Desalination and Water Treatment
www.deswater.com
6 (2009) 138–143

Scaling potential calculations using different methods

Case study: Klazienaveen UF/RO plant

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Received 15 September 2008; accepted 20 April 2009

ABSTRACT

In this paper, the scaling potential of various sparingly soluble compounds was calculated in the concentrate of a full scale reverse osmosis (RO) plant, using various methods and commercially available software programs. The critical compounds calculated were $CaCO_3$, $CaSO_4$, $BaSO_4$, $SrSO_4$, and SiO_2. Since July 2000, the Drenthe Water Supply Company (WMD) supplies high-quality water to the Activated Carbon Manufacturing plant (Norit) in Klazienaveen. The production capacity is between 230,000 and 455,000 m^3/year. The water source is canal water and shows high variations in water quality. To produce this capacity and to meet the water quality standard required for industrial use (boiler feed water), high chemical dosages are applied. Antiscalant is one of the chemicals currently dosed in order to avoid scaling and ensure smooth operation of the RO system. All the software programs employed (ROSA, IMS Design Hydranautics, 4Aqua care, and Phreeqc) and manual calculations with the ASTM method, showed different scaling potentials for the same feed water. All methods employed suggested that the RO concentrate was under-saturated with respect to $CaSO_4$, $SrSO_4$, and SiO_2. In addition, $BaSO_4$ was not expected to occur based on Boerlage's scaling risk limits. In winter periods no antiscalant was needed since the pH was always below the critical pH limit of 7.0. In the summer period, the temperature increased to 25°C, and the possibility of $CaCO_3$ scaling existed, since the critical pH of 6.5 was exceeded. However, based on the results of scaling calculations made in this study, the antiscalant can be stopped and scaling is not expected to occur, if the pH feed is decreased to 6.5 or lower.

Keywords: Scaling; Antiscalant

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1. Introduction

Controlling fouling and scaling of reverse osmosis (RO) membranes is a real challenge. When scaling occurs the resistance of the membranes will increase and resulting in higher required pressure to maintain constant capacity and consequently higher energy consumption. In addition, chemical cleaning is necessary to avoid irreversible scaling and damage of the membranes. Frequent cleaning might shorten the life time of the membranes.

Drenthe Water Supply is operating a RO plant to produce high-quality water for an industrial client. The plant takes the feed water from a canal. Since the fouling potential of this water is high and varying, extended pre-treatment is applied to control fouling of the membranes. The pre-treatment consists of:

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Table 1
Variations in water quality of the source between 2000 and 2005

Parameter	Unit	Max	Min
Temperature	°C	25.5	0.8
pH	–	7.6	6.07
Turbidity	NTU	136.5	7.98
Suspended solids	mg/L	49.6	1.43
Iron (Fe)	mg/L	9.51	1.11
Magnesium (Mg)	mg/L	6.06	3.45
Conductivity EC	μS/cm	573	222
Chloride	mg/L	111	27
DOC	mg C/L	42.74	20.85
UV (254 nm)	abs/m	242.35	19.46

dosing poly aluminum chloride (coagulant), followed by moving bed filtration and ultrafiltration.

In addition antiscalant (no acid) is added to control scaling. Membrane cleaning (in the RO unit) is performed with chemical 12 times a year.

Since the cost of chemicals is high, a study was initiated by Drenthe Water Supply to reduce the consumption of chemicals in the plant. This study focused on the need for the antiscalant or acid to control scaling. A challenging factor in this study was the large and frequent variation in the feed water quality and the variability in the amount of poly aluminum chloride employed in the pre-treatment.

2. Methodology

2.1. Water quality of the source

The water quality in the canal changed with the seasons. Table 1 shows the water quality range for a selected number of parameters.

During the winter period the canal, is fed by run off water of a peaty area, resulting in high iron and organic matter concentrations and a high turbidity. In the summer period, the canal is fed by another source of water, namely the IJssel Lake. This lake gets the water from the Rhine River and polders. The results of chemical analysis of 24 different parameters, which were obtained during a period of 5 years, were taken into account. In addition the data of the continuously monitored conductivity and temperature were used.

From the data collected, it is concluded that the following compounds might exceed the solubility in the concentrate of the RO plant, which is operating at a constant recovery of 75%. The most common mineral scalants [1] are: $BaSO_4$, $CaCO_3$, $CaSO_4$, $SrSO_4$, SiO_2, $Ca_3(PO_4)_2$

Calcium phosphate is expected not to precipitate since the limited data show low levels of phosphate, which is obvious since, poly aluminum chloride will precipitate phosphate in the filtration step.

2.2. Methods and computer programs used in scaling potential:

a. The computer programs were used in the scaling calculation:
   (i) IMS design (Hydranautics), (ii) ROSA (Dow), (iii) 4Aqua and (iv) Phreeqc
b. ASTM [2] manual method

2.3. Assumption used in the calculations:

- The Langlier's approximation was used to determine the Ionic strength (I):

$$I_{\mathrm{mol/L}} = 2.5\times\ 10^{-5}\times \mathrm{TDS} \tag{3}$$

where I is the ionic strength in mol/L
TDS is the total dissolve solid in mg/L.

- Because the missing in some data, the TDS has been calculated from electrical conductivity (EC):

$\mathrm{TDS}_{\mathrm{mg/L}} = \mathrm{EC}_{\mathrm{mS/m}} \times 0.65$ at temperature 20°C.

2.4. Worst-case definition and worst days

2.4.1. Worst case

The full data matrix available comprises weekly measurements of 26 parameters during 5 years. To limit the number of scaling calculations, data are selected on ''worst case'' criteria.

Worst-case scenarios comprise: artificially composed sets of data, assuming the critical parameters are all present in the water on the same day (pH, temperature, highest concentrations of scaling compounds, etc.).

The results for these combinations were six data sets, one per year and one overall for the period. As an example, the worst case in 2000 was composed of the following set of data: The highest temperature 21.5°C was in 15/08/2000, where the highest recorded pH 7.9 was in 1/09/2000. The highest concentrations for each ion were also added to the set of data. However, the highest temperature was 21.9°C (Table 2).

2.4.2. Worst days

During the operation, water quality was monitored and recorded in the Klazinaveen plant. The pH and EC

Table 2
The worst-case data set of the year 2000

Parameters 2000	Worst case	
Temperature	Max	21.5°C
pH	Max	7.9
TDS_{conc}	Max	364 mg/L
$[Ca^{2+}]_{conc}$	Max	140 mg/L
$[HCO_3^-]_{conc}$	Max	538 mg/L
$[Sr^{2+}]_{conc}$	–*	–
$[SO_4^{2-}]_{conc}$	–*	–
$[Ba^{2+}]_{conc}$	–*	–
$[PO_4^{3-}]_{conc}$	–*	–

* Lake in the recorded data.

Table 4
Number of dates was used per year in the worst-days check

Year	Set of dates were used
2000	3
2001	3
2003	4
2004	5
2005	4

were recorded weekly, while some other parameters where measured every two weeks or more frequently. Due to the differences in frequencies of measuring parameters, not all sets were complete. Based on the following parameters a number of days where chosen in each year: (1) max, min temperature, (2) max, min pH feed and (3) max, min EC feed.

For each year (2000 to 2005) and regarding to the above parameters, the days with the highest temperature and the days with the lowest temperature in the year were chosen as worst days. Furthermore, the days with the highest pH or highest EC were also chosen as worst days. In some years, the max pH was in the same day with the max temperature, this combination lead to choose less days per year. The final results of this exercise were three to 6 days per year with full parameters data. As example, the set of data which used in the scaling calculation of the year 2000 illustrated in Table 4.

3. Results and discussion

3.1. pH concentrate calculation

To calculate the SI for calcium carbonate in the concentrate it is necessary to know the pH_c, hydrogen carbonate, carbon dioxide (and calcium). The concentration of calcium carbonate changes gradually in a vessel, and in the stages of the plant due to increasing recovery in the pressure vessel and plant. The pH in the concentrate can be calculated with the Henderson-Hasselbalch equation:

$$pH_{conc} = pK_a + \log\frac{[HCO_3^-]_{conc}}{[CO_2]_{conc}} \quad \text{for pH} < 8$$

$$pH_{conc} = pK_a + \log CF_{actual} + \log\frac{[HCO_3^-]_{feed}}{[CO_2]_{feed}}$$

Where: $CF_{actual} = \frac{1}{1-R} \times \text{rejection} = 4$ in the Klazienaveen plant, since $R = 0.75$.

Assuming that rejection for HCO_3^- is 100%.

- $[CO_2]$: The membrane shows 0% rejection for dissolved gases in water. Thus the concentration of $[CO_2]$ will not change in the concentrate or permeate streams.

$$[CO_2]_{feed} = [CO_2]_{conc} = [CO_2]_{product}$$

- $[HCO_3^-]$: can be calculated base on the recovery of the plant and the $[HCO_3^-]$ rejection: $[HCO_3^-]_{feed} = CF \times [HCO_3^-]_{conc}$

where CF is the concentration factor and can be calculated:

$$CF = \frac{1 - R \times (1 - r)}{1 - R}$$

Table 3
The data set of worst days in the year 2000

Date	Parameters in the concentrate 2000								
	Temp. (°C)	pH	TDS	$[Sr^{2+}]$	$[HCO_3^-]$	$[Ca^{2+}]$	$[SO_4^{2-}]$	$[Ba^{2+}]$	$[PO_4^{3-}]$
8/15/2000	22		341.9	0.07	470.91	79.08	7.5	0.06	0
11/15/2000	19.6		115.1	0.06	45.18	57.08	24.37	0.08	0
12/28/2000	19.5		168.4	0.08	114.51	77.16	23.87	0.12	0

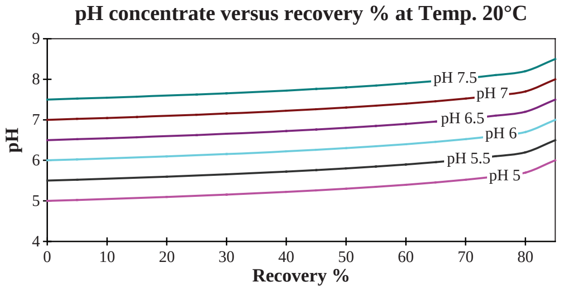

Fig. 1. pH concentrate based on pH feed at different recovery.

where R is the plant recovery, r is the ion rejection, with rejection 100%, $\mathrm{CF} = \frac{1}{1-R}$.

The Hydranautics program shows that the rejection of the $[\mathrm{HCO}_3^-]$ is between 97.9% and 99.8%, which keep the CF value close to 4 for recovery of 75%.

$$\mathrm{pH}_{\mathrm{conc}} = \mathrm{constant} + \mathrm{pH}_{\mathrm{feed}} \quad \text{where constant} = \log \mathrm{CF}$$

In the Klazienaveen plant, log (CF) = 0.6, since $R = 0.75$.

Figure 1 illustrated the pH concentrate at different recovery base on the pH feed.

3.2. Scaling potential

Several programs and method are using in scaling potential calculation in RO system. ASTM manual method and the computer software: Phreeqc, ROSA, 4Aqua, and IMS design were used to calculate the scaling potential of the critical compounds in the Klazienaveen RO system.

$$\mathrm{SI} = \log \frac{[\mathrm{M}^{+y}]^x [\mathrm{X}^{-z}]^y}{K_{sp}} = \log(S),$$

where K_{sp} is the solubility product constant, for example

$$\mathrm{SI} = \log \left[\frac{\mathrm{IAP}}{K_{sp}}\right] = \log \frac{[\mathrm{Ba}^{2+}] \times [\mathrm{SO}_4^{2-}]}{K_{sp}} = \log(S),$$

where IAP is the actual ion activity.

For comparison a temperature of 25°C has been used, because the ASTM program just gives K_{sp} values at this temperature only.

Table 5
The scaling risk limit for BaSO_4 Sr [5]

Super-saturation ratio limit	Temperature				
	5	10	15	20	25
High scaling risk	6.0	5.7	5.5	5.2	5
Low scaling risk	5.4–6	5.2–5.7	5–5.5	4.8–5.2	4.6–5
No scaling risk	5.4	5.2	5	4.8	4.6

Table 6
The scaling risk limit SI for BaSO_4

Super-saturation ratio limit	Temperature				
	5	10	15	20	25
High scaling risk	1.56	1.51	1.48	1.43	1.40
No scaling risk	1.46	1.43	1.40	1.36	1.33

3.2.1. $BaSO_4$

The scalant BaSO_4 has low solubility (1×10^{-5} mol/L) in pure water [4]. When the saturation index is higher than 0 (SI > 0) scaling might occur. The computer programs and ASTM approach were used to estimate the scaling potential in the scenarios (worst case).

However, Boerlage [5] observed that barium sulphate might be substantially supersaturated, while no scaling occurred. She defined the safe super-saturation limits (SSr) that result in no scaling risk, operation above or equal to the risky super-saturation limits (RSr) are given in Table 4.

Table 6 show the scaling limit SI for the component BaSO_4 on the Boerlage's scaling risk limit RSr.

From Figure 2, at 25°C the scaling potential in the concentrate are calculated by ASTM and computer programs. ASTM and the programs show close results and lower Boerlage's scaling risk limits. The results show large differences between the used methods.

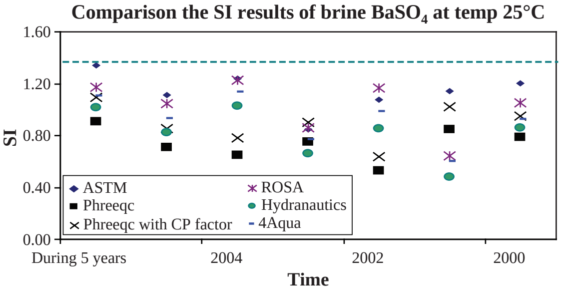

Fig. 2. SI of BaSO_4 for the artificial concentrate composed w-cases at 25°C.

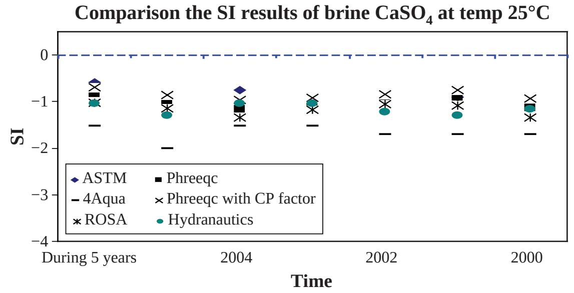

Fig. 3. SI of $CaSO_4$ for the artificial concentrate composed w-cases at 25°C.

3.2.2. $CaSO_4$

Figure 3 illustrates the SI results of the component $CaSO_4$, calculated using the ASTM and the programs, however, large differences are between the different methods. All calculations show that the SI is below the scaling limit (SI < 0).

Consequently scaling of calcium sulphate is not expected to occur in the Klazienaveen plant.

3.2.3. $SrSO_4$

$SrSO_4$ has a very low solubility. Similar to the calculation for barium and calcium sulphate, large differences in calculated SI levels are observed. However, the SI in all calculations SI is below zero, so no scaling is expected to occur (Fig. 4).

3.2.4. SiO_2

Figure 5 shows that The SI results are lower than the saturation limit and the differences minor compared with the results on barium strontium and calcium sulphate.

However, the program Phreeqc is a geological simulation program for the chemical reaction underground water.

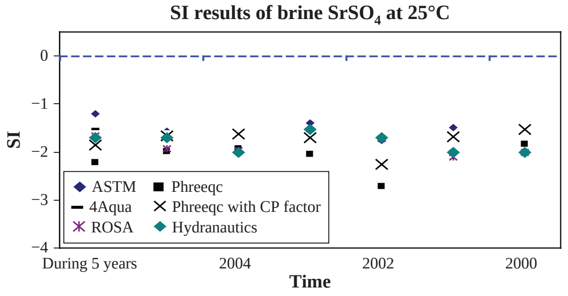

Fig. 4. SI of $SrSO_4$ for the artificial concentrate composed w-cases at 25°C.

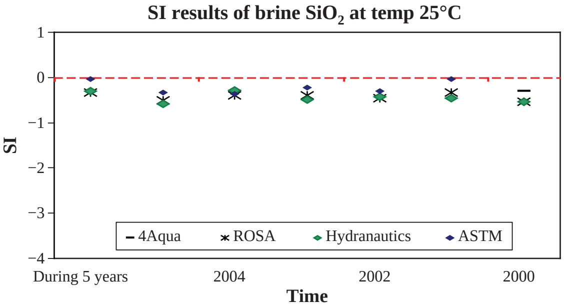

Fig. 5. SiO_2 scaling in the concentrate stream for w-case at 25°C.

In this program is assumed that quartz will be formed, as a result the concentrate will be highly super saturated with silica. This assumption is not right, since in practice amorphous silica, having a much higher solubility, is being formed; for this reason the Phreeqc results were ignored. From the above results, no silica scaling was observed during the operation period between 2000 and 2005.

3.2.5. $CaCO_3$

The $CaCO_3$ scaling potential is governed by $[Ca^{2+}]$ and $[HCO_3^-]$. For low salinity water Langelier Saturation Index (LSI) is commonly applied

$$LSI = pH - pH_s,$$

where $pH_s = C - \log[Ca^{2+}] - \log[HCO_3^-]$, C is the constant depends on temperature and TDS.

The possibility of the $CaCO_3$ scaling is high during the summer due to increase the $[Ca^{2+}]$ and $[HCO_3^{-1}]$. The summer period has a number of days with the highest temperature. In order to check the $CaCO_3$ scaling (LSI), the days with the highest temperature were chosen during the summer period.

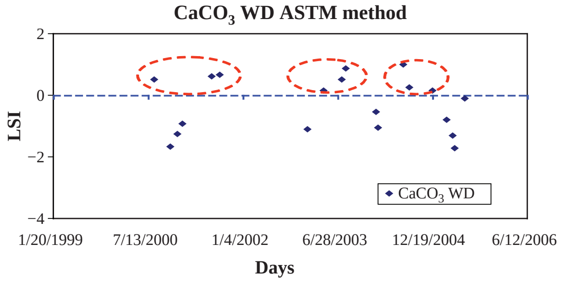

Fig. 6. LSI of $CaCO_3$ in the concentrate of worst days (WD).

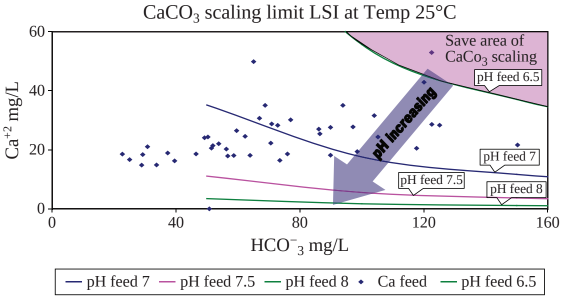

Fig. 7. Ca^{2+} vs with the pH scaling limits at temperature 25°C.

4. Controlling scaling of calcium carbonate

In a graph with calcium and hydrogen carbonate of the feed water on the two axis, pH lines of the feed water can be constructed (calculated) which corresponds with SI $= 0$ in the concentrate at a fixed recovery, e.g. 75%. In Figure 7, the line for pH $= 6.5$ shows that the plant will be safe for $CaCO_3$ scaling if the pH of the feed water is lower than 6.5 for the whole summer period. Since almost no combinations of calcium and hydrogen carbonate combination occurred which were located above the pH $= 6.5$ line. pH values higher than 6.5 represent a situation in which the probability of scaling increases due to the increasing calcium/hydrogen carbonate combinations located in the area.

According to Klazinaveen data, during the winter period, the $[Ca^{2+}]$ and $[HCO_3^-]$ combinations were all located below the pH $= 7$ line. Operating the plant with pH feed equal or lower than 7 during the winter will be safe by adding acid [6]. However, the pH of the feed water used to be 6.8 so usually no acid dose will be necessary.

The in Figure 7 and Figure 8 could be useful for any plant works under same conditions to estimate the limit of pH feed, $[Ca^{2+}]$ and $[HCO_3^-]$ for safe operation. The positioning of the critical pH lines depends on recovery. However, the effect of recovery is incorporated in the calculations.

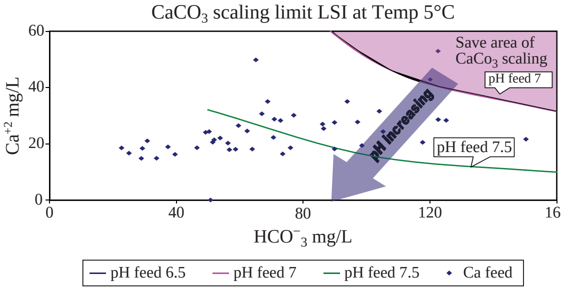

Fig. 8. Ca^{2+} vs. with the pH scaling limits at temperature 5°C.

5. Conclusions

- The pH in the concentrate can be easily calculated with the formula: $pH_{conc} = constant + pH_{feed}$, where constant is: log CF.
- Calculations of SI values with different programs/methods, for barium, strontium and calcium sulphate, show large differences.
- It is very likely that no antiscalant is needed when the pH is below 6.7. The safe pH depends on the temperature and in winter time was higher than 6.7.
- The safe operation, with respect to controlling calcium carbonate scaling in RO plants can be read off the graphs showing the critical pH level of the feed water at a fixed recovery as a function of the concentration of calcium and hydrogen carbonate and the temperature of the feed water.

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