Limits of RO recovery imposed by calcium phosphate precipitation

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Abstract
The presence of phosphate ions causes a difficulty confronting RO purification of secondary treated wastewater and limits the water recovery. These ions can readily lead to membrane blockage by precipitation of sparingly soluble calcium phosphate salts. Currently, it is far from clear if calcium phosphate scale deposition can be reliably inhibited by dosage of antiscalants. Major efforts were devoted to a systematic evaluation of the effectiveness of currently available calcium phosphate antiscalants. The inhibitory capability of the tested antiscalants was assessed using a continuous-flow laboratory system, equipped with a tubular RO membrane. Feed solution of controlled composition, dosed with an antiscalant, was continuously passed through the membrane. Both concentrate and permeate recycled to the feed vessel. Antiscalant effectiveness was evaluated from the rate of membrane permeability decay. Five antiscalants were tested under various solution supersaturation conditions and antiscalant concentrations. All antiscalants proved to be ineffective over most solution compositions tested. Results of this study delineate the restricted range of conditions under which currently available antiscalant are likely to provide an acceptable calcium phosphate scale inhibition.

1. Introduction

Use of treated sewage effluents for irrigation purposes can alleviate the increasing water scarcity difficulty. Common wastewater processes do not remove mineral salts dissolved in sewage effluents, even after tertiary treatment. Wastewater purified by MF/UF processes has restricted irrigation usages because of its high salinity [6]. Unrestricted irrigation usage of secondary treated wastewaters requires salinity removal by the

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proven method of reverse osmosis (RO). Widespread application of RO purification of secondary treated wastewaters is hindered by the calcium phosphate scaling problem.


The major difficulty in wastewater effluent purification by RO lies in effective control of the calcium phosphate scaling problem. The scaling species generally encountered in the desalination of seawater and brackish water feeds, mostly CaCO₃, CaSO₄ and silica, are commonly controlled by a wide variety of inhibiting compounds ("antiscalants"). Available information, as regards the possibility of coping with the problem by antiscalant treatment, is confusing.

Antiscalants were considered in an RO wastewater effluent purification project sponsored by the US Bureau of Reclamation (2002) [8], for coping with the calcium phosphate scaling problem. The wastewater effluent contained 356 mg/L Ca and 14 mg/L P. The final project report discarded the use of antiscalants, stating that "...based on discussions with several scale inhibitor manufacturers, calcium phosphate precipitation is not effectively prevented by commercially available RO antiscalants".

Field experience reported in recent publications is somewhat confusing. Some reports provide experimental evidence on the failure of antiscalants to mitigate calcium phosphate precipitation while in some major RO effluent projects, it is claimed that the calcium phosphate problem can be overcome by the use of antiscalants with control of the pH and of the recovery limits. An RO pilot plant was operated in Israel to purify effluents emanating from conventional secondary biological treatment [3]. The effluent contained 4–48 mg/L PO₄, 40–140 mg/L SO₄, 90–120 mg/L Ca and its pH was in the range of pH = 7.5–8.3. No antiscalant was able to prevent calcium phosphate precipitation at these high supersaturation conditions. Rapid blockage of the membranes was noted- a 40% decline in permeate flow rate occurred within less than two hours of operation. Another RO pilot plant endeavor in Israel [4] examined effluents containing 12–31 mg/L PO₄, 90–120 mg/L SO₄, 100–130 mg/L Ca and having a pH in the range of pH = 6.7–8.0. It was concluded that prevention of calcium phosphate scaling might be achieved through a combination of antiscalant dosage, lowered pH and low water recovery.

Recent papers on wastewater effluent purification by RO clearly acknowledge that the problem of calcium phosphate scaling is a limiting factor but claim that antiscalant dosage enables reasonable operation. In Kuwait’s giant water reuse project, which is currently the world’s largest membrane-based (UF and RO membranes) water reuse project (375,000 m³/day), the feed contains 5 mg/L P, and the RO operation is planned to achieve 85% recovery “limited by calcium phosphate precipitation” [7]. The Bedok (Singapore) wastewater reclamation RO plant treats wastewater containing 2.8 mg/L P, producing 32,000 m³/day of permeate [1]. The feed contains 34 mg/L Ca, 2.8 mg/L P and TDS of 694 mg/L (pH = 6.9, T = 30°C), while the concentrate contains 180 mg/L Ca, 14.6 mg/L P and TDS of 3535 mg/L (pH = 7.5). It is reported that the water recovery is 80%. Under these conditions, the concentrate is highly supersaturated with respect to TCP. Information on the calcium phosphate difficulty was not elaborated and no data were disclosed on the nature and concentration of the antiscalants used.

A very recent publication making reference to the calcium phosphate problem is a UK paper describing the Flag Fen plant, which treats municipal wastewaters to
provide cooling water for a power station [2]. The plant, undertaken since 1995, treats 1200 m$^3$/day effluents using MF and RO technologies. Fouling of the RO membranes proved to be the main challenge. Initial operation showed increase of the RO feed pressure at a rate of up to one bar per hour, due to calcium phosphate scale. The paper states that changes in upstream operation have effectively solved the problem without giving specific details.

It may be concluded, that the recently encountered calcium phosphate scaling difficulty has so far no accepted solution and this problem sorely needs R&D efforts. The main goal of the present research was to investigate the reliability of calcium phosphate scale control by currently available antiscalants of leading companies.

2. Experimental system

The experiments were conducted in a continuous flow pilot RO system equipped with a tubular membrane. The system was designed to enable partial or total recycle of the concentrate and permeate back to the feed vessel. The feed vessel has a capacity of 26 L. The system, shown schematically in Fig. 1, is designed to function unattended.

The tubular element installed in the RO system consisted of a high rejection polyamide/polysulfone composite RO membrane, acquired from X-FLOW, Holand (WFC 0995). The membrane was 14.5 mm in diameter, 1 m long; initial flow rate at 40 Bar is 50 L/m$^2$ h of a 0.35% NaCl at a pH of 6.2; NaCl rejection of 99±0.5% at 25 C. The membrane is held inside a stainless housing.

Total phosphate concentration was determined, using a HACH spectrophotometer, by the Phosphorus Reactive method. Dissolved calcium concentration was determined by EDTA titration, using Murexide as indicator, while dissolved magnesium concentration was determined from hardness measurements by
EDTA titration, using Eriochrome Black T as indicator. The total alkalinity of water was determined by HCl titration up to pH 4.3.

The test solution adopted in this study simulated the main ions present in the concentrate of a wastewater RO pilot plant, located at the Shafdan wastewater site. The feed to the RO pilot plant is a UF filtrate of secondary treated wastewater. The test solution simulated the RO concentrate at about 80% recovery and had the following composition: PO₄ = 28 mg/L, Ca = 330 mg/L, Cl = 587 mg/L.

2.1. Experimental routine

All experiments were carried out with a total recycle of both the concentrate and permeate to the feed vessel, so as to maintain a constant composition. The system was operated under one of the following flow conditions, both of which were in the turbulent regime:

- Feed flow rate of about 140 L/h, providing a Reynolds number (Re) of 4400, a mass transfer coefficient (kDa) of 1.9*10⁻⁵ m/s and leading to a relatively high concentration polarization (CP) modulus in the range of 2.0–2.4.
- Feed flow rate of about 240 L/h, providing a Reynolds number (Re) of 7100, kDa of 2.9*10⁻⁵ m/s and leading to a relatively low CP modulus in the range of 1.3–1.7.
- The net driving pressure (NDP) was 22–40 Bar and the temperature was held constant at 30°C by a thermostatically controlled electrical heating element and a water-cooled heat exchanger.

2.2. Monitoring of the calcium phosphate scaling process

The calcium phosphate scaling process was evaluated from measurements of the permeate decline. To enable comparison of experimental results, permeate flux data were normalized with respect to the initial, scale-free, membrane permeability, correcting also for the slight flux changes caused by temperature and NDP fluctuations, with respect to a normalized temperature of 30°C and a normalized NDP (usually 40 Bar).

Cumulative evidence indicated that the precipitating phosphate species in the present work was three calcium phosphate (TCP)-Ca₃(PO₄)₂. The supersaturation level (SI) of dissolved TCP is given by:

\[
SI = \frac{[Ca]^2[PO_4]^3}{K'_{SP}}
\]  
\[ (1) \]

where \( K'_{SP} \) is the solubility product of TCP, corrected for the ionic strength of the solution. Values of SI were calculated using the Minteq software [5]. The supersaturation level prevailing on the membrane is given by:

\[
SI_W = SI(CP)^5
\]  
\[ (2) \]

where \( SI_W \) is the concentration polarization modulus and the power index 5 results from the ionic product formula of TCP. Finally, scaling rates were characterized by evaluating \( \Delta L_p \), the percentage hourly decrease of the normalized permeability.

3. Results

3.1. Experimental program

The experimental program described below was designed to provide data on calcium phosphate scaling rates under various permeate flux conditions and concentration polarization levels with various concentrations of different antiscalants. Personal contacts with leading antiscalant experts led to the selection of the following five
recommended antiscalants for this study: AF-1025 (GOODRICH), PHREEGAURD 4500 (NALCO), EL-5301 (NALCO), HYPERSPERSE (BETZ) and PHO (GENESYS).

Table 1 summarizes the experimental conditions. The effect of the CP level was tested in two main sets of experiments. In Series A, antiscalant effectiveness was investigated under rather harsh conditions emanating from relatively high concentration polarization levels (concentrate flow velocity of 0.24 m/s) and relatively high permeate levels (NDP of 40 Bar). Since all antiscalants failed to inhibit precipitation under these conditions, the subsequent experiments (Series B, C and D) were performed under milder conditions provided by relatively low concentration polarization levels (concentrate flow velocity of 0.40 m/s) and relatively low permeate fluxes (NDP below 25 Bar).

3.2. Antiscalants effectiveness under relatively high CP conditions

The aim of Series A was to investigate the effects of the nature of the antiscalant and of the antiscalant concentration level on permeate flow decline. The experiments were carried out under feed flow conditions leading to relatively high CP level of 2.0–2.4, as described in section 2.1.

A comparison of four antiscalants (AF 1025, PHREEGUARD 4500, EL 5301 and PHO) was carried out by measuring permeate flux decay in solutions having identical compositions (Ca = 310–330 mg/L and PO₄ = 26–28 mg/L). The initial pH was 6.7 and it remained constant throughout the experiments. Antiscalant dosage covered the range of 15–45 mg/L

As shown below, in all cases the antiscalants proved to be largely ineffective in suppressing the permeate flow decay generated by the calcium phosphate scaling. In all cases, a decline in permeate flow rate and a slight drop in phosphate concentration were observed, indicating a scaling process on the membrane.

3.2.1. Scale suppression at various SI levels with antiscalant AF 1025- (Series A-I) Figs 2 and 3 describe the performances of the GOODRICH AF 1025 antiscalant in runs conducted with feed solutions in the SI range of 0.1–17. As expected, a constant permeate flow rate was maintained with the feed solution of SI = 0.14, which is undersaturated at bulk conditions. However, even in the presence of the relatively high AF 1025 antiscalant concentration of 15 mg/L, permeate flow decay was very high, amounting to 22% at SI = 9 and 34% at SI = 18 in a period of two hours.

The following experiments of series II were conducted using solutions with constant composition, in order to isolate the effect of the antiscalant and its concentration.

3.2.2. Scale suppression at various concentrations of the antiscalant AF 1025- (Series A-II) Figs. 4 and 5 show the performance of the antiscalant AF 1025 at three concentration levels of 15, 30 and 45 mg/L with feed solutions having a substantially constant composition (SI in the range of 30–39). It is seen that the antiscalant is ineffective at all concentrations. With the lowest antiscalant concentration of 15 mg/L permeate flow decreased by 28% in 40 min. An increase of the antiscalant concentration of up to 45 mg/L resulted in a marginal improvement- a permeate flux decline of 16–22% in 40 min.

3.2.3. Scale suppression at various concentrations of the antiscalant PHREEGUARD 4500- (Series A-III) Figs. 6 and 7 shows the performances of NALCO’s PHREEGUARD 4500 antiscalant at two concentration levels of 15 mg/L to 30 mg/L using feed solutions having the same composition as before (SI in the range of 29–31). This antiscalant also displayed a poor performance. The permeate flux decrease after 40 min was about 20–30%.
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<td>25</td>
<td>7.2</td>
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<td>25</td>
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\(^a\)At the beginning of the experiment. Temperature- 30°C; Values of CP, SI/SIw and permeate flux at the beginning of a run/stage.

\(^b\)Initial values of CP, SI/SIw and permeate flux at the lowest pH.
Within the accuracy of the experimental data, there is not much difference in the performances of PHREEGUARD 4500 as compared with AF 1025.

Fig. 2. Performance of antiscalant AF 1025 (15 mg/L).

Fig. 3. Normalized performance of antiscalant AF 1025 (15 mg/L).

Fig. 4. Performance of antiscalant AF 1025 at three dosages levels.

Fig. 5. Normalized performance of antiscalant AF 1025 at three dosages levels.
3.2.4. Scale suppression at various concentrations of the antiscalant EL 5301 (Series A-IV) Figs. 8 and 9 show the performances of NALCO’s EL 5301 antiscalant at two concentration levels of 15 mg/L to 30 mg/L using feed solutions having the same composition as before.
(SI in the range of 24–31). The performance of this antiscalant was slightly better. The permeate flow decrease after 40 min was about 15%. However, the data show a tendency for almost linear decrease with time indicating that this antiscalant also displayed a poor performance as the two previously tested antiscalants.

3.2.5. Scale suppression at various concentrations of the antiscalant PHO- (Series A–V) Figs. 10 and 11 show the performances of GENESYS’s PHO antiscalant at two concentration levels of 15 mg/L (Run 82) and 30 mg/L (Run 83) using feed solutions having the same composition as before (SI in the range of 32–35). The rate of flux decay in the higher antiscalant dosage experiment (Run 83) was higher than that of the lower dosage experiment (Run 82). The flux decline rate of the high dosage run (about 17% /h) was substantially similar to that of the other antiscalants. The results of Run 82 seem unreliable and need to be checked by repeat experiment.

It may therefore concluded that the four tested antiscalants are not capable of exerting a meaningful scale suppression effect in feed solutions having an SI level of the order of 20–40 at the CP level of 2.0–2.4.

3.3. Effect of the pH on HYPERSPERSE effectiveness under relatively low CP conditions (Series B)

Series B was designed to examine the influence of the pH, which is known to have a profound effect on the supersaturation level. Concentrate flow rate was about 240 L/h (except Run 81) in runs conducted in both the presence and absence of an antiscalant. An attempt was made to determine the exact pH range in which the supersaturation is high enough to cause deposition. The aim of Runs 89 and 94 was to determine the critical pH level at which a dosage of 30 mg/L HYPERSPERSE antiscalant might effectively inhibit phosphate precipitation.
The general view reflected in the few publications that refer to phosphate scale control by antiscalants is that favorable conditions are low TCP SI values. In practice, such conditions may be approached by maintaining a low solution pH value, a low permeate flux and high concentrate flow rates, which act to reduce the level of the concentration polarization modulus. In Series B runs, the concentration polarization level was reduced to about 1.6 by increasing the concentrate flow rate, but without a significant reduction of the permeate flux. The permeate fluxes were measured at successive solution pH values of 7.0, 7.25 and 7.5 in runs conducted with and without the presence of 30 mg/L HYPERSPERSE [Table 4.2]. Calculated bulk SI values were about 260 at pH = 7.0, 2900 at pH 7.5, while membrane surface SIW values were about 1200 at pH = 7.0, 14,000 at pH 7.5.

Figs. 12 and 13 showing permeate results in the absence of an antiscalant (Run 89) indicate a negligible decay at pH = 7.0 and significant decays at the higher pH values (8%/h at a pH = 7.25 and 14%/h at a pH = 7.5). The decay results in Figs. 14 and 15 obtained in the presence of the antiscalant

![Fig. 12](image1.png)  
**Fig. 12.** Effect of pH on permeate flux in the absence of an antiscalant.

![Fig. 13](image2.png)  
**Fig. 13.** Effect of pH on normalized permeability in the absence of an antiscalant.

![Fig. 14](image3.png)  
**Fig. 14.** Effect of pH on permeate flux in the presence of antiscalant HYPERSPERSE (30 mg/L).
(Run 94) show that the rate of decay was substantially constant at the three pH levels amounting about to 6%/h. It is evident that the HYPERSPERSE antiscalant was ineffective in controlling the phosphate scaling at the test conditions.

An attempt to regenerate the original permeate flux was made at the end of Run 94 by recirculating through the membrane an acidified solution (pH = 4) obtained by adding citric acid. As seen in Figs 14 and 15, the flux was restored but did not return to its initial value.

Finally, the results of the data in Figs 12 and 13 indicate that in the absence of an antiscalant, the critical pH at which rapid calcium phosphate precipitation may be expected is above 7.0–7.25, for solutions of 330 mg/L Ca and 28 mg/L PO\textsubscript{4}, and a CP of about 1.6 (concentrate flow rate of 240 L/h).

Two Runs [81,85] performed in the absence of an antiscalant explored the effect of pH over a wider range. These preliminary runs were of poor accuracy but despite their experimental scatter, they indicated similar pH trends as found in the better-controlled Runs 89 and 94.

It may be of interest to summarize data measured in Series A-B by plotting the rate of permeate flux decline vs. the supersaturation level prevailing on the wall of the membrane, calculated on the assumption that scaling is controlled by TCP precipitation. The data in Fig. 16 show the expected trend, that permeability decline increases with the supersaturation level and also reflects the inability of the tested antiscalants to moderate the scaling process.

3.4. Effect of the permeate flux on HYPERSPERSE effectiveness under relatively low CP conditions (Series C)

The aim of these experiments was to investigate the effect of the net driving pressure (NDP) on the rate of flux decline. The initial pH was 7.2 and the concentrate flow rate was 240 L/h. The initial NDP in Run 91 was 25
Bar and was gradually increased to 40 Bar (about 5 Bar about every 1 h). The initial NDP in Run 92 was 22 Bar and was gradually increased to 28 Bar (about 3 Bar about every 2 h). Both solutions contained no antiscalant. Run 96 was identical to Run 92, except that 30 mg/L of HYPERSPERSE antiscalant was dosed to the feed solution.

As stated before, it is generally agreed that lowering the permeate flux level acts to moderate scaling difficulty. This effect was investigated in Runs 91 and 92, conducted in the absence of an antiscalant and in Run 96, conducted in the presence of antiscalant HYPERSPERSE. In Runs 91 and 92 [Figs. 17 and 18] the permeate flux level was varied by successive increases of the operating pressure from 22 to 40 Bar, while in Run 96 [Figs. 19 and 20] the flux level was varied by increase of the pressure from 22 to 28 Bar.

Figs. 17 and 18 clearly demonstrate that the rate of permeate flux decay increases with operating pressure. Below 28 Bar, the decay is relatively slow (less than 4%/h), while above 30 Bar there is sharp increase in the decay rate, reaching 13%/h. Further supporting evidence to the direct influence of the permeate flux on the rate of permeability decay is found by comparing the rate of flux decay obtained at two different operating pressures but with an initial identical permeate flux. These conditions were achieved in the data measured at operating pressures of 35 and 40 Bar, starting with the same initial permeate flux of 41–42 L/m² h. The decay rate at 35 Bar was 12.5–12.7%/h which is substantially identical to the rate of 12.4–12.8%/h at 40 Bar.

Figs 19 and 20 show that the presence of the antiscalant in Run 96 arrested the permeability decay process, due to phosphate scaling, observed in Runs 91 and 92. The rate of permeability decay of 1%/h in Run 96 was repeatedly measured in experiments in which distilled water was circulated in the system. Further supporting data are found in Fig. 21, which compares the virtually constant permeate flow rate in Run 96, conducted at low operating pressure, with significant permeate flow decay obtained in Run 94, conducted at 40 Bar (6%/h).

It seems therefore that successful suppression of phosphate scaling by antiscalants is...
restricted to low supersaturation conditions corresponding to pH levels below 7.0–7.2 combined with low permeate flux levels, below about 30 L/m² h and a low CP modulus below about 1.3.

The aim of Series D was to compare the scale suppression effectiveness of four antiscalants (AF 1025, PHREEGUARD 4500, EL 5301 and HYPERSPERSE) under identical solution compositions, in the low permeate level flux range. Low permeate fluxes were obtained by operating the system at 25 Bar. The SI level in all runs was within the range of 80–180, the pH was 7.2 and the antiscalant concentration was 30 mg/L. Each experiment was started by recycling distilled water through the membrane for one hour in order to normalize results with respect to the flux decline attributable to a distilled water fouling effect rather than to phosphate scaling. A reference run was also carried out (Run 307) using the same test conditions but without dosage of an antiscalant in order to observe clearly the scale suppression effect exerted by the antiscalant. Run 308 served to verify that the increase of NDP to 40 Bar was responsible for an accelerated flux decline.
3.5. Scale suppression effectiveness of various antiscalants at a low permeate flux level (Series D)

The permeate flux results displayed in Figs 22 and 23 clearly show that the permeate flux decay of one antiscalant (PHREEGUARD 4500) is almost identical to the flux decay observed in the absence of any antiscalant. It is evident that the performance of the other antiscalants (AF 1025, EL 5301 and HYPERSPERSE) is far superior. In fact, the initial distilled water points of these three runs indicate a permeate flux decline of the same magnitude as that measured in recycling the phosphate solution dosed with the antiscalants. It may be concluded that the antiscalants arrested completely the phosphate scaling process performance under the test conditions.

Finally, an additional test was carried out to confirm the importance of the permeate flux level. Run 308 was conducted with AF 1025 under identical conditions as Run 311 but with a operating pressure increased from 25 to 40 Bar. Figs. 24 and 25 confirm that permeate flux is a crucial parameter that should be maintained below a critical value in order to achieve successful scale control.

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**Fig. 22.** Comparison of various antiscalants at a dosage of 30 mg/L.

**Fig. 23.** Normalized comparison of various antiscalants at a dosage of 30 mg/L.

**Fig. 24.** Comparison between NDP of 25 and 40 Bar in the presence of 30 mg/L AF 1025.
4. Conclusions

The results of the study on the effectiveness of currently available antiscalants on calcium phosphate scale inhibition may be summarized as follows:

- All tested antiscalants proved to be ineffective over most solution conditions.
- The experimental data indicate that antiscalants are likely to prove ineffective when operating conditions are as follows: solution pH above 7.0–7.2, permeate flux above 40 L/m² h and CP modulus higher than about 1.5.
- A dosage of about 30 mg/L antiscalant is more likely to suppress phosphate scaling when operating conditions as follows: pH lower than 7.0, permeate flux below 30 L/m² h and CP modulus lower than 1.3.

At the current state of art with the available antiscalants it seems that control of phosphate scaling by antiscalants is problematical and must be very carefully monitored.

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References