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The performance of polycarboxylates as inhibitors for $CaCO_3$ scaling in reverse osmosis plants

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ABSTRACT

A new membrane-based method was applied to investigate the performance of three phosphorus-free antiscalants of different chemical structures to prevent calcium carbonate scale. Apart from a polyacrylate homopolymer, two copolymers were studied, one of it also being free of nitrogen. The results show that an inhibition of $CaCO_3$ scale on reverse osmosis (RO) membranes is possible with phosphorus-free antiscalants. The individual performance strongly depends on the chemical structure of the polycarboxylate. A specially adapted copolymer clearly outperforms the polyacrylate homopolymer in case of severe scaling conditions. The average residence time of the water in the test plant is approximately 1 h, compared to around less than a minute in a full-scale RO plant. So the operating conditions in the test plant make it more difficult for an AS to inhibit scaling compared to a full-scale RO plant. By energy-dispersive X-ray fluorescence (EDXRF), the scaling layer thickness can be estimated. The SEM images and the 3D images from CLSM showed that the water quality and the applied antiscalant have a great influence on the scaling layer morphology. The effective blocking of the membrane does not only depend on the amount of precipitated $CaCO_3$ but there is also a great influence of the scaling layer structure. With a normal scaling potential of the water, the scaling layer consists of calcite, and at higher LSI values of the feed water, there was also aragonite found on the membrane. From the three antiscalants AA/AMPS shows, as it was expected, the lowest performance as calcium carbonate scale inhibitor, because it is designed predominantly as a disperser and as stabilizer for calcium phosphate. PAA proved to be an efficient inhibitor for hardness at standard applications. For the application in waters with high scaling potential, AA/EA is very suitable, because this inhibitor is able to serve as a good stabilizer for hardness and at the same time as a disperser. A combination of different polymers enables special solutions for high requirements.

Keywords: Polycarboxylates; Calcium carbonate; Scale inhibition; CLSM; SEM; Reverse osmosis

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1. Introduction

The formation of scale on membrane surfaces comprises complex phenomena involving both crystallization and transport mechanisms. Crystallization becomes feasible when the solution is supersaturated, expressed by the activity of ions in the water. For the extent of the membrane scaling, the kinetics of the precipitation is the key factor and has to be considered.

Scale in membrane systems is a combination of surface crystallization and bulk crystallization, and these mechanisms are influenced by the membrane properties and the process conditions [1–6].

In the case of surface crystallization, the scale deposit on the membrane surface grows laterally, leading to an increasing surface blockage and flux decline. In bulk crystallization, small crystal particles are formed through homogeneous crystallization. They may deposit on membrane surfaces and form a cake layer that also leads to flux decline. In supersaturated scale forming conditions, these two effects occur simultaneously, resulting in scale growth and agglomeration.

Even though the brines of reverse osmosis (RO) plants are usually supersaturated, the scale formation on the membrane is mainly governed by the availability of sufficient crystallization nuclei. The time to induce formation of detectable nucleation crystals, the induction time, is important for scale formation of RO membrane.

To assess the risk of scaling, the induction time has to be compared with the residence time of the water in the membrane modules. The typical average residence time of the feed water, respectively, the concentrate is around 1–2 min. But due to the feed spacers, there are dead zones which locally enlarge the residence time significantly and also increase the supersaturation.

The addition of antiscalants (AS) disrupts one or more mechanisms of the scaling process. Generally, AS do not eliminate the scaling tendency, but they delay the onset crystallization (nucleation phase of crystallization), retard the growth of the crystals (growth phase of crystallization) [7] or disperse the precipitates, and distort the lattice of the crystals.

Phosphonates are well known to be highly efficient scale inhibitors and are widely applied in RO plants and cooling systems. However, due to the phosphorous content of the molecule, they contribute to eutrophication of water. Furthermore, aminomethylphosphonate, which is a metabolite of glyphosphate, a herbicide, can be formed as a metabolite during its photodegradation [8]. Therefore, a phosphorus-free treatment can be required by legislation if the phosphate concentration of the brine is limited.

Polycarboxylates, due to the anionic nature, are generally good dispersers for crystals with multivalent cations and are promising additives to prevent scaling, because they are highly efficient in preventing the nucleation and crystallization via adsorption onto developing nuclei [9–11]. The different crystal forming and scaling mechanisms have a strong influence on the morphology of resulting scaling layer on the membrane surface. Polyacrylates with molecular weights in the range of 5,000–6,000 g/mol are the most widely used due to their high-scale inhibition power and environmental compatibility [1,12].

Choosing the optimum dosage of polyacrylates is very important since a lower concentration of polyacrylates will not effectively inhibit scale formation, whereas a high concentration is uneconomical and may additionally have other adverse effects such as gelation [1,9].

The effectiveness of an AS is often determined in laboratory tests like the NACE Standard Test Method 03–74 for calcium carbonate and calcium sulfate [13,14]. In these tests, the AS is added to the sample and after a defined reaction time, a period to settle the scales follows. The concentration of Ca ions in the solution is used to calculate the efficiency of the inhibitor.

These test methods have the advantage that they are easy to apply, but the interaction with the membranes under real operating conditions is neglected, because the test results are strongly affected by the relatively long reaction and settling time. During this time, crystal morphologies are formed which might not be comparable to those in an RO plant. Therefore, only limited statements about the blocking of the membrane can be made with these test methods.

For this reason, a new membrane-based method was applied to investigate the performance of three phosphorus-free antiscalants of different chemical structures to prevent calcium carbonate scale. Apart from a polyacrylate homopolymer, two copolymers were studied, one of it also being free of nitrogen.

2. Materials

2.1. Antiscalants

Common to all polycarboxylates is the same repetitive structural unit, i.e. the carboxylic acid group which can be partially or completely neutralized. The group of polycarboxylates comprises a huge number of commercial products and experimental substances. Contrary to the phosphonates, they are not well-defined chemical substances, but consist of a number of different substances of same or similar structure due to the polymerization process. Generally polycarboxylates are free of phosphorous, which enables the use of antiscalants in areas with restrictions on the phosphorous entry into waste water [15].

The whole group of substances is usually classified by the composition, i.e. by the monomers which have been used during production. Depending on the number of monomers, different subgroups can be distinguished: homopolymers consist of only one monomer, whereas copolymers can be produced from two or more different monomers.

Homopolymers are produced from, e.g. acrylic acid, methacrylic acid, maleic acid, and aspartic acid. One representative has been selected for this study: a homopolymer of the most important monomer, i.e. acrylic acid, partially neutralized (PAA).

The major part of all copolymers is based on acrylic acid. Therefore, this article focuses on copolymers of acrylic acid with two commonly used other monomers: acrylamidopropylsulfonic acid (AA/AMPS) and ethylacrylate (AA/EA).

All antiscalants discussed are characterized by a low aquatic and human toxicity, which is a precondition for a widespread application in water treatment [15]. The antiscalants selected for this study is commercially available, and Fig. 1 shows their chemical structure.

2.2. Membrane plant

In order to closely simulate operating conditions, a membrane-based test method is applied using a RO pilot plant. The fully automated test setup for this work is shown in Figs. 2 and 3, and also provides a screen shot of the control panel.

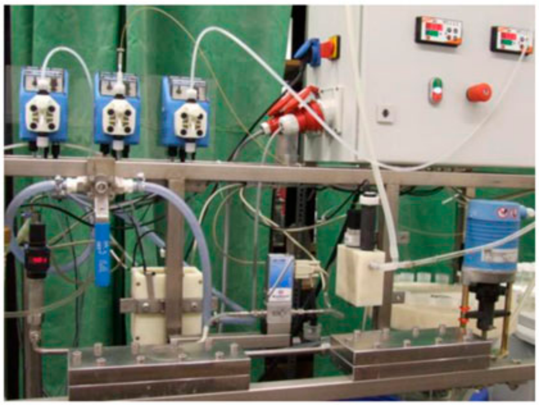


Fig. 2. PC-controlled membrane test plant.

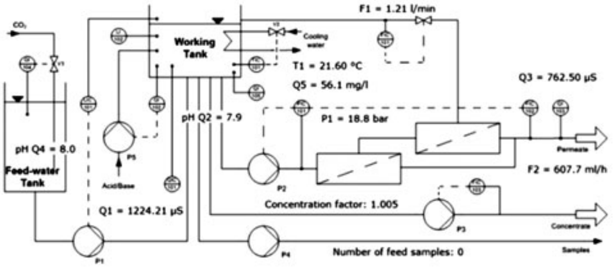


Fig. 3. Screen shot of the control panel.

The water to be examined is fed from the feed water tank (100 L) into a small working tank (1 L) via pump P1. From that working tank, the water is pumped by the high-pressure pump P2 through two RO test cells of 80 cm (4 × 20 cm) membrane area each. The channel height is 2 mm and the cross flow velocity is 0.25 m/s. In order to avoid dead areas in

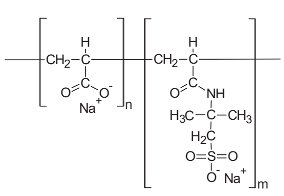
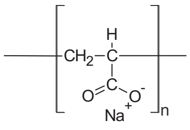
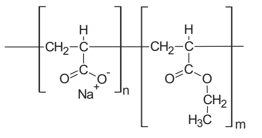
AA/AMPS	PAA	AA/EA
		
Acrylic Acid / Acrylamidopropylsulfonic acid	Acrylic acid, partially neutralized	Acrylic Acid / Ethylacrylate

Fig. 1. Chemical structure of the tested antiscalants.

the feed channel, there are no spacers in the feed channel. The permeate flow is adjusted at a constant value of 480 mL/h, equivalent to a permeate flux of 30 L/mh. Under these hydraulic conditions, the average residence time of the water in the test plant is around 1 h whereby the requirements for an AS increase significantly compared to the conditions in a full-scale plant.

The water level in the working tank is controlled by adding feed water from the feed water tank via pump P1. The concentrate can be discharged via pump P4 and a concentrate sample can be taken via pump P3 for analysis.

2.3. Feed water quality

All experiments were carried out at a constant temperature of 25°C and with standardized test water as shown in Table 1. The test water is prepared by dissolving the salts in two jars with 5 L of demineralized water, one containing the salts with the necessary amount of Ca^{2+} ions, the other containing the salts with the required amount of CO_3^{2-} ions. These solutions were mixed into 100 L of demineralized water and stirred for 24 h to adjust the equilibrium. Finally, the AS was added to the feed water.

To operate the test plant at constant hydraulic conditions in all experiments, the variation of the scaling potential of the actual test water was achieved by multiplying the ionic concentration of the standard test water by a so-called relative feed water concentration (RFWC). For this study, the RFWC has been chosen between 0.8 and 1.3. The Langelier Scaling Index (LSI) calculated according to DIN 38404 C10-R2 (1995) was used to characterize the scaling tendency of the water. The dosing level of the antiscalants was varied between 2.5 and 20 ppm in the feed water. The volumetric concentration ratio (VCR) in the tests was 3 corresponding to a recovery rate of 66.7%.

3. Methods

3.1. Membrane test procedure

At the beginning of a test run, the permeate is discharged and the concentrate is recycled back into the working tank. The water level in the working tank is controlled by adding feed water from the feed water tank via pump P1.

In that manner, the test water is concentrated up to the desired concentration level. As soon as the desired volumetric concentration ratio (VCR, in this study: VCR = 3) is reached, the concentrate is also discharged, and the test plant is operated continuously at that concentration level and at the desired permeate flux. If scaling occurs, the membrane becomes partly blocked and so the pressure is automatically increased to keep the permeate flux at a constant value. The test is stopped, when the maximum achievable pressure of 60 bar is reached, or if the feed reservoir is nearly empty, typically after 100–120 h. At a low feed water level, the pH could not be controlled properly any more, which led to distortions of the trial. Therefore, all data obtained for a running time above 100 h are not taken into consideration.

The pH value in the feed water tank is controlled by adding carbon dioxide by a dosing valve. In order to exclude influences from the membrane on the results in all test runs, FilmTec SW 30 RO membrane sheets from a 2.5´´ element were used.

Table 1
Test water composition

		RFWC		
Parameter	Unit	0.8	1	1.3
Cations				
Na^+	mg/L	81.8	102.2	132.9
Mg^{2+}	mg/L	10.4	13.0	16.9
Ca^{2+}	mg/L	74.4	93.0	120.9
Anions				
Cl^-	mg/L	96.0	120.0	156.0
SO_4^{2-}	mg/L	55.4	69.2	90.0
NO_3^-	mg/L	79.5	99.4	129.2
HCO_3^-	mg/L	180.6	225.8	293.5
pH		8.2	8.2	8.2
LSI of the feed water		0.85	1.07	1.25
Calculated LSI of the concentrate		1.8	2.0	2.2

The advantage of the applied test method is that the operation of the test plant is highly adapted to a full-scale RO plant, namely in terms of reaching the supersaturation by starting from a feed water with only moderate scaling tendency, and with a relatively low residence time of the concentrate in the plant.

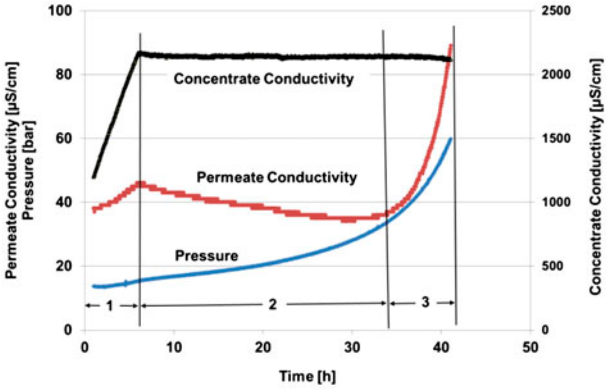


Fig. 4. Typical test phases.
Notes: (1) concentration phase, (2) period of permeance decline, and (3) period of rapid membrane blocking.

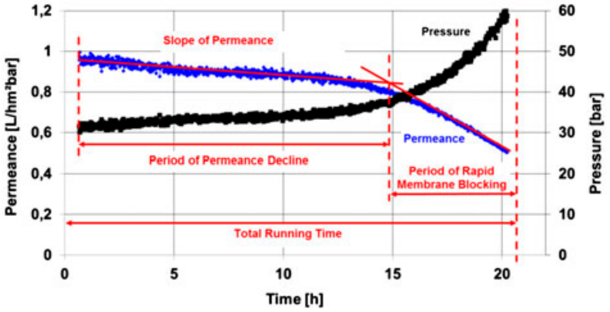


Fig. 5. Permeance and pressure vs. time for typical test phases.

3.2. Water analytics

In addition to the continuous monitoring of the operating parameters of the plant, the ionic composition was generally analyzed once per hour by inductively coupled plasma optical emission spectroscopy (ICP-OES). For each test run, the total alkalinity of the feed water and the brine at the end of the experiment were measured.

3.3. AS efficiency evaluation

In a typical test run, three different phases can be distinguished. For the first 6 h, the water is concentrated to the desired VCF of 3. This phase is followed by a second phase, where relatively moderate scaling occurs, and therefore the pressure rises, respectively, the permeance declines slowly (Figs. 4 and 5).

The duration of this phase is controlled by the induction time and is an important indicator for the performance of an AS. In the third phase, rapid membrane blocking happens. From the measured data which are recorded by a PC-system, the permeance is calculated by dividing the actual permeate flow rate by the corresponding driving transmembrane pressure difference.

3.4. Membrane characterization

To characterize the scaled membranes, the amount of $CaCO_3$ on the membrane is estimated as the thickness of an average scaling layer covering the total membrane area, by energy-dispersive X-ray fluorescence analysis (EDXRF). Furthermore, different microscopic techniques, including scanning electron

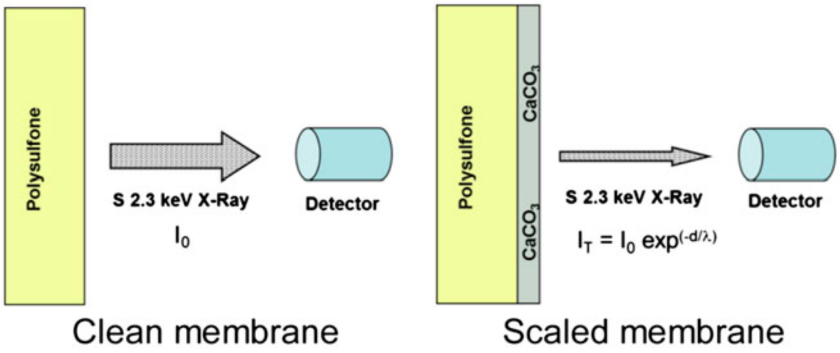


Fig. 6. Principle of estimating the scaling layer thickness.

microscope (SEM) and confocal laser scanning microscope (CLSM), were used to determine the scale morphology. The composition of the scale of selected membranes was determined by wet analysis.

To estimate the average layer thickness, a sample from the scaled membrane was analyzed by a SPECTRO XEPOS unit, and the TURBOQUANT Powder analytical software was applied. Because the analyzed membrane area is an ellipse of 6 mm by 13 mm, the result is very representative.

When a clean membrane is analyzed by EDXRF, the sulfur of the polysulfone midlayer of the membrane is excited by the primary X-rays and emits its characteristic 2.3 keV X-rays (see Fig. 6 left).

A scaled membrane, however, consists of the different layers of the asymmetric membrane material

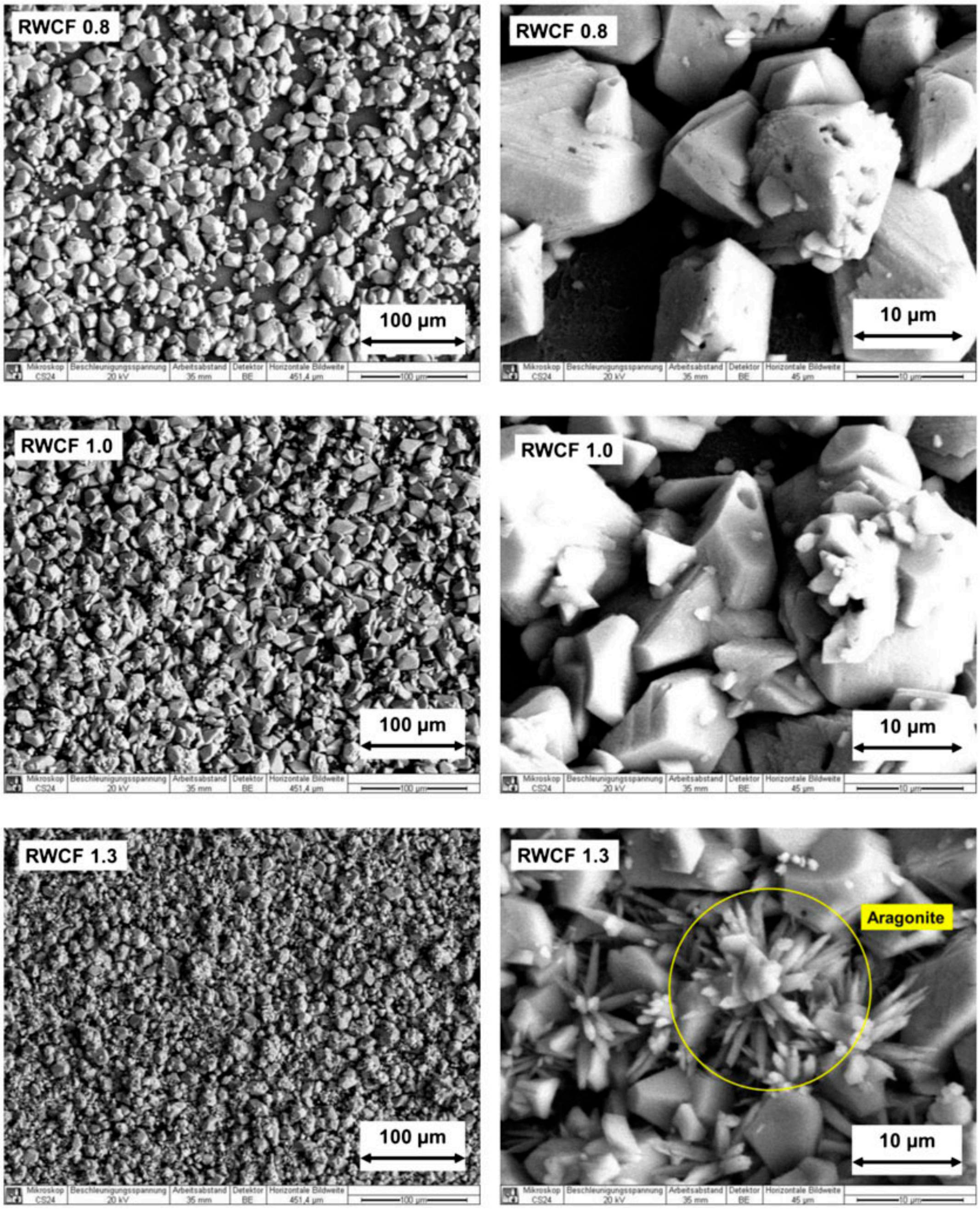


Fig. 7. SEM images at different magnifications of the scaled membranes for increasing RFWC (top 0.8, middle 1.0, bottom 1.3), no antiscalant.

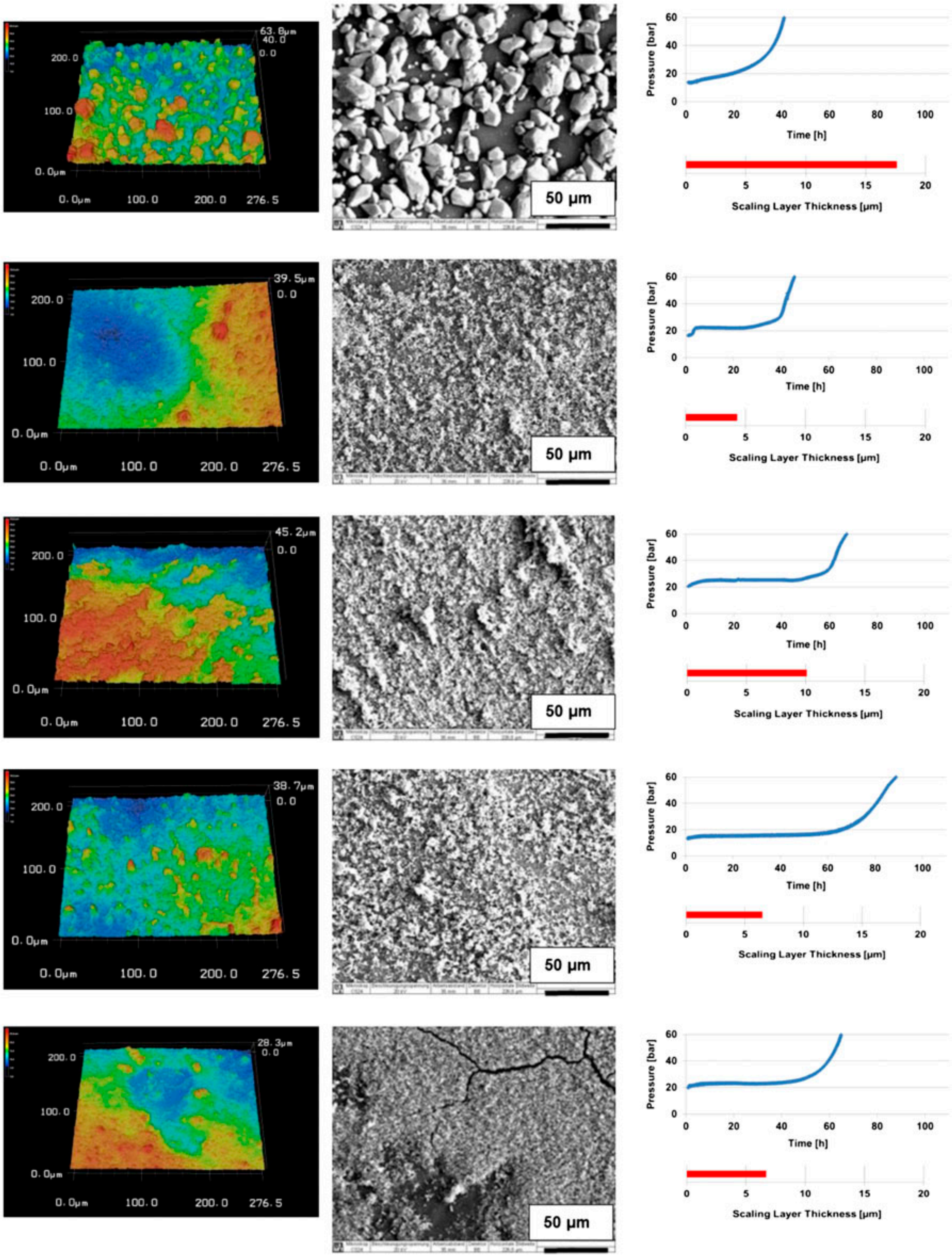


Fig. 8. CLSM image (left), SEM image (middle), pressure dependence vs. time and scaling layer thickness (right), of test runs with AA/AMPS copolymer, RFWC 0.8, dosage 0.0, 2.5, 5.0, 10, and 20 mg/L (top to bottom).

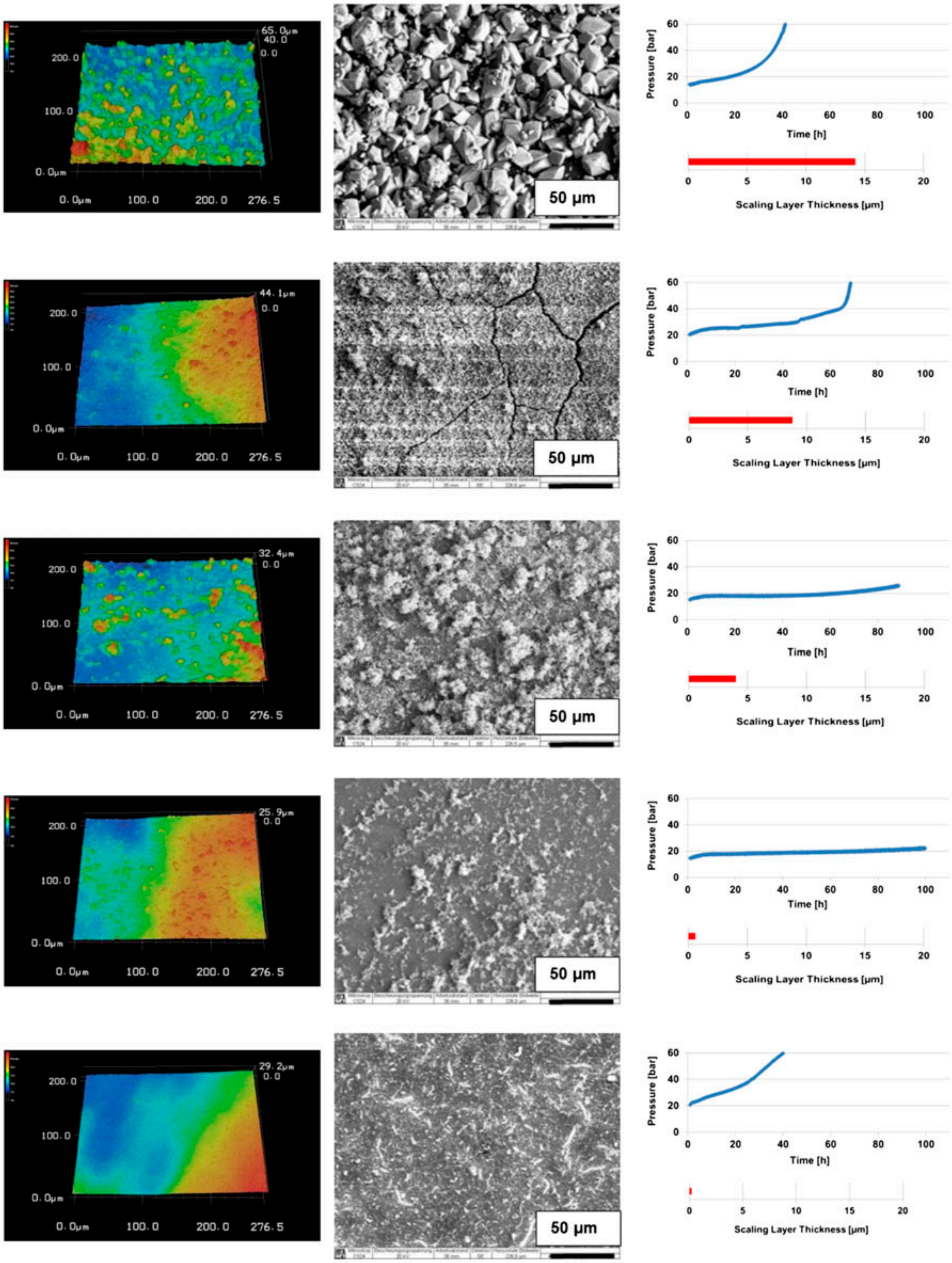


Fig. 9. CLSM image (left), SEM image (middle), pressure dependence vs. time and scaling layer thickness (right), of test runs with PAA homopolymer, RFWC 1.0, dosage 0.0, 2.5, 5.0, 10, and 20 mg/L (top to bottom).

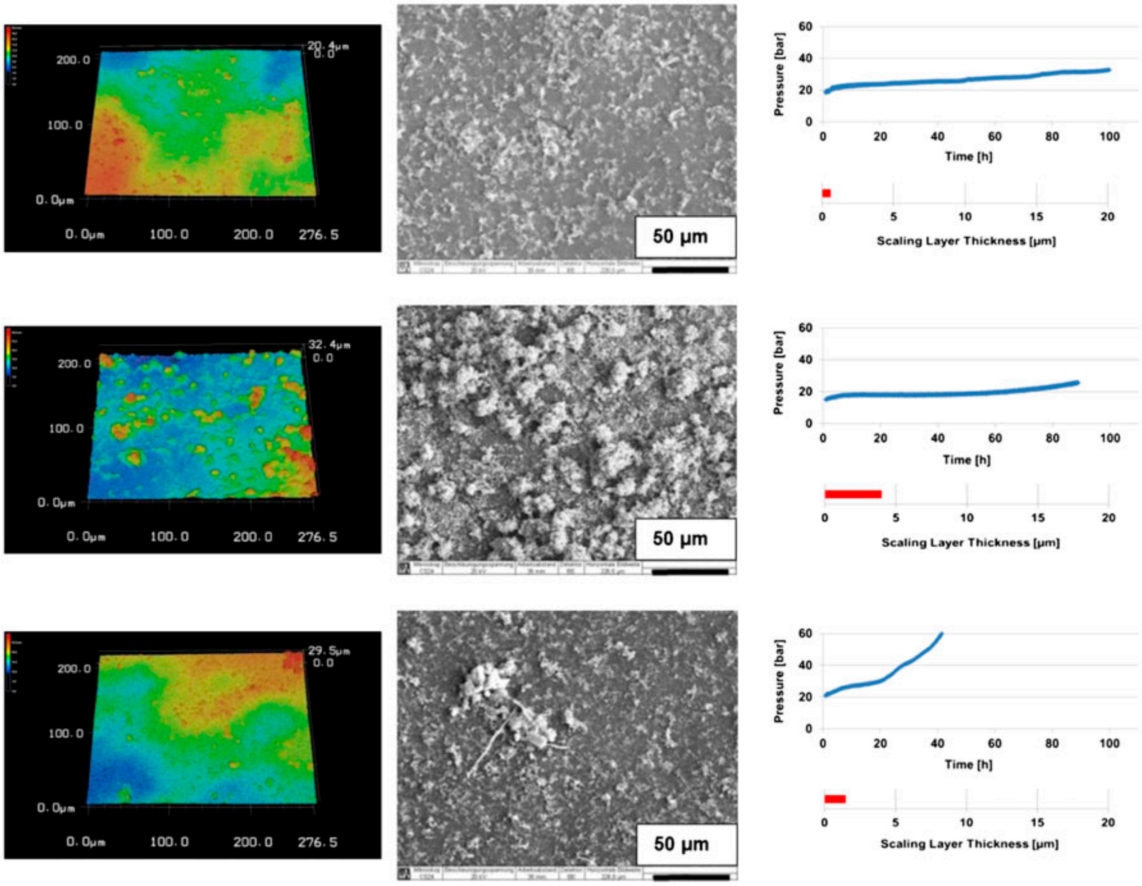


Fig. 10. CLSM image (left), SEM image (middle), pressure dependence vs. time and scaling layer thickness (right), of test runs with PAA homopolymer, dosage 5.0 mg/L, RFWC 0.8, 1.0, 1.3 (top to bottom) PAA, RFWC 0.8; 1.0, 1.3, Dosage 5.0 mg/L.

and the scaling layer on top of them (see Fig. 6 right). The intensitivity of the detected sulfur signal is influenced by different phenomena of the EDXRF-method. But due to the typical particle size in the scaling layer of some microns, the main attenuation effect of the sulfur X-rays happens on their way to the detector through the scaling layer.

By passing through a homogenous scaling layer of the thickness d, the intensity of the X-rays from the sulfur is attenuated down from I_0 (no scale) to I_T by absorption following the Beer–Lambert law. Comparing the sulfur content of a clean membrane to a scaled membrane, the scaling layer thickness d can be estimated, because the attenuation length λ of $CaCO_3$ is known (9.8 µm at a detection angle of 45°) [16]. After passing the attenuation length, the transmitted intensity I_T is reduced down to $1/e$ of the initial intensity I_0.

Although the scaling layer is not homogenous in all experiments (see Figs. 7–12), the amount of $CaCO_3$ can be estimated as a first approximation.

4. Results

4.1. Scaling layer morphology

The following figures are presented to illustrate the morphology of the scaling layer. First in Fig. 7, SEM images of the scaled membranes for different RWCF are shown for tests runs without antiscalant. The images on the left side show that the average size of the crystals decreases with increasing RFWC, corresponding to the extent of supersaturation. The total amount of $CaCO_3$ on the membrane is the same in all three cases. The average scaling layer thickness is approximately 15–20 µm. At a RFWC of 1.3, aragonite crystals appeared combined with calcite.

The reason for the formation of aragonite is that the morphology of calcium carbonate crystals is controlled mainly by the rate of crystallization and the Mg and Na concentrations of the precipitating water. It was reported that magnesium at high concentrations selectively poisons the sideward growth of calcite;

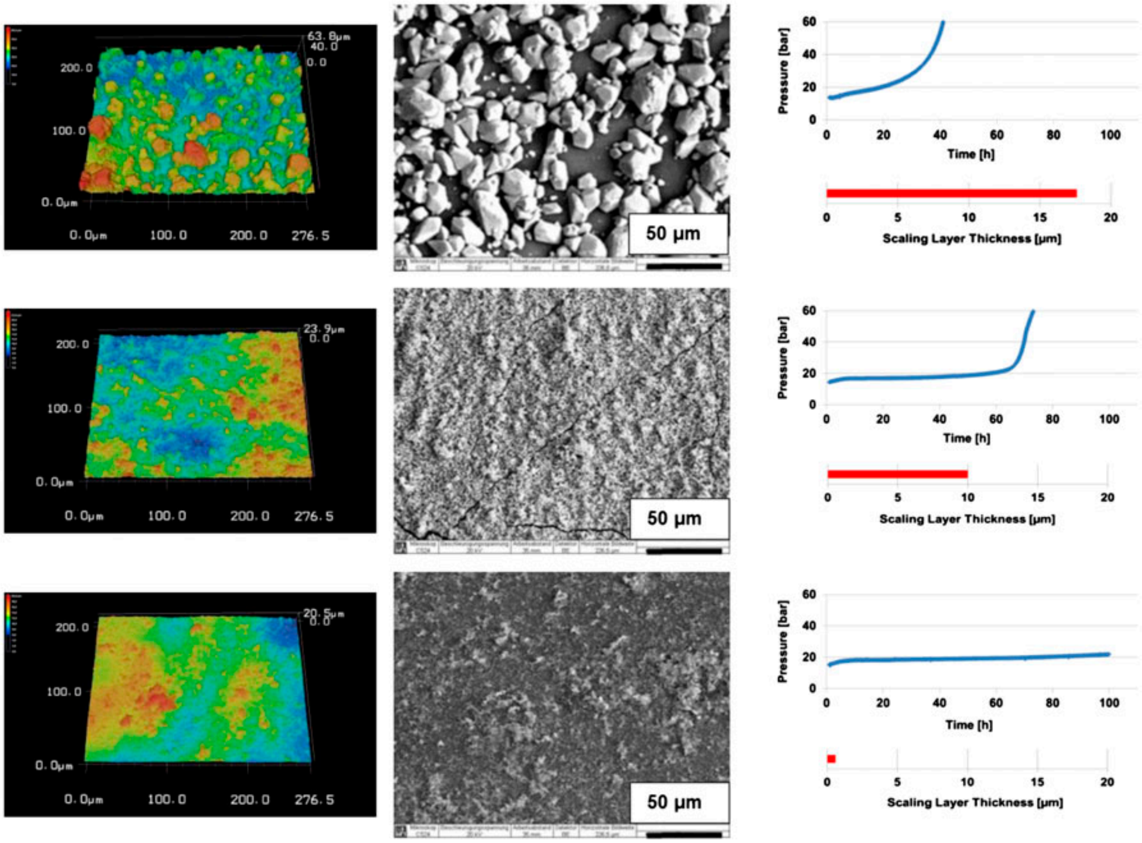


Fig. 11. CLSM image (left), SEM image (middle), pressure dependence vs. time and scaling layer thickness (right), of test runs with AA/EA copolymer**,** RFWC 0.8, Dosage 0.0, 5.0, 10 mg/L (top to bottom)).

thus $CaCO_3$ prefers to crystallize as aragonite, whose sidewise growth is generally stopped at widths of a few microns [17].

For selected test runs, a 3D plot of the scaling layer measured by a KEYENCE VK 8,700 CLSM (Figs. 8–12, left) and the equivalent SEM image (CamScan 24) (Figs. 8–12, middle) are shown. As at all SEM images, the backscattered electrons were detected, the brighter areas correspond to calcium in the scaling layer and the darker areas refer mainly to the sulfur from the membrane material. For easy reading, the development of the pressure vs. time is plotted and the scaling layer thickness is also shown (Figs. 8–12, right).

In the series presented in Fig. 8, the RFWC was adjusted to 0.8. The 3D image taken by the CLSM and the SEM image in the top row show very clear the calcite crystals of the scaling layer, if no AS is added. The precipitate consists of well-defined single crystals that cover the major part of the membrane surface. The scaling layer thickness is around 17 µm and the TRT was 40 h.

In the second row, the morphology of scaling layer is completely different due to the dosage of 2.5 mg/L of AA/AMPS. The average crystal size is much smaller and the crystals form scale patches. The scaling layer thickness decreases down to 4 µm and the pressure development vs. time shows an extended period of permeance decline.

It is remarkable that with a dosage of 5 mg/L, the period of permeance decline is almost doubled despite the scaling layer thickness is also doubled. With a dosage of 10 mg/L, the scaling layer thickness is further reduced and the TRT is extended due to a slower pressure increase in the period of rapid membrane blocking. At 20 mg/L, the amount of $CaCO_3$ on the membrane is nearly the same than with 10 mg/L but the TRT is reduced. The inconclusive scaling layer thicknesses may be caused by an erroneous estimation of the film thickness (due to the limitation of the method).

The RFWC in the series of trials with PAA (Fig. 9) was adjusted to 1.0. According to the resulting higher scaling potential of the feed water, the membrane surface is almost completely covered by calcite crystals and the TRT was only about 40 h in the test run without antiscalant. With increasing dosage from 2.5 to

10 mg/L, the TRT is extended very well (the test runs for 5 and 10 mg/L PAA were stopped after TRT of 100 h) and the scaling layer is reduced down to 1 µm.

The morphology of the scaling layer varies very much with the dosage of the PAA. At low dosage, the scaling layer is still relatively thick and shows cracks probably due to drying. With increasing dosage, the coverage decreases. At a dosage of 20 mg/L, there is nearly no $CaCO_3$ on the membrane, but in spite of this, the membrane is blocked. Wet analysis of the membrane scale could detect the PAA besides some calcium in the layer. This could indicate a calcium sensitivity of the PAA.

The results from the test runs with PAA at a constant dosage 5 mg/L and increased RFWC are presented in Fig. 10. With increasing scaling potential of the water, the TRT decreases and the scaling layer thickness increases. For normal feed waters, PAA serve as a good AS, but for waters with very high scaling potential, the performance of this AS is limited.

Fig. 11 summarizes the results concerning AA/EA at a RWCF of 0.8 with dosages from 5.0 and 10 mg/L. The TRT is extended and at 10 mg/L, there is a scaling layer of less than 1 µm on the membrane and no remarkable pressure increase. The appearance of the scaling layer corresponds quite well to PAA.

The results from the test runs with AA/EA at a constant dosage 20 mg/L and increased RFWC are presented in Fig. 12. With increasing scaling potential of the water, the TRT decreases very little and the scaling layer thickness remains in the range of a few microns.

4.2. Influence of the AS on main operating parameters

The following figures show the typical time dependence of the operating pressure and other main parameters for a test run without AS (Fig. 13) and with an effective AS at optimized dosage.

For all experiments, the concentration phase takes around 6 h, because the water hold-up in the plant is

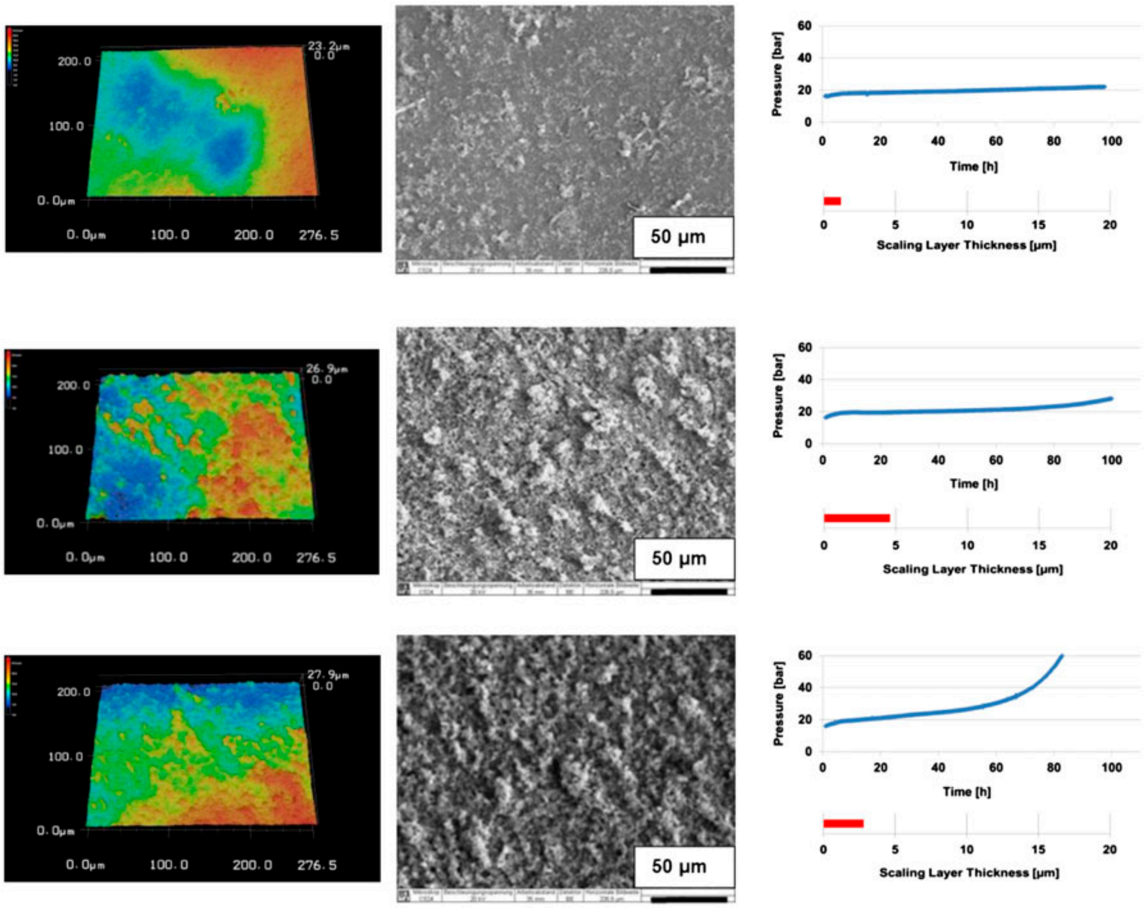
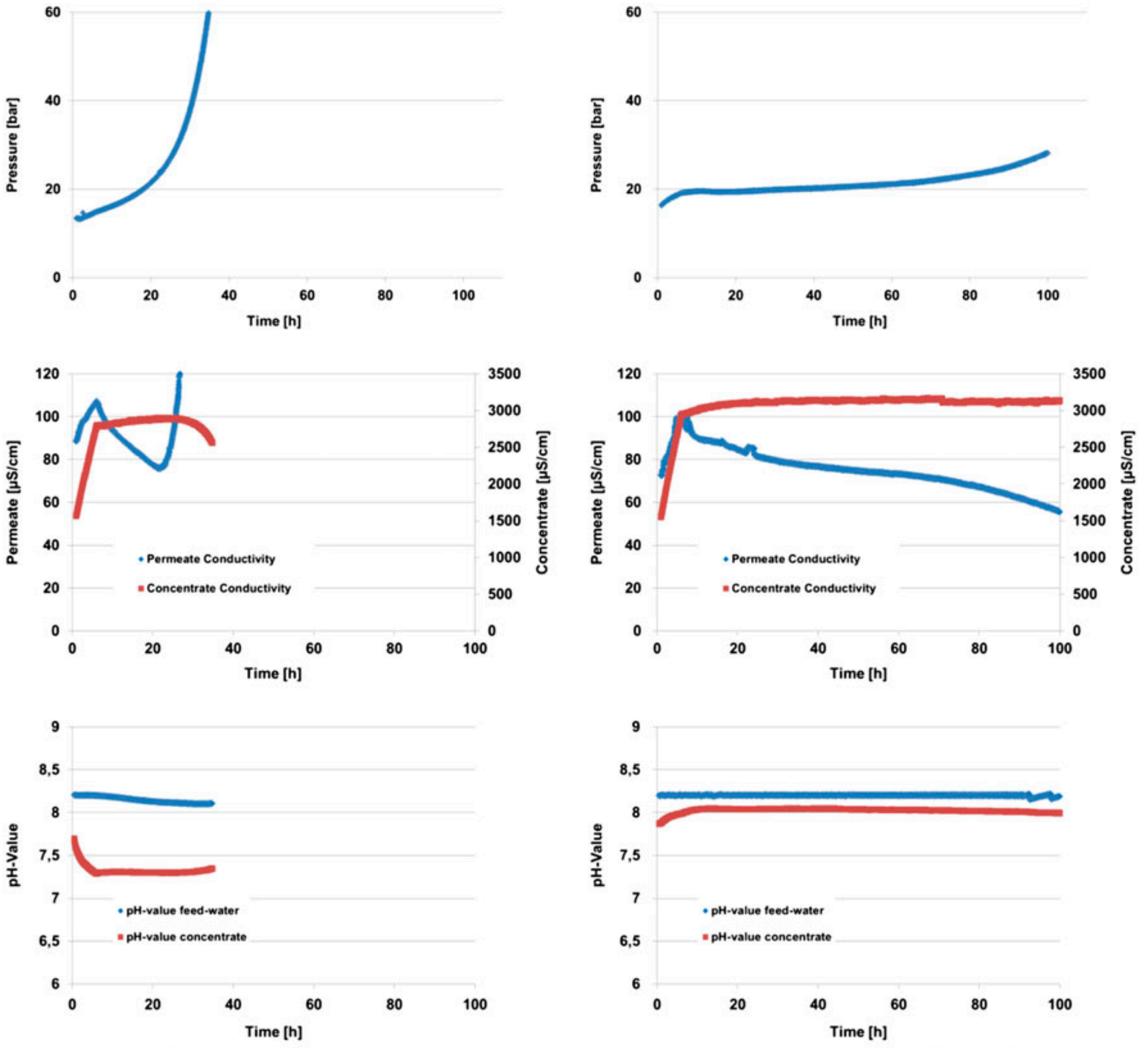


Fig. 12. CLSM image (left), SEM image (middle), pressure dependence vs. time and scaling layer thickness (right), of test runs with AA/EA copolymer, dosage 20 mg/L, RFWC 0.8, 1.0, 1.3 (top to bottom).

very small. Due to the required constant permeate flux, the pressure has to be adjusted if membrane blocking occurs. In the case without an AS, the diagram shows that the pressure increases from the very beginning of the test run. The period of permeance decline is very short, and it lasts for approximately 20 h, followed by the period of rapid membrane blocking. In the case with an AS, there is only a modest pressure increase for the first 6 h during the concentration phase. The period of permeance decline is extended by the AS until about 80 h, and the pressure increase during the rapid membrane blocking phase is not as steep as in the case without AS.

The conductivity of the concentrate increases during the concentration phase and it stays nearly constant for the rest of the test run, if an AS is used. Without an AS, the conductivity decreases due to the very intensive precipitation of $CaCO_3$. The permeate conductivity increases during the concentration phase and decreases continuously during the test run. This slight decrease of the permeate conductivity is due to the hold-up in the permeate volume of the test cells and the membrane properties, while the strong increase of the permeate conductivity in the case without AS (20 h) is an indicator for very rapid membrane blocking due to scaling.

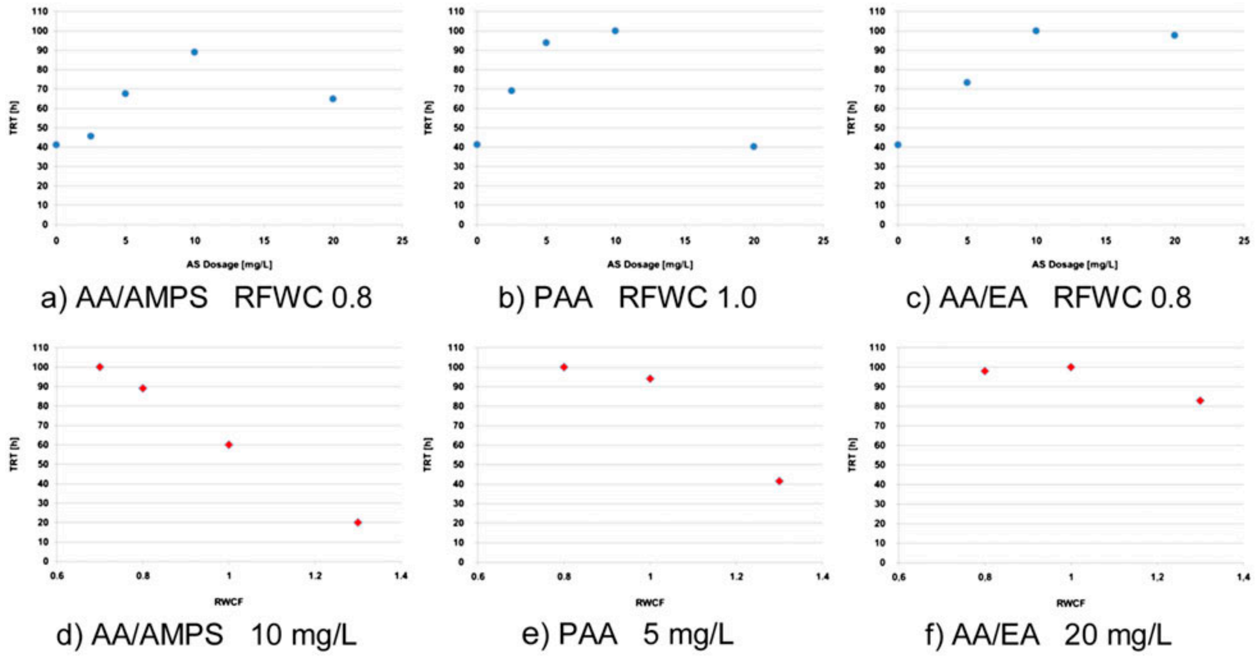
The pH value in the feed water tank is kept constant at 8.2, and if no scaling occurs the pH value in the concentrate is constant during the whole run. If no



Without antiscalant

With 20 mg/L AA/EA, RWCF 1.0

Fig. 13. Pressure (top), conductivity in permeate and concentrate (middle), pH value in permeate and concentrate as function of running time for a test run without antiscalant (left) and as an example with 20 mg/L AA/EA (right).



a) AA/AMPS RFWC 0.8 b) PAA RFWC 1.0 c) AA/EA RFWC 0.8

d) AA/AMPS 10 mg/L e) PAA 5 mg/L f) AA/EA 20 mg/L

Fig. 14. TRT vs. Antiscalant dosage (top: a–c) and TRT vs. RFWC (bottom: d–f).

AS is applied, severe precipitation starts already during the concentration phase.

The pH value of the concentrate decreases immediately and drops down to 7.4 due to the reduction of the CO_3^{2-} and Ca^{2+} concentration. After the concentration phase, the Ca^{2+} concentration decreases continuously, obviously caused by the ongoing $CaCO_3$ precipitation.

With an effective AS, the conductivity of the brine remains constant during the whole test run. There is no increase of the permeate conductivity at the end of the test run that indicates scaling. The pH values of the brine and permeate stay also constant during the test run and there is no significant reduction in the Ca^{2+} concentration.

The precipitation of $CaCO_3$ in the test water is leading to a measurable reduction in the calcium concentration only in case of severe scaling. A few micrometers of scale lead to a complete blocking of the membrane, but the reduction in the concentration of Ca^{2+} amounts only to some mg/L. Therefore, the permeance and the conductivity of permeate are more sensitive parameters to indicate scaling.

4.3. Total running time

In Fig. 14, the performance of the tested AS is presented by the TRT in dependence of the RFWC and the dosage of the inhibitor. The comparison of the TRT as a function of the dosage of the AS shows that all three AS clearly extend the TRT (Fig. 14(a), (b), and (c)). The degree of the extension of the TRT increases with increasing dosage, but there seems to be the possibility for overdosing for PAA (Fig. 9(b)).

In general, the TRT decreases with increasing RFWC at a fixed dosage of AS (Fig. 14(d), (e), and (f)). The AA/EA copolymer shows only a small decrease compared to the other two AS. In Fig. 15, the TRT for the three AS is plotted against the RFWC for a dosage of 20 mg/L. It is obvious that the performance of AA/AMPS as a calcium carbonate scale inhibitor is

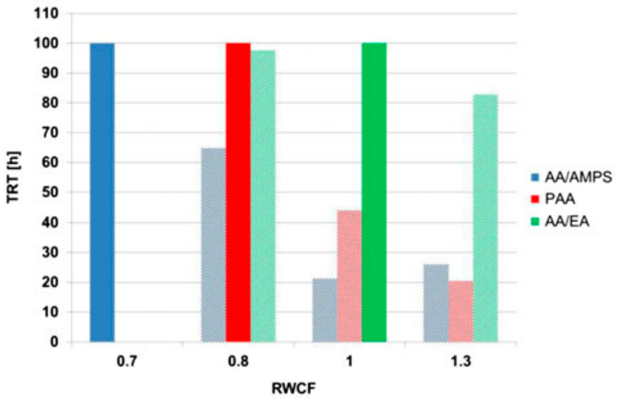


Fig. 15. Comparison of TRT as function of RWCF for three different antiscalants. The dosage was 20 mg/L (Test runs interrupted after 100 h are plotted in full bars).

limited compared to PAA and AA/EA. It should be noted that AA/AMPS is mainly used as disperser. AA/EA shows the best performance of the inhibitors in this work.

5. Conclusions

The pilot RO plant was used to characterize the efficiency of antiscalants against calcium carbonate scale. By EDXRF, the scaling layer thickness was estimated. The SEM images and the 3D images from CLSM showed that the water quality and the applied AS have a great influence on both the scaling layer thickness and the scaling layer morphology. The total running time (TRT) does not only depend on the amount of precipitated $CaCO_3$, but there is also a strong influence of the scaling layer structure. At a normal scaling potential of the water, the scaling layer consists of calcite and at higher LSI values for the feed water, also aragonite was found on the membrane.

The results show that a complete inhibition of $CaCO_3$ scale on RO membranes is possible with phosphorus-free antiscalants. The individual performance strongly depends on the chemical structure of the polycarboxylate. A specially adapted copolymer outperforms the polyacrylate homopolymer under severe scaling conditions. The AA/EA copolymer is suitable also under severe conditions.

From the three tested polyacrylates, AA/AMPS shows, as it was expected, the lowest performance as a scale inhibitor against calcium carbonate, because it is designed mainly as a disperser and as stabilizer for calcium phosphate. PAA proved to be an inhibitor for hardness at normal applications, but there might be some problems at overdosing. For the application for waters with high scaling potential, AA/EA proved to be very suitable, because this inhibitor is able to serve as a good stabilizer for hardness and at the same time as a disperser [18,19]. A combination of different polymers enables special solutions for high requirements.

It should be noted that the average residence time of the water in the test plant is approximately 1 h compared to less than a minute in a full-scale RO plant. So the operating conditions in the test plant make it more difficult for an AS to inhibit scaling compared to a full-scale RO plant.

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