

Monitoring scaling in nanofiltration and reverse osmosis membrane systems

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Abstract

In nanofiltration and reverse osmosis membrane systems 75–90% of the feed water is converted to product, and as a consequence dissolved salts are concentrated in the membrane concentrate. Subsequently, sparingly soluble inorganic compounds such as calcium carbonate and barium sulphate become supersaturated and may precipitate in a membrane element (scaling). Scaling leads to an increase in energy consumption and chemical cleaning frequency. From an economic and environmental point of view this is not desired and early detection of scaling is therefore necessary. With the aim to detect scaling in an early stage a scaling monitor has been developed and tested. The scaling monitor, named ScaleGuard[®], measures the normalised flux of a small membrane element fed by a part of the concentrate of the full-scale plant. This scaling monitor was tested at a pilot plant treating anaerobic groundwater for the production of drinking water. The monitor demonstrated to be able to detect scaling before it took place in the last stage of the pilot plant.

Keywords: Nanofiltration; Reverse osmosis; Scaling; Scaling monitor; ScaleGuard[®]; Supersaturation; Barium sulphate; Membrane filtration; Fouling; Monitoring

1. Introduction

1.1. Scaling

In nanofiltration and reverse osmosis membrane systems the dissolved salts in the feed water

are roughly concentrated 4–10 times (dependent of the conversion and retention) and discharged with the membrane concentrate.

Due to this effect, sparingly soluble inorganic compounds can exceed their solubility product and may precipitate on the membrane surface (scaling). Compounds commonly present in feed

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water and with a low solubility are calcium carbonate, barium sulphate, silica and calcium phosphate.

When scaling occurs the permeability of the membranes decreases and the head-loss in the feed-brine channel increases. A higher feed pressure should be applied to maintain the desired flux causing an increase in energy consumption. In addition, the membranes should be cleaned more frequently, which can result in a shorter membrane life expectancy.

When scaling does not occur, the conversion of the membrane system may be increased. This will reduce the amount of feed water and energy consumption and therefore reduce total costs. However, at a higher conversion the dissolved salts become more concentrated and the conversion is often limited by the risk of precipitation of sparingly soluble inorganic compounds.

1.2. Supersaturation ratio

From a thermodynamic point of view precipitation can occur when the solubility is exceeded. The extent of supersaturation can be expressed as the Supersaturation ratio (S_r). The supersaturation ratio can be calculated with the following equation, example for calcium fluoride:

$$S_r = \left[\frac{(\gamma_+ \cdot c_+)^{v^+} \cdot (\gamma_- \cdot c_-)^{v^-}}{K_{sp}} \right]^{\frac{1}{v}} = \left[\frac{\gamma_{Ca} \cdot c_{Ca} \cdot (\gamma_F \cdot c_F)^2}{K_{sp, CaF_2}} \right]^{\frac{1}{3}} \quad (1)$$

Where c_+ and c_- is the total concentration of free cations and anions respectively. $v = v^+ + v^-$ is the amount of cations and anions in the precipitate (for $BaSO_4$ is $v^+ = 1$ and $v^- = 1$, for CaF_2 is $v^+ = 1$ and $v^- = 2$). K_{sp} is the temperature dependent solubility product.

Until an ionic strength of 1 mole/l, the Debye Hückel-Jones/Davies equation can be used for calculation of the activity coefficient [1]. When the membrane concentrate is more saline, up to an ionic strength of 6 mole/l (for example when treating industrial effluents or seawater), the Debye Hückel-Brömley or the Pitzer-method should be applied [2].

Phreeqc-2 is a computer program using the Debye Hückel-Jones/Davies-equation for calculation of the activity-coefficients. Moreover, the program also calculates a number of inorganic complexes in the water matrix resulting in lower free cations and anions. Phreeqc-2 therefore enables to calculate the Supersaturation ratio of almost all inorganic sparingly soluble salts in water [3].

1.3. Precipitation kinetics

However, besides supersaturation the kinetics of precipitation determines the risk of scaling. When the supersaturation exceeds a critical value, nucleation (formation of tiny crystals from a pure solution) can occur following by growth of the crystals [4]. Both nucleation and growth strongly depend on the supersaturation and temperature of the solution.

In practice, membrane and anti-scalant suppliers recommend not to exceed the solubility product or to apply an acid and/or an anti-scalant to avoid scaling of the supersaturated compounds on the membrane surface. Acid reduces the supersaturation of the alkaline scale forming compounds such as calcium carbonate. Anti-scalants contain active substances that can retard nucleation or growth of the formed crystals.

Boerlage demonstrated that (even without an anti-scalant dose) a considerable supersaturation of barium sulphate (up to S_r 4.6–5.4, depending on temperature) in the membrane concentrate of a reverse osmosis system will commonly not result in scaling [4]. This observation indicates

that there is potentially room for increasing the conversion in full-scale plants. Furthermore, suppliers of anti-scalants need to be on the safe side in their recommended maximum achievable conversion. This situation emphasises the need for a method able to predict accurately whether scaling will occur or not.

1.4. Traditional monitoring methods

In pilot plants detection of scaling can be carried out by frequently measuring the mass balance of the species which may precipitate [5,6]. However, mass balances often suffer from inaccuracies in flow measurements and analysis. Furthermore, this method is laborious and by continuous monitoring also very costly.

In full-scale plants detection of scaling takes place by measuring the normalised flux or Mass Transfer Coefficient (MTC) of the last stage of the membrane plant [7–9].

The Mass Transfer Coefficient is defined as:

$$MTC = \frac{Q_p \cdot TCF}{A_{mem} \cdot NDP} \quad (2)$$

$$TCF = e^{U \left(\frac{1}{T+273} - \frac{1}{T_{ref}+273} \right)} \quad (3)$$

$$NDP = (P_f - 0.5 \cdot \Delta P_{fb} - P_p) - \left(\frac{\pi_f + \pi_b}{2} - \pi_p \right) \quad (4)$$

$$\pi_f = x_\pi \cdot EC_f \cdot \frac{273+T}{273+T_{ref}} \quad (5)$$

The Mass Transfer Coefficient (MTC) represents the flux corrected for temperature variations and the Net Driving Pressure (NDP).

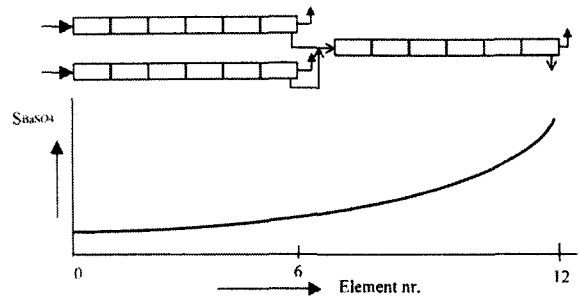


Fig. 1. The increase of the Saturation ratio of barium sulphate in the concentrate in a nanofiltration or reverse osmosis membrane system.

The osmotic pressure can be estimated by measuring the electrical conductivity and temperature of the water. The factor x_π translates the electrical conductivity to the osmotic pressure calculated with osmotic pressure relations [10].

When scaling occurs the product flow will decrease and/or the required feed pressure will increase causing the MTC to drop.

Initially scaling will take place in the last element in the last stage because the supersaturation of the sparingly soluble salts is in this element at maximum, see Fig. 1.

Because the supersaturation is in the last element at maximum, nucleation and subsequently growth of the crystals will initially take place in this element.

The decline in MTC due to the scaling in this element will have only a small effect on the measured average MTC decline of the whole last stage, which may contain e.g. 6 to 7 spiral wound membrane elements per vessel. As a consequence this method is inaccurate, so severe scaling might already have been taken place when a significant MTC decline is observed.

Therefore a method is desired which can detect scaling just before it appears in the membrane element in the full-scale plant.

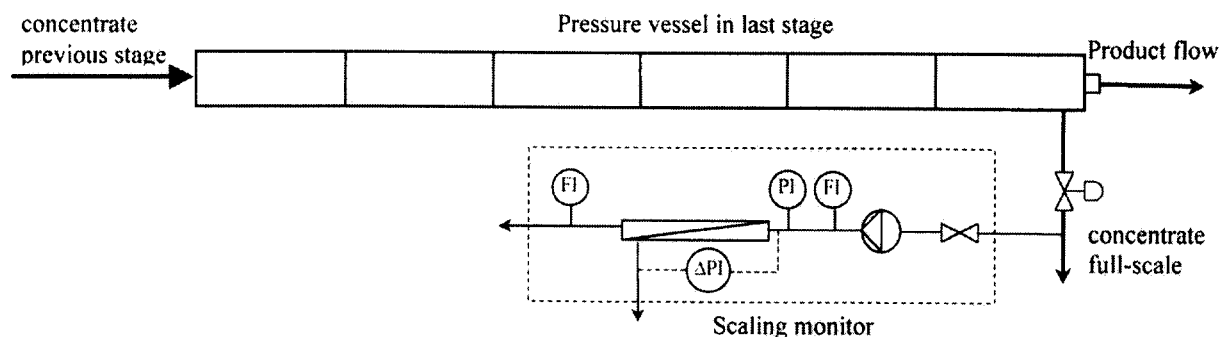


Fig. 2. Principal of the scaling monitor connected to the concentrate of the membrane system.

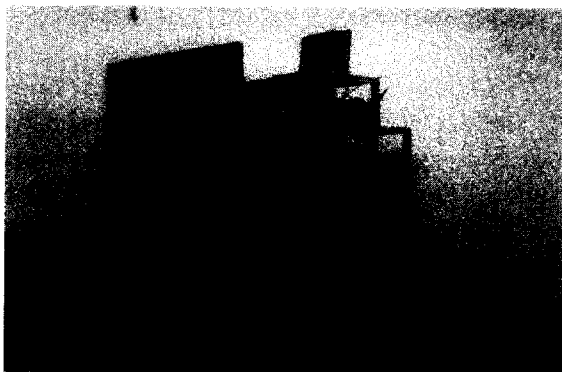


Fig. 3. The ScaleGuard®.

2. Materials and methods

2.1. ScaleGuard®

With the aim to develop such a method, a scaling monitor has been built. The monitor consists of a membrane element fed with membrane concentrate of a pilot or full-scale plant (Fig. 2).

The MTC of the element is continuously estimated by on-line measurement of flow, pressure, temperature and electrical conductivity and calculation with Eqs. (2–5). In the monitor the conversion is increased with about 1–4%, depending of the flow conditions. Due to the

extra conversion it is expected that the first parts of scaling will take place on this membrane element due to the increased supersaturation. Besides that, it is expected that the scaling can be detected more rapidly than in a full-scale plant because the MTC is measured of just one membrane element. When the MTC of the element in the scaling monitor decreases, it will be an indication that scaling occurs.

A photograph of the monitor can be found in Fig. 3.

2.2. Application of the scaling monitor

At a location in the Netherlands of Water Supply Company Overijssel the first prototype of the scaling monitor was connected to the concentrate of a pilot plant treating anaerobic groundwater with nanofiltration. The pilot plant (5–3–2 staging) consisted of four nanofiltration membrane elements per pressure vessel. The goal of the research was to determine the maximum conversion that can be achieved without the risk of scaling, when dosing an anti-scalant based on organo-phosphonates.

The settings during the pilot research can be found in Table 1.

With the model of the membrane supplier in combination with Phreeqc-2 the supersaturations

Table 1
Settings during the pilot research

Parameter	Period 1	Period 2	Period 3	Period 4*
Time, d	14	17	22	7
Conversion, %	75	80	80	80
AS** dose, mg/l	2.3	2.3	3.1	3.1
Settings scaling monitor				
Water flux, l/m ² h	13.5	19	19	19
Conversion, %	9	19	19	19
Add. conversion, %	2	3	3	3

* New membrane applied in the scaling monitor

** AS = anti-scalant

of the sparingly soluble salts in the concentrate at 75% and 80% conversion were calculated.

3. Results and discussion

3.1. Supersaturation

With the model calculations of the membrane supplier it was found out that calcium carbonate and barium sulphate were supersaturated in the concentrate. In addition calculations with Phreeqc showed that also four other inorganic compounds were supersaturated. Results of the calculations of Phreeqc-2 can be found in Table 2.

Iron carbonate shows the highest supersaturation. The supersaturation of barium sulphate is below the critical supersaturation value as found by Boerlage [4]. Scaling of barium sulphate is therefore not expected.

3.2. Monitoring of scaling

Fig. 4 shows the MTC of the four membranes in one of the two last pressure vessels in the third stage and the MTC of the membrane element in the scaling monitor.

In the first period, at a conversion of 75%, 2.3 mg/l anti-scalant based on organo-phospho-

Table 2
Supersaturations ($S > 1$) at 75% and 80% conversion. Calculated with Phreeqc-2 (temp = 11°C)

Compound	Formula	S	S
AT conversion		75%	80%
Calcium carbonate	CaCO ₃	3.8	5.6
Barium sulphate	BaSO ₄	4.5	5.1
Manganese carbonate	MnCO ₃	6.3	8.3
Iron carbonate	FeCO ₃	11.1	17.6
Iron phosphate	Fe ₃ (PO ₄) ₂ ·8·H ₂ O	1.9	2.1
Calcium phosphate	Ca ₅ (PO ₄) ₃ OH	2.3	3.2

ates was dosed. No MTC decrease was observed, either in the four membranes in the third stage and the membrane of the scaling monitor, obviously no scaling occurred. After two weeks of operation, the conversion of the pilot plant was increased to 80%. In this second period the MTC of the membrane elements in the third stage was still constant while the MTC of the membrane in the scaling monitor directly and continuously decreased. After a chemical cleaning with hydrochloric acid at a pH of 2, the MTC was almost fully restored. This showed that an inorganic scaling had taken place, which could almost completely dissolve by the acid. Subsequently, the anti-scalant dose was increased to a higher amount than predicted by the anti-scalant supplier. Again a rapid decrease of the MTC of the membrane element in the scaling monitor was observed. Obviously, an anti-scalant dose of 3.1 mg/l was not able to avoid scaling. To be sure that the (probable insufficient) acid cleaning didn't cause the strong decrease in MTC, the membrane element in the scaling monitor was replaced by a new one. Also in this fourth period a rapid decrease in MTC was observed, while still the MTC of the four membranes in the third stage of the pilot plant was constant.

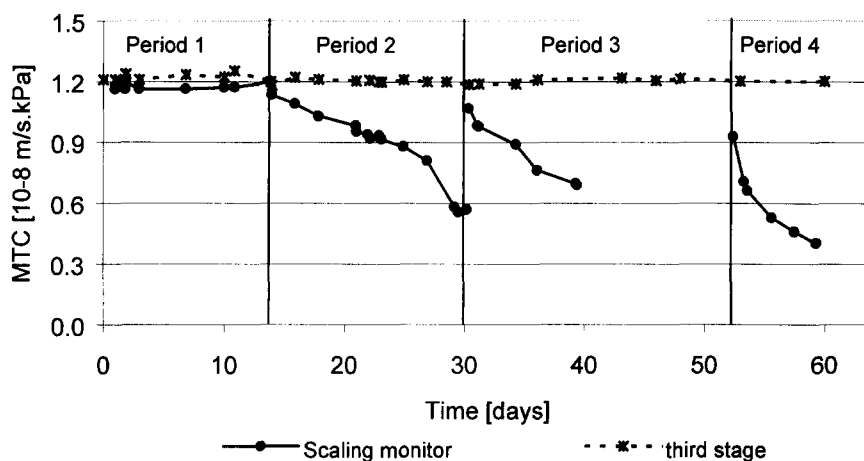


Fig. 4. Average MTC of the four membranes in one of the two pressure vessels in the third stage and the MTC of the membrane in the scaling monitor during the pilot research.

3.3. Scanning electron microscopy analysis

The membrane element from the scaling monitor (from the fourth period) was opened for an autopsy. A thin uniform brown/grey deposit was observed. The characteristics of the deposit were analysed with scanning electron microscopy (SEM). With SEM inorganic elements can be identified. The atomic ratio of the detected elements is listed in Table 3.

Also carbon was identified in the deposition. The exact percentage can not be given, because carbon was also used as a material for conduction during the SEM-analysis.

From these results it is clear that an inorganic scaling had been formed on the membrane surface, which almost certainly consists of a mixture of iron carbonate, calcium carbonate, iron phosphate, calcium phosphate and a small amount of manganese carbonate. This illustrates that actually five of the six supersaturated compounds predicted by Phreeqc-2, precipitated on the membrane surface. As expected, no barium was detected in the scaling.

Table 3

Atomic ratio of the identified elements (in %) in the membrane element in the scaling monitor

Element	Atomic ratio, %
Ca	22
P	12
Fe	26
Mn	2
O	37
Other	1

Fig. 5 shows a SEM-photograph of the amorphous scaling in the membrane of the scaling monitor with a composition according to Table 3.

3.4. Scaling in the pilot plant

After circa three months of operation, the four membrane elements in one of the two pressure vessels in the third stage were removed. The MTC of these membrane elements were measured individually on a test-skid and compared with the individual MTC-value at



Fig. 5. SEM-photograph of the amorphous scaling in the membrane of the scaling monitor (magnitude 1000 X).

Table 4
MTC-decrease of the membrane elements from the third stage in the pilot plant

	MTC-decrease, %
Element 1	3,5
Element 2	6
Element 3	8,5
Element 4	24,5

start-up. The decrease in MTC of the four membrane elements can be found in Table 4.

From these results it is clear that the decrease in MTC per element increases further to the concentrate side of the pilot plant, which is typically for scaling. A cleaning of the membranes with citric acid showed that the MTC of the membranes fully recovered. Also the same inorganic elements as listed in Table 3 were analysed in the cleaning liquid.

From Fig. 4 it was clear that the scaling on these membranes could not be detected by determination of the average MTC of the four membranes in the third stage. While in contrast the scaling monitor shows a very fast detection of

scaling, almost certainly before the scaling enters the membranes in the pilot plant.

4. Conclusions

The scaling monitor demonstrated to be able to detect scaling before it took place in the last stage of a pilot plant.

In order to verify whether this conclusion has general validity the method will be tested in combination with pilot- and full-scale plants fed with different types of water. If so and it is expected that the scaling monitor will be a strong tool in:

- Optimising the operating conditions of the full-scale plant, i.e. conversion and the required anti-scalant/acid dose;
- Identifying the nature of scaling without the need to interrupt the operation of the full-scale plant;
- Optimising the chemical cleaning procedure and frequency.

5. Symbols

- A — Membrane area, m^2
 c_i — Free concentration of species i , mole/l
 EC — Electrical conductivity, mS/m
 K_{sp} — Thermodynamic solubility product, mol^2/l^2
MTC — Mass transfer coefficient of water through the membrane, $m/(s \cdot kPa)$
NDP — Net driving pressure
 S_r — Saturation ratio
 P — Pressure, bar
 T — Temperature, $^{\circ}C$
 U — Membrane dependent temperature factor
 x_{π} — Factor which translates electrical conductivity to osmotic pressure, $kPa \cdot m/mS$

Greek

- Δp_{fb} — Pressure difference over feed-brine spacer, bar
 ν — Number of ions in the precipitate
 π — Osmotic pressure, bar
 γ_{\pm} — Activity coefficient

Subscripts

- + — cations
 – — anions
b — concentrate
f — feed
p — permeate
ref — at reference
w — water

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References

- [1] O. Söhnel and J. Garside, *Precipitation, Basic Principles and Industrial Applications*, Butterworth-Heinemann Ltd, Oxford, 1992, pp. 6–110.
- [2] S.F.E. Boerlage, M.D. Kennedy, G.J. Witkamp, J.P. van der Hoek and J.C. Schippers, *J. Membr. Sci.*, 159 (1999) 47.
- [3] D.L. Parkhurst, *User's Guide to PHREEQC—a Computer Program for Speciation, Reaction-Path, Advective-Transport, and Inverse Geochemical Calculations*, Lakewood, Colorado, 1995.
- [4] S.F.E. Boerlage, M.D. Kennedy, I. Bremere, G.J. Witkamp, J.P. van der Hoek and J.C. Schippers, submitted for publication in *J. Membr. Sci.*, 2000.
- [5] J.P. van der Hoek, P.A.C. Bonné, E.A.M. van Soest and A. Graveland, *Proc., AWWA Membrane Technology Conference, New Orleans, LA, USA, (1997) 1029.*
- [6] J.P. van der Hoek, J.A.M.H. Hofman, P.A.C. Bonné, M.M. Nederlof and H.S. Vrouwenvelder, *Desalination*, 127 (2000) 89.
- [7] J.S. Taylor, J.A.M.H. Hofman, S.J. Duranceau, J.C. Kruithof and J.C. Schippers, *Aqua*, 43 (5) (1994) 238.
- [8] J. Verdouw and H. Folmer, *Proc., Membrane Technology Conference, New Orleans, (1997) 1001.*
- [9] G. Schock and A. Miquel, *Desalination*, 64 (1987) 339.
- [10] DuPont, *Technical information manual*, USA, 1980.