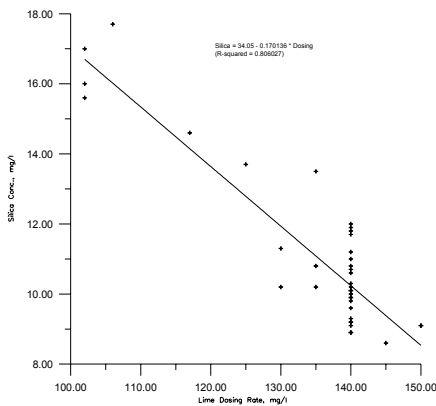


Fig 4 Silica Concentration at Various Lime Dosing in Salbukh Water Treatment Plant.

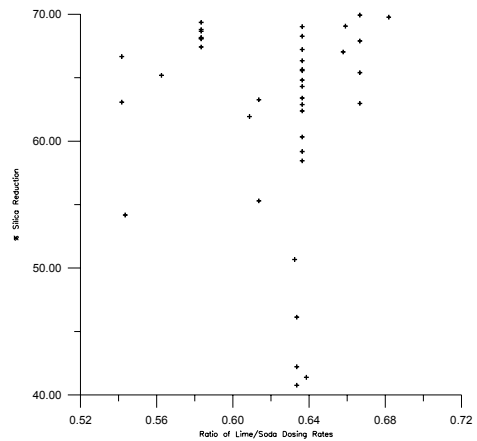


Fig 5 Silica Reduction versus Ratio of Lime to Soda Ash Dosing.

5. CONCLUSIONS

Effect of pH increase, sodium aluminate, lime and soda ash on silica reduction was examined in the field tests and relationships for them were obtained. pH increase in lime softening was much more effective in silica reduction than addition of sodium aluminate and up to 70% reduction in silica was obtained ay pH of 10.2 as opposed to 50% reduction with sodium aluminate at about 22 ppm dosing rate. Hence the sodium aluminate addition was

discontinued. Increase in lime dosing, increased silica reduction but no clear relationship between silica reduction and lime/soda-ash was obtained. Lime dosing of 150 ppm was also able to reduce the silica by about 70%.

The effect of silica removal examined with actual field waters in the laboratory indicated that lime, soda ash and sodium aluminate were not as effective in silica removal as they were in actual field experiments. The reason is attributed to the existence of flocs generated due to addition of flocculants in actual field operations. This indicates the need for addition of flocculants and also stresses the fact that catalytic effects are significant in silica polymerization. In addition, it highlights that in order to examine the effectiveness of a silica removal strategy, it is not sufficient to monitor only the presence of precipitants; presence of flocculants as well as catalytic effects are of great importance.

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