Silica Removal During Lime Softening in Water Treatment Plant

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Abstract

Silica, SiO_2, is typically found in well water supplies. Most of the silica found in well waters is a result of dissolving silica-containing rock. Silica content in brackish water is generally in the range of 20 to 60 ppm. In Salbukh water treatment plant, silica concentration of raw water is about 30 ppm. High concentration of silica causes membrane fouling in the reverse osmosis units.

During lime softening process calcium and magnesium are precipitated. Calcium is deposited as calcium carbonate while magnesium is deposited as magnesium hydroxide. Upon precipitation, magnesium hydroxide forms larger floc that more readily adsorbs or entraps silica particles in the water. So silica will be removed with the precipitation of magnesium hydroxide in the lime softening by adsorption on the magnesium precipitates. In this paper, silica concentrations of raw water and softened water will be monitor during the softening process in Salbukh water treatment plant. Measurements of silica content of softened water will be performed at different pH level in the precipitator. The effect of lime concentration on silica removal during softening was investigated.

Introduction

Salbukh water treatment plants was on operation since 1979 to supply the city of Riyadh with drinking water by treating deep-well water by reverse osmosis. It is located about 60 km north of Riyadh. It receives raw water from wells field, which contains of 18 deep-wells. The depths of these wells are 1200-1800 m.

The raw water has a high temperature ranging between 60-70 ^{o}C, high hardness, high silica content and high salts concentration. So this water needs cooling and softening to meet membranes specifications, besides desalting to meet drinking water specifications. Table 1 shows the chemical analysis of raw water and RO feed water in Salbukh water treatment plant.

The water treatment process in Salboukh water treatment plant as shown in figure 1 is carried out in two main stages, pre-treatment stage (cooling, sodium, softening, acidifications, filtration and other chemical additions) and post-treatment stages which include desalination, chlorination and water mixing [1-3].

Silica concentration of raw water is usually reduced during a lime-soda softening process where calcium, magnesium concentrations are reduced. Lime softening is considered an effective method to reduce soluble and insoluble silica, although its primary purpose is to control water hardness [4,5]. During softening hardness caused by calcium and magnesium are precipitated as calcium carbonate and magnesium hydroxide.

Silica concentrations of raw water and softened water will be monitor during the softening process in Salbukh water treatment plant. Removal of silica at different lime dosing in the softening will be investigated.
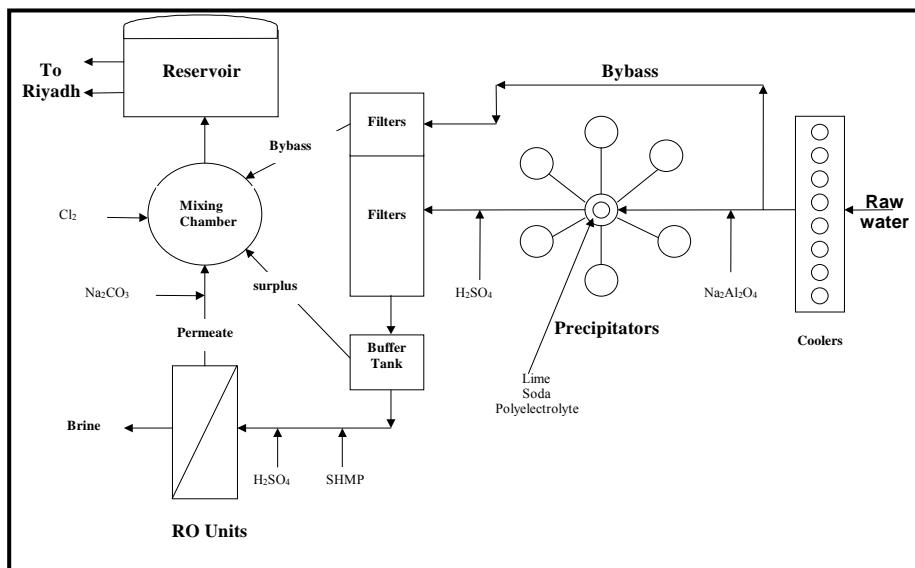

Figure 1 Schematic Flow Diagram of Salbukh Water treatment plant

Lime Softening Process

In Salbukh water treatment plants, lime and soda ash softening process is utilized. Lime ($Ca(OH)_2$) and soda ash (Na_2CO_3) are used for softening. The softening process takes place in six precipitators; only four are working with two as standby. Each precipitator consists of five zones (primary mixing and reaction, secondary reaction, sludge blanket, clarified water zone, sludge concentrators) as shown in figure

2. Lime and soda ash are added into the primary mixing and reaction zone. Each precipitator receives cooled raw water at a rate of 450 m^3/hour with an added fraction of the recycled water from the wastewater tanks. Lime, soda ash and the polyelectrolyte enter the precipitator through a timer that opens for about 10 minutes for each 10 m^3 of input water, i.e. it gives 45 dosing for each hour.

Table 1. Chemical Analysis of Raw Water and RO Feed Water in Salbukh Water Treatment Plant

Parameter	Raw Water	RO Feed
pH	8.13	6.19
Temp, ^{o}C	60	33
T.Hardness, (mg/l)	718	272
Ca Hardness, (mg/l)	426	149
Mg Hardness, (mg/l)	292	123
T.Alklinity, (mg/l)	143	6
Conductivity, (uS/cm)	2016	2015
TDS, (mg ion/l)	1450	1450
Sulfate, (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 objective of lime softening process is to reduce the hardness and thus prevent scaling of membranes in the RO system. Lime–Soda softening reactions can be summarized by the following categories:
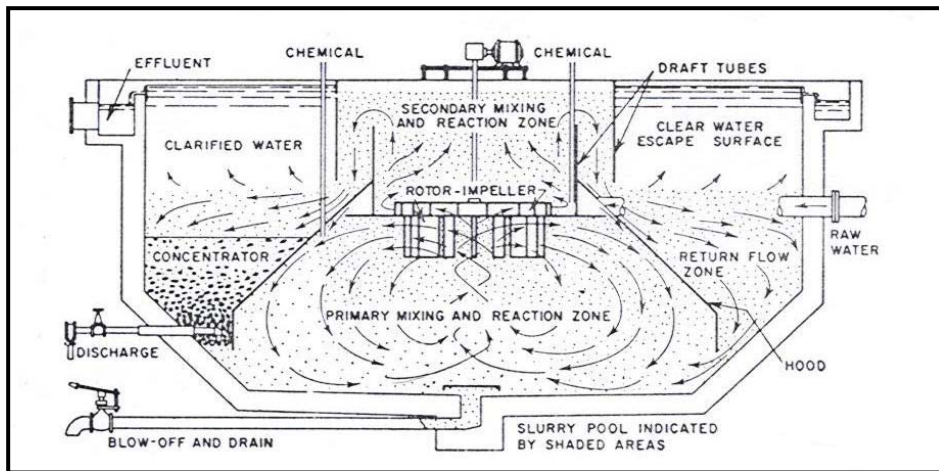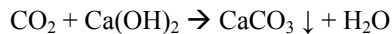

Figure 2 Schematic Diagram of a Precipitat
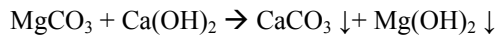
a) Removal of carbon dioxide:
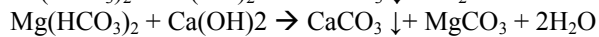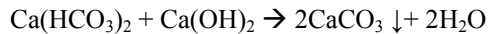The following reaction is completed at pH of 8.3.

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + H_2O$$

or

b) Removal of carbonate hardness:
Carbonate hardness caused by calcium and magnesium bicarbonates are precipitated as calcium carbonate and magnesium hydroxide by the addition of lime, calcium hydroxide $Ca(OH)_2$. Magnesium bicarbonate is first converted to magnesium carbonate at a pH of 9.4. Since magnesium carbonate is soluble, excess lime is added to precipitate it as magnesium hydroxide. The pH is raised to 10.6.
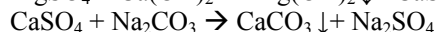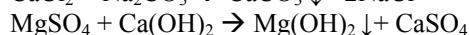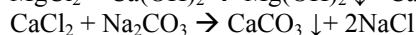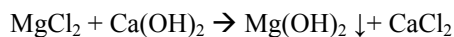
$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$$
$$Mg(HCO_3)_2 + Ca(OH)2 \rightarrow CaCO_3 \downarrow + MgCO_3 + 2H_2O$$

$$MgCO_3 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + Mg(OH)_2 \downarrow$$

c) Removal of calcium non-carbonate hardness:

Non-carbonate hardness caused by calcium sulfate and calcium chloride are precipitated as calcium carbonate by the addition of soda ash, sodium carbonate (Na_2CO_3).

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + Na_2SO_4$$

$$CaCl_2 + Na2CO_3 \rightarrow CaCO_3 \downarrow + 2NaCl$$
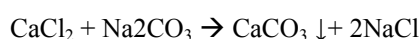
d) Removal of magnesium non-carbonate hardness:

Non-carbonate hardness caused by magnesium sulfate and magnesium chloride are precipitated as magnesium hydroxide by the addition of lime, calcium hydroxide $Ca(OH)_2$. These reactions produce calcium non-carbonate hardness, $CaCl_2$ and $CaSO_4$. So soda ash, sodium carbonate (Na_2CO_3), must be added to precipitate these calcium non-carbonate hardness, $CaCl_2$ and $CaSO_4$, to calcium carbonate.

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow + CaCl_2$$
$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2NaCl$$
$$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow + CaSO_4$$
$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + Na_2SO_4$$

During lime softening silica content is reduced significantly. This is due to the attachment of silica on the surface of the precipitated magnesium ions. At high pH values calcium-magnesium silicates are formed and precipitated.

Results and Discussion

Experimental measurements were performed in the field to find the silica concentration of raw water and softened water in Salbukh water treatment plant. Measurements of silica content of softened water will be performed at different pH level in the precipitator. The field tests were carried out on the Salbukh water treatment plant during 1413H and 1418H to assess in studying the effectiveness of lime softening in silica removal.

The 1413H data represent the behavior of the plant during the addition of sodium aluminate into the precipitator feed. While 1418H data reflect the opertation of the plant with no sodium aluminate was added. The addition of sodium aluminate was stopped in Salbukh water treatment plant on August 18,1997 and restarted for one day on November 17,1997 and completely terminated since November 18,1997.

Silica concentrations against pH of precipitator effluent water are plotted on figure 3 for year 1413H (i.e. during addition of sodium aluminate). The silica concentrations vary from the minimum silica concentration of 9.6 ppm to the maximum silica concentration of 19.9 ppm. The average silica concentration during 1413H is 16 ppm. The pH value is ranging from minimum pH value of 8.2 to maximum pH value of

9.9. The average pH value is 8.89. There is no clear relationship between pH and silica concentrations because pH is still not high enough to reduce the silica significantly. Generally optimum pH for silica removal by sodium aluminate is somewhat higher than 9 [6,7].
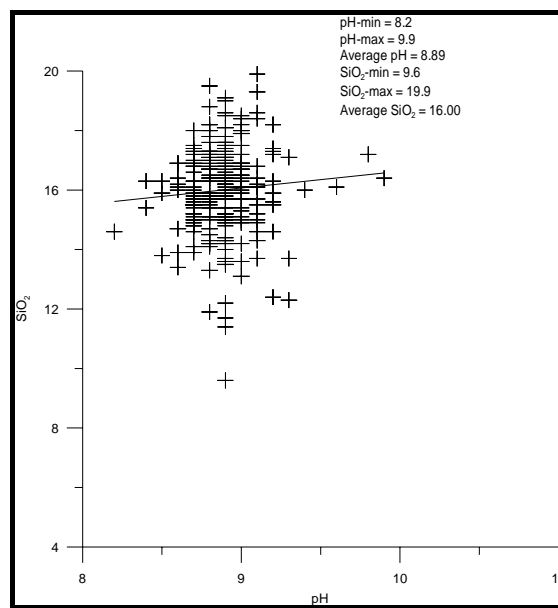

Figure 3 Plot of pH After Precipitators Water vs. Silica Concentration for Salboukh Water Treatment Plant in 1413H.

Figure 4 shows a plot of percentage silica removal and the pH of precipitator effluent water for year 1413H. Percentage of silica removal varies from minimum percentage of silica removal of 26.89 to maximum percentage of silica removal of 66.66. The average percentage of silica removal is 43.97. pH values are between a minimum value of 8.2 and a maximum value of 9.9. The average pH value is 8.89.

Silica concentrations against the pH of precipitator effluent water are plotted in figure 5 for year 1418H (i.e. after termination of sodium aluminate addition). The silica concentrations vary from a minimum silica concentration of 5.8 ppm to the maximum silica concentration of 17.6 ppm. The average silica concentration during 1418H is 10.57 ppm. The pH value is between a minimum value of pH = 9 to the maximum pH value of 10.8. The average pH value is 10.

It is clearly observed from figure 5 that silica content decreases as the pH values increase. Only 10% of soluble silica is ionized at a pH of 8.5. As pH reaches 10, about

50 % is ionized. On other hand silica is precipitated on magnesium hydroxide at pH about 10. However, the solubility of magnesium hydroxide drops steeply as the pH rises above 9.5 and approaches zero a little below 10.5 [8].
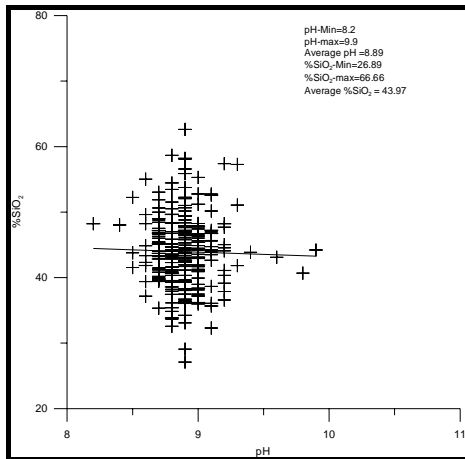

Figure 4 Plot of pH After Precipitators Water vs. Silica Percentage Removal for Salboukh Water Treatment Plant in 1413H.
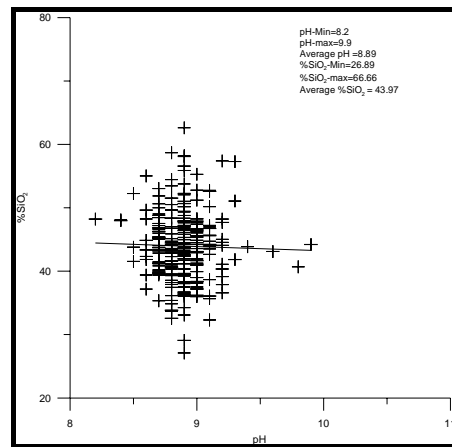

Figure 5 Plot of pH After Precipitators Water vs. Silica Concentration for Salboukh Water Treatment Plant in 1418H.

Figure 6 shows the percentage of silica removal against the pH of precipitator effluent water for year 1418H. Percentages of silica removal vary from a minimum value of 33.84 to a maximum value of 79.86. The average percentage silica removal is 60.54. The pH values are between 8.8 and 10.8. The average pH value is 10.

It is clear from figures 3 to 6 and table 2 that the percentage of silica removal in 1418H, when silica is removed by lime softening with pH rise, is more efficient than the percentage of silica removal in 1413H when silica is removed by addition of sodium aluminate. Silica is removed by adsorption on the magnesium precipitates. Silica is significantly reduced with the precipitation of magnesium hydroxide at high pH values. The precipitation of magnesium hydroxide and calcium carbonate is pH-dependent [6,9].

pH-Min=8.25
pH-max=10.8
Average pH =9.91
%SiO2-Min=33.84
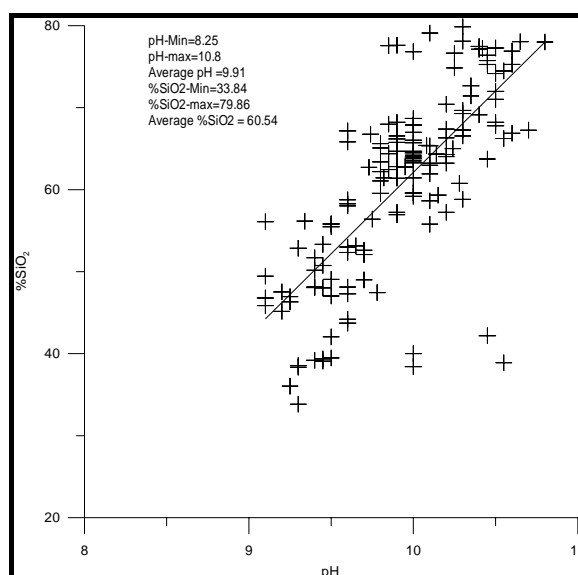%SiO2-max=79.86
Average %SiO2 = 60.54

Figure 6 Plot of pH After Precipitators Water vs.Silica Percentage
Removal for Salboukh Water Treatment Plant in 1418H.

Table 2. Comparisons between 1413H and 1418H Data

	1413H			1418H		
	Min.	Max.	Avrg.	Min.	Max.	Avrg.
SiO_2 content	.6	9.9	6	8	6	.57
%SiO_2 removal	.89	6.66	97	.84	86	.54
pH value	2	9	9	.25	8	

The solubility of magnesium hydroxide drops steeply as the pH rises above 9.5 and approaches zero a little below 10.5 [6]. Although the solubility of silica increases with pH, the solubility of the alkaline silicates decreases with increasing pH. However, at pH 7 and higher, $Si(OH)_4$ begins to ionize to silicate ions in increasing degree, and these are adsorbed and can form a silicate-type bond with a variety of hydroxides that are in a highly dispersed state. Magnesium is the commonest reagent

[9,10]. Soluble silica can also be removed by magnesium bicarbonate as the following reaction;

$$Mg(HCO_3) + 2H_4SiO_4 \rightarrow MgSi_3O_6(OH)_2 + 6H_2O + 2CO_2$$

Conclusion

The precipitation and adsorption of silica by magnesium hydroxide is widely used in water treatment technique for silica removal. Very little attention has been paid to the increases of absorption of OH^- ions on the silica surface with high pH values. The optimal pH for silica adsorption onto $Mg(OH)_2$ was found to be around 10–11, which coincides nicely with the conditions created during lime softening.

So increasing the pH value in the precipitators helped in reducing silica content to a limit that would make the addition of sodium aluminate not necessary. For that reason sodium aluminate addition was stopped. Salbukh water treatment plant was a unique place to study the reduction of silica during softening with and with out the addition of sodium aluminate since it experienced these two situations.

References

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