Silica pretreatment for a RO brackish water source with high magnesium

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Abstract A brackish water source containing high magnesium concentration (333 mg/L as CaCO3) for reverse osmosis (RO) was studied for silica scaling. Threshold limit for RO recovery and required silica removal were firstly determined by a removal–saturation–recovery curve. Three different ratios of lime/soda ash combination were used to test the efficiency of silica removal as well as the impact of calcium and magnesium. Higher pH was more effective for silica removal due to electrostatic attraction since \( \text{H}_2\text{SiO}_3^- \) and \( \text{H}_2\text{SiO}_4^2^- \) were dominant when pH > 9.9. The precipitation of \( \text{Mg(OH)}_2(s) \) has assisted more for silica removal than that of \( \text{CaCO}_3(s) \) and the ratio of 0.044 mg SiO\(_2\)/mg \( \text{Mg(OH)}_2(s) \) and 0.027 mg SiO\(_2\)/mg \( \text{CaCO}_3(s) \) were statistically determined. Moreover, the presence of high magnesium causes \( \text{Mg(OH)}_2(s) \) to precipitate at lower pH (9.41) instead of formation of forsterite (\( \text{Mg}_2\text{SiO}_4(s) \)), which typically occurs at pH > 12.3. Therefore, no forsterite was observed and was verified by X-ray diffraction (XRD) analysis. Consequently, adsorption is more dominant than chemical reaction in this study. Silica removal was also enhanced by coagulation. With the addition of coagulant (PACl), highest silica removal was achieved at pH of 10, but was decreased when the pH was over 10, due to the amphoteric properties of aluminum hydroxide to reduce the electrostatic attraction to silica at higher pH. Since both softening and coagulation were effective for silica removal, seven decision-making criteria were developed to compare the pros and cons of these two processes.

Keywords Forsterite; magnesium; silica scaling; softening; XRD

Introduction

Silica scaling is a common problem encountered in membrane separation processes due to its low solubility of about 100–140 mg/L in amorphous form. Presence of silica in water is due to the dissolution of silica to become silicate based on the following reaction: \( \text{SiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 \). The most common method of silica removal is by precipitation with polyvalent metal hydroxides at high pH, such as: \( \text{Fe(OH)}_3 \), \( \text{Al(OH)}_3 \), and \( \text{Mg(OH)}_2 \). Adsorption, chemical reaction or both are responsible for silica removal (Darton, 1999; Sheikholeslami and Tan, 1999; Bremere et al., 2000; El-Manharawy and Hafez, 2000; Sheikholeslami and Zhou, 2000; Taleb-Ahmed et al., 2002; Semiat et al., 2003). The adsorption of \( \text{Mg(OH)}_2(s) \) and \( \text{CaCO}_3(s) \) for silica removal has been studied by varying the ratio of calcium and magnesium (Sheikholeslami and Zhou, 2000). Both species were proven functional for silica removal but the higher ratio of Mg/Ca at constant total harness achieved higher silica removal, indicating the precipitation of \( \text{Mg(OH)}_2(s) \) has assisted more for silica removal than that of \( \text{CaCO}_3(s) \). In addition, silica could also be precipitated as \( \text{Mg}_2\text{SiO}_4(s) \) or \( \text{Ca}_2\text{SiO}_4(s) \). Sheikholeslami and Bright (2002) propose a possibility where silica was removed due to formation of \( \text{Mg}_2\text{SiO}_4(s) \) (forsterite) from a strong chemical bonding between silicate and magnesium, or \( 2\text{Mg}^{2+} + \text{SiO}_4^{4-} \rightarrow \text{Mg}_2\text{SiO}_4(s) \), instead of adsorption by \( \text{Mg(OH)}_2(s) \). \( \text{SiO}_4^{4-} \) becomes more predominant at pH greater than 11, which would favor the formation of forsterite. The author did not mention the mechanism of \( \text{Ca}_2\text{SiO}_4(s) \) formation, but \( \text{Ca}_2\text{SiO}_4 \) would...
be less possible to form unless no alkalinity is presented to precipitate calcium. On the other hand, testing on coagulant was also conducted. Alum addition to an optimum lime and soda ash dosage did not significantly improve silica removal (Sheikholeslami and Bright, 2002). However, in another study, precipitation aids such as alum, sodium aluminate, or ferric chloride were found necessary for improving performance of the lime-soda ash process to reduce silica to the acceptable level (Al-Rehaili, 2003).

From the above study, silica removal by either adsorption or chemical reaction is not clearly distinguished as the formation of Mg$_2$SiO$_4$(s) was never analyzed. Also, the removal mechanism by either calcium carbonate or magnesium hydroxide was described but not qualitatively determined. Moreover, the presence of high magnesium concentration in this study would be favorable for silica removal. Therefore, three major issues are discussed in this article: (1) Development of a removal–saturation–recovery curve to determine the threshold limits of RO recovery and silica removal; (2) qualitatively determining the effects of Ca and Mg for silica removal and verifying removal mechanism by XRD; (3) determining the enhanced effect for silica removal by adding coagulant. In addition, seven decision-making criteria were also developed to compare the advantages and disadvantages of softening and coagulation processes for silica pretreatment for RO membrane process.

**Methods**

The raw water is obtained from a brackish groundwater source for a 600 CMD drinking water treatment plant located in Penghu County, Taiwan. This water treatment plant uses RO membrane process, but silica is the limitation for water recovery due to the possibility of scaling. BW30-400 membranes from Dow-Filmtec Company are currently used in this plant. The raw water qualities were listed in Table 1. As seen in Table 1, the water has very high hardness, especially for magnesium. Silica is not extremely high but can easily exceed the solubility at high recovery. Therefore, the intention is to pretreat hardness and silica at same time. Standardized jar testing procedures were established which mimic as best possible plant operating conditions while optimizing conditions for hardness and silica removal. Rapid mix was performed for 30 seconds at 100 rpm, whereas slow mixing conditions for floc formation were carried out for 15 minutes at 30 rpm. These mixing speeds for rapid and slow mix correspond to velocity gradients ($G$) at 25 °C of roughly 33 and 350 s$^{-1}$, respectively. Samples for analysis were collected from each jar following a 5 minute settling period. These samples were collected at roughly 10 cm below the water surface with the jar. Upon collection, the samples were filtered with 0.45 micron glass fiber filter paper. All chemicals used are of reagent grade. pH was adjusted by either caustic soda or hydrogen chloride. Silica was measured according to the methods 4500-SiO$_2$ listed in the 20th edition of the *Standard Methods* (1999), using a UV-Vis spectrophotometer (HACH Model DR-4000). The calcium and magnesium concentrations were measured by an ion chromatography (DIONEX ICS-90). Crystal structures of the precipitated species were analyzed by an X-Ray Diffraction, a DMAX 2200 VK type manufactured by Rigaku Co. in Japan.

<table>
<thead>
<tr>
<th>pH</th>
<th>SiO$_2$ (mg/L)</th>
<th>Magnesium (mg/L as CaCO$_3$)</th>
<th>Calcium (mg/L as CaCO$_3$)</th>
<th>Alkalinity (mg/L as CaCO$_3$)</th>
<th>chloride (mg/L)</th>
<th>TDS (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.8</td>
<td>21</td>
<td>333.3</td>
<td>221</td>
<td>225</td>
<td>1,550</td>
<td>3,451</td>
</tr>
</tbody>
</table>
Results and discussion

Determination of threshold limits for water recovery and silica removal

The optimum operation for water recovery and silica removal was determined based on the solubility of silica. For chemistry of amorphous silica, Equations 1–3 were the three most important equations. Based on Equation 1, the solubility is $10^{-2.74}$ M or 120 mg/L when pH is less than 9.5, where silicic acid, Si(OH)$_4$ or H$_4$SiO$_4$, was dominant. When pH is greater than 9.5, where H$_3$SiO$_4$ was predominant, the solubility becomes $10^{pH-12.64}$ M. Typically, the pH entering RO should be controlled to much lower than 9.5 to prevent the scaling of calcium carbonate.

$$\text{SiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 \quad K = 10^{-2.74}$$  \hspace{1cm} (1) \\
$$\text{Si(OH)}_4 \rightarrow \text{H}_2\text{SiO}_4^- + \text{H}^+ \quad K_1 = 10^{-9.5}$$  \hspace{1cm} (2) \\
$$\text{H}_3\text{SiO}_4^- \rightarrow \text{H}_2\text{SiO}_4^2^- + \text{H}^+ \quad K_2 = 10^{-12.3}$$  \hspace{1cm} (3)

Equation 4 can be developed to determine the threshold limits of optimum operation, where $a$ is the fraction remaining in the concentrate stream and $X$ is the operated water recovery for the RO membrane.

$$\text{Solubility} = \left( \frac{a[\text{SiO}_2]}{1 - X} \right) = \left[ a \times \frac{21 \text{ mg/L}}{1 - X} \right] = 120 \text{ mg/L}$$  \hspace{1cm} (4)

A silica removal–saturation–recovery curve was developed and shown in Figure 1 based on Equation 4, where saturation (%) is defined as:

$$\text{Saturation (\%)} = \frac{\text{SiO}_2 \text{ concentration}}{120 \text{ mg/L}} \times 100 \%$$  \hspace{1cm} (5)

In other words, more than 100% saturation in Equation 5 represents solubility is over 120 mg/L, which causes silica scaling. The fraction remaining in the concentrate stream, or the $a$ value in Equation 4, can be predicted by a ROSA program® for the BW30-400 membranes from Dow-Filmtec Company. The result shows, in raw water, or 20% silica removal case, if the water recovery is high, the saturation (%) will exceed 100% and silica scaling will occur. There are two ways to solve the possible silica scaling problems: (1) decrease the recovery to 80%, where the saturation (%) will be less than 100% for raw water; (2) remove the silica concentration at least 40%, where the saturation (%) will be less than 100% even the recovery is 90%. The first method is easier but can only be accepted if less water quantity is allowed. Consequently, in order to achieve the desired recovery of 85%, the targeted SiO$_2$ concentration before entering RO is set up at 10 mg/L, which is equal to 52% removal of silica for the influent. Since this calculation is solely based on thermodynamics, super saturation for silica and concentration polarization for RO membrane can
slightly alter the above calculation but this approach still is the best estimation to predict the possible threshold limits required.

Effects of pH, magnesium hydroxide and calcium carbonate on silica removal

Silica removals were first determined for different pH, as shown in Figure 2. When the pH was less than 9, only less than 20% silica was removed. However, when the pH was greater than 9, the silica removal was rapidly increased to 80% up to pH 12. Based on the solubility products of CaCO₃(s) and Mg(OH)₂(s), it can be determined that for pH < 9, the precipitation of CaCO₃(s) was dominant whereas for pH > 9, Mg(OH)₂(s) was dominant. According to the calculation based on the calcium and magnesium concentration and their solubility product constants, the pHs for precipitation were calculated as 6.72 for CaCO₃(s) and 9.41 for Mg(OH)₂(s). Moreover, for silicate speciation (pKₐ1 = 9.5), uncharged Si(OH)₄ was dominant for pH < 9.5 but charged H₂SiO₄⁻ and H₄SiO₄⁻² were dominant for pH > 9.5. Apparently, the presence of the charged silicate species also favored the reduction of silica. Excellent silica removal at high pH was probably due to the formation of both Mg(OH)₂(s) and charged silicate, where electrostatic attraction between Mg(OH)₂(s) and negative charged silicate could occur. Therefore, high pH softening is proven effective for this water.

Additional experiments were designed to vary lime/soda ash dosages to determine the effect of Mg(OH)₂(s) and CaCO₃(s) on silica removal since lime/soda ash was the most popular softening method in traditional water treatment plants. Lime and soda ash dosage were added based on the fundamental softening equations, where lime is used for raising pH and soda ash is used for providing carbonate. Lime dose (mg/L)/soda ash dose (mg/L) ratios were 1:0, 1:3 and 1:4, with lime dosages varying from 100 mg/L to 300 mg/L and soda ash dosages varying from 0 mg/L to 1,200 mg/L. Therefore, in total 15 batches of jar tests were conducted. Soda ash was added more than lime since in this particular water, the alkalinity was not enough for calcium carbonate to precipitate. The silica removal and precipitated calcium and magnesium for different dosages of lime and soda ash are presented in Table 2, where the precipitated amounts of calcium and magnesium are calculated by subtracting the finished mass of calcium or magnesium from the initial mass of calcium or magnesium.

From Table 2, higher dosages of lime/soda ash and precipitations of calcium and magnesium for higher silica removal are observed. In order to clearly distinguish the results, Figure 3 was plotted to present the silica removal versus different dosages of lime/soda ash. From Figure 3, increases of lime are very effective for silica removal, and an increase of soda ash is also effective from dosage ratio of 1:0 to 1:3, due to enough carbonate sources being provided. It seems that the addition of either lime or soda ash (or both) to form CaCO₃(s) was capable of removing silica. However, the pH increases due to adding lime or soda ash can also contribute the precipitation of Mg(OH)₂(s), especially for the tested water.

![Figure 2: Silica removals for different pH values](https://iwaponline.com/ies/article-pdf/6/4/179/418207/179.pdf)
with high magnesium. The impact of Mg(OH)$_2$(s) and CaCO$_3$(s) on silica removal has been mentioned by Sheikhholeslamian and Zhou (2000), but was not quantitatively evaluated. In order to differentiate between the effects of CaCO$_3$(s) and Mg(OH)$_2$(s) on silica reduction, instead of using percentage removal, Figure 4 plots the silica mass removal (as mg) versus the precipitation amounts of the magnesium and calcium (mg as CaCO$_3$) based on the data in Table 2, since the rejection of silica can contribute to the adsorption onto these two solid species. It is clearly observed that both CaCO$_3$(s) and Mg(OH)$_2$(s) are directly correlated with silica mass removal, and less Mg(OH)$_2$(s) was capable of removing the same amounts of silica, corresponding to the previous study. In order to quantitatively determine the effects, a multiple regression approach using Statistica® to derive an equation based on the experimental data is shown in Equation 6:

\[
\text{Silica removal} = -9.13 + (0.028 \times \text{CaCO}_3(s)) + (0.045 \times \text{Mg(OH)}_2(s))
\]  

(6)

With $R^2 = 0.851$ for Equation 6, it is able to describe the effect of Mg(OH)$_2$(s) and CaCO$_3$(s) on silica removal. In this equation, the minus sign for the intercept term may represent the dosage or precipitation amount of calcium and magnesium. If it is too low, no silica removal will be achieved due to no nucleation forming in this groundwater with almost no turbidity. Therefore, the ratio of 0.045 SiO$_2$/Mg(OH)$_2$(s) and 0.028 SiO$_2$/mg

<table>
<thead>
<tr>
<th>Dosage ratio (mg/L of lime / mg/L of soda ash)</th>
<th>Silica removal (%)</th>
<th>Precipitated amount (mg as CaCO$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Magnesium</td>
</tr>
<tr>
<td>100/0</td>
<td>9.2</td>
<td>73.6</td>
</tr>
<tr>
<td>150/0</td>
<td>10.1</td>
<td>99.1</td>
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<tr>
<td>200/0</td>
<td>17.7</td>
<td>112.2</td>
</tr>
<tr>
<td>250/0</td>
<td>39.8</td>
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</tr>
<tr>
<td>300/0</td>
<td>61.5</td>
<td>163.8</td>
</tr>
<tr>
<td>100/300</td>
<td>13.1</td>
<td>96.0</td>
</tr>
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<td>150/450</td>
<td>13.5</td>
<td>139.2</td>
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<td>200/600</td>
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</tr>
<tr>
<td>250/1,000</td>
<td>54.9</td>
<td>172.1</td>
</tr>
<tr>
<td>300/1,200</td>
<td>65.0</td>
<td>154.9</td>
</tr>
</tbody>
</table>

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Figure 3 Silica removals for different ratios of lime and soda ash dosage

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Table 2 Silica removal and precipitated calcium and magnesium for different dosages of lime and soda ash

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Figure 4 Silica mass removal (as mg) versus the precipitation amounts of the magnesium and calcium (mg as CaCO$_3$) based on the data in Table 2.
CaCO₃(s) were statistically determined once the dosage was capable of passing through the nucleation stage. Thus, the presence of high magnesium concentration is beneficial for silica precipitation. About 22 mg of Mg(OH)₂(s) can remove 1 mg of silica (1 mg Si/8.8 mg Mg) and 36 mg CaCO₃(s) can remove 1 mg of silica (1 mg Si/14.4 mg Ca). This result is also close to literature values, where 7 ppm of magnesium to 1 ppm of silica was reported (Faust and Aly, 1998).

Equation 6 can be faulty if one assumption from previous research is true. Sheikholeslami and Bright (2002) propose a possibility where silica was removed due to formation of Mg₂SiO₄(s) (forsterite) from a strong chemical bonding between silicate and magnesium, or 2Mg²⁺ + SiO₄⁻² → Mg₂SiO₄(s), instead of adsorption by Mg(OH)₂(s). Therefore, an XRD test was conducted using the precipitated species at pH 10.5 with silica removal over 80%. The result is shown in Figure 5. Although the formation of Mg₂SiO₄(s) was proposed in the literature, it was not observed by XRD (no corresponding peak for Mg₂SiO₄(s)). It can be attributed to the following reason: the formation of Mg₂SiO₄(s) is theoretically possible but since SiO₄⁻² is only present at pH at least > 12.3 according to Equation 3, SiO₄⁻² will not have the opportunity to form with

![Figure 4](https://iwaponline.com/ws/article-pdf/6/4/179/418207/179.pdf)

Figure 4 Amount of SiO₂ removal (mg) versus precipitated Mg and Ca for different ratios of lime/soda ash

![Figure 5](https://iwaponline.com/ws/article-pdf/6/4/179/418207/179.pdf)

Figure 5 XRD spectra for precipitation species for softening at pH 10.5
Mg$^{2+}$, because Mg$^{2+}$ has been precipitated out at much lower pH values (9.41 for Mg(OH)$_2(s)$ formation in this case). Therefore, the precipitation of Mg(OH)$_2(s)$ occurred before Mg$_2$SiO$_4(s)$. Consequently, in these precipitated species, Mg(OH)$_2(s)$, CaCO$_3(s)$ and silica were still the dominant species, as shown in Figure 5. Therefore, the most probable mechanism is still the adsorption of silica on the surface of Mg(OH)$_2(s)$ and CaCO$_3(s)$ and adsorption is more dominant rather than chemical reaction in this study.

Enhanced silica removal by coagulation

Silica removal could also be enhanced by coagulation. Polyaluminium chloride (PACl) was selected in this study since it is the most popular used coagulant in Taiwan. Figure 6 presents the silica removal versus PACl dosage for pH 4–11. At the point of zero PACl dosage, silica removal was increased as pH was increased. Silica was removed about 80% at pH 11. The addition of PACl was capable of enhancing silica removal for all the pHs other than 11. Therefore, the addition of PACl for silica removal cannot be applied for pH values higher than 10, which causes an adverse effect for silica removal. It can be explained when the pH is lower than 10, the addition of coagulant (PACl) can increase silica removal either by precipitation of Al(OH)$_3(s)$ to absorb the silica or formation of the positive charge polynuclear hydroxoaluminium species to help complexation of slight negative charge species SiO$_4^{2-}$/H$_4$SiO$_4^{4-}$. However, at pH values higher than 10, the negative charge species aluminium hydroxide Al(OH)$_3$ was presented due to the amphoteric properties of aluminium hydroxide. At that pH for silicate species, negative charge H$_3$SiO$_4^{2-}$ and H$_2$SiO$_4^{2-}$ were also dominant. Therefore, the charge repulsion between the two species results in less silica reduction. Therefore, the use of PACl for enhanced silica removal has to be careful for pH not to exceed 10.

Both coagulation and softening process are capable of removing silica but both have their pros and cons. In Table 3, we list seven decision making criteria for users to judge their benefits for silica removal before entering RO membrane.

1. For silica removal efficiency, higher silica removal was seen for softening (80%) compared to coagulation (40%).
2. Softening removes silica and hardness simultaneously, but coagulation cannot remove hardness.
3. For pH adjustment requirement, pH needs to be increased for silica removal for softening, but then the pH needs to be decreased before entering the RO membrane to prevent calcium carbonate scaling. No extreme high pH is needed for coagulation. For example in Figure 6, pH around 8–9 is capable of removing silica to less 10 mg/L for softening.

Figure 6 SiO$_2$ removal versus PACl dosage for different pH values
No magnesium is required for coagulation, but is needed for softening to remove silica.

More sludges are generated for softening since most of existed hardness and added hardness (lime) are removed simultaneously.

For corrosion control, since all the calcium is removed together with alkalinity in the softening process, corrosion problem could occur resulting from low Langelier Saturation Index (LSI).

For cost comparison, using coagulants is cheaper than using softening reagents since coagulation is widely used in many water treatment plants, and one chemical (coagulant) can solve the silica problem instead of two chemicals (lime/soda ash). Moreover, less sludge cost is needed for coagulation.

Consequently, the listed seven criteria can be used for qualitative determination of silica removal processes.

Conclusions

The presence of magnesium in the water was beneficial for silica removal. From the removal–saturation–recovery curve, both decreasing recovery and removing the influent silica concentration can solve the scaling problem, but the latter is more feasible since required water quantity is still maintained. Higher pH values were more effective for silica removal due to electrostatic attraction since $\text{H}_2\text{SiO}_4$ and $\text{H}_2\text{SiO}_4^-$ were dominant when pH $>9.9$. The precipitation of Mg(OH)$_2(s)$ has assisted more silica removal than that of CaCO$_3(s)$ and the ratios of 0.044 mg SiO$_2$/mg Mg(OH)$_2(s)$ and 0.027 mg SiO$_2$/mg CaCO$_3(s)$ were statistically determined. Moreover, the presence of high magnesium causes Mg(OH)$_2(s)$ to precipitate at lower pH (9.41) instead of formation of forsterite (Mg$_2$SiO$_4(s)$), which typically occurred at pH $>12.3$. Therefore, no forsterite was observed and was verified by XRD analysis. Consequently, adsorption is more dominant than chemical reaction in this study. With the addition of coagulant (PACl), the highest silica removal was achieved at pH 10, but was decreased when the pH was over 11, due to the amphoteric properties of aluminium hydroxide to reduce the electrostatic attraction to silica at higher pH. Since both softening and coagulation were effective for silica removal, seven decision making criteria were developed to compare the pros and cons of these two processes.

References


