Analyses of calcium carbonate scale deposition on four RO membranes under a seawater desalination condition

Nam Wook Kang, Seockheon Lee, Dooil Kim, Seungkwan Hong and Ji Hyang Keown

ABSTRACT

Inorganic fouling is one of the critical operational issues in reverse osmosis membrane. Few researches investigated effects of membrane surface characteristics on inorganic fouling and on anti-scaling techniques although the fouling occurs on the membrane surface. The objective of this paper was to examine whether different characteristics of deposition of calcium carbonate solids would occur on four membranes having distinctive surface properties. A lab-scale cell reactor with a crossflow velocity was installed and two coupons were used for one type of membranes. Two feed waters were examined: concentrated synthetic seawater simulating a 30% recovery and a concentrate from a seawater RO plant in operation at Changwon, Korea. The amounts of solid deposition on the attached membranes were increased in all four membranes but the degree of deposition on each membrane was different. Various types of calcium carbonate solids were clearly detected by both XRD and SEM analyses. In general, a membrane with greater roughness and negative surface charge appeared to form more scales. This implied that membrane surface characteristics such as roughness and surface charge affected inorganic fouling, presumably by providing favourable sites for precipitation and enhancing attraction of species to the membrane surface.

Key words | CaCO₃ scale, inorganic scale, membrane surface characteristics, seawater reverse osmosis desalination

INTRODUCTION

Reverse osmosis (RO) has been one of the most frequently used desalination technologies since it was first introduced in the 1950s by research teams of UCLA and University of Florida. According to the statistical research by Greenlee et al. (2009), membrane and thermal distillation processes almost equally shared the desalination market with reverse osmosis dominating the membrane process. RO membrane is increasingly being used for the production of drinking water, brackish or seawater and wastewater reuse. The seawater reverse osmosis (SWRO) desalination has operational issues caused by various fouling including particulate, inorganic, organic and biological fouling. Fouling leads to the increase of operational energy, cleaning frequency and the reduction of life of membrane elements. Antifouling strategies on an SWRO system are therefore required to prevent fouling of membranes, maintain performance of process and extend service period of a system (Prihasto et al. 2009).

Inorganic scales occur when concentrations of sparingly soluble salts, i.e. divalent ions, exceed their solubility limit. Inorganic salts which are the most likely causes of scaling are Ca²⁺, Mg²⁺, CO₃²⁻, SO₄²⁻, silica and iron. The common scale types are Ca-phosphate, CaCO₃, CaSO₄, SiO₂ and CaF. CaCO₃ precipitates have been the most probable foulants for seawater and wastewater reuse application (Tzotzi et al. 2007).

According to Lee & Lee (2000), there are three mechanisms to explain flux decline due to scale formation in...
MEMBRANES RO membranes, i.e. cake layer formation by bulk crystallization and surface blockage by surface crystallization and crystallization by both mechanisms (Figure 1). In the bulk crystallization, ions combine in a random order under the supersaturated concentrate condition and the combined ions deposit on membrane surface and then grow to a crystal form. On the other mechanism, surface crystallization forms precipitates directly on surface. Finally, when both mechanisms occur in a system, crystal particles formed in the bulk phase come up to deposition and growth of the crystals’ progress on membrane surface. Presumably, both bulk and surface crystallization mechanisms affect scaling formation in a real SWRO system.

Membranes from various manufacturers have their own surface characteristics, such as roughness and hydrophobicity (Norberg et al. 2007). Lee et al. (2010) found that in general, less negatively charged surfaces accumulated more bacterial cells. The other researchers (Rahardianto et al. 2006) confirmed that doses of antiscalant added to control scales were different in accordance with four membranes in their study. Few researchers investigated effects of membrane surface characteristics on those inorganic fouling and on anti-scaling techniques. Due to the fact that fouling occurs on a membrane surface, membranes with different surface properties such as roughness and charges might show different aspects of inorganic fouling and thus need different strategies of scale inhibition.

The common methods to prevent inorganic scales are pH adjustment by acids and addition of antiscalants (or inhibitors) (Fritzmann et al. 2007; Tzotzi et al. 2007; Greenlee et al. 2009). pH adjustment is an efficient way to control CaCO3 scale but requires large amounts of acid addition. Recently, use of antiscalants composed of various polymers has increased extensively (Li et al. 2006; Shih et al. 2006). Antiscalants are made from polycarboxylate, polyacrylate, polyphosphate, or polyphosphonate compound. They are added to feed water before the feed water enters a RO module. Antiscalants cannot completely prevent precipitation when ion concentrations become high as a salt concentration increases in the concentrate.

The objective of this paper was to evaluate CaCO3 scale deposition by both bulk and surface crystallization mechanisms on four different RO membrane surfaces. The deposition was analysed quantitatively by increases in dried weights and dissolution of calcium ions from each membrane coupon and qualitatively by XRD and SEM images of the fouled surfaces. Two feed solutions are used; concentrated synthetic seawater (SW) and concentrates from a real seawater RO plant.

METHODS AND MATERIALS

Schematic diagram of lab-scale systems

A cylindrical cell reactor was built to simulate cross-flow water stream to each membrane in parallel. The outer diameter and the length of the reactor were 2 and 32 cm, respectively. In the reactor, eight acrylic coupons were inserted as shown in Figure 2. The individual membrane area was cut to the same size, i.e., 19.6 cm² (4 cm × 4.9 cm), and attached to a coupon. Two coupons were used for one type of membranes for duplicated samples. The crossflow velocity was maintained at approximately 0.14 m/s. The membrane coupons were taken out at a designated time one by one for further surface analyses. Four membranes from Filmtec SW-30HR, Toray TM820-400, Hydranautics SWC-5 and Woongjin Chemical RE 2540-SR respectively were selected to elucidate effects of different surface characteristics such as surface charge and roughness on scale formation. Table 1 summarizes the membrane surface characteristics.
characteristics. Over 50 h of operation were conducted for concentrated synthetic SW and 15 days of operation for the concentrates from Changwon seawater RO (CSWRO) plant. The experiment was terminated when turbidity of the feed reservoir started to increase rapidly, which indicated the occurrence of inorganic precipitation. Various factors in the real seawater interfered to form CaCO₃ scale and yielded the long operation.

Feed water

The concentrated synthetic seawater was formulated followed by Standard Method 8.11. To simulate the condition in the concentrate part of SWRO, 30% of recovery was selected. The rejection was decided to be 99.6%. The concentration factor (CF) in a RO system can be expressed by Equation (1).

$$CF = \frac{C_c}{C_f} = 1/(1 - R)$$  \hspace{1cm} (1)

where $C_c$ is concentration in concentrate water, $C_f$ is concentration in feed water, and $R$ is water recovery. Therefore, the feed waters using synthetic seawater (SSW) had concentration factors of 1 and 1.43. To simulate seawater in ion concentrations and to remove background effects of sulphate ions for exclusive precipitation by CaCO₃, an adjustment of ion balances was performed as shown in Table 2. Some compounds were left out because they do not affect CaCO₃ scale formation and exist in infinitesimal amounts; NaF and SrCl₂6H₂O. The concentrate from a seawater RO plant was sampled from the SWRO pilot plant at Chang-Won, Kyung-nam province, southern part of Korea. Table 3 shows water qualities of concentrate from the pilot plant, which was operated at a recovery rate of 10–20%. The conductivity of the concentrate of the Changwon SWRO was almost similar to that from the concentrated synthetic SW with concentration factor of 1.43 in this study.

Surface characteristics of RO membranes

Membrane characteristics are critical to understand membrane fouling mechanisms. Increases in dried weight and calcium concentrations extracted from each coupon

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Unit</th>
<th>1</th>
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<tr>
<td>KCl</td>
<td>mg/L</td>
<td>750</td>
<td>1,082</td>
</tr>
<tr>
<td>CaCl₂2H₂O</td>
<td>mg/L</td>
<td>1,450</td>
<td>2,959</td>
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<tr>
<td>MgCl₂6H₂O</td>
<td>mg/L</td>
<td>11,000</td>
<td>16,035</td>
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<tr>
<td>NaCl</td>
<td>mg/L</td>
<td>25,000</td>
<td>32,467</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>mg/L</td>
<td>270</td>
<td>388</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>mg/L</td>
<td>395</td>
<td>564</td>
</tr>
<tr>
<td>TDS</td>
<td>mg/L</td>
<td>52,266</td>
<td>60,747</td>
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<tr>
<td>Ionic strength</td>
<td>mol/L</td>
<td>0.6</td>
<td>1.2</td>
</tr>
<tr>
<td>Conductivity</td>
<td>μS/cm</td>
<td>22,586</td>
<td>42,523</td>
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<table>
<thead>
<tr>
<th>Compounds</th>
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<tbody>
<tr>
<td>Ca²⁺</td>
<td>mg/L</td>
<td>225</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>mg/L</td>
<td>984</td>
</tr>
<tr>
<td>Na⁺</td>
<td>mg/L</td>
<td>17,431</td>
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<tr>
<td>TDS</td>
<td>mg/L</td>
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<tr>
<td>pH</td>
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<tr>
<td>Conductivity</td>
<td>μS/cm</td>
<td>46,000</td>
</tr>
<tr>
<td>Turbidity</td>
<td>NTU</td>
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</table>
were measured to characterize the depositions on the membranes. The membrane detached from each coupon was dried in a desiccator at room temperature. The weight was measured by the balance (AB265-S/FACT, Mettler Toledo, Switzerland) before and after the cell reactor operation. The Ca$^{2+}$ ion in the deposition was extracted by acid addition (0.1 N H$_2$SO$_4$) and analysed through atomic absorption (AA) spectroscopy (AA-6501F, Shimadzu, Japan). A Field-Emission Scanning Electron Microscope (FE-SEM) (SIRPA 55VP, Carl Zeiss, Germany) and Powder X-ray Diffractometry (XRD) detector (D5005, Bruker, Germany) were used to directly examine the membrane surface. The surface roughness of the membranes was measured by atomic force microscopy (AFM, SIS, Pucostation, Germany) followed by the methods of Yang et al. (2009).

**RESULTS AND DISCUSSION**

Liquid samples from the cell reactor were analysed for pH, turbidity, conductivity, TDS and temperature during operation. In addition, turbidity in the feed reservoir was regularly checked as an indicator of an initiation of CaCO$_3$ precipitation. Figure 3 showed the results of turbidity and pH in the feed reservoir that were used to conclude sufficient scale formations. The turbidity of the two feed waters increased over time. In the case of synthetic seawater, turbidity rapidly increased and the pH decreased after 48 h, at which the operation was ended and the membrane coupons were sampled for analyses. The concentrate from Changwon SWRO (CSWRO) plant rapidly built up scales after 15 days. Temperature during the operation was maintained at 18.5 ± 1.5 °C for synthetic seawater and 27 ± 1 °C for Changwon seawater.

**Quantitative analyses of CaCO$_3$ precipitation**

Extracted Ca$^{2+}$ concentration and dried weights. Analyses were conducted to investigate amounts of calcium carbonate solids formed on membrane surface as shown in Figure 4. The amounts of solid deposition were increased in all four membranes but the degree of deposition on each membrane was different. First of all, differences in dried weights of RO membrane filters before and after the operation were positive; approximately 0.4 mg/cm$^2$ for concentrated SSW and 0.2 mg/cm$^2$ for the concentrates from CSWRO. In addition, Ca$^{2+}$ ions existed on all membrane surfaces but with the various quantities of Ca$^{2+}$ ions. In general, the inorganic scaling from the concentrates of CSWRO was much lower than that from the SSW, which was consistent with the low salt concentrations in the concentrates from CSWRO. Increases in the extracted Ca$^{2+}$ ions and the dried weights appeared relatively greater in Woongjin and Filmtec membranes than the other membranes. The membrane with the smallest increase was the Toray membrane. Table 1 showed that the Toray membrane had relatively low roughness and more negative charge than others. Lee et al. (2010) examined that less negatively charged surfaces accumulated more bacterial cells. In general, the Filmtec membrane with greater roughness and negative surface charge seemed to form more solids than Toray membrane with lower roughness and less negative surface charge. According to Jarusutthirak et al. (2007), experiments with divalent cations (Ca$^{2+}$) showed greater flux decline compared to the experiments with monovalent cations (Na$^+$). The more positively charged feed waters by divalent ions reduced electrostatic forces between the negatively charged membrane and the feed water and therefore yielded greater fouling in the processes. The less
negatively charged membrane was more susceptible to the attraction of divalent ions to the membrane surfaces. This implied that membrane surface characteristics such as roughness and surface charge affected inorganic fouling, presumably by providing favourable sites for precipitation and enhancing attraction of species to the membrane surface.

**Structural characterization of CaCO₃ precipitation**

The XRD spectra were analysed to learn presence of scales on membrane surfaces and types of CaCO₃ scales. In the case of CaCO₃, 2θ values correspond to the values for calcite crystals (Shakkthivel & Vasudevan 2006). Figure 5 revealed that three different forms of calcium carbonate...
solids were formed, i.e., calcite, vaterite and aragonite, on the membranes treating the concentrated SSW (Tang et al. 2008). The aragonite was discovered on only Filmtec membrane. The peaks at the same degree showed different intensities on the four membranes. The calcite peak at 30–35° among other peaks was the highest for three membranes except the Toray membrane. The highest peak in the Toray membrane was revealed to be vaterite form. A variety of crystal types were apparently formed on the Filmtec membrane with greater roughness and negative surface charge than the other membranes. The XRD spectra from the membrane coupons treated with concentrates from CSWRO are shown in Figure 6. The calcite was the major crystal in all four membranes although the Woongjin membrane showed the highest peak at 2θ value for vaterite forms of crystals. For example, coupons from Hydranautics and Filmtec membranes had no vaterite peaks at 30–35°. The similarity of the peaks was greater for the same membrane (Figure 5(a) and Figure 6(a)) than for the same feed properties. The results in the two types of feed water were different due to other factors affecting CaCO₃ precipitation in the concentrates from CSWRO. The numbers of peaks detected by the XRD spectra were greater for the concentrated SSW than for the concentrates from CSWRO. According to Berner (1975), dissolved Mg²⁺ in seawater had no effect upon rate of seeded precipitation of aragonite

Figure 7 | Field-emission scanning electron micrographs of the membrane surfaces fouled by concentrates from CSWRO. (a) and (e) RE 2540-SR, (b) and (f) TM820-400, (c) and (g) SWC-5, (d) and (h) SW30HR.
but severely retarded rate of seeded precipitation of calcite. The XRD result of the CSWRO indicated that the less peaks might be yielded from numerous dissolved compounds such as Mg$^{2+}$ and organic matter in the natural seawater.

SEM analyses were conducted to examine direct images of the scales on the membrane surface treated with the concentrates from CSWRO as shown in Figure 7. The SEM images magnified at 500 times were used to observe a common pattern of crystallization in a wide area of the surfaces. The detailed images of each crystal were taken at ×10,000 magnification. The amounts and the shapes of each scale were relatively different. Various sizes of CaCO$_3$ crystals were shown on all cases of the membranes. At low resolution, comparatively many scales were observed on the Filmtec membrane, which was distinguished from the other three membranes. Relatively large amounts of crystals were detected on the Filmtec membrane but lumps of crystals were located sparsely on the other three membranes. All membranes clearly showed the calcite crystals in the membrane surface at high resolution, as shown in Figure 7 (e), (f), and (g). The most common structure of calcite is trigonal crystal structure, which is the only crystal system whose point groups have more than one lattice system associated with hexagonal and rhombohedral lattice. The unique hexagonal crystal structure was shown in the Woongjin membrane surface. The almost hexahedron types of crystals were detected on the membranes from Toray and Hydranautics. The detailed shapes of the crystals on the Filmtec membrane were somewhat different from the other membrane surfaces. The results implied that shapes and types of crystals could be different depending on the surface properties of membranes although the same feed water was treated.

CONCLUSIONS

The effect of membrane characteristics on the deposition of inorganic scales was investigated with four different RO membranes. The deposition was analysed quantitatively by increases in dried weights and dissolution of calcium ions from each membrane coupon and qualitatively by XRD and SEM images of the fouled surfaces. Two feed waters were examined: concentrated synthetic seawater simulating a 30% recovery and a concentrate from a seawater RO plant in operation at Changwon, Korea.

The increases in turbidity of the two feed reservoirs corresponded well to sufficient amounts of inorganic scale depositions on the membranes although the concentrates from CSWRO took longer time for precipitation. Various types of calcium carbonate solids were clearly detected by both XRD and SEM analyses. The presence of calcium carbonate scales implies that an anti-scaling strategy is necessary for a SWRO plant.

The amounts of solid deposition measured by increases in the extracted Ca$^{2+}$ concentrations and the dried weights became greater after the operation in all four membranes but the degree of deposition on each membrane was different. It appeared that the increases in the Woongjin and the Filmtec membranes were relatively more substantial than the other membranes. The smallest increase was occurred to the Toray membrane that had relatively low roughness and more negative charge than the others. This implied that membrane surface characteristics such as roughness and surface charge affected inorganic fouling, presumably for providing favourable sites to precipitation and enhancing attraction of species to the membrane surface.

Outcomes of this research help to enhance RO membrane performance and to extend the use of reverse osmosis membranes to various fields including seawater desalination, industrial water recycling and wastewater reuse.

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