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Effect of concentrate recycle on anti-scalant performance

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ABSTRACT

A convenient reverse osmosis (RO) laboratory technique for rapid initial screening of anti-scalant performance is based on full recycling of concentrate and permeate to the feed vessel and observing the scale suppression effectiveness under different operating conditions. Once-through flow tests in which both permeate and concentrate are continuously withdrawn from the RO system simulate more closely actual plant conditions but are usually impractical as they require a large inventory of the feed solution.

In the recycle mode of operation, the residence time of the anti-scalant in the system is increased. The objective of the present study was to investigate if the increased residence time leads to a deviation between results measured by the simple recycle technique with those obtained by the more elaborate once-through technique.

A comparison between inhibition results observed in full recycle and once-through tests respectively was carried out in a continuous flow pilot RO system. Tests were performed with three anti-scalants applied to solutions having a $CaCO_3$ scaling propensity. In all cases permeability decline data measured in the full recycle and in the once-through modes of operation respectively were in substantial agreement, within the experimental accuracy of $\pm 5\%$. Data previously obtained with $CaSO_4$ scaling solutions gave similar results. It may be therefore concluded, that recycle tests of anti-scalant performance simulate reasonably well once-through flow conditions.

Keywords: Reverse osmosis; $CaCO_3$ scale; Anti-scalants testing; Once-through; Recycle

1. Introduction

The commonly used technique for scale control in reverse osmosis (RO) desalination is based on dosage of an anti-scalant. The difficulties in the application of anti-scalants are that there are hundreds of commercial products, all shrouded in commercial secrecy, and that the effects of operating parameters on inhibition effectiveness are largely unpredictable. An elaborate R&D program on a large scale pilot plant aiming to identify optimal scale control conditions is often unavoidable.

The test program can be considerably simplified by performing initial screening experiments according to several laboratory procedures developed at the Rabin Desalination Laboratory [1–5]. The scaling propensity of a given water feed dosed with an anti-scalant is tested in a laboratory RO system operated under hydrodynamic conditions, simulating as closely as possible the Reynolds number and geometry of the

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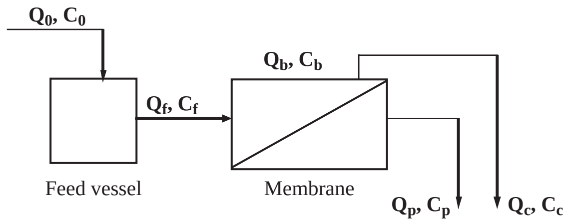

Fig. 1. Once-through mode of operation.

industrial module. The anti-scalant effectiveness is evaluated by determining the rate of scale precipitation and/or of the flux permeability decline.

The once-through mode of operation provides the closest simulation to real plant conditions. In this test method, water of controlled composition is continuously supplied to a laboratory RO system (Fig. 1) and the scaling potential is characterized by monitoring the rate of permeability decline. However, unless the test can be carried at the site of the raw feed water, this method is not practical. Costs of the chemicals required for supplying large quantities of water of the required composition are rather high and elaborate measures may be required for ensuring a constant scaling potential.

Convenient techniques obviating the need to prepare large volumes of the feed water, are based on recycling of the tested solution Two recycle techniques enable determination of the two major scaling propensity parameters – *the upper scaling threshold limit and the lower scaling threshold limit*.

The upper scaling limit denotes a concentration level at which the supersaturation degree attained by the concentrate triggers an immediate precipitation process. This parameter is determined by recycling the tested feed solution by either continuous [1] or intermittent [3] permeate withdrawal (Fig. 2). The concentration effect induces a continuous increase of the scaling potential in the system. The upper scaling threshold limit is detected by a sharp increase in the scale precipitation rate and/or an abrupt drop in permeability. This parameter is very useful for rapid assessment of the relative effectiveness of anti-scalants.

The upper scaling threshold limit does not take into account time effects. It is well known that when the supersaturation level of a solution is not sufficiently high, precipitation commences only after a certain delay time, denoted in the literature by terms such as induction time or nucleation time or incubation period. Thus, full characterization of the scaling propensity requires determination of this delay time. This is given by the lower scaling threshold limit which defines the maximum concentration level, attained by the concentrate in the meta-stable zone, at which precipitation is prevented or at least delayed for a long period of time. The lower scaling threshold limit is determined by full recycle operation of the tested solution, with both concentrate and permeate returned to the feed vessel (Fig. 2b). Information on the onset of scale deposition is obtained from periodic measurements of permeate flow rate and solution concentrations of the scaling species [4,5]. Lower scaling limits have been successfully correlated by models based on nucleation theories [4–6].

Real industrial systems operate in a once-through flow mode. The residence time of the brine in the RO module is therefore much shorter than that prevailing in the recycle tests described above. Recalling that the recycling solution is actually a supersaturated solution stabilized by the presence of an anti-scalant, it is conceivable that a long residence time might accelerate nucleation processes and enhance scaling tendencies. The end result of such an effect would be that recycle tests evaluate a higher scaling tendency than that prevailing in a once-through flow system.

The objective of this study was to clarify if results of recycle tests show a substantial difference from measurements in the once-through flow mode.

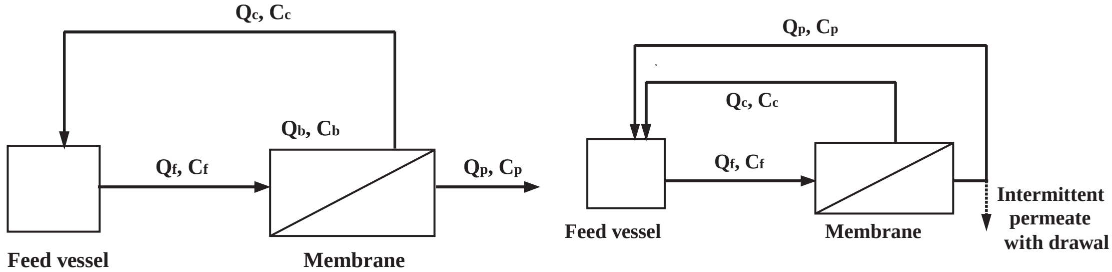

Fig. 2. Membrane tests for characterizing scaling propensity. (a) Recycle with permeate withdrawal and (b) recycle without permeate withdrawal.

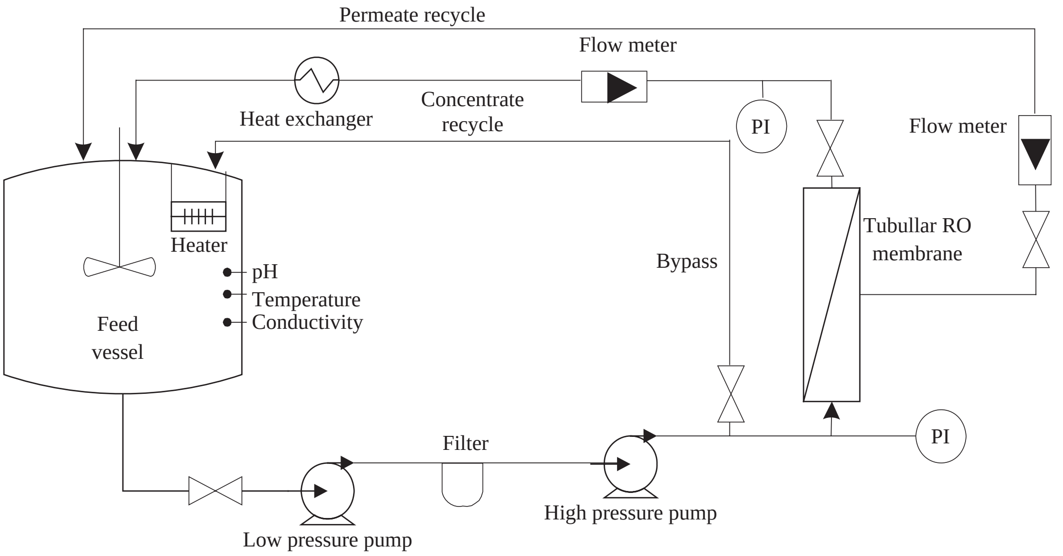

Fig. 3. Continuous flow RO system.

2. Experimental

2.1. Experimental system

The experiments were conducted in a continuous flow pilot RO system (Fig. 3) equipped with a tubular membrane so as to ensure a well defined flow system.

The tubular element, housed in a stainless steel tube, was supplied by X-FLOW Co., Holland (catalogue item WFC 0995). It consisted of a high rejection polyamide/polysulfone composite, 14.5 mm in diameter, 1 m long. The nominal flow specified in the catalogue for a 0.35% NaCl solution at 25°C was 50 L/m^2 hr at a pressure of 40 bar and a salt rejection of 99 $\pm$ 0.5%. The actual permeability of the various elements used in this study varied considerably from tube to tube.

The recycling solution was held at a constant temperature by the thermostatic controlled heating element and the water cooled heat exchanger. Solution pH was held constant at a desired level by a pH controller. A pH increase was achieved by actuating a NaOH dosing pump or by opening a solenoid valve to inject air into the feed solution. Air bubbling releases dissolved CO_2 from the solution, thus causing a pH increase [7]. A pH decrease was achieved by opening a solenoid valve feeding CO_2 into the solution.

2.2. Anti-scalants tested

The experiments were carried out in conjunction with a study comparing the $CaCO_3$ scale inhibition provided by zinc ions with that of conventional organic anti-scalants [8]. Recent studies [9,10] indicate that Zn^{2+} ions, which are environmentally friendly and can be conveniently released to the water by contact with Cu-Zn alloy redox media, can exert useful $CaCO_3$ scale suppression effects within a certain range of solution conditions.

The anti-scalants tested in the comparison of once-through and recycle tests were Zn^{2+} ions, PermaTreat PC-191 and Genesys CAS. PermaTreat PC-191, a product of Nalco Co., is a phosphonate based anti-scalant recommended for $CaCO_3$ scale control at a dosage of 1.0–3.5 ppm for solutions at Langelier Saturation Index (LSI) <2.6. Genesys CAS, a product of Genesys International, is a blend of phosphonates with carboxylic acids in a bisulfate base, recommended for $CaCO_3$ scale control at substantially similar conditions as Permatreat.

The Zn^{2+} ions were added to the feed stream either by simple dosage of a $ZnCl_2$ solution or by contacting the feed solution with a woolen bed of Zn-Cu alloy, KDF, supplied by Fluid Treatment Co., USA.

2.3. Experimental measurements

Periodic measurements were made of permeate flow rate, solution composition and solution turbidity. Solution turbidity was measured using a HACH turbidimeter, model 2100P. Dissolved Ca^{2+} was analyzed by the EDTA method, carbonate species were determined by total alkalinity titrations and Zn^{2+} ions concentration was measured by a HACH spectrophotometer, Model DR 2010, using the Zincon method (No. 8009).

Table 1
Experimental conditions in the once-through and in the recycle tests

Parameter	Recycle tests	Once-through tests
Ca^{2+} concentration (ppm)	200–220	450–550
Mg^{2+} concentration (ppm)	10–15	35–42
Na^{+} concentration (ppm)	140–150	130–150
Cl^{-} concentration (ppm)	350–390	980–1200
Talk (ppm as $CaCO_3$)	290–330	120–140
pH level	8.2	8.3–8.5
LSI_{bulk}	1.53–1.55	1.45–1.55
LSI_{wall}	1.8–2.0	1.8–2.0
Operating pressure (bar)	33–42	38–42
Feed velocity (m/s)	0.30–0.49	0.30–0.46
Reynolds number	5400–8900	5400–8200
Temperature (°C)	23–31	24–31
Initial permeate flux (L/h m^2)	35–50	42–50
Zn^{2+} concentration (ppm)	1.9–2.2	2.2–2.5
Genesys CAS concentration (ppm)	3.0	1.5–3.0
Permatreat concentration (ppm)	1.5–3.0	1.5–3.0

2.4. Characterization of the scaling propensity

The occurrence of scale deposition on the membrane can be conveniently detected by observing the decline in membrane permeability L_p defined by:

$$L_p = \frac{J_v}{\Delta P - \pi_m} \tag{1}$$

where J_v is the permeate flux, ΔP is the operating pressure and π_m is the osmotic pressure prevailing on the membrane wall. The magnitude of π_m is affected by the concentration polarization (CP) phenomenon. In the present work osmotic pressure was significantly lower than the operating pressure so that little error was introduced by approximating wall osmotic pressure π_m with bulk osmotic pressure π_b. Osmotic pressures were calculated using the ROPRO 6.1 software [11].

The effectiveness of the various tested inhibitors was assessed by comparing the intensity of flux decline, represented by the membrane permeability ratio, L_{p_f}/L_{p_i}, in the presence and in the absence of the inhibitor, where L_{p_f} and L_{p_i} are the final membrane permeability and initial clean membrane permeability respectively.

2.5. Evaluation of the CP

The fundamental parameter dictating the scaling potential is the supersaturation level prevailing on the membrane surface. The value of the CP modulus, which is required for determining the supersaturation level on the membrane surface, was evaluated from the film model using the mass transfer coefficient correlation for turbulent flow through pipes [12]:

$$\mathrm{Sh} = \frac{k \cdot d_h}{D} = 0.023 \cdot \mathrm{Re}^{0.875}\mathrm{Sc}^{0.25}$$

The CP level was maintained constant in each run by suitable adjustment of the operating pressure and feed velocity. The value of the CP modulus in the various runs was in the range of 1.6–2.0. The $CaCO_3$ precipitation potential indicated by the LSI was evaluated using the MINTEQ 2.32 software [13]. LSI levels were maintained in a rather narrow range of 1.45–1.55, in the solution bulk and of 1.8–2.0, on the membrane surface.

2.6. Experimental conditions

Permeability decline data obtained in full recycle tests (permeate and concentrate streams returned to the feed tank, Fig. 2b) were compared with data measured in once-through tests carried under nominally identical precipitation and hydrodynamic conditions. Table 1 summarizes experimental conditions.

The once-through tests were preformed by continuous flow of about 300 L/h tap water into the feed tank. Solution composition was adjusted by dosage of a concentrated $CaCl_2$ solution providing Ca^{2+} ions concentrations in the range of 450–550 ppm. The pH was adjusted by controlled dosage of NaOH to the range of 8.3–8.5. Zinc ions were introduced into the feed solution by contacting the tap water with a bed of woolen KDF, Zn-Cu alloy. According to Hasson et al. [9], about

Table 2
Comparison between once-through and full recycle results in the Zn^{2+} inhibition tests

Mode	Run no.	Duration (h)	pH	C/P	LSI_{bulk}	LSI_{wall}	Zn^{2+} (ppm)	Induction time (h)	L_{p_f}/L_{p_i}
FR	2	6.75	8.2	1.83	1.54	1.94	0	1.33	0.84
	20	6	8.2	1.8	1.54	1.9	0	No bulk precipitation	0.78
	22	9	8.2	1.64	1.54	1.9	0	No bulk precipitation	0.73
OT	62	9.6	8.4	1.65	1.5	1.86	0	9.5	0.73
	62a	10	8.4	1.68	1.5	1.83	00	9	0.72
FR	1	12.75	8.2	1.82	1.54	1.94	2.15	No bulk precipitation	0.66
	4	7.2	8.2	1.75	1.54	1.94	2	No bulk precipitation	0.88
	14	10.5	8.2	1.67	1.53	1.88	1.85	No bulk precipitation	0.856
	21	11.1	8.2	1.6	1.55	1.86	2.5	No bulk precipitation	0.88
OT	60	8.5	8.3	1.75	1.45	1.8	2.5	No bulk precipitation	0.74
	61	10	8.5	1.67	1.5	1.85	2.5	No bulk precipitation	0.77
	61a	9	8.4	1.7	1.5	1.82	2.2	No bulk precipitation	0.75

1.4 kg woolen KDF is required in order to obtain the desired Zn^{2+} ions concentration of about 2.5 ppm. Solution analyses confirmed this criterion. The organic anti-scalants were added by dissolution the desired concentration into the feed solution. In the full recycle tests, the feed solution was prepared by dissolving in distilled water appropriate amounts of $CaCl_2$, $NaHCO_3$ and $MgSO_4$ and adding either a $ZnCl_2$ solution or dissolving one of the organic anti-scalants.

3. Results

3.1. Zn^{2+} ions inhibition tests

Table 2 compares results of full recycle and once-through tests measured in the Zn^{2+} ions inhibition experiments. Permeability data for both modes of operation are plotted in Fig. 4 for the blank tests (no anti-scalant added) and in Fig. 5, for the Zn^{2+} ions inhibition tests. The blank data show excellent agreement between permeability decay measurements of the once-through and the full recycle tests. The data of the Zn^{2+} ions inhibition tests show a slight scale suppression improvement in the full recycle tests. This small deviation is within the accuracy of $\pm 5\%$ of results measured in repeat experiments.

3.2. Genesys inhibition tests

Table 3 compares results of full recycle and once-through tests measured in the Genesys inhibition experiments. The permeability decline data plotted in Fig. 6 show a slight scale suppression improvement for the once-through mode, contrary to the trend observed in the Zn^{+2} ions inhibition experiments. This result reinforces the conclusion that permeability data measured in full recycle and once-through modes are

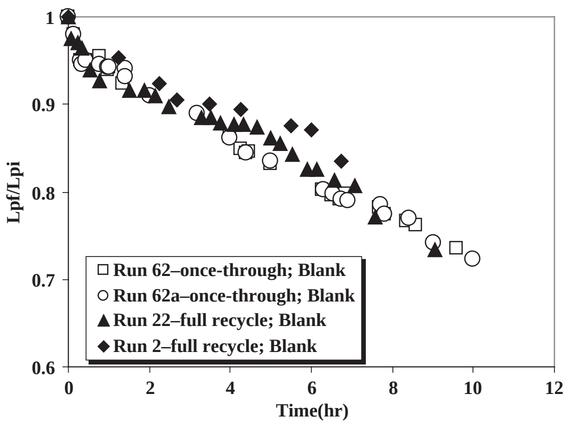

Fig. 4. Comparison of permeability decline data measured in once-through and in full recycle modes in the blank tests ($LSI_{bulk} = 1.5$).

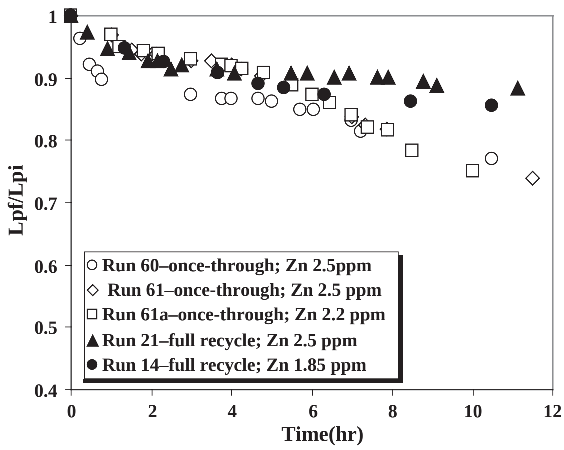

Fig. 5. Comparison of permeability decline data measured in once-through mode and in full recycle modes in the Zn^{2+} ion inhibition tests ($LSI_{bulk} = 1.5$).

Table 3
Comparison between once-through runs and full recycle results in the Genesys inhibition tests

Mode	Run no.	Duration (h)	pH	C/P	LSI_{bulk}	LSI_{wall}	Genesis (ppm)	Induction time (h)	L_{p_f}/L_{p_i}
FR	53	9.3	8.2	1.68	1.5	1.8	3	No bulk precipitation	0.88
	53a	9	8.2	1.65	1.5	1.85	3	No bulk precipitation	0.87
OT	66	7.7	8.35	1.72	1.49	1.85	3	No bulk precipitation	0.93
	67	8	8.35	1.7	1.49	1.85	1.5	No bulk precipitation	0.88
	68	7.5	8.4	1.7	1.49	1.85	3	No bulk precipitation	0.91

in substantial agreement within the experimental accuracy of $\pm 5\%$.

3.3. Permatreat inhibition tests

Table 4 compares results of full recycle and once-through tests measured in the Permatreat inhibition experiments. The permeability decline data plotted in Fig. 7 show substantially similar scale suppression results for the once-through mode and the full recycle mode, in agreement within the experimental accuracy of $\pm 5\%$.

4. Conclusions

A convenient laboratory technique for characterizing scale suppression effectiveness is based on full recycling of concentrate and permeate to the feed vessel and observing the scale suppression effectiveness with different feed solutions and different anti-scalants. The residence time of the anti-scalant in a recycle test is enhanced and it has been suggested that an increased residence time would diminish the scale suppression capability of the anti-scalant [14]. The $CaCO_3$ scaling data obtained in this research clearly show that, at least under the experimental conditions covered in this study, there is no significant difference

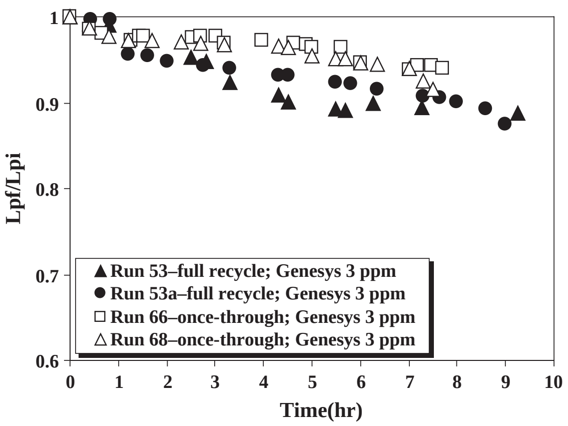

Fig. 6. Comparison of permeability decline data measured in once-through and in full recycle modes in the Genesys inhibition tests ($LSI_{bulk} = 1.5$).

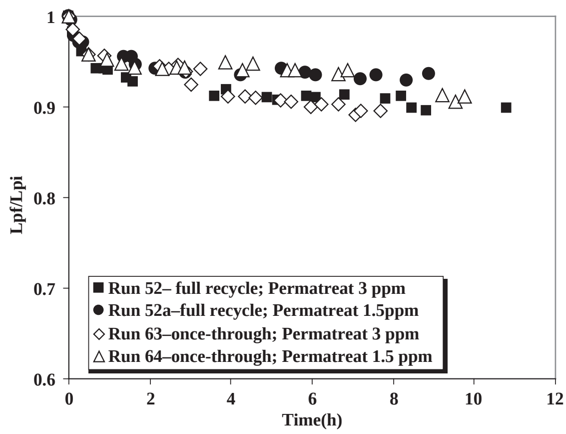

Fig. 7. Comparison of permeability decline data measured in once-through mode and in full recycle modes in the Permatreat inhibition tests ($LSI_{bulk} = 1.5$).

Table 4
Comparison between once-through runs and full recycle results in the PermaTreat PC-191 inhibition tests

Mode	Run no.	Duration (h)	pH	C/P	LSI_{bulk}	LSI_{wall}	Permatreat (ppm)	Induction time (h)	L_{p_f}/L_{p_i}
FR	52	10.8	8.2	1.65	1.5	1.8	3	No bulk precipitation	0.90
	52b	9.3	8.2	1.68	1.5	1.8	3	No bulk precipitation	0.88
	52a	8.5	8.2	1.7	1.5	1.8	1.5	No bulk precipitation	0.93
OT	63	8	8.4	1.65	1.49	1.8	3	No bulk precipitation	0.89
	63a	9	8.4	1.67	1.5	1.82	3	No bulk precipitation	0.88
	64	9.75	8.45	1.7	1.5	1.85	1.5	No bulk precipitation	0.91

between scale suppression results measured in full recycle and in once-through flow systems. A few tests comparing permeability declines in once-through and recycle systems in a $CaSO_4$ scaling solution inhibited by PermaTreat 191 yielded similar results [5], reinforcing the conclusions of this study.

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