Desalination and Water Treatment
www.deswater.com

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doi: 10.5004/dwt.2011.2340

31 (2011) 326–330
July

Silica scaling on reverse osmosis membranes — Investigation and new test methods

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Received 3 June 2010; Accepted 22 March 2011

ABSTRACT

Scaling calculations are usually only based on the silicate concentration in the feed water, because suitable test methods for the interaction of silica with other ions are missing. As the contents of the other ions, i.e. above all calcium and magnesium are not considered, this method is incorrect and can lead to substantial problems. In this paper first the results of laboratory experiments investigating the influence of different cations on the behaviour of supersaturated solutions of silica in different test waters are discussed. Subsequently, the results of the new membrane-based test method considering the influence of Ca^{2+} and Mg^{2+}, the pH value and the addition of antiscalants are discussed. Different methods of analysis made it possible to distinguish three groups of silicates: 'monomeric', 'polymeric' and 'filterable'. Ca^{2+} and Mg^{2+} ions have a strong influence on the formation of filterable silicate and on the kinetics of the formation of the different silicate species. The 'polymeric silica' is mainly responsible for the membrane scaling, and the kinetic of its formation is strongly influenced by the cations and the pH value. The antiscalant Osmotech 1309 makes it possible to operate the plant at significantly higher recovery rates, resp. at higher SiO_2 concentrations.

Keywords: Antiscalants; Membrane scaling; Osmotech 1309; Reverse osmosis; Silica scaling

1. Introduction

In many reverse osmosis systems with high silica containing water, the problem is severe and irreversible membrane scaling. The engineering task is to find out the appropriate antiscalant agent and the optimal dosage. However, suitable test methods are missing [1,2]. Usually only the silicate concentration in the feed water is regarded. As the contents of the other ions, i.e. above all calcium are not considered, this method is not reliable and can lead to substantial problems.

In this paper first the results of laboratory experiments investigating the influence of ions on the behaviour of supersaturated solutions of silica in different test waters are discussed. After that the new developed membrane-based test method to determine the effectiveness of antiscalants is presented. Subsequently, the results of test series about the influence of Ca^{2+} and Mg^{2+}, the pH value and of the addition of antiscalants on silica membrane scaling are discussed. The standard test conditions for the results

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Presented at EuroMed 2010 — Desalination for Clean Water and Energy: Cooperation among Mediterranean Countries of Europe and MENA Region, 3–7 October 2010, David Intercontinental Hotel, Tel Aviv, Israel. Organized by the European Desalination Society.

presented in this paper are a volumetric concentration ratio of 3, a constant permeate flux of 30 L/m²h, and for the test runs with Ca^{2+} and without pH control an LSI = 1.8 (LSI = Langelier Saturation Index).

2. Different forms of silicates in water

The detailed structure of silicates in water is hardly known. The literature provides only the basic information about the general chemistry of silicates. The silicates present in natural waters exist in various forms. The main equilibria involved are the following [3]:

$$SiO_2 + 2H_2O = Si(OH)_4 \tag{1}$$

$$Si(OH)_4 + OH = HSiO_3^- + 2H_2O \tag{2}$$

However, when the concentration of silica increases, the soluble silica tends to polymerise, following an ionic mechanism [4]. The dimerisation reaction is

$$Si(OH)_4 + OH^- = SiO(OH)_3^- + 2H_2O \tag{3}$$

$$SiO(OH)_3^- + Si(OH)_4 = (OH)_3SiOSi(OH)_3 + OH^- \quad \text{(dimerisation)} \tag{4}$$

It can last a long time before polymerisation starts. During this time, the monomeric solution is quite stable. But once the polymerisation has begun, the monomer disappears very rapidly. Indeed, the monomer reacts more rapidly with dimer and higher oligomers than with another monomer. So, it is difficult to observe the polymerisation of silica and to predict the resulting molecules and their concentrations.

The kinetics of the polymerisation of silicic acid have been studied by many authors. Baumann [5] provided the first systematic studies on the polymerisation and depolymerisation at 30°C and pH-values between 5.8 and 9. The work of Rodriguez [6] gives an overview about the recent work on this topic. Sheikholeslami et al. [7] reported about the dependence of the polymerisation time from the pH-value at SiO_2 concentrations at 360–400 mg/L. Between pH 6.5 and 8.5 the polymerisation is relatively fast but it decreases to very low values at pH 5.5.

The silicate ions polymerisation leads to the formation of "silica scale", which is a complex and amorphous product, a complicated mixture of numerous components, and it is impossible to know precisely which species are present and how they will react. The limit (e.g. in molecular weight) between the species which stay dissolved and the others is also not really determined.

So it is difficult to act on silicates because of the impossibility to know precisely the distribution and behavour of species.

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

- Small-size units ('monomeric silicates').
  SPM (Spectro-Photometric Method), Hach method 8185
  This method allows to determine the small-size units ('monomeric silicates'). It includes not only the monomer silicate ion, but also some small oligomeric species such as dimers, trimers, etc. The exact number of reactive units is not known.
- Total amount of silicates
  AAS (atomic absorption spectrometry) / ICP (inductively coupled plasma).
  These two methods allow determining 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 resp. gel is determined ('filterable' silicate).

3. Laboratory experiments on the influence of cations

According to Neofotistou and Demadis [8] and Koo et al. [9], the presence of calcium or magnesium ions favours the formation of silicate deposits. Iler [3] reported that at pH 7, the silica particles are negatively charged and repel each other. But if salt is added, the charge repulsion is reduced and aggregation and gel formation occurs.

Figs. 1 and 2 show the influence of the Ca^{2+} concentration on the measured silica concentration vs. time. In these experiments different amounts of NaCl and $CaCl_2$ are added to the initial solution of 1,000 mg/L SiO_2. The total concentration of the added salts is kept to be 25 mval/L and the ratio between NaCl and $CaCl_2$ was varied, i.e. 5 mmol/L NaCl plus 10 mmol/L CaCl2 or 20 mmol/L NaCl plus 2.5 mmol/L $CaCl_2$.

The results of the AAS show that the more calcium the solution contains, the higher is the final amount of 'filterable' and 'polymeric' silicates, and the quicker this final concentration will be reached. In the case of the SPM values it was found that there is almost no influence of the $CaCl_2$ concentration on the final monomeric silica concentration.

4. Development of the membrane test method

To investigate the observations from the laboratory experiments at a reverse osmosis plant, a new test method was developed. The test set-up for this work and its flow scheme are shown in Figs. 3 and 4.

The water, to be examined, is concentrated to a defined level with two reverse osmosis test cells of 80 cm² membrane surface each. Until the test water is concentrated

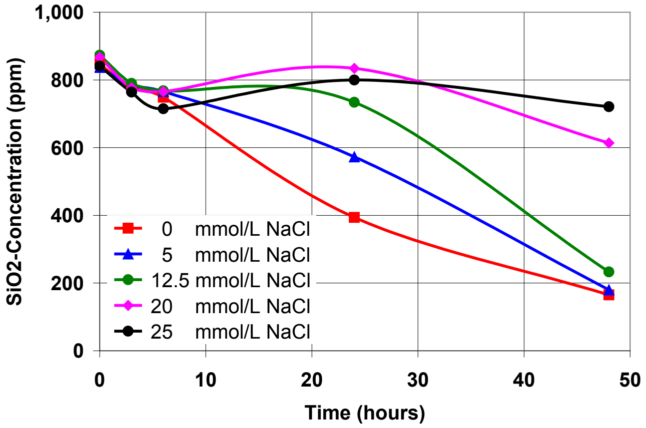

Fig. 1. SiO_2 concentration by AAS vs. time and NaCl/$CaCl_2$ ratio.

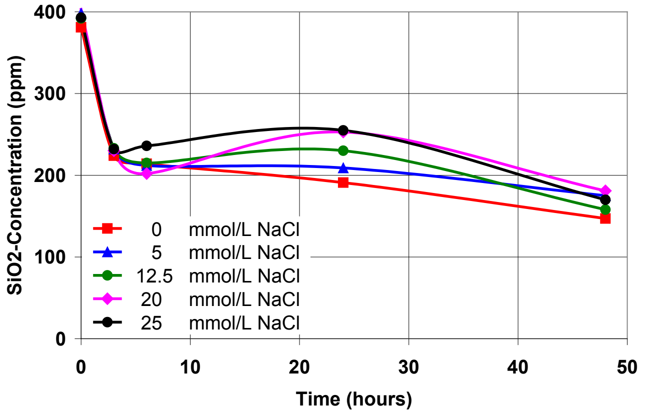

Fig. 2. SiO_2 concentration by SPM vs. time and NaCl/$CaCl_2$ ratio.

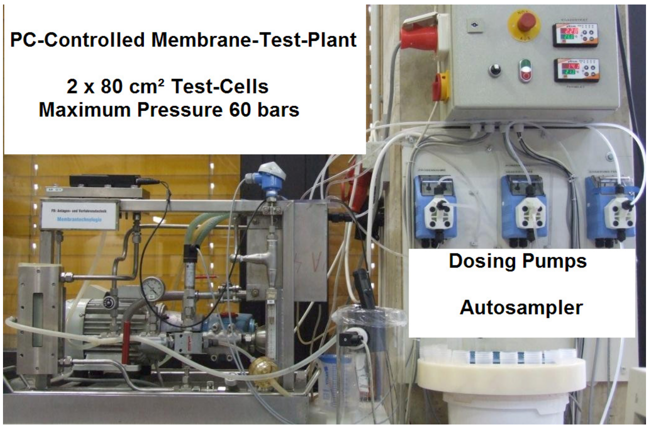

Fig. 3. Membrane test set-up.

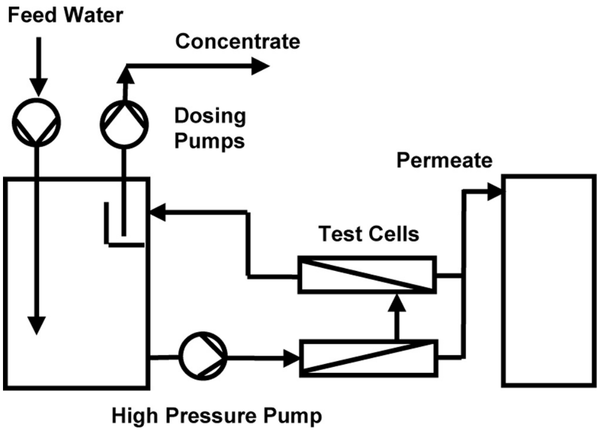

Fig. 4. Flow scheme of the test set-up.

up to the desired concentration level, a constant amount of permeate is produced and the concentrate is recycled to the feed tank.

As soon as the desired volumetric concentration ratio is reached, the test plant is operated continuously at that concentration level at a constant permeate flux due to pressure adjustment. The first criterion for the scaling potential of the test water is the total permeate amount produced up to a pressure of 60 bar. In cases where the scaling potential of the test water is low or if an appropriate antiscaling agent is used, as second criterion serves the slope of the pressure increase versus the produced permeate amount.

Besides the operating parameters of the plant, the ionic composition was generally analyzed once per hour by means of ICP.

5. Results from the test runs

The entirely produced permeate amount depends on the composition of the water, in particular on the LSI, the SiO_2 concentration and the antiscalant agent. With rising SiO_2 concentration the totally produced permeate amount decreases. The test runs, which were accomplished with an urban drinking water and with two model waters, show that Ca^{2+} ions and silicate are influencing each other as to membrane scaling.

The scaled membranes were examined under a scanning electron microscope (SEM), and the element distribution of the scaling layer was determined by energy dispersive X-ray spectroscopy (EDX).

Fig. 5 shows the distribution of Ca and Si in a scaling layer. One clearly recognizes that these elements form the scaling layer in separate structures. In case with no Ca^{2+} in the test water but with high concentrations of silicate, scaling occurs in an amorphous layer (Fig. 6).

The different impact of Ca^{2+} and Mg^{2+} ions on the rate of scaling for different silica concentrations is very clearly shown in Fig. 7. In the case of Ca^{2+} at an LSI = 1.78 even small concentrations of SiO_2 have an important influence

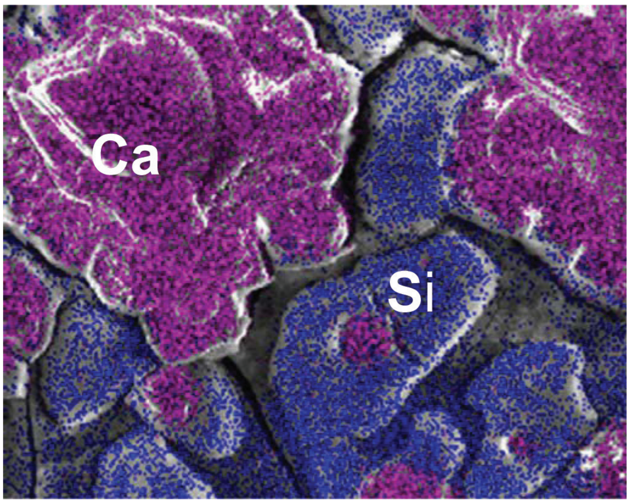

Fig. 5. Distribution of Ca and Si in a $CaCO_3/SiO_2$ deposit on a membrane.

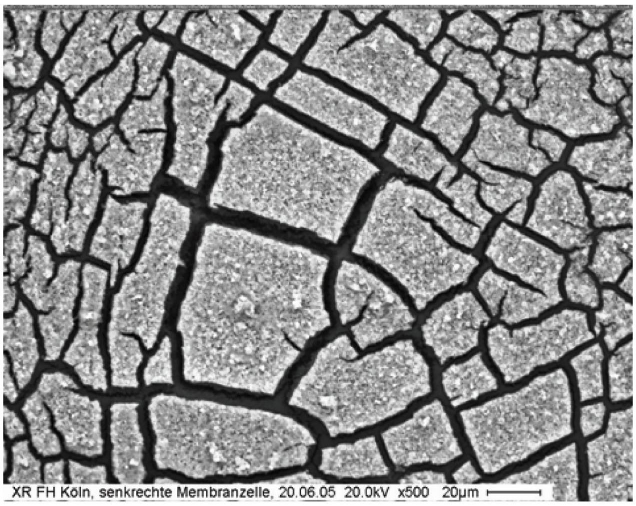

Fig. 6. SiO_2 deposit on a membrane.

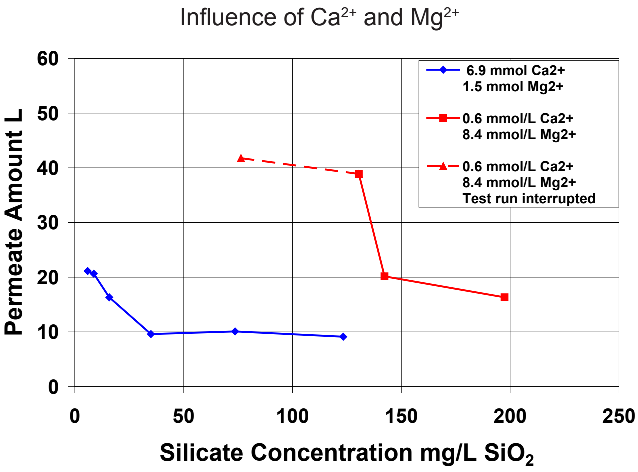

Fig. 7. Produced permeate amount vs. SiO_2 concentration in brine.

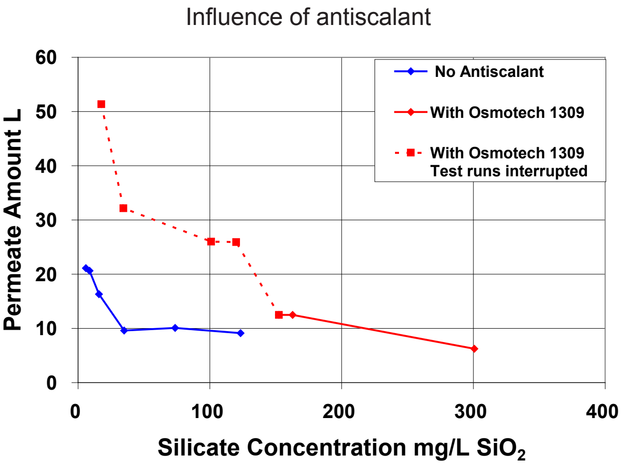

Fig. 8. Produced permeate amount vs. SiO_2 concentration in brine (6.9 mmol/L Ca^{2+}/1.5 mmol/L Mg^{2+}).

on the scaling potential of the water. If the Ca^{2+} ions are replaced by Mg^{2+} ions scaling occurs only at significantly higher SiO_2 concentrations.

Fig. 8 shows the big influence of the added antiscalant Osmotech 1309. Osmotech 1309 is an antiscalant and antifoulant used for the prevention of inorganic scale deposits in membrane systems. This antiscalant is a liquid product based on phosphonic acids, phosphonocarboxylic acids and special polycarboxylic acids. It is an efficient scale inhibitor against various minerals and designed especially against silica fouling.

Compared to the test runs without antiscalant, the produced permeate amount by adding Osmotech 1309 could be reached at three times higher SiO_2 concentrations. Test runs with lower SiO_2 concentrations were interrupted when no scaling was found and the produced permeate amount had reached three times the corresponding value for test runs without antiscalant.

To investigate the dependence of the scaling potential of the test waters on the pH value at different SiO_2 concentrations, the pH was varied between 5.5 and 6.5. Because the scaling potential at that conditions is quite low, the slope of the pressure increase versus the produced permeate amount is used as criterion to rate the results.

Fig. 9 shows the results for test runs at a pH value of 5.5 at SiO_2 concentrations of 150 mg/L and 275 mg/L with and without antiscalant Osmotech 1309.

Up to SiO_2 concentrations of 150 mg/L the pressure increase at constant flux could be kept relatively low by using Osmotech 1309. At significantly higher SiO_2

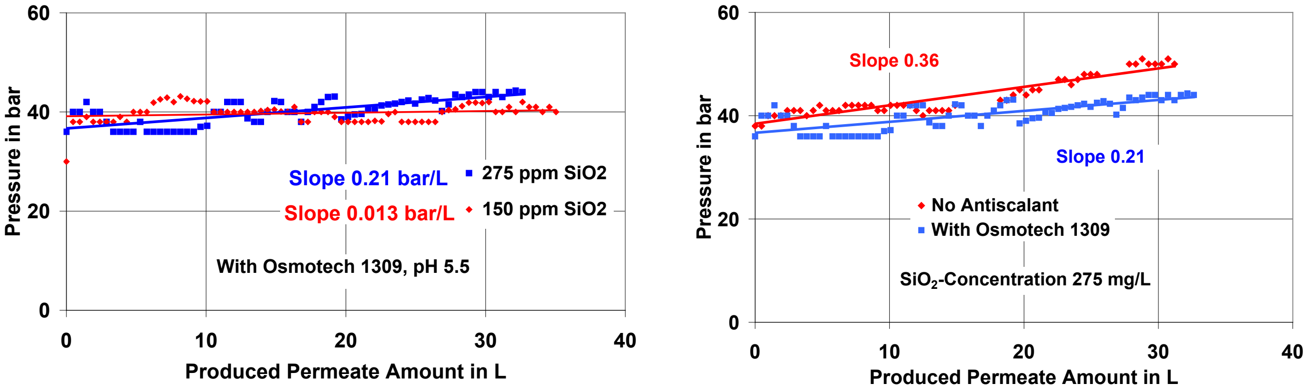

Fig. 9. Influence of SiO_2 concentration in brine (left) and antiscalant Osmotech 1309 (right) on pressure increase at pH of 5.5 at constant permeate flux.

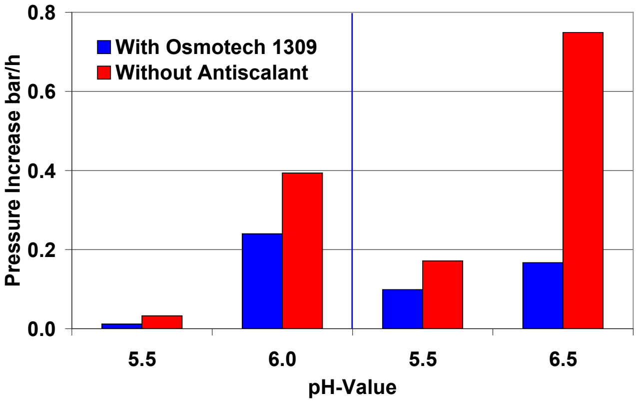

Fig. 10. Pressure increase vs. antiscalant and pH left side at 150 mg/L SiO_2, right side at 275 mg/L SiO_2.

concentrations of 275 mg/L the used antiscalant is able to decrease the pressure increase per produced volume of permeate by a factor of 1.7 (0.36 bar/L without antiscalant/ 0.21 bar/L with Osmotech 1309).

In Fig. 10 the influence of the used antiscalant is shown for test runs at different pH-values and SiO_2 concentrations. The pressure increase rises with increasing pH and increasing SiO_2 concentration. But by adding a suitable antiscalant the pressure increase could be reduced in comparison to the respective test run without antiscalant.

6. Conclusions

The different methods of analysis made it possible to distinguish three groups of silicates: 'monomeric', 'polymeric' and 'filterable'. Ca^{2+} and Mg^{2+} ions have a strong influence on the formation of filterable silicate and on the kinetics of the formation of the different silicate species. With this new membrane test method the strong impact of silicate scaling was proved, even if only small amounts of scale were formed. It could be shown, that the 'polymeric silica' is mainly responsible for the membrane scaling. The kinetic of the formation of 'polymeric silica' is strongly influenced by the cations and the pH-value.

It could be demonstrated that the use of a suitable antiscalant makes it possible to operate the plant at significantly higher recovery rates.

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