Role of phosphate and humic substances in controlling calcium carbonate scaling in a groundwater reverse osmosis system

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A B S T R A C T

The role of phosphate and humic substances (HS) in preventing calcium carbonate scaling and their impact on antiscalant dose was investigated for a reverse osmosis (RO) system treating anaerobic groundwater (GW) (containing 2.1 mg/L orthophosphate and 6–8 mg/L HS).

Experiments were conducted with the RO unit (treating anaerobic GW), and with a once-through lab-scale RO system (operating with artificial feedwater). Additionally, (batch) induction time (IT) measurements were performed with, i) real RO concentrate, and ii) artificial RO concentrates in the presence and absence of phosphate and HS.

It was found that at 80% recovery (Langelier saturation index (LSI) 1.7), calcium carbonate scaling did not occur in the RO unit when the antiscalant dose was lowered from 2.2 mg/L (supplier’s recommended dose) to 0 mg/L. The IT of the real RO concentrate, without antiscalant, was longer than 168 h, while, at the same supersaturation level, the IT of the artificial concentrate was approximately 1 h. The IT of the artificial concentrate increased to 168 h with the addition of 10 mg/L of phosphate, humic acid (HA), and fulvic acid (FA). Furthermore, in the lab-scale RO tests, the normalized permeability (Kw) of the membrane decreased by 20% in 2 h period when fed with artificial concentrate of 80% recovery containing no phosphate, whereas, with phosphate, no decrease in Kw was observed in 10 h period.

These results indicate that phosphate and HS present in the GW prevented calcium carbonate scaling in the RO unit and reduced the use of commercial (synthetic) antiscalants.

1. Introduction

In the Netherlands, over 60% of the produced drinking water by Dutch water supply companies is obtained from the treatment of GW [1, 2]. Although, in general, the quality of GW is already very good, it is often desirable to remove a wide range of components, such as salinity, specific ions, organic micropollutants (OMPs), color, all of which can be obtained by RO. For this reason, several of the Dutch water supply companies have embraced (or are exploring) the use of RO technology for producing drinking water of impeccable quality.

In RO applications, the recovery (ratio of the permeate water to the feed water) strongly affects the economic and operational performance due to the total energy consumption per unit volume of product water, concentrate volume, and the scale of the pretreatment. When treating seawater, the osmotic pressure limits the recovery of the system. Conversely, in brackish water RO (BWRO), it is usually economically favorable to increase the recovery. However, membrane scaling is the main obstacle in operating BWRO systems at high recovery rates. The consequences of scaling are increase in feed channel pressure drop, increase salt passage, higher feed pressure requirement resulting in higher operational costs and shorter lifetime of membranes caused due to frequent cleanings [3].

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Scaling is the precipitation of poorly soluble species (e.g., calcium carbonate, calcium sulphate, barium sulphate, calcium phosphate, etc.), which become oversaturated as the retained salts are concentrated in the RO system. Thus, scaling in RO systems is related to the composition of feed water (e.g., concentration of inorganic compounds, pH, temperature etc.), as well as to the recovery of the RO [4].

In this study, we focus on calcium carbonate scaling, which is one of the most common type of scale encountered in RO systems [4]. The formation of calcium carbonate in RO concentrate is directly related to the concentration of calcium and bicarbonate/carbonate and various other factors including but not limited to temperature and pH. The solubility of calcium carbonate in water decreases with an increase in temperature and pH. The scaling potential of calcium carbonate for a given water composition can be expressed by various indicators, such as the saturation ratio (S), the saturation index (SI), and the LSI. These indices only provide information about the saturation level. Whether calcium carbonate may or may not precipitate on the surface of the membrane depends not only on supersaturation, but also depends on the precipitation kinetics such as nucleation and growth rates. The mentioned indices do not provide information about the precipitation kinetics or the time required for precipitation to occur. To obtain information about reaction kinetics, growth tests and/or IT measurements are generally performed. In this study, we focused on IT measurements where IT is considered as the elapsed time between the development of the supersaturated conditions and the detection of crystallization [5-7].

At supersaturated conditions, the precipitation of calcium carbonate in RO applications is controlled by the addition of antiscalants. Antiscalants allow much higher supersaturation without scale formation. The crystallization process of calcium carbonate and other scaling species (e.g., calcium sulphate, barium sulphate, etc.) is hindered in the presence of antiscalants, resulting in prolonged IT [8-10]. Various types of antiscalants are available such as polyphosphates, phosphonates/organophosphates, polyacrylates and biobased, and their effectiveness is reported to depend on the functional groups of the molecules, their molecular weight, and charge density [4,11]. Threshold inhibition is one of the main mechanisms of antiscalants by which the process of crystallization is hindered by the adsorption of antiscalants on the active sites of the first nucleating crystals [12,13]. More specifically, when the crystal formation starts to occur at submicroscopic level, the negative groups of the antiscalant attach to the cationic sites of the scale nuclei which then disrupts the electronic balance that is required to encourage the growth of the crystals [4,12,14]. As a result, antiscalants not only delay the formation of calcium carbonate, i.e., prolonging the IT, but also decreases the crystal growth rate of calcium carbonate [12].

In applications other than RO, researchers have reported that the crystal growth rate of calcium carbonate is also reduced when a water solution contains some common inorganic ions, including but not limited to the magnesium ion [15-17], orthophosphate ion [18-20], and sulphate ion [21] as well as when it contains dissolved organic substances such as HS [22-26]. It is, therefore, likely that when these substances are present in RO feed, they may have an inhibitory effect on calcium carbonate scaling and could result in the reduction of antiscalant dose. Operating the RO with the lowest antiscalant dose at which scaling does not occur is necessary, since high doses of antiscalant not only result in additional costs, but may pose environmental concerns. To the authors’ knowledge, no study to date has examined the effects of aforementioned ions and HS on reducing the antiscalant dose to tackle calcium carbonate scaling in RO plants [4].

The objective of this paper is to investigate the effect of inorganic ions, particularly phosphate, and HS on calcium carbonate scaling for an RO system treating anaerobic GW in the Netherlands. We combine results from an RO pilot, operating with anaerobic GW, a lab-scale RO system, operating with artificial feedwater, and controlled precipitation experiments. By systematically varying the composition of the artificial feedwaters, different aspects of the complex anaerobic GW are isolated and investigated separately.

### 2. Materials and methods

#### 2.1. Chemicals

In this study, to investigate the effects of inorganic ions (e.g., phosphate, magnesium and sulphate) and HS on the inhibition of calcium carbonate scaling in RO processes, experiments (e.g., IT measurements (described later in Section 2.3)) were performed with both real RO concentrates and artificial RO concentrates. To identify the effect of the mentioned ions and HS individually on the precipitation of calcium carbonate, it was necessary to carry out experiments with the artificial RO concentrates, which was not possible with the real RO concentrate. The artificial solutions were prepared using Milli-Q water (Merk Millipore, conductivity < 10 µS/cm and TOC < 30 µg/L). The chemicals used include Na₂SO₄, CaCl₂·2H₂O, KH₂PO₄, and MgCl₂·6H₂O (Analytical Grade, Merck), NaHCO₃, NaOH, and NaHSO₃ (Analytical Grade, J.T. Baker), HA and FA (International Humic Substances Society, (IHSS)). For pH adjustments, 0.2 M solutions of HCl (Analytical grade, ACROS Organics) or NaOH were employed. The artificial concentrate solutions are prepared such that the Ca²⁺ and HCO₃⁻ concentrations were equivalent to the concentration of real ground water (Table 1, Section 2.2) treated at a certain recovery value. The antiscalant used in this study was OSM92 (Aquacare Europe) which is a phosphate antiscalant.

#### 2.2. GW composition

The anaerobic GW was abstracted from several wells of a drinking water production plant in Kamerik, Netherlands. The composition of the anaerobic GW (RO feed) is presented in Table 1. The values in Table 1 represent an average obtained from the regular feedwater monitoring of the drinking water production plant, and was performed by a commercial lab (Vitens Laboratorium, Netherlands). For the identification and quantification of HS, the dissolved organic carbon (DOC) was characterized with liquid chromatography–organic carbon detection (LC–OCD) (DOC-Labor, Germany).

The assessment of the scaling potential of the RO concentrates at various recoveries was performed using the projection programs of antiscalant manufacturers. For the scaling tendency of calcium carbonate, the programs calculated LSI, where a positive LSI value for a solution implies that the solution is supersaturated in calcium carbonate and precipitation might occur, while a negative LSI value denotes that the solution is undersaturated and calcium carbonate will not precipitate. In addition, the projection programs also suggested a required antiscalant dose to prevent scaling. To determine the speciation of calcium and phosphate ions, Visual MINTEQ program (version 3.1) was employed.

### Table 1

| Anion               | Concentration (mg/L) |
|---------------------|----------------------|
| Sulphate            | 38.2 [20-44]         |
| Chloride            | 79.4 [70-95]         |
| Fluoride            | 0.1 [0.1-0.14]       |
| Bicarbonate         | 391.8 [380-410]      |
| Carbonate           | –                    |
| Nitrate             | < 0.2                |
| Silica              | 16.7 [14.6-16.7]     |
| Orthophosphate      | 2.1 [1.8-2.5]        |

#### Other properties of the feedwater:

| pH                  | 7.0-7.1               |
| DOC (mg/L)          | 750-800               |
| Temperature (°C)    | 12                    |
| Turbidity (NTU)     | < 0.1                 |

◊ Values in brackets [] represents the range of concentrations that could be present in the RO feed due to the various combination of wells, a TDS = Total dissolved solids.
Furthermore, the Visual MINTEQ program was also used to identify the complexation of calcium ions with HS.

2.3. IT measurements

A schematic diagram of the IT setup is illustrated in Fig. 1. This setup was also used by Waly et al. [27]. An air-tight double wall 3 L Applikon glass reactor was used for the IT experiments. The Applikon reactor had an internal diameter of 12 cm and a height of 24 cm. The reactor included a mixing controller with mixing shaft that was used to adjust the stirring rate of the solution. The stirring rate could vary between 0 and 1250 rpm. A stirring rate of 150 rpm was used for the IT measurements [7,27]. The top of the reactor was closed using a stainless-steel lid equipped with a thin rubber gasket to avoid the escape of CO₂ from the solution into the air and vice versa. In this study, IT experiments were performed by measuring the pH of the solution using a pH probe (Endress + Hauser) with an accuracy of ± 0.01 pH units. The probe was inserted in the reactor and the pH values were continuously recorded during the entire experiment. The interval for pH measurements was set to 1 min. IT was defined as the time when the solution pH decreased by 0.03 units from the initial value, due to calcium carbonate precipitation [28]. It is worth mentioning that a part of the measured IT may also include (part of) the growth phase of calcium carbonate.

At the end of each experiment, the reactor was filled with 0.1 M HCl to dissolve any crystals formed during the experiment. Acid cleaning was performed for 30 min and the stirring rate was set to 1250 rpm. After acid cleaning, the reactor was flushed twice with demineralized water (demi-water) for 10 min. A thermostat was used to maintain a constant temperature of 20 °C during the experiments.

IT measurements were performed using both anaerobic real RO concentrates (Table 2) and artificial concentrate solutions (Table 3). It should be noted that the real RO concentrates (Table 2) include all the ions (substances) present in the anaerobic GW, but only the relevant ions to this study are listed in Table 2.

It was crucial to keep the anaerobic RO concentrate anaerobic and eliminate the oxidation of Fe²⁺ while filling the reactor. For this, the 3 L reactor was filled (at approximately 10 L/min flow rate) with the anaerobic RO concentrate, in a bottom to top manner, from a tube equipped with fine nozzles located 3 cm from the bottom of the reactor. At the same time, the concentrate was drained from the overflow tube (Fig. 1) located on the top of the reactor. After 30 min, the concentrate flow was stopped and the overflow tube of the reactor was closed. Thus, the reactor was completely filled with the anaerobic RO concentrate. In the case of the presence of some (trace) amount of dissolved oxygen that might have intruded during filling, NaHSO₃ (< 10 mg/L) was used to prevent Fe²⁺ oxidation, and then NaOH was used to correct the pH.

To run an IT experiment with the artificial concentrate, the 3 L reactor was initially half-filled with the NaHCO₃ solution and the pH was set at the desired value. Afterwards, the remaining half of the reactor was filled with the CaCl₂·2H₂O solution through the fine nozzles located 3 cm from the bottom of the reactor to maintain the uniform distribution of the solution. While adding the CaCl₂·2H₂O solution, the stirring rate inside the reactor was set to 150 rpm to allow uniform mixing of the solutions and avoid the formation of any local supersaturated zones.

2.4. RO pilot

The RO pilot plant is schematically represented in Fig. 2. The RO consisted of three stages, with a variable number of parallel pressure vessels containing three 4 in. membrane elements (Hydranautics ESPA2-LD-4040) each. The anaerobic GW, after passing through a cartridge filter (10 µm), was directly fed to the RO unit and the unit was operated at constant permeate production. The normalized Kₑ (Eq. (1)) and the normalized pressure drop (ΔP, Eq. (7)) for the last element of the third stage (internal scale guard) were recorded separately. The equations used to normalize the RO operational data were obtained from the membrane manufacturer (Hydranautics). An example calculation for normalizing the operational data, i.e., Kₑ of the internal scale guard is given in the Supplementary Material. The purpose of including an internal scale guard in the last pressure vessel is to monitor the occurrence of scaling. The internal scale guard is the last element in the last stage of RO for which the permeate flow (thus Kₑ) and the ΔP across the element are measured. The permeate of the internal scale guard is collected separately from the permeate outlet (located on the concentrate side of the pressure vessel) and the permeate of the other membrane elements in the pressure vessel is collected from the permeate outlet which is located on the feed side as illustrated in Fig. 2 and Fig. S1.

$$K_e = \frac{Q_p}{NDP \times A} \times \frac{TCF_r}{TCF_t}$$

(1)

Where: $Q_p$ = permeate flow (L/h); $NDP$ = net driving pressure (bar); $A$ = membrane area (m²); $TCF_r$ = temperature correction factor at reference conditions (25 °C) which is equal to 1; $TCF_t$ = temperature...
correction factor at time t.

\[ \text{NDP} = P_f - \Delta P_{fc} - P_p - \pi_{fc} + \pi_p \]  

(2)

Where: \( P_f \) = feed pressure (bar); \( \Delta P_{fc} \) = pressure drop (bar); \( P_p \) = permeate pressure (bar); \( \pi_{fc} \) = feed-concentrate osmotic pressure (bar); \( \pi_p \) = permeate osmotic pressure (bar).

\[ \pi_{fc} = 0.002654 \times C_{fc} \times \frac{(T + 273)}{(1000 - \frac{C_{fc}}{1000})} \]  

(3)

\[ \pi_p = 0.002654 \times C_p \times \frac{(T + 273)}{(1000 - \frac{C_p}{1000})} \]  

(4)

\[ C_t = C_x + C_c \]  

(5)

Where: \( C_t \) = TDS of the feed (mg/L); \( C_c \) = TDS of the concentrate (mg/L); \( C_p \) = TDS of the permeate (mg/L); \( T \) = Temperature (°C)

\[ \text{TCF} = e^{2700 \left( \frac{T}{12} - 1 \right)} \]  

(6)

In RO processes, it is essential to normalize the operational data (e.g., \( K_w \), etc.) to account for the changes occurring in the RO feed. It can be misleading if the data is not normalized. For instance, if the temperature of the RO feed drops, the \( K_w \) will decrease suggesting that fouling/scaling is occurring which in reality may not be the case. To account for the temperature changes in the RO feed, temperature correction factor (Eq. (3)) is given by the membrane manufactures. It is assumed that by normalizing the data (e.g., \( K_w \)) with the temperature correction factor, the effect of temperature change on the \( K_w \) is omitted completely. It is worth mentioning that the RO feed in this study is anaerobic GW which has more or less constant temperature, and therefore the effect of temperature change on the \( K_w \) is negligible.

\[ \Delta P = \Delta P_t \times \left( \frac{Q_{c,ref}}{Q_{c,act}} \right)^m \times \left( \frac{\eta_{T,ref}}{\eta_{T,act}} \right)^n \]  

(7)

Where: \( Q_{c,ref} \) = average reference feed/concentrate flow; \( Q_{c,act} \) = average feed/concentrate flow at time t; \( \eta_{T,ref} \) = viscosity at reference temperature; \( \eta_{T,act} \) = viscosity at actual temperature; \( m = 1.4; n = 0.34 \).

The RO pilot was operated with various antiscalant doses and without dosing antiscalant as described in Table 4. In the first set of experiments, the RO unit was operated at 70% and 80% recoveries initially with the antiscalant dose recommended by the projection programs of the antiscalant suppliers, and then the dose was lowered by 0.5 mg/L and/or 0.2 mg/L after each 12 h of RO operation to a final dose of 0.2 mg/L. In the second set of experiments, the RO unit was...
operated without antiscalant addition. The average operating flux of the last stage was in the 10–20 L/h/m²/bar range for all experiments.

2.5. Lab-scale RO measurements

Lab-scale RO measurements were done with a system schematically represented in Fig. 3. The setup comprised of a SEPA CF cell (140 cm², Sterlitech Corporation, USA) and the OMSO Inspector unit (Convergence Industry B.V., Netherlands). Membrane sheets harvested from a Hydranautics ESPA2-LD-4040 element were used. A new membrane sheet was used for each experiment. In all experiments, the recovery was in the range of 0.5–0.7% and the cross-flow velocity was approximately 0.12 m/s. Both permeate and concentrate were directed to the drainage. All experiments were carried out at room temperature (20–23 °C). When a drop in K_w was observed, scanning electron microscopy (SEM) (JEOL JSM-6010LA) was used to examine the membrane sheets.

Several artificial feed solutions (Table 5) were used, that were realized by continuous dosing of additives (e.g., Ca²⁺, HCO₃⁻, PO₄³⁻, etc.) to the feed stream of demi-water as illustrated in Fig. 3a. If no chemical dosing was applied, Milli-Q water was dosed instead. The final solution (artificial concentrate solution) was introduced to a 5 L reactor in which the artificial concentrate solution was stirred at a rate of 150 rpm with a residence time shorter than 1 min. The residence time of less than 1 min was achieved by maintaining equal flow rates (32 L/h) of the artificial concentrate solution entering and leaving the 5 L reactor and by keeping the volume of the artificial concentrate solution in the reactor to approximately 0.5 L.

In this study, the once-through lab-scale RO measurements with the HA and FA (IHSS) were not performed as those experiments were cost-wise not feasible.

| Run | Recovery (%) | Recommended dose (mg/L) | Initial dose (mg/L) | Final dose (mg/L) | Pressure vessel configuration | Run period (days) |
|-----|--------------|-------------------------|---------------------|-------------------|------------------------------|------------------|
| A   | 70           | 2.8                     | 3.0                 | 0.2               | 6–2–1 (3 elements)           | 10               |
| B   | 80           | 2.2                     | 2.2                 | 0.2               | 6–2–1 (3 elements)           | 16               |

Recommended dose was the antiscalant dose determined by the projection program of the antiscalant manufacturer.
6 in the feed water was approximately 2.8 mg/L for the RO operation at some concerns with the results from the projection software. Firstly, scaling at 70% and 80% recoveries. It is worth mentioning that we have compounds, of the anaerobic RO concentrate at recovery values of 70% and 80% recoveries varying the feedwater composition, we noticed that the recommended dose must increase with the recovery, because the system operating at 80% contains, at some location, concentrate that is equivalent with 70% recovery and therefore requires at least a dose that is required for 70%. Secondly, by varying the feedwater composition, we noticed that the recommended dose (given by the projection programs) does not depend on phosphate, magnesium, sulphate or DOC concentration. For instance, at 80% recovery, the recommended dose by the projection program was 2.2 mg/L when the feed water contained 2.1 mg/L of phosphate and when phosphate was eliminated from the feedwater input of the projection program. However, precipitation studies suggest that these factors affect the precipitation of calcium carbonate [18,19,21–26,29].

3. Results and discussion

3.1. Scaling potential and the recommended antiscalant doses at 70% and 80% recoveries

The scaling tendency, for several commonly encountered scaling compounds, of the anaerobic RO concentrate at recovery values of 70% and 80% with and without antiscalant addition is presented in Fig. 4. The figure shows that both calcium carbonate and barium sulphate are supersaturated and may be expected to cause scaling in the absence of antiscalant. The LSI values were 1.2 and 1.7 for the real RO concentrates at 70% and 80% recovery, respectively. The supersaturation level of the different phases of calcium carbonate is given in Table S1. We expect that calcium carbonate will precipitate prior to barium sulphate. Boerlage et al. [6] demonstrated that barium sulphate has very slow precipitation kinetics even at saturation levels as high as 4.5.

Furthermore, Fig. 4 shows that calcium carbonate and barium sulphate scaling may not occur in the presence of antiscalant. The projection software recommended a phosphonate antiscalant for controlling scaling at 70% and 80% recoveries. It is worth mentioning that we have some concerns with the results from the projection software. Firstly, according to the projection program, the recommended antiscalant dose in the feed water was approximately 2.8 mg/L for the RO operation at 70% recovery and a lower dose of about 2.2 mg/L for operation at a higher recovery of 80%. We consider that the required dose must increase with the recovery, because the system operating at 80% contains, at some location, concentrate that is equivalent with 70% recovery and therefore requires at least a dose that is required for 70%. Secondly, by varying the feedwater composition, we noticed that the recommended dose (given by the projection programs) does not depend on phosphate, magnesium, sulphate or DOC concentration. For instance, at 80% recovery, the recommended dose by the projection program was 2.2 mg/L when the feed water contained 2.1 mg/L of phosphate and when phosphate was eliminated from the feedwater input of the projection program. However, precipitation studies suggest that these factors affect the precipitation of calcium carbonate [18,19,21–26,29].

3.2. Effect of antiscalant dose on RO pilot performance

The appropriate antiscalant dose was determined experimentally by operating the RO pilot with 70% and 80% recovery and varying antiscalant dose. The results are illustrated in Fig. 5.

In Fig. 5a, the normalized $K_w$ and the normalized $\Delta P$ of the last element (the internal scale guard) are shown when the RO unit was operated at 70% and 80% recoveries with various doses of a phosphonate antiscalant. As shown, the RO unit was operated for 10 days at 70% recovery (LSI 1.2) with an initial dose of 3 mg/L (0.2 mg/L higher than the recommended dose) which was then lowered every 12 h to a final dose of 0.2 mg/L. During this period, the normalized $\Delta P$ remained constant and also no decrease in the normalized $K_w$ was observed even when the antiscalant dose was as low as 0.2 mg/L. It could be that the antiscalant dose of 0.2 mg/L was sufficient to target calcium carbonate scaling or perhaps calcium carbonate scaling might not occur in 6–10 days of RO operation at 70% recovery.

After 10 days of RO operation at 70% recovery, the RO recovery was increased to 80% (Fig. 5a) where calcium carbonate was highly supersaturated (LSI 1.7). The starting antiscalant dose was 2.2 mg/L (equivalent to the supplier’s recommended antiscalant dose) for the first day of the RO operation at 80% recovery which was afterwards lowered by 0.2 mg/L after every 12 h of operation to a final dose of 0.2 mg/L. As can be seen, the normalized $K_w$ remained constant and also no increase in the normalized $\Delta P$ was observed when the RO unit was operated for 12 days with an antiscalant dose as low as 0.2 mg/L.

The RO unit was operated at 80% recovery without antiscalant addition (Fig. 5b). As can be seen, both the normalized $K_w$ and the normalized $\Delta P$ remained constant for an experimental period of 32 days at 80% recovery which indicated that there was no need to add antiscalant even when the LSI of the RO concentrate was as high as 1.7. This suggested that calcium carbonate scaling might have been inhibited by some constituents (possibly phosphate and HS) present in the feedwater (anaerobic GW) that might have functioned as natural antiscalant.

| Exp. # | Feed solution | Equivalent recovery (%) | Flow rate | pH | Ca²⁺ (mg/L) | HCO₃⁻ (mg/L) | PO₄³⁻ (mg/L) |
|-------|---------------|-------------------------|-----------|----|-------------|--------------|--------------|
| 1     | Artificial concentrate | 80 | 32 L/h | 7.4 | 576 | 1959 | 0 |
| 2     | Artificial concentrate | 80 | 32 L/h | 7.4 | 576 | 1959 | 10 |

* Feed solution to the SEPA CF cell.
3.2.1. Comparing anaerobic real RO concentrate and artificial concentrate
To understand why the RO pilot did not scale at high supersaturation levels, IT measurements were performed with the anaerobic real RO concentrate at 70% and 80% recoveries in the absence of antiscalant (Exp. A and B, Table 2). In parallel, IT measurements were also executed using artificial concentrate solutions (Exp. A and B, Table 3).

In Fig. 6, we show that the measured ITs of the real RO concentrate at 70% and 80% recoveries were both longer than 168 h (7 days), while for the artificial concentrates corresponding to 70% and 80% recoveries, the measured ITs were approximately 6 h and 1 h, respectively. Thus, at the same supersaturation level, the IT of the real RO concentrate at 80% recovery was at least 168 times longer than that of the artificial concentrate. This result clearly shows that the formation of calcium carbonate was suppressed in the anaerobic real RO concentrate by some

Fig. 6. (a) IT of the (▾) real RO concentrate at 70% recovery without antiscalant, (▽) artificial concentrate at 70% recovery without antiscalant, (b) IT of the (▴) real RO concentrate at 80% recovery without antiscalant, (△) artificial concentrate at 80% recovery without antiscalant.
constituents present in the RO feedwater (anaerobic GW).

3.3. Effects of phosphate and HS on the precipitation of calcium carbonate

In Table 6, the DOC characterization of the anaerobic GW with LC-OCD analysis is presented. The analysis revealed that from 8.62 mg/L of DOC in the GW, 5.26 mg/L (61.1%) was represented by HS of FA type. We consider that the difference between the ITs of the anaerobic RO concentrate and the artificial concentrate, demonstrated in the previous section, is caused by phosphate and/or HS present in the GW (Table 1, Table 6). We investigated this hypothesis by varying the composition of the artificial concentrate (Table 3), evaluating the effect of magnesium and sulphate (Fig. 7a), phosphate (Fig. 7b), FA (Fig. 7c) and HA (Fig. 7d) which is presented in the next section.

3.3.1. IT measurements

In this section, the effects of phosphate and HS on hindering calcium carbonate precipitation is presented with the IT measurements. Additionally, IT tests with some other ions such as Mg$^{2+}$ and SO$_4^{2-}$, which are reported in literature to have a positive effect on the suppression of calcium carbonate, are also presented here to identify if those ions have played a role in the long IT of the real RO concentrate.

Fig. 7a compares the ITs of the artificial concentrate of 80% without the addition of Mg$^{2+}$ and SO$_4^{2-}$, with the addition of Mg$^{2+}$, and with the addition of SO$_4^{2-}$ (Exp. B, C, and D in Table 3). As can be seen, in the absence of mentioned ions, IT was approximately 1 h, whereas with 87 mg/L of Mg$^{2+}$ and with 217 mg/L of SO$_4^{2-}$, IT increased to approximately 2 h and 1.2 h, respectively. This result is in agreement with the findings of Waly et al. [27], where they reported that Mg$^{2+}$ ions offer stronger inhibition for calcium carbonate than SO$_4^{2-}$ ions. In addition, the results of Fig. 7a are also in line with the observations of other researchers, such as Berner [15], Bischoff [16] and Chen et al. [16], that the formation of calcium carbonate is hindered in the presence of Mg$^{2+}$ ions. However, it is clear from Fig. 7a that neither Mg$^{2+}$ nor SO$_4^{2-}$ was accountable for the long IT (>168 h) of the real RO concentrate at 80% recovery.

In Fig. 7b, the measured ITs of the artificial concentrate of 80% recovery in the presence of various concentrations of phosphate (Exp. E, F, and G in Table 3) are illustrated. We show that phosphate has a considerable effect on delaying calcium carbonate precipitation. In the presence of 10 mg/L of phosphate (which is equal to the concentration of phosphate in the real RO concentrate of 80% recovery), IT of the artificial concentrate increased from 1 h to a period longer than 168 h which indicated that phosphate was one of the constituents of the feedwater which was responsible for the long IT (>168 h) of the real RO concentrate. When 5 mg/L of phosphate was added to the artificial concentrate solution, the measured IT was also longer than 168 h, which suggested that if the GW contained 1 mg/L of phosphate, it would still need the role of antiscalants to control calcium carbonate scaling at 80% recovery. However, in the presence of 2.5 mg/L phosphate, the formation of calcium carbonate was not hindered substantially, as IT with the mentioned phosphate concentration increased to 4 h.

It should be noted that the aforementioned phosphate concentrations are referred to the total dissolved phosphate which includes various species of phosphate such as HPO$_4^{2-}$, H$_2$PO$_4^-$, PO$_4^{3-}$, etc. In other words, when 10 mg/L of phosphate was added to the artificial concentrate solution of 80% recovery, not all the mentioned concentration existed in the form of PO$_4^{3-}$ ion. Actually, based on the speciation of phosphate which was carried out with the Visual MINTEQ, the PO$_4^{3-}$ form was negligible in the artificial concentrate and the dominant species was HPO$_4^{2-}$. Reddy [18], Simkiss [30], Griffin and Jurinak [31], and Pytkowicz [32] have demonstrated that phosphate adsorbs onto the calcium carbonate crystals and hinder their growth. Among the various forms of phosphate, PO$_4^{3-}$ and HPO$_4^{2-}$ are the adsorbing species that hinder the crystal growth of calcium carbonate [33]. This suggests that the long IT of the artificial concentrate in Fig. 7b could be due to the adsorption of phosphate, i.e., HPO$_4^{2-}$ on the newly formed calcium carbonate nuclei in the nucleation phase, consequently preventing the nuclei from growing further and initiating crystalization.

In summary, the results of Fig. 7b indicate that when phosphate is present in the feedwater in concentrations that can hinder calcium carbonate precipitation, the antiscalant dose to target calcium carbonate scaling can be reduced significantly, as demonstrated in Fig. 5, where the antiscalant dose at 80% recovery of the RO pilot (Kamerik, Netherlands) was lowered from the recommended dose of 2.2 mg/L to 0.2 mg/L and then to zero dose. It is worth mentioning that the presence of high concentrations of phosphate in the feed water should not be considered as a way to prevent calcium carbonate scaling and to reduce the dose of antiscalants, since they may lead to calcium phosphate scaling at high recovery rates when the solubility limits of calcium phosphate is exceeded. If, however, they are present in the RO concentrate at concentrations where they do not lead to calcium phosphate scaling, then their effect on the reduction of antiscalant dose and in determining the optimum dose of antiscalants should not be neglected.

The effect of HS was investigated by comparing the IT of the artificial concentrate of 80% with and without HA and FA (Exp. B, H, I, J and K in Table 3). Fig. 7(c) presents the ITs of the artificial concentrate of 80% recovery in the presence of FA. As shown, the effect of FA on prolonging the IT of calcium carbonate is also noticeable. In the presence of 5 mg/L and 10 mg/L FA, IT of the artificial concentrate of 80% recovery increased from 1 h to a period longer than 168 h. Fig. 7(d) illustrates the ITs of the artificial concentrate solution of 80% recovery when HA was used. The IT values, when 5 and 10 mg/L HA were used, were approximately 116 h and longer than 168 h, respectively. These results suggested that the formation of calcium carbonate was also considerably hindered by HA. The results of Fig. 7c–d are in agreement to the findings of Klepetsanis et al. [24]. In their study, they investigated the effects of HA and FA at concentrations in the 0.1–0.5 mg/L range on the IT of

### Table 6

| DOC | HOC | CDOC | LDOC | Approximate molecular weight (g/mol) |
|-----|-----|------|------|-------------------------------------|
|     |     |      |      | Building blocks | LMW$^a$ neutrals | LMW$^a$ acids |
|     |     |      |      | Aromaticity (SUVA-HS) | Molecular weight |
|     |     |      |      | % DOC | % DOC | % DOC | % DOC | % DOC |
|     |     |      |      | L/(mg m) | (g/mol) | % DOC | % DOC | % DOC |

| ppp-C$^b$ | ppp-C | ppp-C | ppp-C | ppp-C | 300–500 | < 350 |
|-----------|-------|-------|-------|-------|---------|-------|
| 8620      | 1023  | 7597  | 46    | 5263  | 3.93    | 679   |
| 100%      | 11.9% | 88.1% | 0.5%  | 61.1% | 11.5%   | 14.5% |

$^a$ HOC: hydrophobic organic carbon.
$^b$ CDOC: chromatographic dissolved organic carbon.
$^c$ LMW: low molecular weight.
$^d$ ppp-C: parts per billion carbon.
calcium carbonate. They reported that both HA and FA prolonged the IT of calcium carbonate. In their study, however, IT tests were performed for a maximum duration of approximately 3 h.

It is well established that Ca\(^{2+}\) ions interact with HS leading to the formation of calcium complexes with HS \([34,35]\). Based on this, one may suggest that upon the formation of complexes, the concentration of free calcium in the artificial concentrate solution of 80% recovery (in Fig. 7c and d) might have reduced, thus resulting in longer ITs. However, this mechanism seemed less likely to predominate, as the concentration of calcium was much higher than those of FA and HA. For instance, in Fig. 7c and d, the concentration of calcium in the artificial concentrate of 80% recovery was approximately 576 mg/L, while the concentrations of FA and HA were each approximately 10 mg/L and that might have not substantially lowered the supersaturation levels. Various models exist that theoretically determine the binding of metal ions with HS. One of the models that is used by researchers is the NICA-Donnan model which is incorporated in the Visual MINTEQ program. With the NICA-Donnan model, it was found that 10 mg/L of each FA and HA would bind approximately 1.8 and 1.2 mg/L of Ca\(^{2+}\), respectively. Therefore, the reduction in the concentrations of free Ca\(^{2+}\) ions due to HS was negligible. This indicated that the complexation of calcium with HS was not the main mechanism for delaying the precipitation of calcium carbonate. It should be noted that the concentrations of Ca\(^{2+}\) ions that might have been complexed with FA (Fig. 7c) and HA (Fig. 7d) could be different from those calculated by the NICA-Donnan model as the structure and chemistry of the HS may differ. The use of the NICA-Donnan model was to illustrate that 10 mg/L of each FA and HA would not complex a high concentration of Ca\(^{2+}\) ions.

Various researchers, such as Hoch et al. \([22]\), Klepetsanis et al. \([24]\), and Amjad et al. \([25]\) have studied the effect of HS on the crystal growth rate of calcium carbonate in seeded growth tests. They all reported that the adsorption of humic molecules on the active growth sites of calcium carbonate crystals (which, as a result, hamper further growth) is the dominant mechanism in retarding the crystal growth of calcium carbonate. This suggest that the long ITs in Fig. 7c and d were due to the adsorption of humic molecules on the newly formed nuclei in the nucleation phase which, as a result, did not allow the nuclei to further grow and to initiate crystallization.

To summarize the effect of HS on calcium carbonate, one can propose that HS, particularly FA, present in the anaerobic GW in Kamerik (Netherlands) could also be one of the reasons for the long IT of the real RO concentrate at 70% and 80% recoveries (Fig. 6) and for preventing calcium carbonate scaling in the RO unit at 80% recovery when no antiscalant was used (Fig. 5b). The results indicated that when HS, which have the same inhibitory effect on calcium carbonate as the HA and FA of IHSS, are present in the RO feed, the required dose of antiscalants can be lowered substantially.

It should be taken into account that although the natural presence of HS in the RO feed may prevent calcium carbonate scaling at high

![Fig. 7.](Image)
recovery rates, it may foul the RO membranes since some researchers [36–39] have reported that HS lead to the fouling of RO membranes. Therefore, the presence of HS in the RO feed should not be favored as a way to control calcium carbonate scaling. It is, however, not known that if HS from every location can lead to the fouling of the RO membranes as their structure and chemistry may differ from one location to another. For instance, in Fig. 5b, the normalized $K_w$ of the last element of the RO unit did not decrease in 1-month period when the unit was operated at 80% recovery (DOC concentration in the concentrate was approximately 42 mg/L) which suggested that HS present in the GW was not causing fouling. Membrane fouling due to HS is a different topic and requires further research to answer if all HS can cause fouling of RO membranes, which fractions of HS lead to the fouling, at what concentrations and operational conditions and in the presence of what ions do they lead to the fouling of RO membranes, etc. Characterization of HS and to investigate their fouling propensity was not in the scope of this paper.

To sum up, the IT measurements for the various artificial concentrate compositions of 80% recovery are summarized in Fig. 8. The figure clearly shows that both phosphate and HS, i.e., HA and FA can substantially hinder the precipitation of calcium carbonate in RO applications.

3.3.2. Lab-scale RO measurements

In the previous section, the effect of phosphate and HS on delaying the formation of calcium carbonate in glass reactors was investigated. However, the condition in such a reactor differs from an RO system, in terms of residence time, geometry, material and hydro-dynamics. In this section, the effect of phosphate on calcium carbonate scaling in RO systems is investigated using the once-through lab-scale RO setup.

Fig. 9a presents the normalized $K_w$ of the Hydranautics ESPA2-LD-4040 membrane when fed with the artificial concentrate of 80% recovery, i.e., in the absence of phosphate and ii) in the presence of 10 mg/L of phosphate (Table 5). The feedwater composition was equivalent with the artificial concentrate used in the IT measurements (Section 3.3.1). In both experiments, the filtration flux was in the 30–35 L/m²/h range which was higher than the average flux of the last stage of the RO pilot unit.

As can be seen, when phosphate was absent, the normalized $K_w$ of the membrane decreased by approximately 20% in less than 2 h due to calcium carbonate scaling. In Fig. 9b, the SEM image of the membrane scaled with calcium carbonate is illustrated. On the other hand, when approximately 10 mg/L of phosphate was added to the artificial concentrate, the normalized $K_w$ of the membrane remained constant for a 10-hour experimental period which is in agreement to the IT results of Fig. 7b. As presented earlier in Fig. 7b, IT of the artificial concentrate in the presence of 10 mg/L of phosphate was longer than 1 week, which suggested that if the lab-scale RO test was continued for a 1-week period or even longer, calcium carbonate scaling would not have occurred. It was cost-wise not feasible to run the lab-scale RO test for a 1-week duration due to the consumption of large amount of chemicals in once-through experiment. The result of Fig. 9 clearly showed that the presence of phosphate can prevent calcium carbonate scaling in RO systems and therefore can reduce the need for the addition of commercial antiscalants. Furthermore, this result verified that phosphate was one of the reasons for the constant normalized $K_w$ of the last element of the RO pilot unit (Kamerik, Netherlands) when no antiscalant was used (Fig. 5b).

Furthermore, one can perceive from Fig. 9 that the addition of antiscalant was a must to prevent calcium carbonate scaling when the membrane (in the lab-scale RO test) was fed with the artificial concentrate of 80% recovery in the absence of phosphate. This result also suggested that, in case, when phosphate (and also HS) were not present in the GW, the dosage of antiscalant to the RO feed would have been crucial to prevent calcium carbonate scaling in the RO unit of Kamerik when the unit was operated at 80% recovery.

We emphasize that it is important to conduct these experiments in a flow through mode, rather than in a circulation mode, due to the difference in residence time and the possibility of recirculating seed crystals. Due to the required feedwater volume, it was not possible to perform these experiments with HS.

From the results in this study, it became obvious that the required antiscalant dose is significantly impacted by the feedwater composition (e.g., the presence of phosphate and HS) and that those factors are insufficiently taken into account when antiscalant dosing is recommended. It is therefore beneficial to experimentally determine optimal dosing or to use feedback control [40].

4. Conclusions

In this study, we investigated the effect of phosphate and HS on membrane scaling. We combined pilot scale RO operation, lab-scale RO operation and controlled precipitation experiments.

The major findings of this study can be summarized as follows:

- We demonstrated that both phosphate and HS considerably hinder the formation of calcium carbonate and therefore can prevent calcium carbonate scaling in RO applications.
- At 80% recovery of the RO pilot unit without antiscalant, the IT of the anaerobic real RO concentrate (containing phosphate and HS) was longer than 168 h, whereas, at the same supersaturation level,
Fig. 9. (a) Normalized K_{sw} of the ESPA2-LD-4040 membrane in the lab-scale RO test when fed with the artificial concentrate of 80% recovery (□) in the absence of phosphate and (●) in the presence of 10 mg/L of phosphate, and (b) SEM image of the ESPA2-LD-4040 membrane after being fed with the artificial concentrate of 80% recovery in the absence of phosphate.

the IT of the artificial RO concentrate (without phosphate and HS) was approximately 1 h.
- With the addition of 10 mg/L phosphate to the artificial RO concentrate of 80% recovery, the IT of the concentrate increased from 1 h to at least 168 h. Likewise, the IT of the artificial RO concentrate of 80% recovery was longer than 168 h when 10 mg/L of HA and FA was added to the artificial concentrate.
- In the absence of phosphate, the normalized K_{sw} of the ESPA2-LD-4040 membrane decreased by approximately 20% in 2 h period when the membrane was fed with the artificial concentrate of 80% recovery containing no phosphate, while the normalized K_{sw} remained constant for a 10-h experimental period when the membrane was fed with the same artificial concentrate in the presence of 10 mg/L of phosphate.

- It was found that the presence of phosphate and HS in the RO feed has a noticeable effect on the reduction of antiscalant dose required to control calcium carbonate scaling.
- The supplier’s recommended antiscalant dose to prevent calcium carbonate scaling in the RO unit at 80% recovery was 2.2 mg/L. Due to the presence of phosphate and HS in the RO feed, the RO unit could be operated with an antiscalant dose as low as 0.2 mg/L and even without antiscalant.

CRediT authorship contribution statement

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2021.105651.

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