

# Silica Scaling in Water Treatment: Mechanism and Mitigation

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## Abstract

Managing the silica scaling is a challenging task in reverse osmosis and thermal desalination process. Silica scaling is governed largely by amorphous silica deposition, polymerisation of monosilica and deposition of metal silicate. The mitigation of silica scaling in process shall consider all three types of silica scaling.

It is well known that condition of scaling for these three types silica scale are very different. While amorphous silica and polysilica scale are mostly mitigated with high pH condition, metallic silicate e.g. Al, Ca, Mg-  $\text{SiO}_4$  starts to precipitate from pH 9.5.

The difference in silica scale behaviour in temperature also causes more challenge in silica mitigation in water treatment, particularly in thermal process. The mono silica and poly-silica showed a normal solubility, i.e. the solubility of the species increases with the temperature. Therefore, for amorphous silica, the highest scaling potential will happen at lower temperature process, e.g. flash chamber ( $\sim 50^\circ\text{C}$ ) of multi-effect distillation (MED). However, the metallic silicate such as Ca-  $\text{SiO}_4$ , Al-  $\text{SiO}_4$ , Mg-  $\text{SiO}_4$  demonstrates the invisible solubility. The potential of scaling will be more severe at high temperature process, e.g. effect -1 of MED.

To better manage the silica scaling issue, brine speciation in different stage of process needs to be simulated to paint a better picture of scaling. This will give an indicator of scaling tendency (thermodynamics) in the different stage of process.

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## Introduction

Scaling is a significant process and flow assurance issue for water treatment facilities. Normally, calcite and other sulphate and carbonate scale are attracted most of attention. While the sulphate and carbonate based scale can be managed through ion exchange by removing alkali earth metal ions, silica will normally remain in the water and cause scaling issue downstream. The impact of silica scaling becomes more eminent in

desalination process. There are three types of silica scaling:

- i) mono silica scaling
- ii) Polymerisation of mono silica
- iii) Metal silicate scaling, e.g. Al-  $\text{SiO}_4$ , Mg- $\text{SiO}_4$ ,  $\text{CaSiO}_4$  and Fe- $\text{SiO}_4$  etc

Chemistry of silica scaling is critical to the mitigate the silica scaling issue in thermal process, e.g. multi-effect distillation (MED) (Al-Shammiri, 1999), as well as reverse osmosis process.

## Silica Scaling Mechanisms

### Amorphous Silica scaling

Amorphous silica scale can be formed in one of following situation:

- 1) Concentrating an under-saturated solution by evaporation
- 2) Cooling a hot saturated solution
- 3) Lowering the pH of an aqueous solution of a soluble silicate below about 10.7

Different to the other popular types of scale, amorphous silica shows normal solubility. Its solubility increases with the temperature. Therefore, the most threat shall be in the process where the lowest temperature is present, e.g. downstream flash chamber.

Silica solubility with temperature can be expressed

$$\text{Log } C = -731/T + 4.52,$$

in which C, ppm SiO<sub>2</sub>, T, K, absolute temperature

### Silica polymerisation

Polymerisation occurs when SiO<sub>2</sub> over 200-300 ppm and no receptive solid surface for the deposition. It was reported polymerisation occurred at pH 7-10 in the absence of salt. (Bouguerra, 2007)

- *Nucleus on deposition (kinetic concern)*

It was reported that nucleus condition having great influence on silica polymerisation rate. At pH 9.0 and 22°C, with nucleus of 8 nm silica sol, silica gel is deposited at very high rate of 500 ppm/hr. while with no presence of nucleus, only 15 ppm/hr of deposition rate was observed at supersaturation was about 200 ppm or three fold of saturation.

This indicated that by controlling the nucleus, it is possible to control the rate of deposition

of colloidal silica. Once nucleus is present, the deposition rate could be spontaneously higher.

- *Electrolyte effect*

In geothermal brine, deposition of silica could be in the order of magnitude faster than deposition of molecular silica. It is the colligations of colloidal particles rather than deposition of monosilica under such condition, e.g. presence of coagulation agent, usually small concentration of polyvalent metal ions or high content of monovalent ions ( 0.3M NaCl)

Cooling water containing more than 300 ppm silica did not deposit a scale if calcium ions were first converted to soluble chelates. Otherwise a deposit of colloidal silica associated with calcium carbonate was formed.

- *Polymerisation mechanism*

Polymerization of silica monomer to form particles is observed with the sequence of following steps

- 1) Polymerisation of monomer to form particles
- 2) Growth of particles
- 3) Linking of particles into branched chains to form gel

At pH>7, where silica begins to dissolve as silicate, the silica particles are negatively charged and repel each other. Therefore, the particles' growth continue without aggregation. However, aggregation will occur if salt is present (0.2 ~0.3mol/L) (Iler, 1987)

### Metal Silicate Scaling

- *Al-silicate*

SiO<sub>4</sub>-Al is "inverse" solubility like CaSO<sub>4</sub> and CaCO<sub>3</sub>, where high process temperature has the most severe threat. At pH 9.0, initial 35 ppm monomeric SiO<sub>2</sub> addition for 20-100 ppm of Al<sup>3+</sup> reduced the concentration production

$[Al^{3+}, ppm][SiO_2, ppm]=300$ , At pH7~8, presence of 0.04~0.10 ppm Al in solution will precipitate amorphous silica, this is more affect the colloidal silica rather than mono silica.

The precipitate Al with soluble silica is optimum at pH 8-9: 20 ppm Al will reduce 100 ppm  $SiO_2$  to 3 ppm. For pH range 5-11, 4 parts of AL are required for 1 parts of  $SiO_2$ . Widely diverse observation suggested complexity of alumina-silica system. This suggested the precipitation of Al-  $SiO_4$  is not a stoichiometric combination. It may co-deposit large quantity of  $SiO_4$

DOW recommend  $Al^{3+}$  less than 0.05 mg/L for FILMTEC to avoid the Al-silicate fouling even silica level is below the saturation (DOW Tech Manual Excerpt).

Higher pH reduces the risk of scaling of Al-silicate as long as it won't promote precipitation of Mg, Ca-silicate (Gunnarsson, Sep, 2003). It was reported that EDTA and citrate will react with the excess  $Al^{3+}$  to inhibit the formation of Al-  $SiO_4$ . However, phosphonate based antiscalant (commonly used for calcite or sulphate scaling) will promote the Al-  $SiO_4$  scaling despite the presence of EDTA and/or citrate (Gabelich, 2005).

- *Mg, Ca-silicate*

Similar to  $SiO_4$ -Al,  $CaCO_3$  and  $CaSO_4$ , Mg, Ca-silicate also show inverse solubility. Therefore the potential for the threat is higher temperature process, e.g. effect 1 of MED, in which the temperature is as high as ~90°C.

The magnesium silicate system is highly pH dependent. Below pH 7, essentially there is no chance of precipitation. Above pH, Magnesium silicate is very likely to form due to reactive silicate ions are formed. (Meyers, IWC-99-64) The temperature is important; precipitation begins at a lower pH if the

temperature is sufficiently high. Comparing to Calcium silicate, magnesium silicate has low solubility in warm waters at a high pH level.

Co-precipitation of  $Mg(OH)_2$  and colloidal silica has also been observed.  $Ca^{2+}$  and  $Mg^{2+}$  are also the catalyst for silica polymerisation reaction.  $Mg^{2+}$  has greater impact than  $Ca^{2+}$ , which indicated higher pH promotes the scaling of M-  $SiO_4$ .

Formation of Mg- $SiO_4$  is a two-step process, under relatively high pH conditions,  $Mg(OH)_2$ , which is an inversely soluble with respect to temperature, the precipitation can take place near the surface of the heat transfer. As a deposition on a solid surface,  $Si(OH)_4$  condenses with any pre-existing solids surface that bears OH groups or any MOH surface, where M is a metal that will form silicate at the pH involved. The process occurs at range of pH7 to pH 11. Deposition is usually carried out at pH above 8 and it progresses faster at high pH until 11. The presence of sodium chloride (0.2N NaCl, 7,000 ppm Cl, 4600 ppm Na) monovalent electrolyte will accelerate deposition. If the silica concentration exceeded about 240 ppm, scale formation occurred when calcium was present and deposition rate was over 100 times faster than would be possible if the silica alone were involved

In a cooling tower operating at a pH level of less than 7.5, soluble silica generally is maintained below 100 ppm as  $SiO_2$ . For a pH level higher than 7.5, soluble silica should be maintained below 100 ppm (as  $SiO_2$ ) despite the high solubility of  $SiO_2$  at higher pH. It is due to the factor of potential of deposition of Mg- $SiO_4$  and Ca-  $SiO_4$

Rough guideline for Mg-  $SiO_4$  control (Amjad, 2010)

pH region	Mg (as CaCO <sub>3</sub> ) xSiO <sub>2</sub>	SiO <sub>2</sub>	Comments
<7.5	< 40,000 ppm <sup>2</sup>	Reactive SiO <sub>2</sub> < 200 ppm	Mg- SiO <sub>4</sub> usually not precipitate
7.5~8.5	<12,000 ppm <sup>2</sup>	Reactive SiO <sub>2</sub> < 150 ppm	Onset of precipitation
>8.5	<3,000 ppm <sup>2</sup>	Reactive SiO <sub>2</sub> < 100 ppm	High risk pH range

Please notice that Mg here is displayed as ppm of CaCO<sub>3</sub>, a conversion factor of 4.1 should be used. This indicates 4.1 ppm of Mg<sup>2+</sup>(as CaCO<sub>3</sub>) in this table equivalent to 1ppm of Mg<sup>2+</sup> in solution

- *Interaction between different types of scales*

In an environment in which CaCO<sub>3</sub> or other mineral precipitate is prevented completely, higher silica levels generally are tolerated in the process water as opposed to those environment in which other scales are controlled ineffectively. (Amjad, 2010) Suppression of calcium carbonate scale will be beneficial to remove crystalline matrix in which silica can be entrapped and grown on it (Amjad, 2010).

## SiO<sub>2</sub> and Hardness Removal

### Activated alumina

- *pH dependent*

It was reported that activated alumina ion exchange process is efficient in silica removal. The process is strongly pH dependant. An optimum silica removal process can be achieved at pH 8.0-8.5 (Bouguerra, 2007).

- *Leaching of aluminium in normal operation*

It was reported Aluminium in activated alumina can be leached through high pH process condition, which is preferable for silica removal. Both high pH and F in RO brine contribute to the leaching of aluminium from alumina. Over 1 ppm of aluminium leaching is

expected. This leachant will result in metal silicate scaling if the process pH is high.

- *Loss of capacity in regeneration*

It was reported that regeneration of alumina (for fluoride removal) with 4% of caustic soda resulted in 5~10% alumina loss. The capacity of the remaining medium is reduced by 30~40%. The medium has to be replaced with 3~4 regenerations.

## Conclusion

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metallic silicate such as Ca- SiO<sub>4</sub>, Al- SiO<sub>4</sub>, Mg- SiO<sub>4</sub> demonstrates the invisible solubility. The potential of scaling will be more severe at high temperature process, e.g. effect -1 of MED.

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Silica scaling is not easily mitigated by simple pH adjustment. For example, operating at a high pH generates the problem of magnesium silicate scale, lowering the pH shifts the magnesium silicate to amorphous silica deposition. In the presence of nucleus, polymerisation of monosilica will occur to form the sol gel aggregation.

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