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The performance of anti-scalants on silica-scaling in reverse osmosis plants

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ABSTRACT

Irreversible membrane scaling caused by silica remains a severe problem in many reverse osmosis plants. The engineering task is to find out the appropriate anti-scalant agent and its optimal dosage. Because suitable test methods are missing, a new membrane-based test method was developed. The fully automatically controlled test set-up and the test procedure are described. The effectiveness of 13 anti-scalants for silica was measured at different pH-values between 7.6 and 9.0 and with silica concentrations from 120 to 275 mg/L. The results show that two of the anti-scalants investigated in this paper have a significant anti-scaling effect for silica. Confocal Laser Scanning Microscope data indicate that even a very thin layer of some 10th of a micrometre can cause heavy scaling on the membrane.

Keywords: Reverse osmosis; Silica; Anti-scalant; Test method

1. Introduction

Irreversible membrane scaling caused by silica remains a severe problem in many reverse osmosis plants. The engineering task is to find out the appropriate anti-scalant agent and its optimal dosage.

However, suitable test methods are missing [1,2], and even the effectiveness of anti-scalants for calcium carbonate and calcium sulphate often is only determined in laboratory tests like the National Association of Corrosion Engineers (NACE) Standard Test Method 03-74. These test methods have the advantage that they are easy to apply, but the interaction with the membrane under real operating conditions, i.e. the surface charge of the membrane, the concentration polarisation, and the simultaneous membrane blocking of other substances are neglected.

Mostly only the silicate concentration in the feedwater is regarded. As the contents of the other ions, i.e. calcium and magnesium, the interaction with the membrane and the polymerisation kinetics of the silicic acid are not properly considered, jar test methods are not reliable. Thus, plant operation based on jar tests results can lead to substantial problems. To avoid such disadvantages a new membrane-based test method was developed, and the results obtained with this method are presented in this paper.

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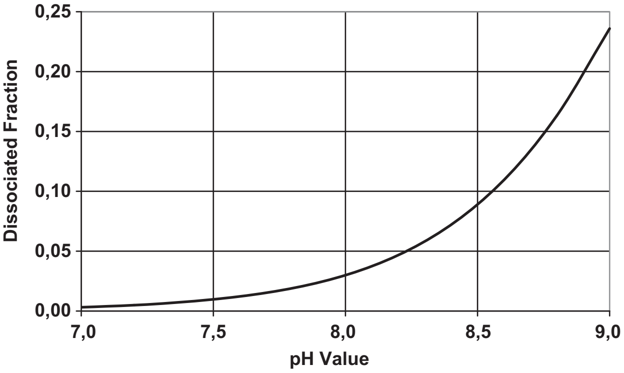


Fig. 1. Dissociated fraction of silicic acid $Si(OH)_4$ vs. pH-value.

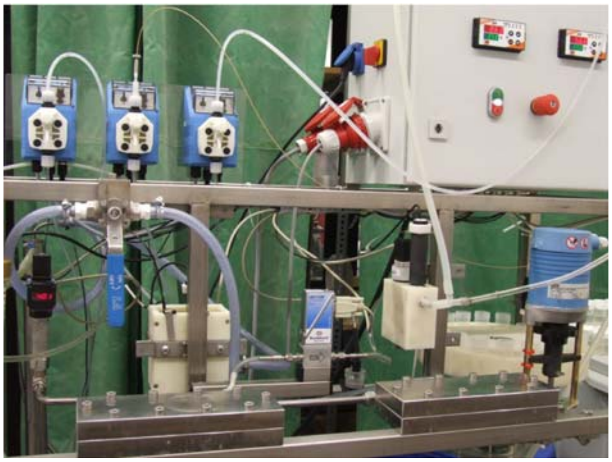


Fig. 2. Main view of the test plant.

2. Behaviour of silica in natural waters

The detailed structure of silicates in water is hardly known because the silicates exist in various forms. The main equilibria involved are the following [3]

$$SiO_2 + 2H_2O = Si(OH)_4$$

$$Si(OH)_4 + OH^- = HSiO_3^- + 2H_2O$$

With rising silica concentration the soluble silica tends to polymerise. The dimerisation reaction is

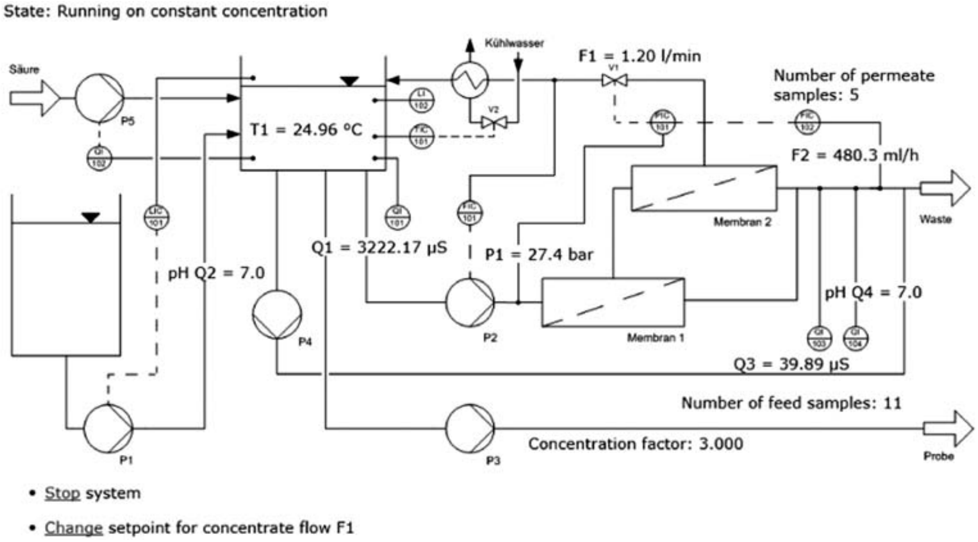
$$Si(OH)_4 + OH^- = SiO(OH)_3^- + 2H_2O$$

$$SiO(OH)_3^- + Si(OH)_4 = (OH)_3SiOSi(OH)_3 + OH^-$$

According to Gill [4] the reaction follows an ionic mechanism, and therefore it is very important to know the dissociated part of the silicic acid as a function of the pH-value. In Fig. 1, the dissociated fraction is shown for the first dissociation step as well as for the important pH-range in RO-applications (pK_{s1} 9.51; pK_{s2} = 11.74).

It may last a while before polymerisation starts, and during this time the monomeric solution is quite stable. But once the polymerisation has begun, the monomer disappears very rapidly. The monomer reacts faster with dimers and higher oligomers than with other monomers. Thus it is difficult to observe the polymerisation of silica and to predict the resulting molecules and their concentrations.

The silicate ions polymerisation leads to the formation of "silica scale", which is a complex and amorphous product, a complicated mixture of numerous components. It is impossible to know precisely which species



State: Running on constant concentration

T1 = 24.96 °C

F1 = 1.20 l/min

Number of permeate samples: 5

F2 = 480.3 ml/h

Q1 = 3222.17 µS

P1 = 27.4 bar

pH Q2 = 7.0

pH Q4 = 7.0

Q3 = 39.89 µS

Number of feed samples: 11

Concentration factor: 3.000

- Stop system
- Change setpoint for concentrate flow F1

Fig. 3. Screen-shot of the PC-control panel.

are present and how they will react. The limit (e.g. in molecular weight) between the species which stay dissolved and the others neither is really determined.

The important parameters for the polymerisation rate of silica besides the silica concentration itself are the pH-value and the concentration of calcium and magnesium [5–7].

3. The membrane-based test method

In order to investigate the performance of different anti-scalants at a reverse osmosis plant, a new membrane-based test method was developed. The test set-up for this work is shown in Fig. 2. Fig. 3 provides a screen-shot of the PC-control panel.

The water to be examined is fed into a small working tank via pump P1. From that working tank the water is pumped by the high pressure pump P2 through two reverse osmosis test cells of 80 cm^2 membrane area each. The permeate flow is adjusted at a constant value of 480 mL/h, equivalent to a permeate flux of 30 L/m^2 h.

At the beginning of a test run the permeate is discharged, and the concentrate is recycled in the working tank. The 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 is reached, the concentrate is also discharged (by pump P4), and the test plant is operated continuously at that concentration level and at a constant permeate flux, due to automatic controlled pressure adjustment.

In order to run the tests at a defined pH-value, the pH-value in the feed water can be controlled by adding acid or caustic soda by a dosing pump (P5).

Via pump P3 a sample is taken every hour and analysed by Inductively Coupled Plasma (ICP).

From the measured data recorded by means of a PC-System, the permeance of the membrane is calculated by dividing the actual permeate flow by the driving pressure difference. There are three criteria investigated in the membrane-based test method to determine the performance of an anti-scalant:

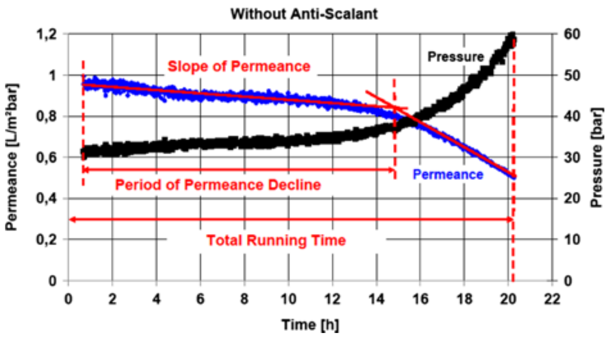


Fig. 4. Typical permeance profile (SiO_2 153 mg/L).

- The time for the period of permeance decline starting after a concentration factor of 3 is reached.
- The slope of the permeance during the period of permeance decline.
- The total running time until a pressure difference of 60 bar is reached.

4. Experimental procedure

The test waters are prepared by adding specific salts (analytical grade) in demineralised water. After adding the salts, SiO_2 is added as a concentrated sodium silicate solution. Then the resulting test water is stirred for 24 h to have the silicates completely dissolved. Before the test starts, the corresponding anti-scalant is added and the pH is adjusted to a defined value by adding sulphuric acid. The test water for the experiments in this paper contains ca. 80 mg/L Mg and 40 mg/L Na. The main anion is SO_4^{2-} with a concentration of around 400 mg/L. Depending on the specific test conditions (pH-values, SiO_2-concentration, pH-control) there are also minor concentrations of NO_3^- and HCO_3^-. The initial pH-setting of the feed water is done with sulphuric acid. Normally the tests were carried out without pH-control of the concentrate, leading to a situation where the pH of the concentrate considerably rises during the test run, e.g. from 7.6 to 8.4. The trials with pH-control of the concentrate were done with nitric acid to keep the sulphur concentration in the feed water constant, for sulphur is used as a tracer to determine the actual concentration factor. With the chosen test water composition the precipitation of other salts besides silicate is almost excluded. Therefore any coprecipitation of silica scale with other species is excluded, especially with calcium carbonate. Coprecipitation can cause membrane scaling even at very low SiO_2-concentrations [1].

The membrane used was Filmtec FT 30 SW grade.

The concentration factor in the reported experiments was 3, and the silica concentration in the concentrate was set at relatively high values between 120 and 275 mg/L. These high SiO_2-concentrations were chosen to simulate the effect of high concentration polarisation in spiral-wound elements, especially in the dead zones of the spacer.

The performances of a variety of different anti-scalants were investigated at different pH-values. Selected membranes were analysed and measured by a Scanning Electron Microscope and a Confocal Laser Scanning Microscope (CLSM).

In order to characterise the chemical structure of the silicates in the water, the samples in this work were analysed according to three different methods:

Small-size units (monomeric silicates). Spectro-Photometric Method (SPM, Hach method 8185). This method allows to determine the small-size units (monomeric silicates). It includes not only the monomer silicate ions, but also some small oligomeric species such as dimers, trimers, etc. The exact number of reactive units is not known.

The Total amount of silicates. Atomic Absorption Spectrometry/ICP. These two methods allow to determine the total amount of silicates present in the solution, including the soluble silica and also the bigger polymeric structures (polymeric silicates).

From the difference between the silicate concentration in filtered water samples at the very beginning of the test and the concentration of "polymeric silicates", the amount of precipitate respectively gel is calculated ("filterable" silicate).

5. Results

In the cases where the membrane is totally scaled, at first the pressure increase is relatively slow for a certain period of time (period of permeance decline), but it is followed by a sudden and strong increase (Fig. 4). Dividing the actual permeate flow rate by the actual pressure difference results in permeance. A typical example for the permeance profile is given in Fig. 4 to illustrate the performance criteria for the tested anti-scalants.

It is clearly seen that there are two different sections of the typical permeance profile in the case of silica scaling. The time for the period of permeance decline and the slope of the permeance serve as main criteria for the performance of an anti-scalant. The lower the slope and the longer period of permeance decline, the better is the effectiveness of the anti-scalant. In addition, the total running time until the pressure has reached 60 bars is taken as a criterion to quantify the anti-scalant effect on the silica-scaling.

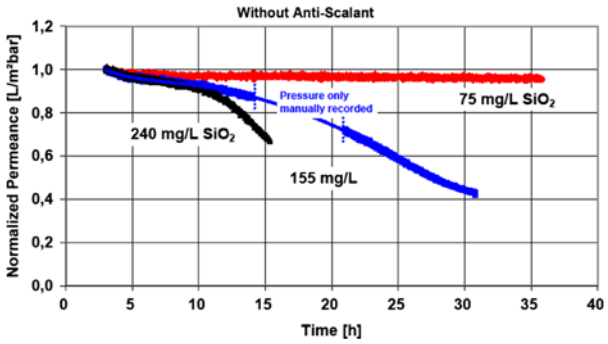


Fig. 5. Normalised permeance for different SiO_2-concentrations, without pH-control.

Fig. 5 shows the influence of the silica concentration on the normalised permeance profile when no anti-scalant is used. The permeances in this figure are normalised to the initial value in order to eliminate the different permeances of the clean membrane samples. At 75 mg/L SiO_2 no scaling occurs and there is no significant decline in the permeance. This test run was interrupted after 35 h. With increasing SiO_2-concentrations the slope of the permeance is higher, and the period of permeance decline as well as the total running time become shorter.

In Fig. 6, the permeance profiles for a test run with no anti-scalant (A) and for test runs with three different anti-scalants (A, B, and C) are shown. The better the performance of the anti-scalant is, the lower is the slope of the permeance and the longer are the period of permeance decline and the total running time. Anti-scalant B influences only the slope of the permeance in the first part of the test run and is not sufficient. By applying anti-scalant B or even better C, the scaling of the membrane is reduced considerably.

From Fig. 6, it is obvious that by using a suitable anti-scalant the period of permeance decline can be prolonged and the slope of the permeance can be reduced considerably.

Fig. 7 gives an overview of the measured period of permeance decline for selected anti-scalants compared to the measured value for the test run without anti-scalant. The chemistry of the anti-scalants was: polyacrylates, polyacrylate copolymers, terpolymers, phosphonates as well as proprietary silicate-anti-scalants. Some anti-scalants show almost no effect while two anti-scalants prolong the period of permeance decline by more than a factor of 2. With the test procedure described in this paper the efficiency of anti-scalant programs against silicate scaling can be quantitatively determined.

The anti-scalant with the best performance (Number C in Fig. 7) was chosen as the reference anti-scalant for further detailed studies. The results are summarised in Figs. 8 and 9. These data clearly prove the efficiency. However, the obtained values for the permeance decline and for the slope of permeance are fluctuating to some extent.

Careful analysis of the test protocols showed that the pH-value of the concentrate was varying to a certain extent, even for trials with the same starting conditions.

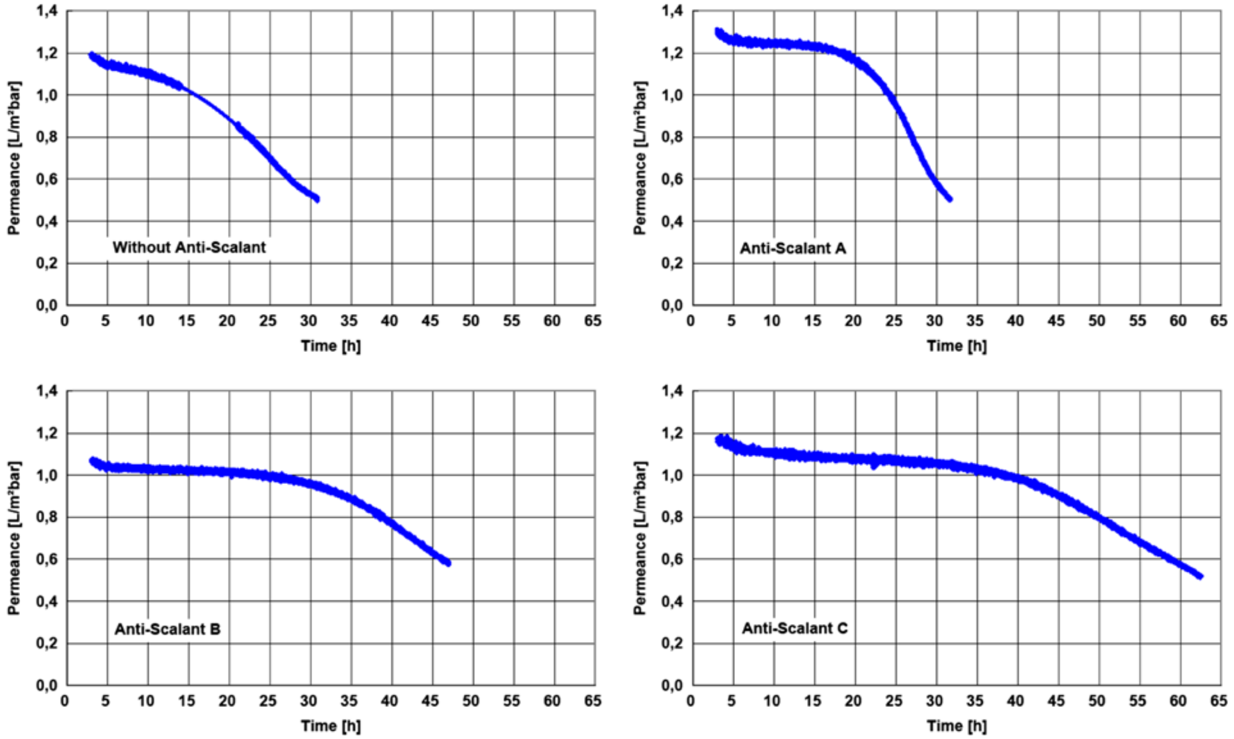


Fig. 6. Permeance profiles for selected anti-scalants without pH-control (150 mg/L SiO_2).

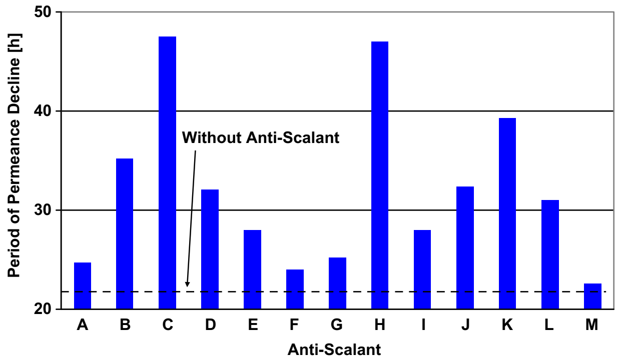


Fig. 7. Period of permeance decline for 13 anti-scalants (150 mg/L SiO_2, without pH-control).

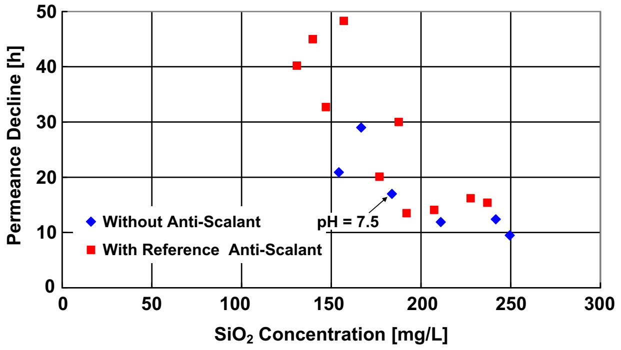


Fig. 8. Time of permeance decline vs. SiO_2-concentration, pH 7.6–8.4.

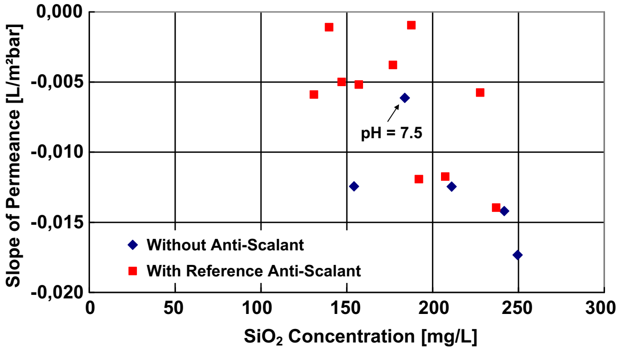


Fig. 9. Slope of permeance vs. SiO_2-concentration, pH 7.6–8.4.

In order to illustrate the influence of a varying pH, two test runs with the same initial pH, but with and without pH-control of the concentrate are presented in Fig. 10. If the pH-value of the concentrate is kept constant at 8.0, the permeance profile differs completely from that obtained for the run without pH-control. This demonstrates that the pH is strongly influencing silica scaling.

Sheikholeslami [7] reported that the polymerisation time of monomeric silica is relatively low for pH-values between 6.5 and 8.5 and increases both for lower and for higher pH-values. But considering that the

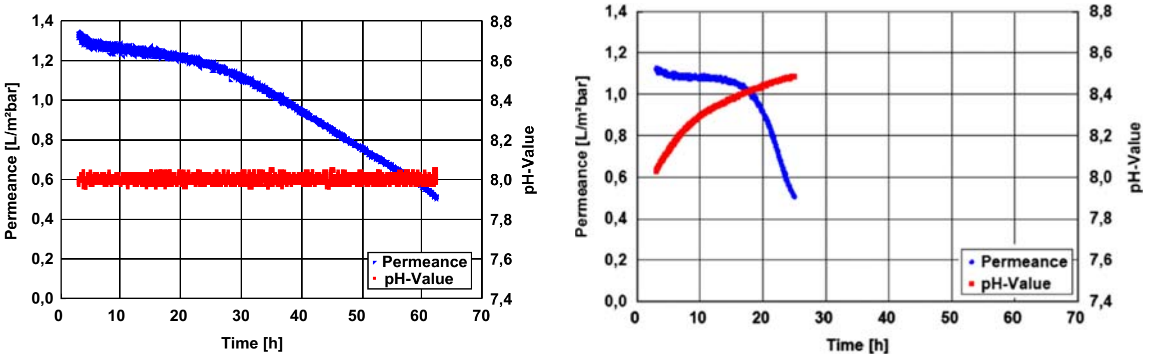


Fig. 10. Influence of pH-Value on the permeance profile, SiO_2 180 mg/L, with anti-scalant.

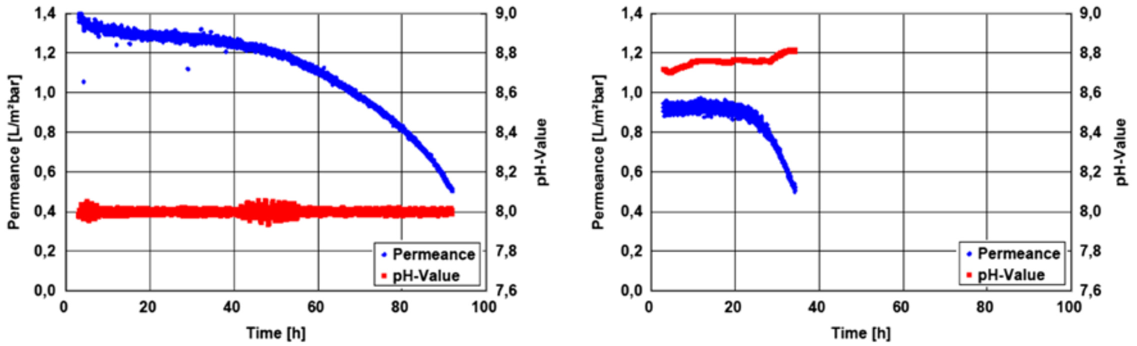


Fig. 11. Influence of pH-Value of the concentrate on the permeance profile, SiO_2 150 mg/L, with anti-scalant.

polymerisation is based on an ionic reaction [4], it is obvious that at higher pH-values the amount of ionic silica species is increased and thus also the probability for scaling.

Fig. 11 shows the permeance profile for test runs with 150 mg/L SiO_2 at controlled pH-values of 8.0 and 8.8. The total running time is longer by a factor of 2.7 at pH 8.0 compared to the running time at pH 8.8, and the period of permeance decline is decreasing from around 50 h at pH 8.0 to 20 h for a pH 8.8.

In Figs. 12 and 13, the three-dimensional profiles of pure silica scaling layers measured with a CLSM are shown. Because CLSM is a non-destructive method, the membrane can be observed during the test procedure.

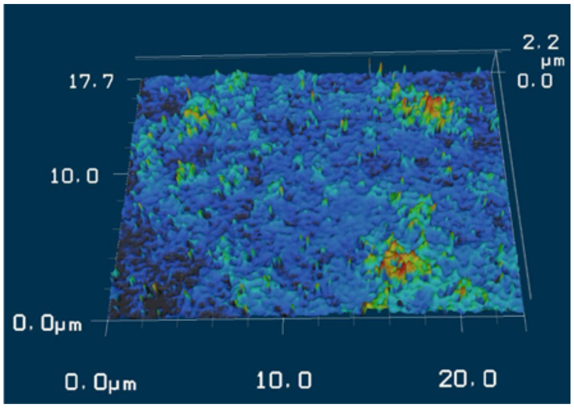


Fig. 12. Membrane partly scaled by a 0.3 μm silica layer.

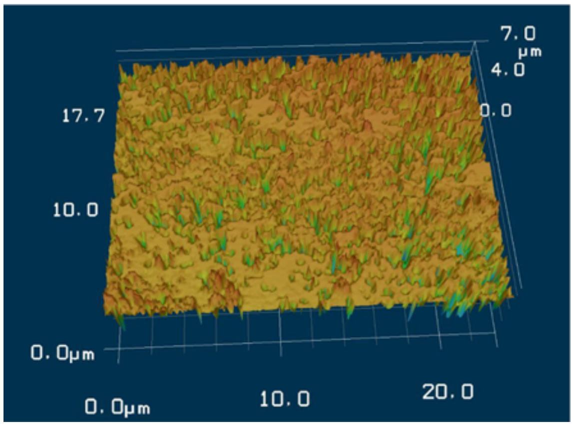


Fig. 13. Membrane totally scaled by a 4.5 μm silica layer.

When scaling starts, it occurs in randomly distributed separated spots on the membrane surface (Fig. 12). These local spots grow mostly in height (up to some micrometres) leaving the non-scaled membrane surface almost clean, so that the permeance decline is very low. But a scaling layer of only some tenth of a micrometre results in a heavy scaling effect (Fig. 12). Such thin scaling layer corresponds to a very small reduction of the silica content in the feed water. To give an example: Assuming a layer of 1 μm of SiO_2 for a test that runs for 50 h at 30 L/m^2h permeate production, the silica content of the feed water is calculated to be reduced by only 0.3 mg/L. Thus it is impossible to determine the scaling of the membrane by SiO_2 from analysis and mass balance. Furthermore it can be concluded that it is neither possible to get reliable information about the effectiveness of anti-scalants for silica from jar tests.

When the scaling is almost completed, the height of the silica is typically around 5 μm and there are only small holes left in the layer (Fig. 13). Even for this deposit that is completely blocking the membrane the calculated reduction of the silica content of the feed water is only approximately 0.5 mg/L, which is within the error of detection.

6. Conclusions

The mechanism of RO membrane scaling by silicate is very complex and depends particularly on the water composition. Especially the pH-value has a strong influence. Jar tests can provide only very limited information. However, for the determination of the optimal operation conditions and the selection of an anti-scalant, pilot plant tests are necessary for reliable results. The efficiency of an anti-scalant depends highly on its chemical structure. Reliable comparative data can only be obtained if all parameters are carefully controlled during the trials. CLSM data indicate that to observe silica scaling, only a very small amount of polymerised silica is necessary. A suitable anti-scalant allows to operate the RO-plant at higher silicate concentrations, and thus to achieve higher recovery rates.

The found results make it possible to develop innovative anti-scalants based on the state-of-the-art-products.

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