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Operational experience of the brackish water reverse osmosis of the water treatment plant in Sant Joan Despí

Albert Teuler[a], Àlex Vega[a,*], Josep Coma[b], Daniela Vidal[b], Jordi Aumatell[b]

[a]*AGBAR, Societat General d'Aigües de Barcelona, S.A. Av Diagonal 211, E-08018 Barcelona, Spain*
Tel. +34 93 342 36 53/+34 618 64 98 72; email: avega@agbar.es
[b]*ADIQUIMICA. C/Albert Llanas 32, 08024 Barcelona, Spain*

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ABSTRACT

To ensure correct operation of any facility that uses membrane treatment technology (ultrafiltration, reverse osmosis, etc.) requires a set of maintenance and cleaning operations, which allow correct operation and optimum duration of membranes, and also ensure the quality of water produced. In 2009, the existing drinking water treatment plant in Sant Joan Despí started operating a treatment combining ultrafiltration and reverse osmosis technologies to ensure compliance with the health limits set by the Spanish Royal Decree RD140/2003. Specific antiscalant was developed especially for controlling calcium carbonate, calcium phosphate, and barium sulfate scales, which are the most problematic insoluble species in the brine of the reverse osmosis at the water treatment plant in Sant Joan Despí. Specific software was developed to calculate the optimum dose of antiscalant based on the feedwater chemistry, the temperature, and the RO plant's conversion, thus minimizing operating costs. Furthermore, Adiconline RO was installed to measure online and in real time the concentration of antiscalant in the feed. This system analyzes the active ingredients of the antiscalant and allows controlling the dosage level of antiscalant at the required level. The operational data of the RO and the results of autopsy of different elements confirmed that actions taken had been appropriate to provide efficient operation.

Keywords: Reverse osmosis; Ultrafiltration; Brackish water; Scale inhibition; Antiscalant monitor

1. Introduction

Since water treatment plant in Sant Joan Despi was first opened in 1955, the plant has undergone several extensions and reforms, in all cases with the aim of allowing it to fulfill its supply commitments with every guarantee as regards health, as required by current legislation.

The last of the important works executed was the start up, in 2009, of a treatment process using ultrafiltration membranes and reverse osmosis on a fraction of the water. This technology makes it possible to guarantee the achievement of the health standards [1] set for trihalomethanes (disinfection by-products), since they eliminate practically all organic and inorganic precursors that are involved in the generation of these compounds.

*Corresponding author.

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1.1. Plant description

1.1.1. Ultrafiltration

For the purpose of achieving the established quality objectives, both with regard to organoleptic improvements and compliance with the most stringent legislation, a fraction of the water from the intermediate pumping process is treated using membrane technology.

This flow requires previous acidification with sulfuric acid to adjust the pH to one that maximizes the retention of residual aluminum during the first ultrafiltration membranes (UF) phase. The UF operates under water and suctioning the water into them. Due to their passage size, they form a total barrier against bacteria, but not against viruses. They also eliminate suspended matter up to the levels required for the correct functioning of the reverse osmosis (RO) membranes.

Through a distribution channel, water is distributed to nine chambers where the UF equipment is submerged. To collect the permeated water, there are nine pumps, one for each chamber, that drive the water to the two collection channels that pour the water into a storage tank with a capacity of $1.600\,m^3$. This tank has 12 vertical pumps which pump the ultra-filtered water to the RO pretreatment area.

From time to time, UF modules must be subjected to counter-current cleaning to recover the facility's capacity, which is reduced through the accumulation of substances on the outer surface of the membranes. The wash water is pumped to the general plant discharge circuit and can then be reincorporate into the process.

1.1.2. Reverse osmosis

Before reaching the reverse osmosis racks, the water from the UF process is pumped into a pretreatment station consisting of ultraviolet radiation, the adding of reagents, cartridge filtering, and more ultraviolet radiation. The purpose of this pretreatment is to protect the osmosis membranes.

The RO process constitutes a total barrier to viruses and bacteria. It also eliminates practically all organic and inorganic compounds present in the water and achieves conductivities and total organic carbon low levels.

High pressure pumping allows the ultra-filtered water to pass through two of the osmosis phases through which it has previously passed for treatment in the RO plant. This process generates brine containing a high concentration of salts. A second pumping process generates enough pressure to the brine that comes from the two previous steps to pass through the third one.

Since water is practically salt-free, subsequent remineralization is needed to ensure that the water is not aggressive.

The rejection of water containing high salt concentration (brine) that is generated is taken to a tank provided for this purpose and the residue is pumped to the brine collector pipe in the Llobregat River which discharges into the sea without causing impact on the environment.

1.1.3. Remineralisation

The purpose of this phase is to adjust the mix of water from the refining process with the water from the osmosis process while guaranteeing that the mineral salt content does not render the water aggressive or cause a build up of lime scale in it.

The remineralization process is executed in the calcite filters, a series of contact chambers in which the osmotized water flows through a calcite bed (calcium carbonate).

2. Scaling control in reverse osmosis membranes at the water treatment plant in Sant Joan Despi

2.1. Simulation study of scale formation in the reject water of the reverse osmosis at a recovery of 90%

The reverse osmosis at the water treatment plant in Sant Joan Despi operates at a recovery of 90%. In these conditions of high recovery, brine water that has highly concentrated scale components exceeds the solubility limits of one or more sparingly soluble salts [2]. This leads to the precipitation of insoluble salts on the membrane surface. The most common scale-forming salts are calcium carbonate, sulfate, fluoride and phosphate, strontium, and barium sulfate [3]. Apart from limiting recovery to avoid exceeding solubility limits, the most common approaches followed to prevent scale formation are pH adjustment through acid addition to reduce the scaling potential and the use of antiscalants. The antiscalants are added to feedwater at very low levels to reduce or prevent the formation of the scales in the concentrate.

A study was performed with scientific software ADICRO to simulate the behavior of the water in reverse osmosis process in Sant Joan Despi. The input variables were the feedwater composition, the temperature, the recovery of the plant, and the membranes used. The program ADICRO calculates osmotic pressure, ionic strength, and the values of the solubility products for sparingly soluble species corrected according to the ionic strength. These values are used to calculate saturation levels (SL), Langelier saturation index (LSI), Stiff and Davis index, fouling index (FI), and scaling potentials to predict the risk of membrane scaling or fouling. The software also recommends the most effective antiscalant and the optimal dosage to protect membranes against scaling phenomena and deposit formation. The program determines the optimal operating range and indicates whether the treated water will be within allowable limits for the different scaling potentials. The program also calculates the amount of sulfuric or hydrochloric acid or base required to decrease or increase the pH of feedwater to reach the desired pH.

Table 1 shows the water chemistry of the feedwater and the reject water at 90% recovery. The composition of the water corresponds to the average values of the analytical parameters of the feedwater during a period of two years. Barium and phosphate concentrations correspond to the maximum concentrations found in the feedwater during the sampling campaign. The study is performed under the most unfavorable conditions with respect to precipitation of calcium phosphate and barium sulfate. The aluminum concentration corresponds to the maximum value of aluminum to the UF effluent (0.05 mg/L Al).

Based on the feedwater analysis in Table 1 and operating at a recovery of 90%, a study of the scaling potential for sparingly soluble species in the concentrate water was conducted using ADICRO scaling prediction software. Fig. 1 shows the scaling potentials without antiscaling treatment at temperature of 20˚C. The scaling potentials are expressed as the percentage of the maximum admissible limit for the SL and FIs. A scaling potential higher than 100% indicates that the saturation level for a compound is greater than the maximum permissible limit for this saturation level, and the compound will tend to precipitate. The results of simulation indicated that the solubilities at 20˚C of calcium carbonate ($CaCO_3$), calcium fluoride (CaF_2), calcium phosphate ($Ca_3(PO_4)_2$), and barium sulfate ($BaSO_4$) would be exceeded without antiscalant treatment in the reject water. For other compounds, scaling potentials were within admissible limits and the plant could be operated without risk of scale formation.

2.2. Development of antiscalant to inhibit the precipitation of $CaCO_3$, CaF_2, $Ca_3(PO_4)_2$, and $BaSO_4$

Calcium carbonate ($CaCO_3$), calcium fluoride (CaF_2), calcium phosphate ($Ca_3(PO_4)_2$), and barium sulfate ($BaSO_4$) were the problematic sparingly soluble compounds in the water reject in reverse osmosis in Sant Joan Despi. To evaluate the effectiveness of various antiscalant formulations to inhibit the $CaCO_3$, CaF_2, $Ca_3(PO_4)_2$, and $BaSO_4$ scale formation in membrane systems, the following dynamic tests were performed:

Table 1
Water chemistry of the feedwater and the reject water at a recovery of 90% of the reverse osmosis

Parameter	Feedwater	Simulated reject water at a recovery of 90% (software ADICRO)
pH	7.00	7.85
Calcium	104 mg/L Ca	1,040 mg/L Ca
Magnesium	31 mg/L Mg	310 mg/L Mg
Sodium	210 mg/L Na	2,100 mg/L Na
Potassium	31 mg/L K	310 mg/L K
Barium	0.104 mg/L Ba	1.04 mg/L Ba
Strontium	1.7 mg/L Sr	17.0 mg/L Sr
Iron	0.008 mg/L Fe	0.080 mg/L Fe
Aluminum	0.050 mg/L Al	0.50 mg/L Al
Manganese	0.026 mg/L Mn	0.260 mg/L Mn
Sulfate	204 mg/L SO_4	2040 mg/L SO_4
Chloride	320 mg/L Cl	3,200 mg/L Cl
Fluoride	0.180 mg/L F	1.80 mg/L F
Bicarbonate	294 mg/L HCO_3	2,940 mg/L HCO_3
Nitrate	9.0 mg/L NO_3	90.0 mg/L NO_3
Silica	2.57 mg/L SiO_2	25.70 mg/L SiO_2
Phosphate	0.466 mg/L PO_4	4.66 mg/L PO_4
Ionic strength (FI)	0.022	0.198

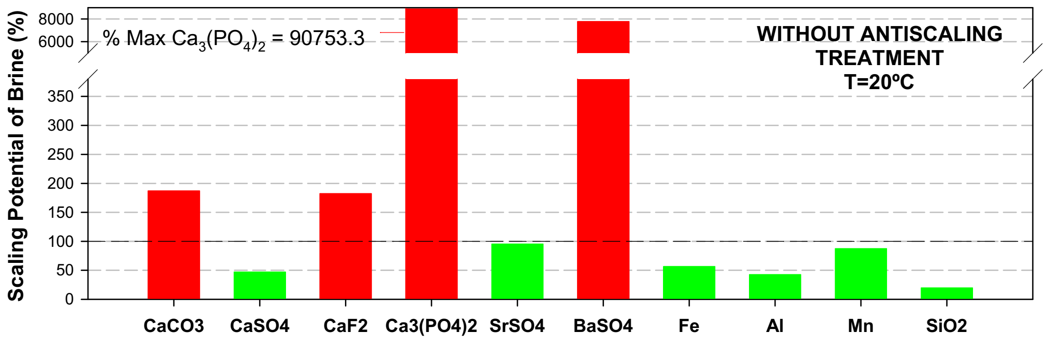

Fig. 1. Scaling potential of brine (recovery = 90%) without antiscaling treatment at $t = 20$ °C.

(1) The first stage of the membrane scaling experiments was conducted in a laboratory cross-flow flat sheet membrane unit. These tests allowed isolating and identifying the best performing antiscalants.
(2) To confirm the ability of selected antiscalants a continuous flow pilot RO plant was used. The pilot plant was equipped with a tubular membrane.

All experiments were carried out with a total recycle of both the concentrate and permeate to the feed vessel, so as to maintain a constant composition. These tests were conducted using synthetic water to work in totally controlled conditions. Separate solutions containing anions and cations were added to the RO feedwater of Sant Joan Despi that already contained the antiscalant to be tested, to obtain water that simulated reject water at a recovery of 90% as shown in Table 1. Sodium chloride was added also to achieve an ionic strength equivalent to the reject water. The RO elements Filmtec LE-440i were used during the tests. The feed pressure is specified by the membrane manufacturer and was controlled at 10.3 bars. The water pH was controlled at 7.85, corresponding to the pH of the brine water obtained from simulation using the software ADICRO (Table 1). The water temperature ranged between 7 and 27°C. A limited number of runs were conducted in this work. Three scenarios were selected depending on the water temperature. The temperatures tested were 7, 20, and 27 °C. For each scenario, various antiscalants were tested at different concentrations.

To evaluate the efficacy of the different antiscalants tested and to calculate the inhibition of scale formation in each pilot plant run, the following operating parameters were monitored during the trials: normalized permeate flux, normalized salt rejection, feed pressure, pressure drop between feed and brine streams (Delt P), pH, and temperature. A complete chemical analysis of the feed and permeate was performed periodically. The concentration of different antiscalants tested during the pilot plant trials was monitored online using the analyser Adiconline RO. At the end of the tests, samples of membrane were cut for SEM–EDX (scanning electron microscopy and energy dispersive X-ray spectroscopy) analyses to study the chemical composition, crystal structure, and morphology of the inorganic deposits and scales deposited on the membrane surface.

In order to calculate the inhibitor efficacy, the results obtained with each test were compared to the performance of operating parameters and analytical values obtained under the same conditions of scale potential without antiscalant treatment (blank).

Table 2 shows the SL and FI of sparingly soluble species at temperatures of 7, 20, and 27 °C for the synthetic water that simulates the rejection at recovery of 90% (Table 1). The SL or FIs greater than one indicate that the solubility of the sparingly soluble salts is exceeded and its precipitation is likely to take place. The table also shows the scaling potentials without antiscalant treatment at the reject. The ADICRO predictions indicated that the solubilities of calcium carbonate ($CaCO_3$), calcium fluoride (CaF_2), calcium phosphate ($Ca_3(PO_4)_2$), and barium sulfate ($BaSO_4$) exceed the maximum allowable scaling potential limit (>100%). The Calcium carbonate exhibited the phenomenon of inverse solubility, that is, the solubility of calcium carbonate decrease with increasing the temperature. The most unfavorable scenario for calcium carbonate was at 27°C. At this temperature, the scaling potential for $CaCO_3$ was higher. However, calcium fluoride, calcium phosphate, and barium sulfate had the lowest solubility at 7°C.

The results obtained from tests allowed isolating the most effective antiscalant to inhibit the formation of inorganic scales. At temperatures of 7, 20, and 27 °C, ADIC RO-17 was clearly the most effective antiscalant. ADIC RO-17 was capable of 100% inhibition of calcium carbonate, calcium fluoride, calcium phosphate, and barium sulfate.

Table 2
SL, FI, and scaling potentials without antiscalant treatment of sparingly soluble species for synthetic water, recovery = 90% and temperatures = 7, 20, and 27 °C

Sparingly soluble species	Saturation level/fouling index			Scaling potential without antiscalant treatment		
	$T = 7$ °C	$T = 20$ °C	$T = 27$ °C	$T = 7$ °C (%)	$T = 20$ °C (%)	$T = 27$ °C (%)
$CaCO_3$	87.42	125.36	149.02	177.98	187.06	191.93
$CaSO_4$	0.76	0.72	0.70	50.17	47.31	45.78
CaF_2	1.05	0.66	0.53	329.74	182.30	134.30
$Ca_3(PO_4)_2$	1,104.52	907.53	813.56	110,452.00	90,753.32	81,356.23
$SrSO_4$	0.48	0.45	0.43	98.78	95.51	93.41
$BaSO_4$	120.27	72.38	47.35	13,016.91	7,776.44	5,083.85
Fe	0.73	0.57	1.35	73.17	56.86	135.43
Al	0.49	0.43	0.40	48.58	42.85	39.73
Mn	0.56	0.88	1.04	56.42	87.71	104.43
SiO_2	0.24	0.20	0.18	23.59	19.85	17.82

Conventional antiscalants have poor results to control calcium phosphate scale. The most common approach followed to inhibit calcium phosphate precipitation is reducing pH by acid dosing. The acid dosing implies an increase in operating costs due to large quantities of acid required as well as the occurrence of corrosion problems.

ADIC RO-17 is a synergistic blend of antiscalants developed to control the calcium phosphate scaling without addition of acid for pH correction. The scale inhibitor developed is also highly effective at preventing the calcium carbonate, calcium fluoride, and barium sulfate scales.

A dosing model for ADIC RO-17 was developed. The model calculates the optimum effective antiscalant dosage to inhibit the formation of scales in the reject stream. The mathematical model was developed from the data obtained from RO pilot plant experimental runs and field data. The antiscalant was tested under various solution supersaturation conditions and antiscalant concentrations. The model predicts the dosage for scale control based upon

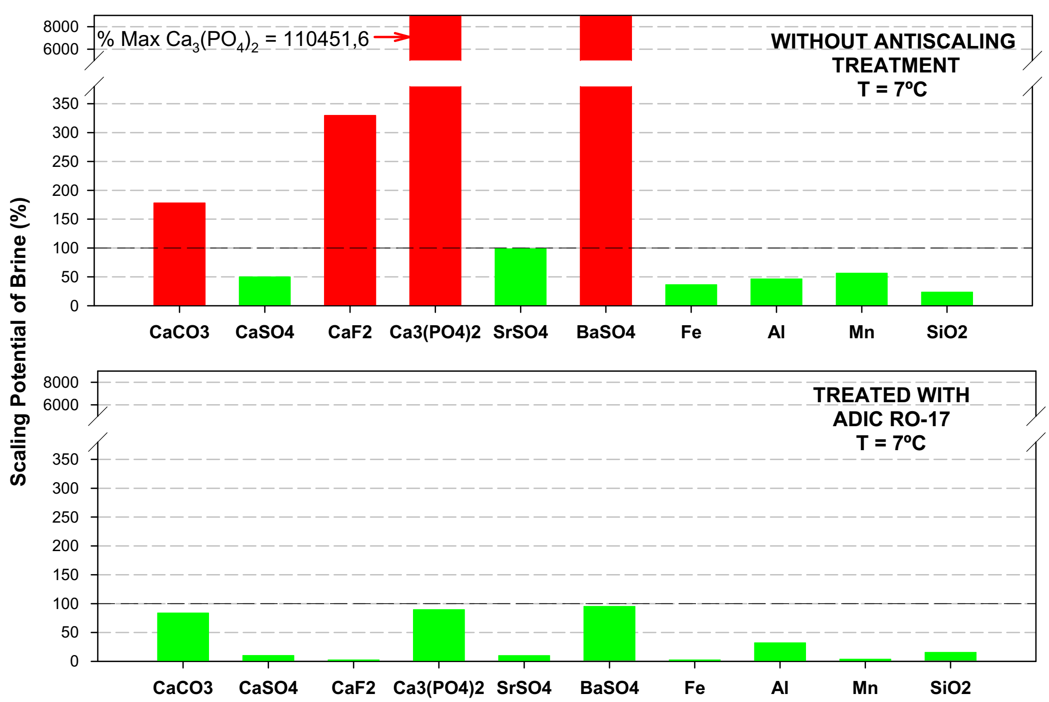

Fig. 2. Scaling potential of brine (recovery = 90%) without and with antiscaling treatment at $t = 7$°C.

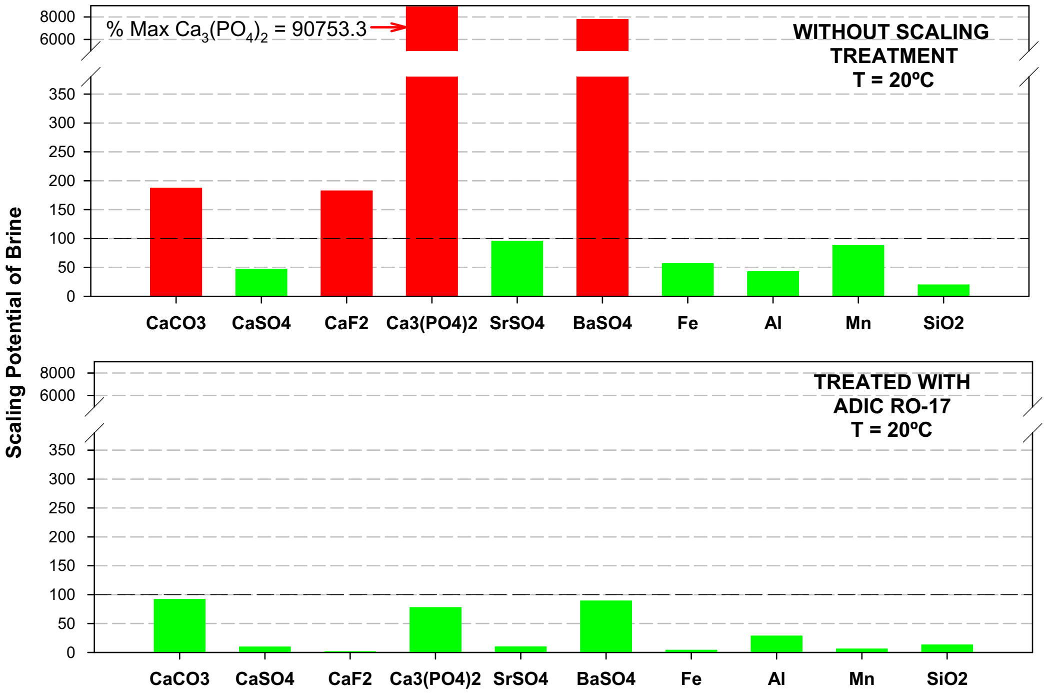

Fig. 3. Scaling potential of brine (recovery = 90%) without and with antiscaling treatment at $t = 20$ ℃.

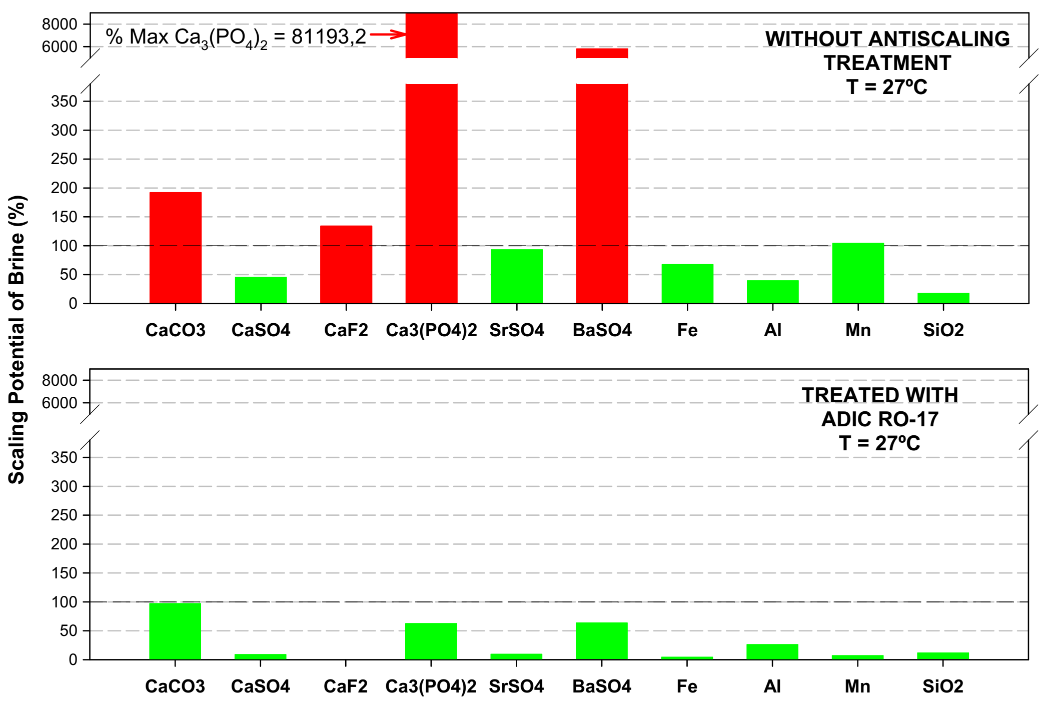

Fig. 4. Scaling potential of brine (recovery = 90%) without and with antiscaling treatment at $t = 27$ ℃.

water chemistry and operating parameters. The model is accurate within operating and water chemistry ranges of the reverse osmosis at the water treatment plant in Sant Joan Despi. The dosage model is accurate within a range of feedwater temperatures of 7–27 ℃.

The experimental results allowed modeling the reduction of scaling potentials for sparingly soluble species as a function of the dose of antiscalant ADIC RO-17. Figs. 2–4 show the reduction of scaling potentials in the reject water of the reverse osmosis at a recovery of 90% (Table 1) and temperatures of 7, 20, and 27 ˚C with required dose rate of antiscalant ADIC RO-17. Scaling potentials for the calcium carbonate, calcium fluoride, calcium phosphate, and barium sulfate were reduced to values lower than 100% for each temperature with ADIC RO-17 dosing. The reverse osmosis membranes were fully protected against scale formation on the membrane surface in the temperature range of 7–27 ˚C.

The dosage of the antiscalant ADIC-RO-17 model and the scaling potential reduction model and the knowledge acquired in the experimental stage were incorporated into the software ADICRO. The program calculates scaling potentials and recommends the optimal dosage of ADIC RO-17 to ensure the effective protection of the reverse osmosis membranes at the water treatment plant in Sant Joan Despi against scaling and fouling.

3. Dosage protocol of antiscalant in order to optimize the antiscalant dose and minimize operational costs in the treatment of reverse osmosis membranes at the water treatment plant in Sant Joan Despi

3.1. Dosage optimization of antiscalant as a function of feedwater composition, temperature, and conversion. Antiscalant performance

The composition of the feedwater to the reverse osmosis system of Sant Joan Despi plant varies depending upon the source of water. The water may come from the Llobregat river collection or wells that draw water from the aquifer. The composition of the feedwater affects reverse osmosis performance. It is therefore essential to know precisely the water composition. In order to determine the optimum dosage of antiscalant ADIC RO-17, simulations with the software ADICRO should be performed. Based on the feedwater analysis, the temperature and the recovery, the program recommends the ADIC RO-17 dosage required to reduce and maintain scaling potentials of sparingly soluble species below 100%. In the case of any compound precipitation, although antiscalant is dosed, i.e. the scaling potential exceeds 100%, different strategies can be applied to avoid problems of scale formation. On the one hand, the pH may be reduced and on the other hand, the recovery may be decreased to lower the scaling tendency.

The performance of the reverse osmosis system in Sant Joan Despi was evaluated using data from the online supervisory control and acquisition system installed in the plant, where parameters such us feed pressure, permeate pressure, reject pressure, pressure drop between feed and brine, feed flow, reject flow, permeate flow, feed quality, reject quality, permeate quality, and feedwater temperature and recovery are recorded. During the operation of reverse osmosis plant, system conditions such as temperature, pressure, and feedwater quality may vary, causing variations in productivity and quality of the permeate water. In order to distinguish between such normal behavior and changes in the operational parameters due to fouling or scaling, the permeate flow and salt passage have to be normalized. To evaluate the performance of the system, it is necessary to compare the behavior under the same conditions. Therefore, it is necessary to convert the operational data obtained from present conditions to a set of selected standard conditions and thus it normalizes the behavior of the reverse osmosis plant. Changes in the normalization parameters indicate a potential problem in the operation of the plant.

To evaluate the efficacy of the antiscalant ADIC RO-17 to inhibit scale formation, normalized permeate flow and salt passage were monitored daily. These normalized parameters are the best indicators of membrane fouling. The evaluation is carried out analytically by standardizing operating data of the rack eight for four months in accordance with the standard method ASTM D 4516 Standard Practice for Standardizing Reverse Osmosis Performance Data [4].

Fig. 5 shows the total normalized permeate flow of the rack eight after four months of operation. Fig. 6 shows the average normalized salt passage of the three stages of rack eight. The results show that the normalized flow and salt passage remained stable and there were no variations in the normalized parameters. These results indicate that the antiscalant is effective to avoid membrane scaling at high recoveries.

To validate the effectiveness of the antiscalant, last position membrane elements for third stages were autopsied. The autopsy results indicated that inorganic scales were not found in the membrane autopsied. The problematic sparingly soluble compounds ($CaCO_3$, CaF_2, $Ca_3(PO_4)_2$, and $BaSO_4$) were not detected on the surface of third stage membranes, where the risk of scale formation is higher.

The antiscalant ADIC RO-17 is effective in controlling inorganic scales, specially prevent calcium carbonate, calcium fluoride, calcium phosphate, and barium sulfate scaling, under the operating conditions of the

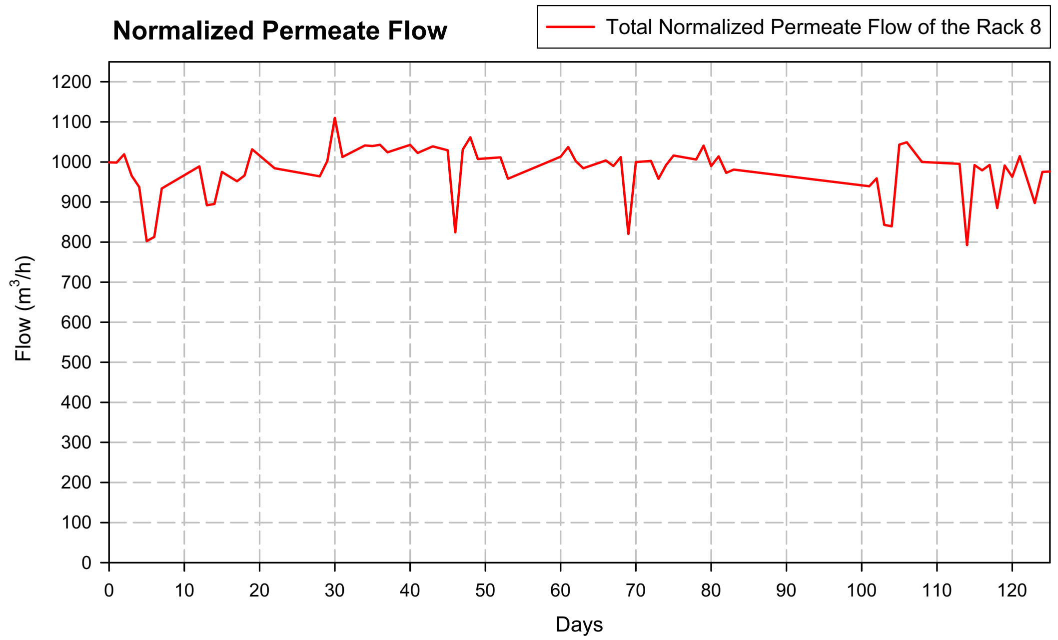

Fig. 5. Total normalized permeate flow of the rack eight for four month of operation.

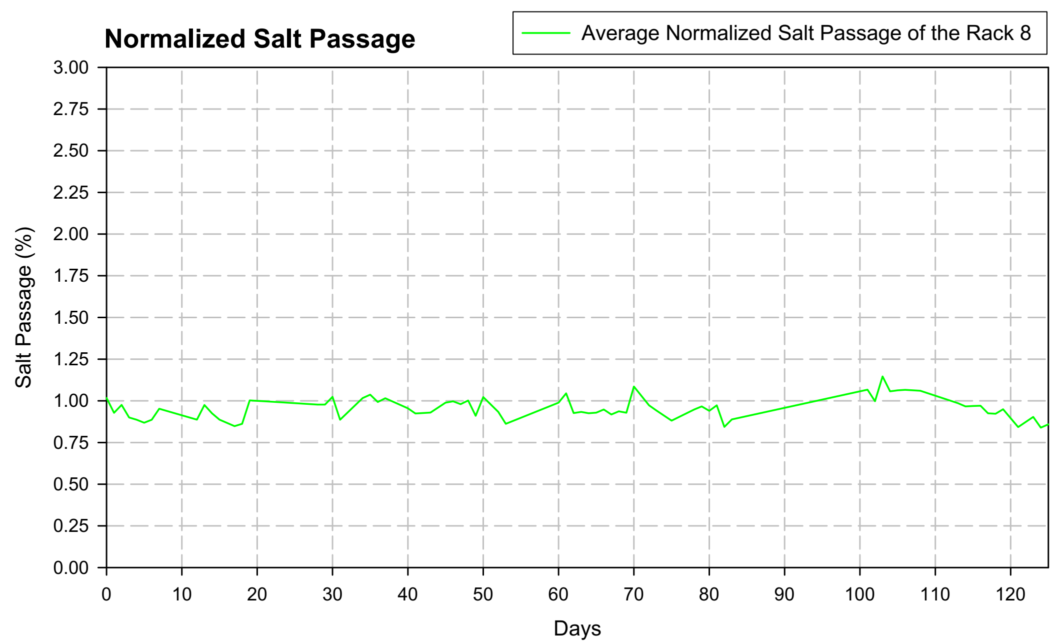

Fig. 6. Average normalized salt passage of the rack eight for four month of operation.

reverse osmosis in Sant Joan Despi. The software ADICRO is a useful tool for optimizing the dosage of antiscalant as a function of feedwater analysis, temperature and plant recovery. The program recommends the minimum effective antiscalant dosage to protect the membranes against inorganic scale formation.

3.2. Monitoring and control of antiscalant to validate the recommended dosing

Adiconline RO (Fig. 7) system was installed in Sant Joan Despi to accurately monitor online and in real time the antiscalant dosing in the feedwater of

Fig. 7. Adiconline RO system.

the reverse osmosis. Adiconline RO allows validating online the recommended antiscalant dosage, thus the antiscalant concentration is controlled without exceeding the recommended dosing, and ensuring the minimum concentration to protect the membranes against scale formation. Dosing the minimum effective antiscalant reduces operating costs for chemical treatment, minimizes treatment chemical discharge to the environment, and prevent under feed of antiscalant.

Adiconline RO analyzes the concentration of active ingredients contained in the antiscalant formulation in few minutes. The system has been developed to analyze antiscalants containing phosphorous in their composition. Since the active ingredients of the antiscalant are analyzed, this provides a direct measure of antiscalant concentration in the feedwater without adding additional chemical tracers for monitoring the antiscalant.

Online quantitative analysis method of the contents of active ingredient of the antiscalant containing phosphorous in feedwater in a reverse osmosis system comprises of the following stages (Fig. 8).

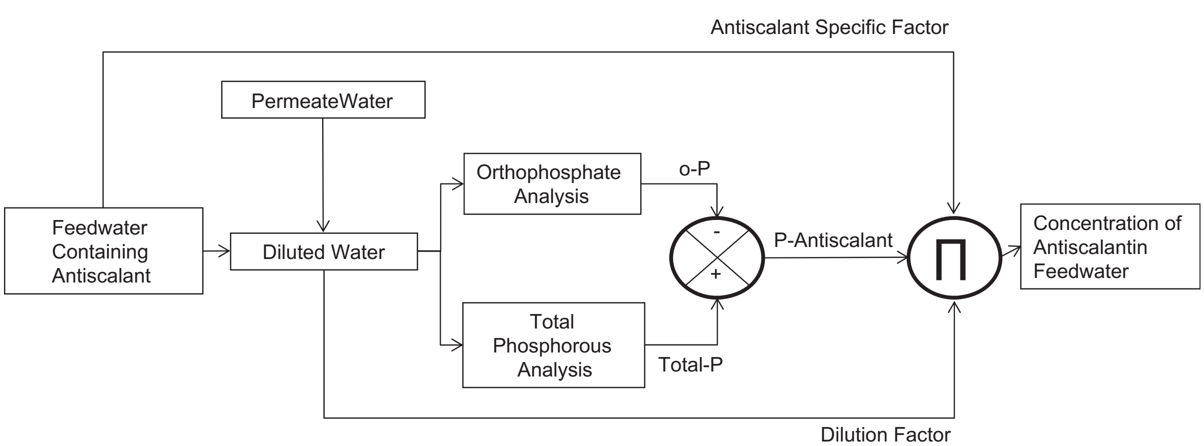

Fig. 8. Flow diagram of the Adiconline RO system.

(1) Dilution of feedwater containing the antiscalant. The dilution depends on the water chemistry and physicochemical parameters of the water containing the antiscalant. Maximum dilution is 80% with reverse osmosis permeate.
(2) Analysis of the concentration of orthophosphate in the diluted water containing antiscalant. A colorimetric analytical method is used to analyze the level of orthophosphate in the diluted water.
(3) Analysis of the total phosphorous concentration in the diluted water containing antiscalant. The antiscalant is not detected by analyzing the orthophosphate analyzed in the previous stage. In a first substage, the antiscalant containing phosphorous is hydrolyzed to orthophosphate. After hydrolysis, the concentration of orthophosphate is analyzed by colorimetric detection. The difference between the total phosphorous and orthophosphate analyzed in the previous stage corresponds to the phosphorous that comes from antiscalant.
(4) Determination of the concentration of the antiscalant in feedwater. The concentration of antiscalant in feedwater is calculated by multiplying the difference between total phosphorus and orthophosphate in the diluted water by the dilution factor and specific factor for each antiscalant.

4. Conclusions

The drinking water treatment plant in Sant Joan Despí, operating with a treatment combining ultrafiltration and reverse osmosis technologies, ensures the compliance with the health limits set by the Spanish Royal Decree RD140/2003.

The reverse osmosis at the water treatment plant in Sant Joan Despi operates at a recovery of 90%. In these conditions of high recovery, calcium carbonate, calcium fluoride, calcium phosphate, and barium sulfate exceed its solubility limits in the water reject in reverse osmosis.

The antiscalant ADIC RO-17 is effective in controlling inorganic scales, specially prevent calcium carbonate, calcium fluoride, calcium phosphate, and barium sulfate scaling, under the operating conditions of the reverse osmosis in Sant Joan Despi.

The software ADICRO is a useful tool for optimizing the dosage of antiscalant as a function of feedwater analysis, temperature, and plant recovery. The program recommends the minimum effective antiscalant dosage to protect the membranes against inorganic scale formation.

Adiconline RO accurately monitors online and in real time the antiscalant dosing in the feedwater of the reverse osmosis. This system analyzes the active ingredients of the antiscalant and allows validating online the dosage level of antiscalant.

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