



Investigation of Fouling of Membranes of a Reverse Osmosis Unit by Silica

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Abstract

A reverse osmosis unit to treat ground water in Saboura/Syria has been in operation for several years. It suffered frequently from severe fouling of membranes. This led to frequent stoppages and losses of flow. Operators of the unit reported the formation of white solid scales on the membranes. It is well known that membranes treating ground water suffer from precipitates such as CaCO_3 , CaSO_4 , Fe, Al, Silica compounds, colloidal matters, bacteria and others. In this study analysis of the solid scales on the membranes showed that silica is the main scaling component. So experiments were carried out to investigate the effect of silica concentration in ground water and other variables such as pressure, pH, metal cations and type of membrane on fouling. The results obtained showed that silica has a direct effect on fouling of membranes. This is influenced by many parameters. Increasing pressure leads to increase in flow rates of water through the membranes. Reduction of pH causes less scaling of silica on the membranes. Cations present in water such as calcium and magnesium help in forming polymeric silicates which cause fouling.

Keywords

Reverse Osmosis, Fouling, Silica, Pretreatment, Membrane

Subject Areas: Chemical Engineering & Technology

1. Introduction

The world suffers from severe shortage of drinking water. Desalination plays an increasingly important role in alleviating this shortage in many parts of the world. Desalination started on a commercial scale in the fifties of last century especially in the Gulfregion using distillation technology. Desalination using reverse osmosis RO started commercially in the seventies and spread all over the world.

Desalination by reverse osmosis suffered from many problems which hindered its wide application. One of the most important problems is fouling of membranes which leads to increase of pressure drop, reduction of water

flux and frequent stoppages to clean or replace the membranes. Fouling of membranes is caused by many compounds such as calcium and magnesium salts, compounds of iron and aluminum, silicates, colloids, micro-organisms and others. So RO depends heavily on pretreatment of feed water. The pretreatment step itself depends on the specifications of feed water and the quality of water produced.

Saboura desalination plant treats ground water in Saboura area in eastern Syria by RO to produce potable water. Pretreatment of ground water consists of cooling and aeration of ground water to increase dissolved oxygen and to oxidize iron to Fe_2O_3 which precipitates on the walls of the cooler. Hydrogen sulfide H_2S is also removed in this step. Sodium aluminate is added to prevent fouling. Colloids are coagulated and removed by passing water through a sand filter. Sulfuric acid is added to reduce pH from 6.5 to 5.5 to prevent precipitation of CaCO_3 on membranes. Finally hexametaphosphate is added as anti-scalent to prevent precipitation of CaSO_4 . But despite this pretreatment Saboura plant suffered from frequent fouling of membranes.

Silica is considered as one of the main causes of scaling. It is present in natural water in concentrations of 1 - 30 $\text{mg}\cdot\text{L}^{-1}$, but its concentration in ground water could reach 159 $\text{mg}\cdot\text{L}^{-1}$. Silica is present in water in the hydrated form such as H_4SiO_4 and $\text{Si}(\text{OH})_4$. It has no bad effect on health so there is no limit to its concentration in drinking water. A study found that silica scaling on membrane was in the form of colloid of nanoparticles of polymeric silica. It reduced the flux to a certain value called the critical flux [1]. Another study found that silica scaling in addition to reducing the flux ruins the membrane itself. A pretreatment by electro coagulation was tried to remove silica. About 80% of silica was removed at 0.5 A and 30 minutes holding time. This led to improvement of the flux through the membranes [2]. A study was carried out to find the effect of physical parameters such as Silt Density Index SDI, Zeta potential, and critical flux on fouling. The study indicated the potential of reducing fouling by chemical coagulation and the use of antifouling compounds [3]. A study to desalinate brackish water concluded that silica is the main cause of scaling and that scales adhere tightly to the membranes. Attempts to remove scales could lead to damage of the membranes. The study found out that many parameters influence precipitation of silica such as the presence of cations such as Ca^{2+} , Mg^{2+} in water which encourage the polymerization of silica. The treatment was done by addition of sodium aluminate in a pretreatment stage to prevent silica precipitation [4]. A study on water with high silica concentration fed to RO unit in the Canary Islands found out that water flux is reduced by high silica concentration [5]. The results of a study of the effect of inorganic compounds such as Ba, Fe, Mn, Ni on silica precipitation showed a strong influence for iron in comparison with other metals [6]. The synergic effect between silica and alginate on scaling by silica was also studied by Higgin [7]. He found out that alginic acid reduces silica scaling and that addition of this acid after fouling leads to its removal.

Silica in brackish water at concentration of 30 mg/L was removed by coagulation/ultrafiltration to prevent scaling in reverse osmosis (RO) membrane [8]. The important factors were pH, coagulant dosage, mixing intensity and velocity gradient. Optimum silica removal of 65% was achieved.

Amjad, Z. and Zuhl, R.W. [9] compared the performance of polymeric additives as silica polymerization inhibitors. They show the impact of impurities (*i.e.*, inorganic and organic coagulant/flocculant) on the performance of silica inhibitors. They illustrated the effect of water chemistry (type and concentration of cations) on the performance of silica inhibitors.

The purpose of this study is to identify the scales in Saboura RO unit and find out the operating parameters which influence it such as pH, pressure, concentration of cations and type of membranes.

2. Experimental Methods and Apparatus

2.1. Chemicals

Solutions of feed water were prepared by adding silica suspension to desalinated water from Saboura station with conductivity of 10 micro Siemens/cm. The silica suspension used has the label Aerosil 200 supplied from Degussa Corporation. Specific surface area was $200 \pm 25 \text{ m}^2\cdot\text{g}^{-1}$, average particle size 12 nanometer and concentration 99.8 wt%.

2.2. RO Equipment

A pilotplant unit of RO was assembled as shown in **Figure 1**.

It consisted of a pressure vessel which contained one membrane with a flux of $900 \text{ L}\cdot\text{h}^{-1}$. The unit was supplied with a pump which gave a pressure of 14 bar and a feed tank of 2000 L. The unit was equipped with a thermometer, a flow meter, a barometer and a pH meter from Hach Company.



Figure 1. Experimental pilot plant RO unit.

The membrane used was of the spiral-wound type CPA3 made from polyamide composite material and supplied from Hydranautics Company. The membrane operates at a maximum pressure of 41.6 bar, temperature of 45°C, pH 3 - 10 and a flow of 17 m³·h⁻¹. It has a minimum salt rejection of 99.6% and nominal membrane area of 37.2 m² (Figure 2). A spectrophotometer of the type DR2010 from Hach Company was used to analyze the precipitates.

2.3. Procedures for Water Treatment

Silica was added in the form of silica powder suspension (Aerosil 200). The temperature, pressure and pH were measured and controlled. Water was pumped at a certain pressure through the RO experimental unit shown in Figure 1. An experiment was carried out on desalinated water from the station with no silica suspension for comparison for a period of 5 hours to clean the membrane and to make the flow steady at F_0 .

3. Results and Discussions

3.1. Analysis of Precipitates

Figure 3 shows a photograph of precipitates on the membranes. This precipitate was in the form of white solid crystalline scales. The precipitate was placed in an oven at 120°C for 1 hour to determine water content. It was then placed in an oven at 550°C for 2 hours to determine its content of organic matter. The sample was dissolved in 37% HCl and 70% HNO₃. The dissolved part was analyzed by Hach Spectrometer and found to consist of calcium and magnesium sulfates. The undissolved silica was weighed. The composition of the precipitate was:

H₂O = 1.48%, organic matter = 21.05%, Ca²⁺ = 3.54, Mg²⁺ = 2.40%, SO₄²⁻ = 8.68%, SiO₂ = 62.82%, losses = 0.03%.

So the precipitate is mainly silica which is the most important foulant in this case.

3.2. Effect of Silica on Fouling

Samples of water with silica content of 10, 25, 40 and 60 mg·L⁻¹ were used. The experiment lasted for 20 hours. The value of flow every two hours was taken F_T . The relative flow F_R was calculated so that:

$$F_R = F_T / F_0 \quad (1)$$

where:

F_0 = Flow rate of water without addition of silica.

F_T = Flow rate of water with silica.

F_R = Relative flow rate.

Values of F_R were plotted versus time of flow in hours. The results are shown in Figure 4. The figure clearly shows that flow through the reverse osmosis membranes decrease steadily due to fouling. This drop in flow is influenced by the concentration of silica in the water ranging from 10 - 60 mg/L.



Figure 2. A photo of the membrane used in the experiment.



Figure 3. Photograph of precipitates on the membranes.

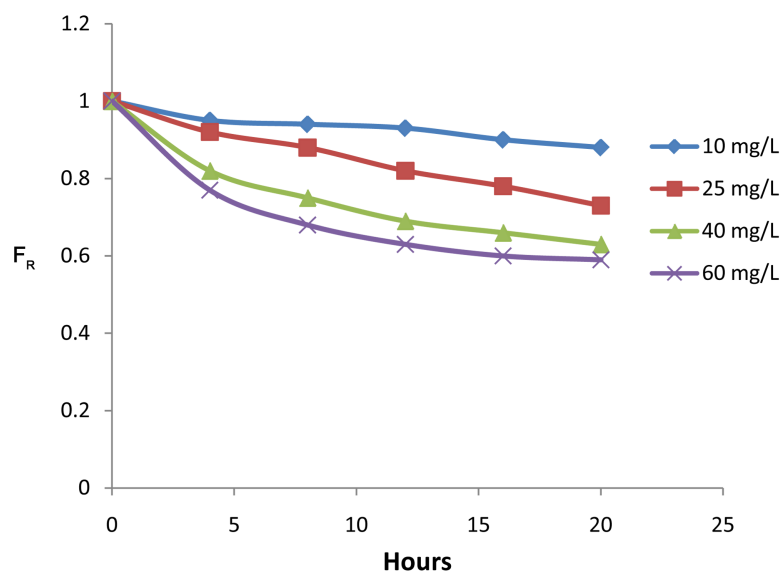


Figure 4. Effect of silica concentration on flow of water through membranes. $P = 10$ bar, $T = 20^\circ\text{C}$, $\text{pH} = 5.5$.

3.3. Effect of Pressure on Flow through RO

The influence of pressure was studied by feeding water with $10\text{ mg}\cdot\text{L}^{-1}$ silicate at a temperature of 20°C and $\text{pH} = 5.5$ with different pressures. The results are plotted in Figure 5. It is clear that increasing pressure leads to higher flow rates. However at high pressure the drop in flow rates versus time is quicker than at low pressures. This is related to the rapid build-up of scales at the membrane surface when operating at high pressure.

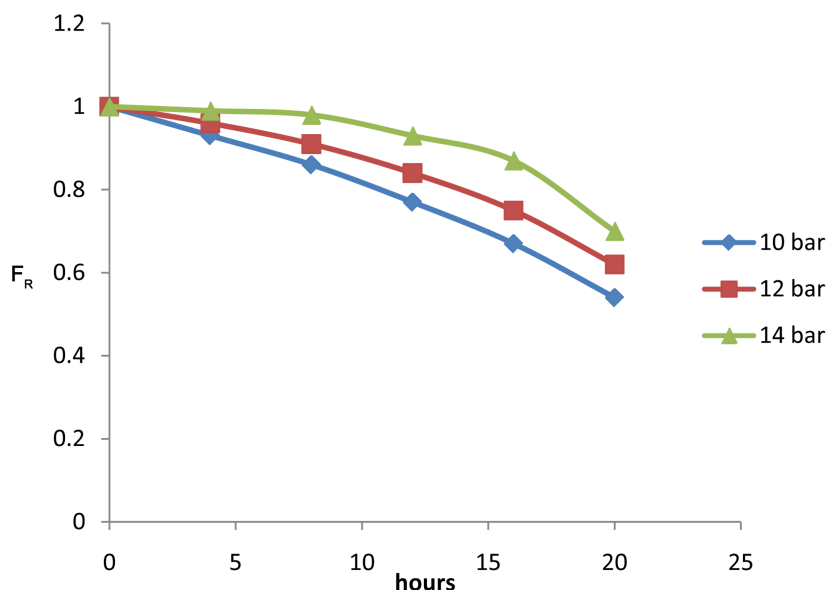
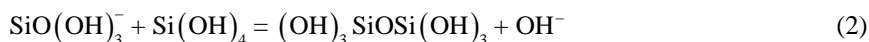


Figure 5. Effect of pressure on flow of water through membranes. $\text{SiO}_2 = 10 \text{ mg}\cdot\text{L}^{-1}$, $T = 20^\circ\text{C}$, $\text{pH} = 5.5$.

3.4. Effect of pH on Flow through RO

The pH plays a key role in the chemical reactions which lead to precipitation of solids and formation of scales. An experiment was carried out using feed water with $10 \text{ mg}\cdot\text{L}^{-1}$ silicates at a pressure of 10 bar and a temperature of 20°C . The pH was varied from 5.5 to 8.5. The results are represented in **Figure 6**. It is clear that increasing pH causes a rapid increase in scaling. This is due to the formation of polymer silicate at $\text{pH} = 8.5$ according to the reactions:



3.5. Effect of Cations Ca^{2+} on Flow through RO

Presence of cations in the water plays important role in the chemical reactions which lead to formation and precipitation of silica scales. This was investigated by preparing solutions with 10 and $60 \text{ mg}\cdot\text{L}^{-1}$ of silicate. The experiment was performed at a temperature of 20°C , a pressure $P = 10$ bar and $\text{pH} = 6$. CaCl_2 was added to make solutions with 100 and $400 \text{ mg}\cdot\text{L}^{-1}$ of Ca^{2+} . The results are shown in **Figure 7**. This shows that flow through membranes dropped quite a bit at high Ca^{2+} concentration. This confirms that Ca^{2+} supports the precipitation of silicates. It is known that silicates are charged with negative charge at natural conditions of $\text{pH} = 7$. But addition of CaCl_2 causes the forces of repulsion to decrease and silica gel to form which plays a great role in scaling and drop of flow.

3.6. Effect of Membrane Type on Flow through RO

The experiment was carried out using water with silicate concentration of $40 \text{ mg}\cdot\text{L}^{-1}$ at a pressure of 12 bar with the pH adjusted to 5.5. The experiment was repeated using exactly the same conditions but on a spiral wound polyamide membrane from a different company called Filmtic Company. This membrane operates at maximum applied pressure of 41 bar and maximum chlorine concentration < 0.1 ppm and maximum operating temperature of 45°C and maximum flow rate of $19 \text{ m}^3\cdot\text{h}^{-1}$.

The results are plotted in **Figure 8**. This shows that at the same conditions membrane B (polyamide from Filmtic Co) is better than membrane A (polyamide from Hydranaut Company). The structure and type of surface of the membrane play an important role in silica deposition. Rough membrane's surface helps scale formation.

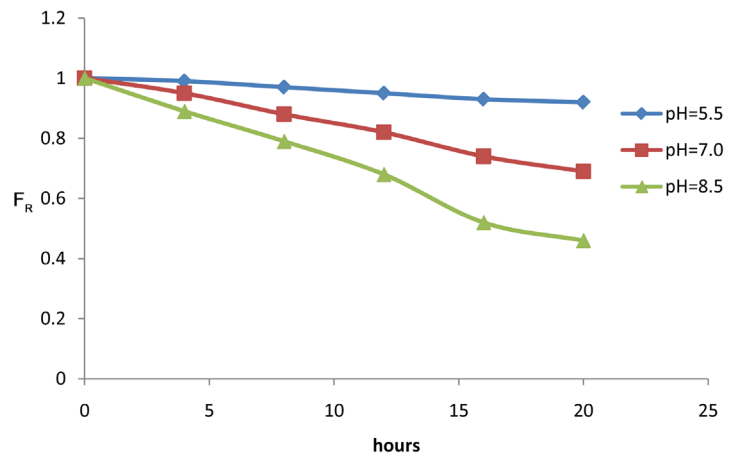


Figure 6. Effect of pH on flow of water through membranes. $\text{SiO}_2 = 10 \text{ mg}\cdot\text{L}^{-1}$, $\Delta P = 10 \text{ bar}$, $T = 20^\circ\text{C}$.

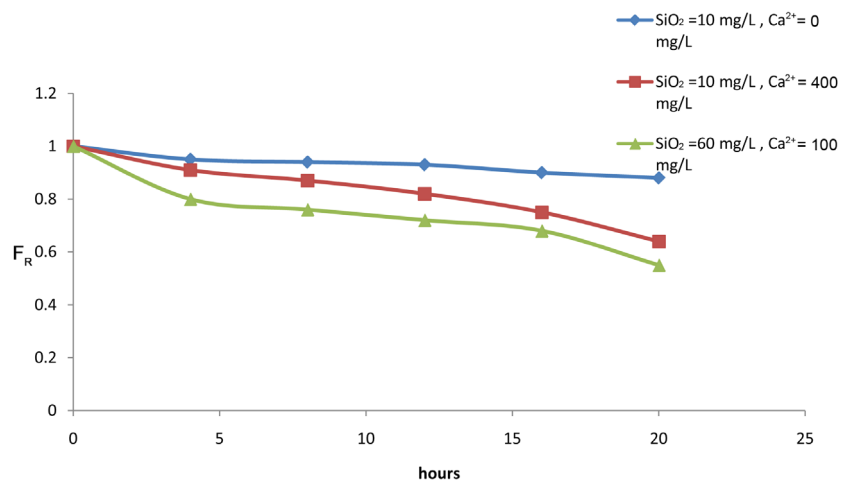


Figure 7. Effect of cations Ca^{2+} on flow of water through membranes. $\text{SiO}_2 = 10 \text{ mg}\cdot\text{L}^{-1}$, $\Delta P = 10 \text{ bar}$, $T = 20^\circ\text{C}$, $\text{pH} = 6$.

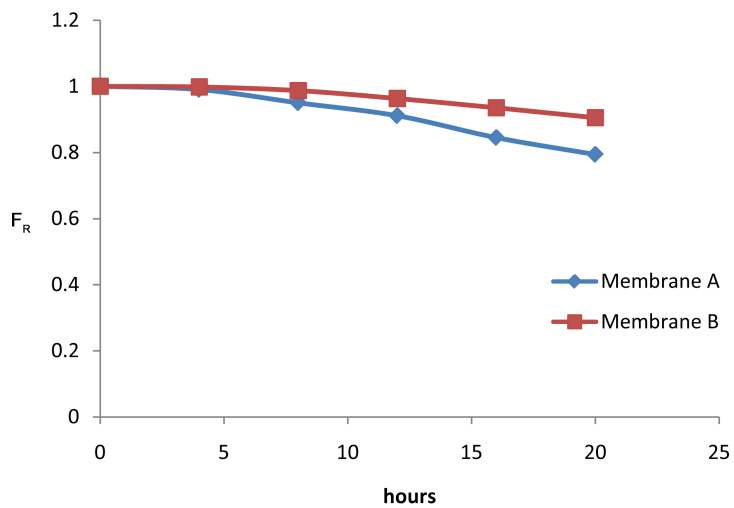


Figure 8. Effect of membrane type on flow of water through membranes. $\text{SiO}_2 = 40 \text{ mg}\cdot\text{L}^{-1}$, $\Delta P = 12 \text{ bar}$, $T = 20^\circ\text{C}$, $\text{pH} = 5.5$.

4. Conclusion

The results shown indicate that silica causes fouling of membrane and increases scales. So with higher silica concentration flow through membranes decreases. Increasing the pressure causes an increase in the flow rates through membranes. But with high pressure the drop of flow with time is higher. This is caused from the rapid deposition of scales on membrane. pH plays important role since high pH values of feed water lead to increase in the precipitation of scales. At pH = 8.5 polymeric silica formation is enhanced and this leads to high scaling and drop in the flow rate of water through membranes. The influence of cations such as Ca^{2+} was investigated and this was found to increase scaling because it supports formation of precipitates of scales. The type of membrane has an influence on scaling. It was found that polyamide membranes from Filmtic Company give better flow rates than polyamide membranes of the type CPA3 supplied by Hydranautics Company used in Saboura RO unit.

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