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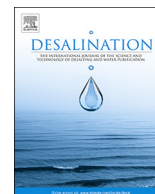Haidari, A. H.; Gonzalez-Olmos, R.; Heijman, S. G.J.

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Scaling after remineralisation of reverse osmosis permeate

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ABSTRACT

Scaling problems are more frequently observed in hot water equipment fed with remineralised reverse osmosis permeate compared to hot water systems fed with conventionally purified water. These problems occur when permeate from reserve osmosis is remineralised to a hardness to meet the regulations. The effects of temperature, initial calcium concentration, and the addition of two types of scaling inhibitors (humic substances and phosphate) on scaling formation were investigated using synthetic water to mimic remineralised RO permeate and tap water. No scaling was observed at room temperature for solutions with an initial concentration of about 40–60 mg/L Ca^{2+}. At higher temperature, the saturation index increased, and scaling occurred. In conventional hot tap water, scaling occurred after prolonged exposure time but was about 50% less compared to synthetic water, probably due to the presence of scaling retarding compounds in the tap water such as humic substances. In hot synthetic water, scaling was also retarded when humic substances were dosed. Humic substances at its optimum dosage (3 mg/L C) was more efficient for inhibition of scaling than phosphate at its optimum dosage (1 mg/L P).

1. Introduction

Reverse osmosis (RO) is a popular technology for the production of highly purified water used in applications such as drinking water, dialysis water, industrial boiler feed water, pharmaceuticals devices, semiconductor manufacturing, and industry (e.g., paper, sugar, beverage, horticulture) as well as in the reclamation of wastewater [1–12]. The undisputed reputation of the RO technique in the current market rests on the capability of RO to produce high-quality permeate that is virtually free of dissolved compounds. During the post-treatment, permeate of RO is conditioned to the desired water quality according to the guidelines and regulations. For instance, electrodialysis or ion exchange is used during post-treatment to remove trace ions and to produce superior water quality, which is required for pharmaceutical production, semiconductor manufacturing or boiler feed water [10]. In applications such as horticulture, essential nutrients needed for the growth of crops are added into the permeate water [11]. For the production of drinking water, minerals are typically added into permeate of RO during post-treatment [13].

The amount and type of minerals added into the permeate of RO for the production of drinking water depends on the local regulations, and therefore, a thorough understanding of these regulations is required before designing the post-treatment steps [10].

Conditioning and disinfection are typical processes during the post-treatment of RO-permeate used for the production of drinking water. Conditioning includes adding minerals, mainly calcium, magnesium and bicarbonate, and adjusting the pH. Conditioning of the permeate serves three goals: (i) reduce the chance of cardiovascular diseases and kidney stones, (ii) prevent corrosion of instruments and piped distribution systems and (iii) add buffering capacity to the water [14] (please see the supplementary materials for more information). The scaling propensity of natural waters is determined using two categories of methods: electrochemical methods and non-electrochemical methods [15].

To achieve these aims, usually in drinking water, the minimum and maximum concentration of Ca^{2+} is determined in addition to a minimum bicarbonate concentration and a pH range.

The goal of this research was to determine the effects of selected variables on the differences in scaling behaviour between normal tap water and remineralised RO-permeate and to find solutions for the enhanced scaling by dosing compounds that can act as antiscalants. In this context, the effects of temperature, initial Ca^{2+} concentration and the antiscalant type (humic acids and inorganic phosphate) and concentration on the amount of calcium carbonate scaling is discussed in
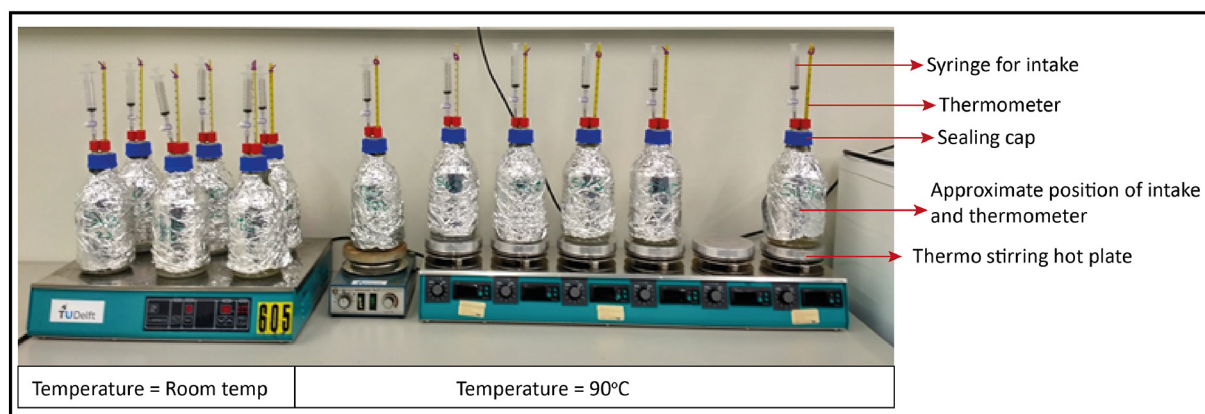

Fig. 1. Experimental setup used in this research.

this study.

2. Materials and methods

2.1. Preparation of water

This study involved the sampling and analysis of synthetic waters that contained calcium (Ca^{2+}). The effect of possible inhibitors on the scaling of calcium carbonate was determined at low and high temperatures. The synthetic water corresponded with the remineralised water produced with RO-permeate to be used as drinking water on ships; i.e. the synthetic water had an initial concentration of 40 mg/L Ca^{2+}. The synthetic water was prepared by mixing identical volumes of a 2 mmol/L calcium chloride ($CaCl_2$) solution with a 4 mmol/L sodium bicarbonate ($NaHCO_3$) solution. Initial solutions were prepared by dissolving $CaCl_2$ (Sigma-Aldrich, > 99.9% purity) and $NaHCO_3$ (Sigma-Aldrich, > 93% purity) separately into ultrapure water. Next, the $CaCl_2$ solution was stirred until a vortex appeared in the solution. Then, the solution of $NaHCO_3$ was slowly added into the vortex. After, the pH of the solution was adjusted to be around 7.0 by addition of a solution of 0.1 M hydrochloric acid (HCl) in very small volumes. Finally, 1 mmol of calcium carbonate ($CaCO_3$) powder and a selected amount of scalant inhibitor was added into the water. The $CaCO_3$ powder was added as seed crystals to provide the dissolved Ca^{2+} with suitable surface area to crystallize, avoiding supersaturation due to a lack of crystallization surface.

In addition to the synthetic water, tap water was also investigated during each experiment. The tap water used during this study had an initial concentration of 45–60 mg/L Ca^{2+}.

2.2. Additives

Two types of additives were used as potential scaling inhibitors at high temperature during this study: humic substances and phosphate. The humic substances was obtained from a solution of Natural Organic Matter (NOM) of a groundwater treatment plant, which is used for the production of potable water. During the water treatment process, NOM is adsorbed on an anion exchange resin column that is regenerated with 10 wt% NaCl. The salt is washed out from the spent regenerant, and the NOM remains in the sample. NOM is identified and quantified using liquid chromatography organic carbon detection (LCOCD) technique. Results showed that NOM consists of 90% aquatic humics substances, 7% building blocks and 4% low-molecular weight Neutrals (Please see the supplementary materials for more information about the NOM composition in this study). Determining the exact type of humic substance was not possible within this study. However, former studies [16,17] showed that majority of NOM in drinking water consists of humic acids while the commercial organic acids are typically soil

extracted and therefore consist of fulvic acids. The salinity of humic substances solutions, which were added to samples, was < 7 mg/L NaCl in the final samples.

Disodium phosphate, Na_2HPO_4 (Sigma-Aldrich, > 99% purity), was also used as potential antiscalant inhibitor. The pH of a Na_2HPO_4 solution is very close to 7, which is in contrast to solutions of other phosphate salts such as trisodium phosphate (high pH) and monosodium phosphate (low pH) [18]. Phosphate is not a common component of drinking water, but it is a known (moderate) antiscalant, and in some countries, it is dosed into drinking water to prevent corrosion of pipelines.

2.3. Experimental set-up

The prepared synthetic solutions were continuously stirred using stirring plates. Each sealed, isolated bottle contained a specific concentration of antiscalant. One set of samples was examined at room temperature while the temperature of the other set was increased up to approximately 90 °C before observation. The bottles were isolated with aluminium foil to minimize the heat exchange of bottles with the environment and also sealed to minimize the evaporation of water and exchange of gases (particularly CO_2). The bottles were sealed using special caps with two connections. One of the connections was used to draw samples from bottles, and the other connection was used to place the thermometer for temperature monitoring (Fig. 1). The thermometer and intake were placed inside the middle of the bottles in order to give the best indication of the average temperature; the temperature close to the heating plate was higher than the middle of the bottle, and the temperature close to the cap was lower than the middle of the bottle.

2.4. Analytical methods

Samples were taken from the bottles with a frequency of two times every hour during the first 2.5 h of the experiment and once every four hours thereafter. Initially, the samples were filtered through a 0.45 μm filter to remove the calcite particles, and then the dissolved calcium concentration was measured using ion chromatography (Metrohm Ion Chromatography equipped with a C4 cation column 150/4.0). To make the comparison of different solutions easier, the calcium concentration was plotted as a normalized calcium concentration in some graphs because the initial dissolved calcium concentration of each solution was slightly different. The normalized dissolved calcium concentration was obtained by dividing the dissolved calcium concentration by the initial calcium concentration ($t = 0$ h, before heating) and is expressed as a percentage.

The measured dissolved Ca^{2+} concentration is used to calculate the saturation index (SI) by using Eq. (1).

$$SI = pH - pH_s \tag{1}$$

The SI is the difference between the actual pH of the solution (pH) and the calculated pH (pH$_s$) of the same solution at which the water is in equilibrium (saturated). The SI provides a qualitative assessment of saturation state of a solution, i.e. it does not indicate the actual amount of minerals that will precipitate if the solution attains saturation equilibrium state [19]. Water with negative SI tends to be corrosive, and water with positive SI tends to scale.

The actual pH of the solutions was measured with a pH-meter (WTW inoLab, Multi 9420). The saturation pH of solutions (pH$_s$) was calculated from the HCO$_3^-$ and Ca^{2+} concentrations using Eq. (2).

$$pH_s = pK_2 - pK_s - log([Ca^{2+}].[HCO_3^-]) \tag{2}$$

pK$_2$ and pK$_s$ are the second dissociation constant (ionization constant of HCO$_3^-$) and the solubility product constant of calcium carbonate, respectively. The equilibrium constants (K$_s$ and K$_2$) in Eq. (2) can be calculated using Eqs. (3) and (4) [20,21]. The values found in Eqs. (3) and (4) are the equilibrium constants for the calcium carbonate and bicarbonate reaction at 25 °C. For the calculations, it is assumed that the concentration of bicarbonate is equal to two times the Ca^{2+} concentration at 25 °C ([HCO$_3^-$] = 2 [Ca^{2+}]).

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-} \quad K_s = [Ca^{2+}] \times [CO_3^{2-}] = 10^{-8.48} \tag{3}$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \quad K_2 = \frac{[CO_3^{2-}].[H^+]}{[HCO_3^-]} = 10^{-10.3} \tag{4}$$

While the pressure variations on the mass action constants have a negligible effect, the temperature plays an important role. In this paper, the van't Hoff equation (Eq. (5)) was used to calculate the variations of mass action constants at different temperatures, where R is the gas constant ($R = 8.314 \cdot 10^{-3}$ kJ/mol·K), T is the temperature expressed in Kelvin [K], and ΔH_r is the heat gained or lost in the chemical system (reaction enthalpy).

$$\frac{d\,In\,K}{d\,T} = \frac{\Delta H_r}{R.\,T^2} \tag{5}$$

The calculation of ΔH_r and the definition of the standard state is analogous to that of the standard Gibbs free energy of the reaction when each product or reactant is present at unit activity at a specified standard state (25 °C and 1 atm) [21]. The effect of temperature on the equilibrium constant can be determined knowing the temperature dependence of enthalpy of the reaction. At 25 °C, the value of the reaction enthalpy, ΔH_r^o, is calculated from the formation enthalpies, ΔH_f^o, which are listed in Table 1.

Typically, ΔH_r^o is constant within the range of a few tenths of a degree, i.e. it can be assumed that it is not a function of temperature within this range; therefore, Eq. (5) can be integrated to give an equation for two temperatures [21]:

$$log\,K_{T1} - log\,K_{T2} = \frac{-\Delta Hr^o}{2.303R}\left(\frac{1}{T1} - \frac{1}{T2}\right) \tag{6}$$

The value of the reaction enthalpy at 25 °C can be calculated using Eq. (7) and the formation enthalpies, which are found in Table 1. T1 is the temperature at 25 °C [298.15 K], and T2 is the actual temperature expressed in Kelvin [K].

Table 1
Enthalpies used for the reactions in this study [22].

Reactants/Products	ΔH_f^o[kJ/mol]
CaCO$_3$	− 1206.9
Ca^{2+}	− 542.8
CO$_3^{2-}$	− 677.1
HCO$_3^-$	− 691.99
H$^+$	0

$$\Delta Hr^o = \sum \Delta H_f^o{}_{Products} - \Delta H_f^o{}_{Reactants} \left[\frac{kJ}{mol}\right] \tag{7}$$

3. Results and discussion

3.1. Effects of temperature

Fig. 2 compares the normalized Ca^{2+} concentration and the SI of tap water produced by a conventional treatment plant with the synthetic water, which represents the permeate of RO. The figure shows the measurements performed at 20 °C and 90 °C. For the comparison of the Ca^{2+} concentration of synthetic water with tap water, normalized values are used because the initial Ca^{2+} concentration was 40 mg/L Ca^{2+} in the synthetic water and 45–60 mg/L Ca^{2+} in tap water.

Fig. 2 shows a decrease in the dissolved Ca^{2+} concentration over time for tap water and synthetic water at both temperatures (at 20 and 90 °C). This indicates the formation of calcium carbonate scaling during the experiments. However, the scaling occurring with 20 °C solutions is insignificant compared to the scaling with 90 °C solutions.

At 20 °C, the Ca^{2+} concentration decreases immediately after the start of experiments in the first four hours ($t = 1$ h) and remains almost constant until the end of experiments in both tap water and synthetic water.

SI of the tap water was almost constant (equal to one) at 90 °C in the first 40 h of the experiment and sharply decreased at $t = 40$ h. Comparing the SI with the Ca^{2+} concentration of this solution indicates that while the solution is supersaturated, the scaling is retarded in the first 40 h of the experiment. While SI of tap water drops sharply at 40 h, the Ca^{2+} concentration variation is insignificant from $t = 20$ h until the end of the experiment, which indicates that the pH decreased at $t = 40$ h. Scaling could decrease the SI in two ways: (i) by the decrease of Ca^{2+} and (ii) by a decrease in pH that occurs due to precipitation of carbonate with Ca^{2+} and a resulting shift of the bicarbonate dissociation equilibrium (Eq. (4)) toward the dissociation of bicarbonate for production of carbonate and protons. The sharp decrease of SI at t = 40 h is primarily represented by the latter.

In the case of synthetic water at 90 °C, the SI remains constant (0.5) because scaling happened during the first 4 h and there was no inhibitor in the solution to prevent or delay the scaling.

The normalized concentration of Ca^{2+} in Fig. 2 shows that the scaling in synthetic solutions is higher and occurs faster than in tap water, likely because of the absence of inhibiting organic and inorganic components.

At 90 °C, the Ca^{2+} concentration dropped sharply at the first 20 h of the experiment for both types of solution. Over this period, the drop in Ca^{2+} concentration was about 20% for drinking water and 40% for synthetic water, respectively. This result suggests that synthetic water had about 50% higher scaling compared to tap water because of the presence of inhibiting organic and inorganic components in tap water. After the first 20 h, the Ca^{2+} concentration remained constant at these values for about 50 h (between $t = 20$–70 h).

3.2. Effects of additives at high temperatures

Figs. 3 and 4 illustrate how solutions of synthetic water at 90 °C are affected by different concentrations of humic substances with regard to dissolved Ca^{2+} concentration and SI, respectively. An average pH of about 7.8 (with a minimum of 7.1 and a maximum of 8.2) was measured after cooling down the samples.

In all solutions, there was a remarkable decrease in the concentration of dissolved calcium between two and 20 h ($t = 2$–20 h), indicating scaling occurring in the first 20 h of the experiment. Then, the Ca^{2+} concentration became almost constant until the end of the experiment. The SI, however, was constant until 40 h after the start of the experiment, when it had a sharp decrease.
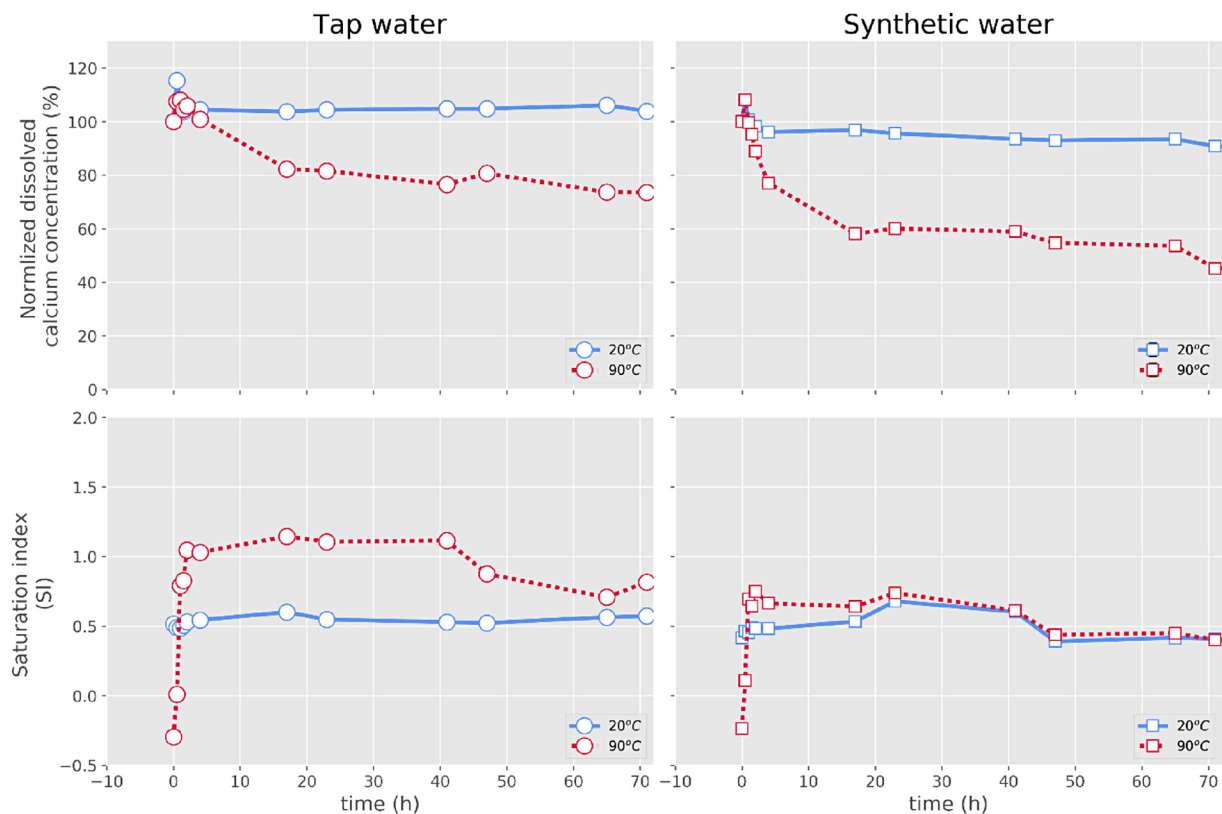
Fig. 2. Effects of temperature on the concentration of dissolved calcium and SI in the examined solutions. Each colour indicates the solution at a particular temperature: room temperature (approximately 20 °C) and boiler temperature (approximately 90 °C). Dotted (red) lines demonstrate solutions at 90 °C, and continuous (blue) lines demonstrate solutions at 20 °C. Circles represent tap water data, and squares represent synthetic water data.

In the solution without humic substances, the SI remained low compared to solutions with humic substances (Fig. 4), the Ca^{2+} concentration decreases very fast in the first 40 h after the start of the experiment, and decrease moderately until 20 h after the start of the experiment after which it remains almost constant until the end of the experiment.

Comparing solutions with a high concentration of humic substances to those without or with a very low concentration of humic substances shows that while the solutions with a high humic substances

concentration are supersaturated, no scaling occurs.

The results obtained for solutions with a low concentration of humic substances (humic substances < 3 mg/L C) are very similar to the tap water experiment at 90 °C. While there is a clear oversaturation of Ca^{2+} in solutions with a humic substances concentration higher than 3 mg/L C, the SI of these solutions remains high until 40 h after the start of the experiment. This indicates that the scaling rate is negligible in these solutions until 40 h after the start of the experiment. Similar to the tap water (90 °C), there is also a sharp decrease of SI at $t = 40$ h in the case
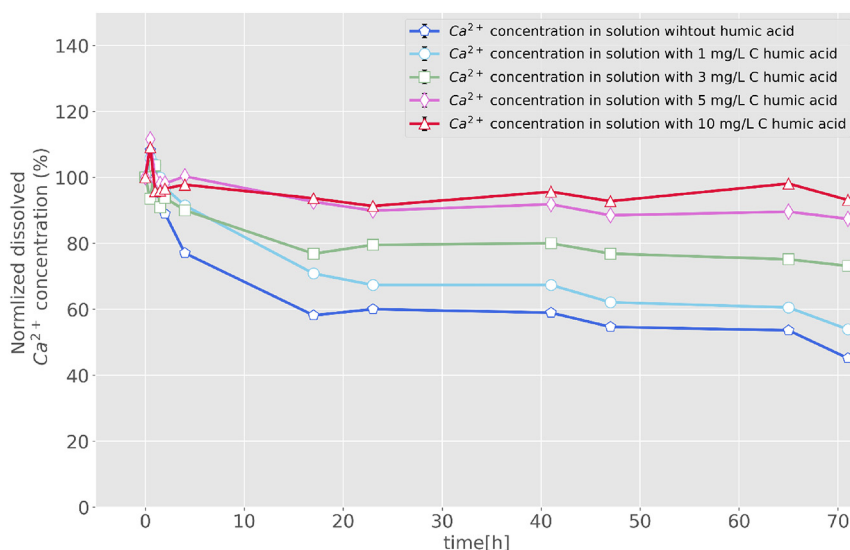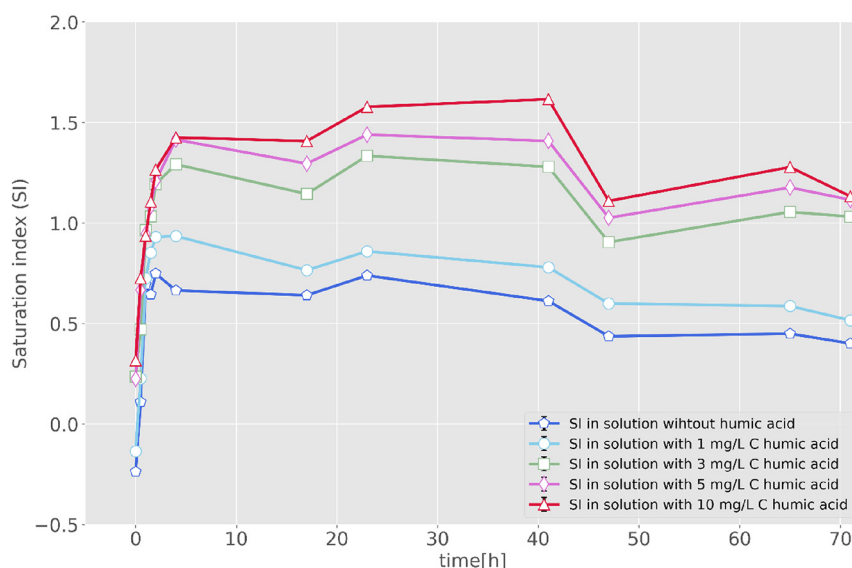

Fig. 3. Effects of humic substances concentration on the concentration of dissolved calcium at 90 °C. Solutions with a higher concentration of humic substances had a higher Ca^{2+} concentration at around 20 h after the start of the experiment.

Fig. 4. Saturation index for solutions with humic substances at 90 °C. While solutions with humic substances concentration of 3 mg/L C and higher were super-saturated, no scaling was observed in these solutions until 40 h after the start of the experiment.

of synthetic water with humic substances, which could be related to pH decrease in these solutions.
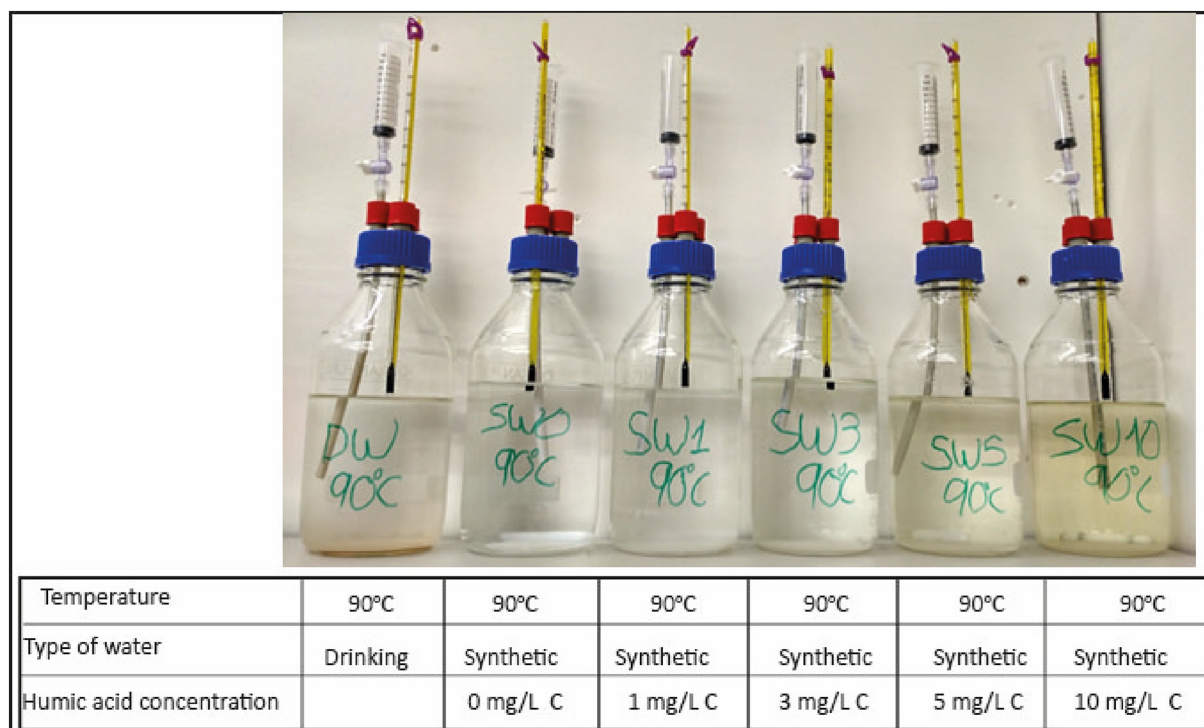
Results from Fig. 3 show that the scaling decreases by increasing the humic substances concentration. This indicates that a higher humic substances concentration could have an increased effect on the crystallization process by disturbing crystal growth. While a higher concentration of humic substances resulted in lower scaling, a humic substances concentration above 3 mg/L C gave a yellowish colour to water (Fig. 5), which is not appealing to consumers because users typically do not trust water with a yellowish colour.

Fig. 6 illustrates the effects of phosphorus concentration on scaling by synthetic water at 90 °C with respect to Ca^{2+} concentration. The

average measured pH after cooling down the 90 °C samples was about 7.8 (with a minimum of 7.4 and a maximum of 8.4) for the solution with added phosphate.

The antiscalant action of phosphate was less effective than humic substances at high temperatures. The dissolved Ca^{2+} concentration was reduced by 15–20% of the initial value in solution with a humic substances concentration > 3 mg/L compared to 20–40% in solutions with phosphate, indicating a higher efficiency of humic substances in the prevention of scaling.

In contrast to humic substances, the increase in phosphate concentration did not necessarily reduce the scaling, i.e. the optimal dosage of phosphate was not the highest concentration (3 mg/L P = 13.75 mg/

Temperature	90°C	90°C	90°C	90°C	90°C	90°C
Type of water	Drinking	Synthetic	Synthetic	Synthetic	Synthetic	Synthetic
Humic acid concentration		0 mg/L C	1 mg/L C	3 mg/L C	5 mg/L C	10 mg/L C

Fig. 5. The colour of solutions at humic substances concentration above 3 mg/L becomes yellowish, which is often not appealing for consumers. (DW = tap water produced by conventional treatment plant; SW: synthetic water; the index "i" in SWi represents the concentration of scaling inhibitor).
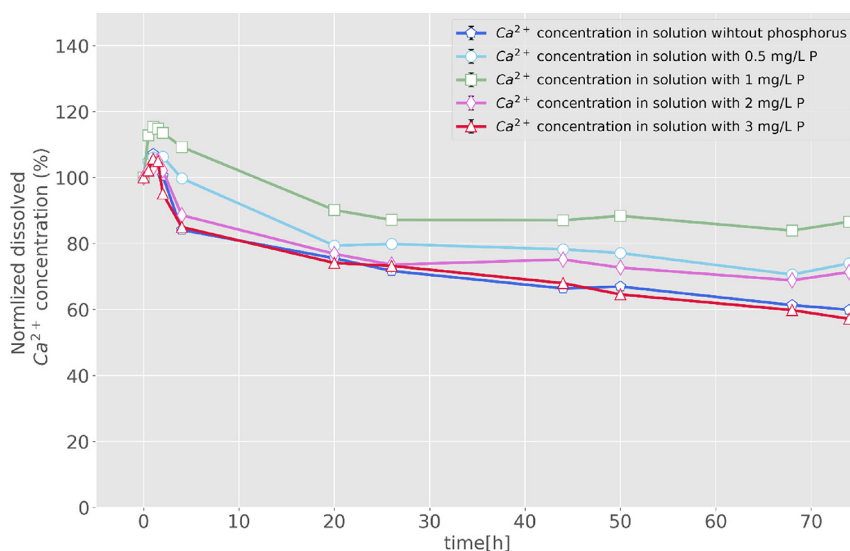
Fig. 6. Effects of phosphorus concentration on the concentration of dissolved calcium at 90 °C.

L Na_2HPO_4) but instead at 1 mg/L P (4.85 mg/L Na_2HPO_4). The optimal phosphorous dosage was in agreement with the practical application of phosphate in boilers, which is a dosage of about 0.6–1.2 mg/L P (2–4 mg/L PO_4^{3+}) [18].

From the economic point of view, the cost of dosing phosphate is higher than humic substances. While phosphate is ranked as one of the valuable minerals in the world due to its scarcity, humic substances are usually considered a residual product of drinking water treatment.

4. Conclusion

The purpose of this study was to determine an explanation for differences in the scaling behaviour between normal tap water and remineralised permeate of reverse osmosis (RO) when these solutions are heated up until 90 °C. The temperature had a high impact on the occurrence of scaling. Precipitation did not take place in experiments with tap or synthetic water with a Ca^{2+} concentration of about 40 mg/L at 20 °C. When the temperature increased up to approximately 90 °C, the Ca^{2+} concentration dropped by 20% and 40% in tap water and synthetic water respectively, i.e. tap water showed about 50% less scaling compared to synthetic water because of the presence of organic and inorganic inhibiting components. The effect of the temperature on scaling was reduced by increasing the concentration of natural humic substances and phosphate, which were added as scaling inhibitors. At optimal dosage, solutions with humic substances (3 mg/L C) showed about 40% less scaling than solutions with optimal phosphate dosing (1 mg/L P). In solutions with humic substances, the scaling was reduced as the concentration of humic substances increased. However, increasing the concentration of humic substances above 3 mg/L C resulted in a yellowish colour to the water.

In summary, humic substances are preferred to be used in RO post-treatment compared to phosphate when the permeate of RO is used for drinking water and in hot water boilers at the same time. That is because humic substances at its optimum dosage (3 mg/L C) is more effective than phosphate to prevent scaling, is more common in drinking water and is cheaper.

Acknowledgement

Appendix A. Supplementary Data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.desal.2019.06.002.

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