Inhibition of CaCO₃ scaling on RO membranes by trace amounts of zinc ions

Dmitry Lisitsin⁹, Qingfeng Yang⁹, David Hasson⁹*, Raphael Semiat⁹

⁹GWRI Rabin Desalination Research Laboratory, Department of Chemical Engineering, Technion-Israel Institute of Technology, Haifa 32000, Israel
Tel. +972 4 829 2936/2009; Fax +972 4 829 5672; email: hasson@tx.technion.ac.il

Abstract

Anti-scalants, which are widely used for scale control in desalination processes, are essentially impurities capable of inhibiting scale precipitation and weakening scale adhesion on a flow surface. Many basic studies indicate that metallic ion impurities, notably Zn ions, can hinder significantly CaCO₃ precipitation from hard waters and alter crystal morphology. Recent studies demonstrate a substantial potential for suppressing CaCO₃ scale formation in hard water heating systems by trace concentrations of Zn ions. The objective of the present work was to explore the possibility of controlling CaCO₃ scale formation in RO membrane systems by a similar technique. Results obtained with a tubular RO system are most promising. A Zn²⁺ concentration of the order of 2 PPM was able to exert a marked suppression effect on both bulk precipitation of CaCO₃ and on membrane scaling on waters of moderate hardness.

Keywords: RO pretreatment; CaCO₃ scaling; Zinc dosage; Antiscalants

1. Introduction

The aim of this paper is to examine the potential of an upcoming scale control technique. Currently, the most commonly used technique for controlling CaCO₃ scale precipitation on RO membranes is by dosage of an antiscalant. When properly applied, an antiscalant has the advantage of inhibiting effectively scale formation at very low dosages, typically below 10 PPM. The most common antiscalants are polymeric organic compounds, usually phosphonates or polyelectrolytes.

A recently proposed technique for controlling scale deposition in heat-exchange systems is by dosage of trace concentrations of Zn²⁺ ions. The presence of Zn²⁺ ions induces scale suppression effects substantially similar to

*Corresponding author

European Desalination Society.
0011-9164/05/$ – See front matter © 2005 Elsevier B.V. All rights reserved
those of organic antiscalants. A conspicuous advantage of Zn\(^{2+}\) ions is that they can be conveniently dosed by contacting the feed water with a redox alloy medium, such as a granular bed of KDF\(^{®}\) Cu-Zn alloys [1,2]. Another advantage is that Zn\(^{2+}\) ions are environmentally friendly and do not raise a problem in concentrate waste disposal. Also, Zn\(^{2+}\) ions meet drinking water criteria. An upper limit of 5 PPM zinc in drinking water is recommended, not because of a health hazard but due to the astringent taste that Zn\(^{2+}\) ions impart to water above the 5 PPM limit.

In a recent study performed in this laboratory [3], the inhibitory effect of Zn\(^{2+}\) ions dosed into hard water by contact with a KDF bed was investigated in heating systems. The supersaturation level with respect to CaCO\(_3\) was in the range of Langelier Saturation Index (LSI) values of 1.0–1.8. Water film temperatures were as high as 80\(^\circ\)C. Zinc dosages as low as 1–1.5 PPM reduced scaling rates measured with no zinc by a factor of over 2–3. In view of these results, it is of interest to examine the potential of the Zn dosage technique for scale control in RO systems.

2. Experimental

2.1. Experimental system

Experiments were conducted in a continuous flow tubular RO system (Fig. 1) which provides a well-defined flow system. The RO tubular element (14.5 mm diameter, 1 m long) consisted of a high rejection polyamide/polysulfone composite RO membrane, supplied by Stork Friesland B.V., Gorredik, Holland (catalogue designation: WFC 0995).

Operating pressures were in the range of 35–45 bars, providing initial permeate fluxes in the range of 20–50 L hour\(^{-1}\) m\(^{-2}\). Feed velocity in the various runs was in the range of 0.25–0.47 m/sec. The recycling solution was held at a constant temperature of 30\(^\circ\)C by a thermostatic controlled heating element and a water cooled heat exchanger. Solution pH was held constant at a desired level by a pH controller which either actuated a NaOH dosing pump or opened a CO\(_2\) solenoid valve.

The experimental system enabled two modes of operation. In the full recycle (FR) mode, both permeate and concentrate streams were returned to the feed tank, thus maintaining a constant composition of the solution flowing through the membrane, till the eventual onset of bulk precipitation. In the permeate withdrawal (PW) mode, permeate was withdrawn from the system, leading to continuous concentration of the recycling solution which eventually led to bulk precipitation.

2.2. Feed solution

Solutions having a propensity for CaCO\(_3\) precipitation were prepared in a 30 L feed

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration PPM</th>
<th>Ion</th>
<th>Concentration PPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(^{2+})</td>
<td>220</td>
<td>HCO(_3)(^-)</td>
<td>370</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>10</td>
<td>SO(_4)(^-)</td>
<td>40</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>140</td>
<td>Cl(^-)</td>
<td>390</td>
</tr>
</tbody>
</table>
tank. The nominal composition of the solution (Table 1) was the same in all experiments, except for the pH level:

The feed solution was prepared by dissolving in distilled water appropriate amounts of CaCl$_2$, NaHCO$_3$ and MgSO$_4$. The saturation pH of the solution was 6.6. A desired supersaturation potential of CaCO$_3$ was adjusted by careful addition of NaOH solution to the pH level providing the desired LSI level. The FR experiments were carried out at initial pH values in the range of 7.6–8.2, providing initial LSI values in the range of 1.0–1.6. The PW experiments were carried out at an initial LSI value of 1.2 and an initial pH level of 7.7. As noted below (see 3.3.2), zinc solubilities were higher in most PW experiments due to the lower pH level.

2.3. Experimental procedure

Characterization of the inhibition effectiveness of Zn$^{++}$ ions in full recycle experiments was carried out by measuring permeate flow rate, solution composition and solution turbidity versus time. In the permeate withdrawal experiments, water recovery fraction versus time was also measured. Feed temperature, operating pressure and permeate flux data were monitored and logged with the TestPoint program via LabJack hardware. Solution turbidity was measured using a HACH turbidimeter, model 2100P. Dissolved Ca$^{++}$ was analyzed by the EDTA method, carbonate species were determined by total alkalinity titrations and Zn$^{++}$ concentration was measured by the HACH spectro-photometric procedure.

In FR runs, the LSI level was maintained constant throughout the experiment by pH control of the recycling solution. Calcium carbonate scaling on the membrane was indicated by permeate flux decline while bulk precipitation was detected by a sharp turbidity increase. At the end of the induction period, the onset of precipitation led to a sharp decrease of the LSI level as a result of the pH decrease accompanying CaCO$_3$ formation and of the depletion of the scaling species from the solution. In PW runs, the pH level was also maintained constant but the LSI level continuously increased as a result of the solution concentration effect. As before, both the LSI and the pH levels rapidly decreased after the onset of precipitation.

Osmotic pressures and LSI levels of the solutions were calculated using the ROPRO 6.1 software. It may be noted that while in the FR mode of operation the solution osmotic pressure remains constant, in the PW mode the concentration effect leads to a continuous increase in the osmotic pressure. This increase in osmotic pressure was taken into account in evaluating changes of membrane permeability.

3. Results

3.1. Method of analysis

Since scale deposition induces a continuous decline in permeate flow rate, the inhibition effectiveness of Zn$^{++}$ ions was assessed by comparing membrane permeability decline with time in the presence and in the absence of Zn$^{++}$ ions. Membrane permeability $L_p$ is given by:

$$L_p = \frac{J_v}{\Delta P - \pi_m}$$  \hspace{1cm} (1)

where $J_v$ is the permeate flux, $\Delta P$—the operating pressure and $\pi_m$—the osmotic pressure prevailing on the membrane wall. The magnitude of $\pi_m$ is affected by the concentration polarization phenomenon. However, since in the present work osmotic pressure was significantly lower than the operating pressure,
little error was introduced by approximating wall osmotic pressure $\pi_m$ with bulk osmotic pressure $\pi_b$.

The fundamental parameter dictating the scaling potential is the supersaturation level prevailing on the membrane surface. The value of the concentration polarization (CP) modulus, which is required for evaluating membrane wall conditions, was roughly calculated by assuming that diffusivity coefficients of all ions except $H^+$ were equal and that $H^+$ diffusivity was an order of magnitude higher.

The permeability of the various membrane tubes used in this study varied considerably from tube to tube. The CP level was maintained constant in all experiments by suitable adjustment of the operating pressure and feed velocity.

### 3.2. Full recycle experiments

Table 2 summarizes the data obtained in the full recycle experiments. The duration of an experiment was 15–20 hours except in runs terminated earlier due to bulk precipitation. Most experiments were replicated and in all cases reproducibility of the results was quite satisfactory. The inhibition effectiveness of $Zn^{++}$ can be roughly assessed by comparing the permeability ratio $L_{pf}/L_{pi}$ in the absence and in the presence of $Zn^{++}$ ions, where $L_{pf}$ is the final permeability and $L_{pi}$ is the clean membrane permeability.

#### 3.2.1. Inhibition effects of 2 PPM $Zn^{++}$ at LSI levels of 1.1, 1.4 and 1.6: Results of the experiments conducted at the lower LSI levels of 1.1 and 1.4 will be first considered. The inhibitory effect of $Zn$ is observed in the permeability data plotted in Fig. 2. At both LSI levels membrane permeability remained substantially constant in the presence of 2 PPM $Zn^{++}$ while a marked permeability decline process occurred in the absence of zinc.

It may be noted that the marked permeability decline observed in Fig. 2 at the relatively low LSI level of 1.1 in the solution was not accompanied by bulk precipitation throughout the 16 hours of the experiment. The dissolved $Ca^{++}$ concentration remained constant and no solution turbidity was detected. The permeability decline was caused by the much higher LSI level of about 1.7 prevailing on the membrane surface due to the CP effect.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Duration (hours)</th>
<th>pH</th>
<th>LSI* sol. bulk</th>
<th>LSI* memb. wall</th>
<th>Zn^{++}</th>
<th>Induction time (hours)</th>
<th>Lpf / Lpi</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16</td>
<td>7.6</td>
<td>1.1</td>
<td>1.75</td>
<td>Blank</td>
<td>No precipitation</td>
<td>0.74</td>
</tr>
<tr>
<td>2</td>
<td>16</td>
<td>7.6</td>
<td>1.1</td>
<td>1.75</td>
<td>2 PPM</td>
<td>No precipitation</td>
<td>0.94</td>
</tr>
<tr>
<td>3</td>
<td>11</td>
<td>8</td>
<td>1.4</td>
<td>2.0</td>
<td>Blank</td>
<td>1</td>
<td>0.88</td>
</tr>
<tr>
<td>4</td>
<td>14.5</td>
<td>8</td>
<td>1.4</td>
<td>2.0</td>
<td>2 PPM</td>
<td>No precipitation</td>
<td>0.94</td>
</tr>
<tr>
<td>5</td>
<td>14.75</td>
<td>8</td>
<td>1.4</td>
<td>2.0</td>
<td>5 PPM</td>
<td>13.5</td>
<td>0.89</td>
</tr>
<tr>
<td>6</td>
<td>9.5</td>
<td>8</td>
<td>1.4</td>
<td>2.0</td>
<td>10 PPM</td>
<td>3.75</td>
<td>0.73</td>
</tr>
<tr>
<td>7</td>
<td>18.5</td>
<td>8.2</td>
<td>1.6</td>
<td>2.2</td>
<td>Blank</td>
<td>4</td>
<td>0.85</td>
</tr>
<tr>
<td>8</td>
<td>15</td>
<td>8.2</td>
<td>1.6</td>
<td>2.2</td>
<td>2 PPM</td>
<td>3.25</td>
<td>0.89</td>
</tr>
</tbody>
</table>

*LSI value held in the solution prior to precipitation which reduces drastically the LSI level.
Fig. 3 shows that at the LSI level of 1.4 bulk precipitation occurred in the Zn\textsuperscript{2+} free solution after a brief induction period of 1 hour. Fig. 4 shows that the presence of 2 PPM Zn\textsuperscript{2+} was able to prevent bulk precipitation throughout an experiment conducted at the same LSI level of 1.4.

Figs. 5, 6 and 7 show that a 2 PPM dosage of Zn\textsuperscript{2+} in a solution having the higher LSI level of 1.6 was not able to prevent the processes of permeability decline and of bulk precipitation. It may be therefore concluded that Zn dosage has a potential for inhibiting CaCO\textsubscript{3} scale deposition when the LSI level in the bulk of the solution is below 1.4 and the level on the membrane surface is below 2.0.
As noted below, the precipitation tendency of Zn ions increases with the increase in the pH level. The LSI level in the various FR runs was fixed by adjusting the pH while maintaining the same solution composition. Thus the poor inhibitory performance of Zn at the LSI level of 1.6 was probably due not only to the increase in the CaCO₃ precipitation potential but also to a decrease in Zn solubility arising from the pH level of 8.2 (as compared to the pH level of 7.6–8.0 prevailing in the runs at LSI = 1.1–1.4 which displayed a marked inhibition effect).

3.2.2. Inhibition effectiveness at LSI = 1.4 with increased Zn⁺⁺ concentrations: The effect of Zn concentration on inhibition effectiveness was investigated in runs 5 and 6, performed with dosages of 5 and 10 PPM Zn⁺⁺ respectively. The data obtained (Figs. 8–10) clearly indicate that increase of the Zn⁺⁺ concentration beyond 2 PPM diminished the inhibition effectiveness. The permeability data (Fig. 8) show a progressive deterioration in membrane permeability with increase of the Zn level. In fact, the decrease in permeability with 10 PPM Zn⁺⁺ is greater than that in the absence of Zn. Bulk precipitation, which was completely prevented by 2 PPM Zn⁺⁺ in Run 4 lasting 16 hours, occurred after 13.5 hours in the presence of 5 PPM Zn⁺⁺ (Fig. 9) and after 4 hours, in the presence of 10 PPM Zn⁺⁺ (Fig. 10).

3.2.3. Zn concentrations: Solubility data indicate that the experimental solutions were
supersaturated not only with respect to CaCO₃ but also with respect to some Zn salts, notably Smithsonite \([\text{ZnCO}_3]\) and Hydrozincite \([\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6]\). The least soluble Zn salt is Hydrozincite which has a very low solubility, given by \(\log(\text{IAP}) = -77.6\) at room temperature.

The solubility of Hydrozincite depends on the hydroxyl activity raised to the 6th power. Thus when augmenting the LSI level by increasing the pH of the solution of Table 1, the precipitation tendencies of both CaCO₃ and Hydrozincite are enhanced.

Fig. 11 shows the depletion of Zn\(^{++}\) from solutions of different initial zinc concentrations but with the same initial LSI level of 1.4 and the same initial pH value of 8.0. As anticipated, the Zn depletion rate is more rapid the higher the initial Zn concentration. Fig. 12 compares the rate of Zn depletion in solutions having the same initial Zn\(^{++}\) concentration of 2 PPM but different pH levels. It is seen that in Run 4 conducted at LSI = 1.4 and pH = 8.0 in which no bulk precipitation occurred, the Zn level remained substantially constant. On the other hand, in Run 8 conducted at LSI = 1.6 and pH = 8.2 in which bulk precipitation occurred, Zn depletion was rapid. It seems that the poor inhibitory effect of Zn at the high LSI value stems from the combined effect of co-precipitation and reduced Zn solubility.
3.3. Permeate withdrawal experiments

The inhibitory effect of Zn in permeate withdrawal experiments was studied by performing a series of runs at initial Zn\(^{++}\) levels of 0 (blank), 2 and 5 PPM respectively. The initial solution LSI level in all experiments was 1.2 and all other experimental conditions were nominally identical. Replicated runs showed good experimental reproducibility. Table 3 summarizes run conditions and provides data on the onsets of precipitation and the decline in membrane permeability. As noted before, permeabilities were evaluated taking into account the increase in osmotic pressure accompanying the solution concentration effect. Fig. 13 shows the increase in osmotic pressure of the solution in the runs analyzed below.

The onsets of membrane scaling and of bulk precipitation were detected from measurements of membrane permeability, from turbidity data and from solution composition analyses. Each experiment lasted about 10 hours and was terminated shortly after the onset of bulk precipitation. Onset of bulk precipitation occurred after a permeate water recovery of 40% to 60%.

3.3.1. Inhibition effects of Zn\(^{++}\): Membrane and solution performance in the PW experiments followed three stages. In the initial stage, membrane permeability remained constant and the experimental Ca\(^{++}\) concentration coincided with the theoretical value calculated from the concentration effect due to permeate withdrawal, assuming no precipitation.

Since the supersaturation level increases with the volume of permeating filtrate, a threshold LSI level, defined as LSI\(_1\), is reached at which CaCO\(_3\) begins to precipitate on the membrane surface. The precipitation process is initiated on the membrane surface since it is exposed to a higher supersaturation level, due to the CP effect. At this stage there is no increase in solution turbidity but a decline in membrane permeability is observed. The depletion in dissolved Ca\(^{++}\) concentration accompanying membrane scaling results in a deviation between measured and theoretically calculated calcium values.

The continuous increase in solution supersaturation generated by permeate withdrawal

### Table 3
Permeate withdrawal experiments

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Initial Zn(^{++}) PPM</th>
<th>Initial LSI</th>
<th>(L_p/b/L_p)</th>
<th>Membrane scaling onset</th>
<th>Precipitation onset</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>sol. bulk</td>
<td>memb. wall</td>
<td>((LSI_1)_b)</td>
<td>((LSI_1)_w)</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>1.2 (pH = 7.7)</td>
<td>1.6</td>
<td>59</td>
<td>1.39   1.78 1.55 1.72</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>1.2 (pH = 7.7)</td>
<td>1.6</td>
<td>90.5%</td>
<td>1.42   1.8  1.75 2.12</td>
</tr>
<tr>
<td>11</td>
<td>5</td>
<td>1.2 (pH = 7.7)</td>
<td>1.6</td>
<td>95.5%</td>
<td>1.52   1.91 1.8  2.18</td>
</tr>
</tbody>
</table>
ultimately leads to a threshold LSI limit, denoted as $\text{LSI}_2$, at which bulk precipitation is initiated. Bulk precipitation induces a rapid drop in the dissolved $\text{Ca}^{++}$ concentration and a sharp increase in solution turbidity, with a concomitant drastic decrease in the solution supersaturation level. Consequently, the process of membrane permeability decline is virtually arrested.

Fig. 14 describes the increase in the solution supersaturation potential LSI with time. The same data are plotted in Fig. 15 versus a more instructive parameter—the fractional water recovery. It is seen that the onset of bulk precipitation ($\text{LSI}_2$) is significantly delayed by the presence of Zn—from 1.55 at a threshold water recovery of 40% in the absence of Zn to about 1.8 at a threshold water recovery of 55% in the presence of 5 PPM $\text{Zn}^{++}$.

Figs. 16–18, showing the changes in calcium concentration and turbidity level with

Fig. 13. Osmotic pressure increase during PW runs.

Fig. 14. LSI vs. time in PW runs.

Fig. 15. LSI vs. % water recovery in PW runs.

Fig. 16. $\text{Ca}^{++}$ and turbidity in the absence of Zn.
the water recovery level highlight the three stages observed in the course of permeate withdrawal. The initial Ca\(^{++}\) concentration is seen to follow the theoretical concentration curve up to a certain recovery level corresponding to LSI\(_1\) after which membrane scaling causes an increasing deviation between measured and theoretically calculated Ca\(^{++}\) values. The threshold LSI\(_1\) level of 1.39 in the absence of Zn increases to 1.52 in the presence of zinc with a corresponding increase of the water recovery level from 18\% to 32\%. At the critical supersaturation level LSI\(_2\), bulk precipitation is seen to cause a rapid increase in turbidity and a sharp decline in Ca\(^{++}\) concentrations.

The beneficial effect of Zn in moderating permeability decline during the membrane scaling phase is well reflected in the data of membrane permeability versus water recovery presented in Fig. 19. It is seen that at a water recovery of 40\%, a permeability decline of about 40\% is observed in the absence of Zn. In the presence of 2 PPM Zn, the permeability decline at a water recovery of 50\% is about 10\% and with 5 PPM Zn, the permeability decline is less than 5\% at a water recovery of over 55\%.

Evidence linking high membrane permeabilities with the presence of Zn is given by the data of dissolved Zn concentration versus water recovery presented in Figs 20 and 21. Comparison of the Zn concentration of the theoretical curve assuming no precipitation with measured Zn values shows that part of the Zn was precipitating throughout experi-

![Fig. 17. Ca\(^{++}\) and turbidity with 2 PPM Zn\(^{++}\).](image)

![Fig. 18. Ca\(^{++}\) and turbidity with 5 PPM Zn\(^{++}\).](image)

![Fig. 19. Relative permeability vs. %recovery without and with Zn dosage.](image)
iment. However it is seen that the residual Zn concentrations in the solution prior to bulk CaCO₃ precipitation were sufficiently high to provide a marked inhibitory effect.

3.3.2. Zn levels in the PW experiments: Figs. 20 and 21 show the measured concentration of free Zn⁺⁺ compared to that predicted by the concentration effect due to permeate withdrawal. As in the FR experiments (Figs 11 and 12), the dissolved Zn⁺⁺ concentration decreased during the run. However, prior to bulk precipitation, relatively high dissolved Zn⁺⁺ concentrations above 2 PPM were maintained in the solution.

The higher dissolved Zn concentration in the PW experiments is most probably the reason why bulk precipitation was suppressed up to LSI₂ levels in the range of 1.55–1.8, in contrast to the lower LSI limit found in the FR experiments. The higher Zn solubility in the PW experiments stems from the lower pH level of the solution—an initial pH of 7.7 as compared to the pH level of 8.2 maintained in the FR experiments carried out at LSI = 1.6.

4. Conclusions

The results of this exploratory investigation indicate that dosage of trace amounts of Zn can induce a marked beneficial scale suppression effect within a certain range of water compositions. The results of the full recycle experiments suggest that a useful scale suppression effect might be exerted in treating concentrates at a membrane wall LSI level below about 2.0. Permeate withdrawal experiments extending over a period of 10 hours indicate the possibility of suppressing membrane permeability decline by 2–5 PPM Zn concentrations.

The preliminary experiments indicate that several effects are involved in the Zn inhibition effect apart from the CaCO₃ supersaturation level, notably Zn ion solubility in a solution of a given composition and Zn ion depletion by a pH related precipitation process.

Ongoing research aims at delineating conditions at which scale inhibition by the Zn technique could be of practical interest.
References

