

## **The Use of FTIR Spectrometry in the Autopsy Membrane of a RO Process of Brackish Water Demineralization (Brédéah Plant, Algeria)**

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### **Abstract**

In Reverse Osmosis (RO), a badly adapted pre-treatment would cause pores obstruction of the membranes by various compounds (inorganic, organic) what would lead to a significant reduction of their output. In the Brédéah demineralization unit of brackish water (salinity from 3000 to 7000 mg/L), producing 34.000 m<sup>3</sup>/day drinking water, the direct autopsy on the membranes used remains impossible. For that, gravimetric and FTIR spectrometry analyses taken on samples with various stages of the process enabled us to determine the dry matter rate and to make a qualitative determination of the compounds retained on the membranes and their effect on possible filling.

**Keywords:** RO, Brackish water, Pre-treatment, Membrane autopsy, Gravimetric method, FTIR spectrometry.

### **Introduction**

Algeria is now confronted to crucial problems in matter of water issues. It disposes of a very limited fresh water potential, particularly in the northern part of the country where lives about the three fourth of the population. In the 100 milliards of m<sup>3</sup> that constitutes the rainfall, 85% are conceded to evaporation while in the remaining that streams on the surface, about 50% goes to the sea or in the saline lakes (Sadi & Kehal., 2002).

So in the north-western, water scarcity is more important than in the North of Algeria. Rainfall, the most important parameter in the water potential varies between 290 and 666 mm/year (Bouanani, 2005).

The desalination of water by Reverse Osmosis is a membrane separation process in which the water from a pressurized saline or brackish solution is separated from the solutes and flows through an appropriate membrane (Dababneh & Al Nimr,

2003). The salt content of permeate flowing through the membrane is reduced while these of the feed solution pressurized on the other side of the membrane increases.

Performance in Reverse Osmosis, is determined by several variables, which can be classified in three categories namely: variables concerning the membranes, variables concerning the feed water and variables concerning the conditions of operation.

The use of membrane filtration in water treatment enables the production of high quality drinking water by removing micro-organisms, inorganic and organic compounds.

However, fouling of membrane elements may cause operational problems of membrane installation. Fouling mainly stems from three sources, namely particles in the feed water, build up of sparsely soluble minerals and by products of growth of micro-organisms (Nicolaisen, 2002). All of these conditions require frequent cleaning which is expensive and leads to shorter service life of the membrane elements. Therefore fouling increases the costs of plant operation and can be a threat for drinking water production. Fouling can ultimately lead to an early replacement of membrane element.

Identifying the cause of fouling of a membrane filtration plant requires a destructive study of one of several spiral wound membrane elements.

This work describes achieving methods and strategies for diagnosis of fouling, which enable prediction, prevention and control of fouling.

An adequate pre-treatment of the feed is mandatory to a well functioning membrane plant.

## Materials and Methods

### Station presentation and description

The Brédéah demineralization station has been operating since 2004. It has a production capacity of 34 000m<sup>3</sup>/day, and produces water, which salt contains is about 163 mg/L. It was conceived to respond to the water need of Oran inhabitants. This water drinking production represents 10% of its total consumption (Dahmani & Bithorel, 2001). The plant is under the responsibility of the DRHW Oran. The current operator of this demineralization unit is Degremont's company (France).

The process used is the RO and the conversion rate is 70%. This desalination station treats brackish water of Brédéah aquifers which are constituted by Miocene limestone and saline alluvium of Plio-quadernary formation (Benziane, 1984). The water is pumped from three wells with a salinity content varying between 3000 to 7000 mg/L.

### Desalination Process of Brédéah plant

The functioning principle of the RO process (Fig.1) consists initially of a pre-treatment of raw water to avoid the suspended matter deposits (SMD) which could lead to the filling of the membranes and thus to a fast reduction in the production flows. The raw water feeding the RO station of Brédéah comes from a mixture of water of 3 wells. This mixture supplies nine sand filters making it possible to remove it from the suspended matter. An injection of a ferric chloride solution is carried out, upstream, in the raw water piping (coagulation and flocculation). The sodium bisulphite, used as a biocide, is injected in case of necessity or as a preventive. Moreover, an injection of sulphuric acid is done in order to avoid calcium carbonate deposits. In this case, the pH control is necessary. The possible filling of the membranes due to many causes

(precipitation of sulphate and carbonate calcium,...) can be avoided by the inhibitors injection of scaling.

Finally a filtration on cartridge allows the retention of the finer particles (size of about 5  $\mu\text{m}$ ). Pre-treated water passes through membranes blocks made of in spiral form. Effluents, saturated with salts, are then evacuated and, permeate (demineralised water) is corrected with lime and chlorine according to the standards.

### Sampling and pre-treatment

The objective of experimental work is to collect suitable typical samples from water feed (brackish water), pre-treated water, permeate and raw water (Fig.1). Feed water concerns the mixture of three wells situated in Brédéah plant.

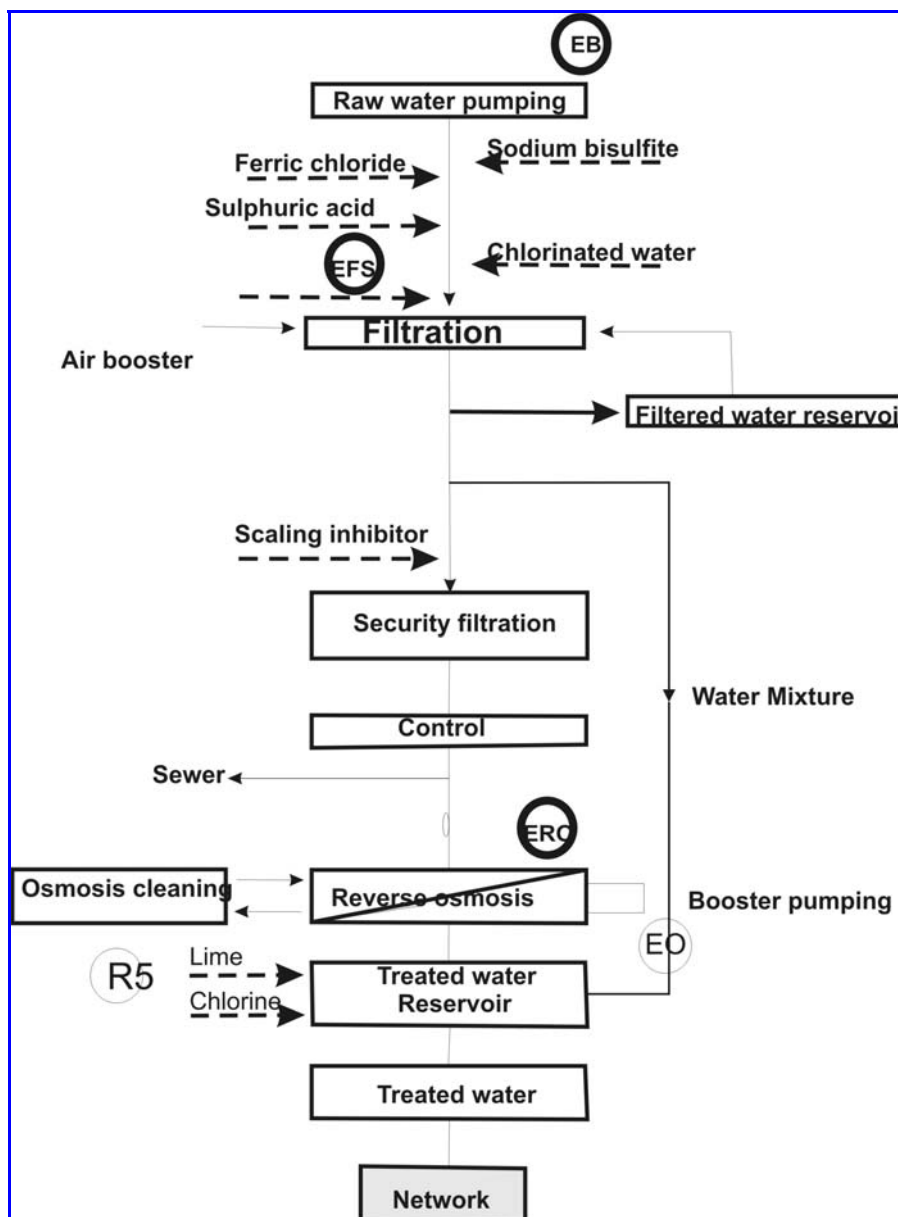


Figure 1: Desalination process of Brédéah plant and sampling point.

## Methodology

Water samples have been made according to ASTM D3370-76 methods. This step is very crucial as well for studying the clogging phenomenon, the samples has been done immediately after the exit of the module spiral (membrane type: polyamide), CPA3 model (Filmtec).

Other samples were taken at different stages of the process (Fig. 1) at:

- Wells P1, P2 and P5 (raw water),
- Pre-treated water (EFS Entry sand filter, EROblock entry reverse osmosis)
- Release of the RO: EO;
- And at the level of rejection: R.

The parameters analyzed are pH, TDS, the water temperature, cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Sr}^{2+}$ ) anions ( $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{NO}_3^-$ ) silica and organic matter. Water temperatures and pH were measured respectively by a temperature probe and pH-meter type Hach.

Cations and anions were analyzed as follows:

- Calcium and magnesium by complexometry (method described in ASTM D511-77 / B);
- Sodium and potassium by flame photometry (ASTMD 1428-64);
- Barium and strontium were assayed by atomic absorption spectroscopy (Methods described in ASTM D3651-78 and ASTM D3352-74);
- Manganese by colorimetric method (ASTM D858-77) whose principle is to dissolve the manganese by hydrochloric acid and then oxidize in the form of permanganate in presence of ammonium persulphate and silver nitrate;
- Bicarbonate ions depending on the method ASTM D513C;
- Chloride ions by volumetric method (ASTM D512 B): it consists on the sample titration by a silver nitrate solution in presence of potassium chromate;
- Sulphate ions by Gravimetric method (ASTM D 516-68) whose principle is to precipitate sulphate ions in the form of barium sulphate;
- Fluorine by potentiometric method (ASTM D 1179-80) with a selective electrode type ISE25F (Radiometer Analytical SA), and a reference electrode Ag/AgCl saturated calomel.
- Nitrate by UV-visible spectrophotometer type Nicolet Evolution 100.

### FTIR spectrometry

The analysis has been performed by an FTIR spectrophotometer (Perkin Elmer Spectrum One) on water samples upstream and downstream the reverse osmosis block. This analysis was preceded by the determination of the organic matter content in raw water sampled from the three wells. This quantification was made possible by weighing the ash rate obtained after drying and calcination of the solid between 120°C and 550°C (Thierrin, 1990 ; Da Cunha, 2000 ; Grossart, 2001; Nagamoutou, 2006).

This ash rate was calculated as follows:

$$R = \frac{100m_C}{m_S}$$

where R is the ash rate (%),  $m_C$ , the weight of the sample after calcination at 550 ° C and,  $m_S$  the mass of the sample after drying at 120 ° C.

The qualitative analysis by FTIR spectrometry has enabled us to make an identification of functional groups that may be present in the sample of the solid.

The majority of these groups are carboxylic acids, phenols and carbonyl. Beyond 550°C, it remains only inorganic compounds, so it is possible to get information after analysis by FTIR spectrometry.

### Results and interpretation

Table 1 lists the values of the elements contents present in waters analysed in the various stages of demineralization process.

The conductivity and TDS of water supplying the demineralization plant are very high. They are respectively between 8620- 9060  $\mu$ S/cm and 6700-7360 mg/L. It also noted high concentrations of sodium, chloride and sulphate contents in these wells. The TDS contents of obtained permeate is 163mg/L and that of the discharging water is very high (24195g/L). The determination, made by the "IMS Design" Software Design, of the saturation percentage (Tableau 2) shows a significant  $\text{CaSO}_4$  saturation in the rejected waters.

Analyses made by FTIR spectrometry have permitted to demonstrate the presence of sulphate (calcium sulphate in particular) in the samples (Raw water EFS, ERO, R) and their trace in the permeate: this shows the strong contribution of sulphate salts in the clogging phenomenon of membranes. This has been proven by the presence of the sulphate band (located at  $1151.54 \text{ cm}^{-1}$ ) of the sample EFS (Fig. 3), which has the same "shape" as that of the plaster (Fig. 4), and which does not appear important in the spectra of raw water, ERO and R samples (Fig. 3, 5, 6). Note that the addition of sulphuric acid at the pre-treatment results in calcium sulphate as salts at the sand filter entrance, and then the using of the scaling inhibitor can remove in large quantities calcium sulphate and thus to obtain a solution with no salts, at the entrance to the osmosis block.

Table1 : Analysis Results. (P1, P2, P5 = EB; R5 = R; permeate = EO)

Parameters	P1	P2	P5	EFS	ERO	EO	R
T (°C)	17,1	17,2	17,8	17,4	17,6	17,5	17,5
pH	8,00	7,84	8,05	6,50	6,80	6,62	8,20
Cond. (µS/cm)	8620	9060	8220	8820	8720	295	26700
TDS (mg/L)	6803	7360	6700	7170	7167	163	24195
Ca <sup>2+</sup> (mg/L)	472,00	483,00	481,00	480,00	484,00	8,80	3200,00
Mg <sup>2+</sup> (mg/L)	480,00	485,00	487,00	485,27	346,25	4,85	861,86
Na <sup>+</sup> (mg/L)	1657,00	1645,00	1655,00	1639,00	1636,00	31,00	3900,00
K <sup>+</sup> (mg/L)	14,25	14,77	14,88	14,75	14,50	1,56	47,05
Ba <sup>2+</sup> (mg/L)	0,00721	0,00721	0,00735	0,00745	0,0074	0,00	0,0125
Sr <sup>2+</sup> (mg/L)	0,00533	0,00533	0,00584	0,00544	0,0054	0,00	0,014
Mn <sup>2+</sup> (mg/L)	1,12	1,56	1,44	1,14	1,12	0,00	7,45
HCO <sub>3</sub> <sup>-</sup> (mg/L)	450,00	312,00	375,00	328,00	327,56	16,10	568,00
CO <sub>3</sub> <sup>2-</sup> (mg/L)	7,1	7,1	6,7	0,2	0,2	0,2	23,1
Cl <sup>-</sup> (mg/L)	3443,00	3240,00	3002,00	2911,00	3017,50	35,50	9585,00
SO <sub>4</sub> <sup>2-</sup> (mg/L)	1440,00	1884,00	1754,00	1770,00	1668,00	54,00	7506,00
F <sup>-</sup> (mg/L)	0,85	0,80	0,83	0,85	0,85	0,08	2,45
NO <sub>3</sub> <sup>-</sup> (mg/L)	24,55	24,35	24,55	24,45	6,15	0,12	0,25
SiO <sub>2</sub> (mg/L)	32,00	32,10	32,45	4,32	3,25	0,01	11,47

Table2 : Saturation Index valus

	P1	P2	P5	EFS	ERO	EO	R	% Saturation (IMS)
SI Silica	22,9	22,9	23,1	2,1	2,3	0	8,1	100
SI CaSO <sub>4</sub>	35,2	45,4	42,8	45,3	44,3	50	500,4	230
SI BaSO <sub>4</sub>	42,2	53,2	50,4	52,2	52	0	144,6	6000
SI SrSO <sub>4</sub>	0	0	0	0	0	0	0,1	800
Langelier's Index	1,7	1,4	1,6	0	0,3	-2,9	2,8	

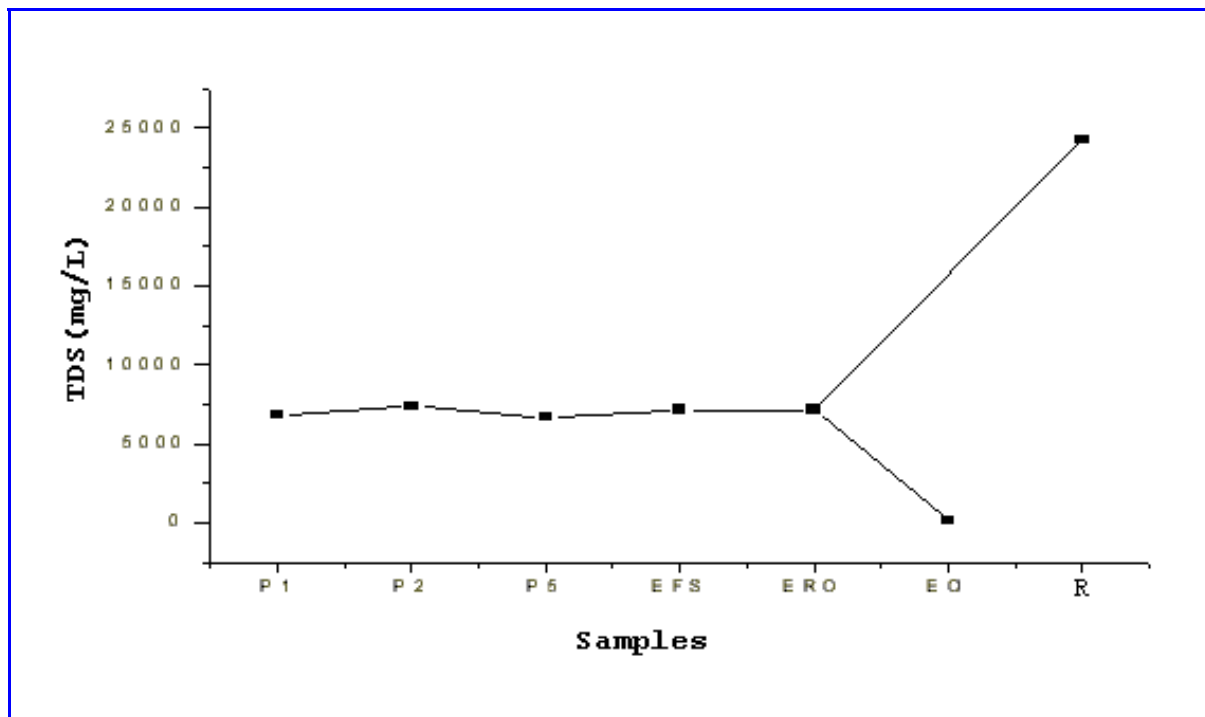


Figure 2: TDS curve variation depending on the sampling location.

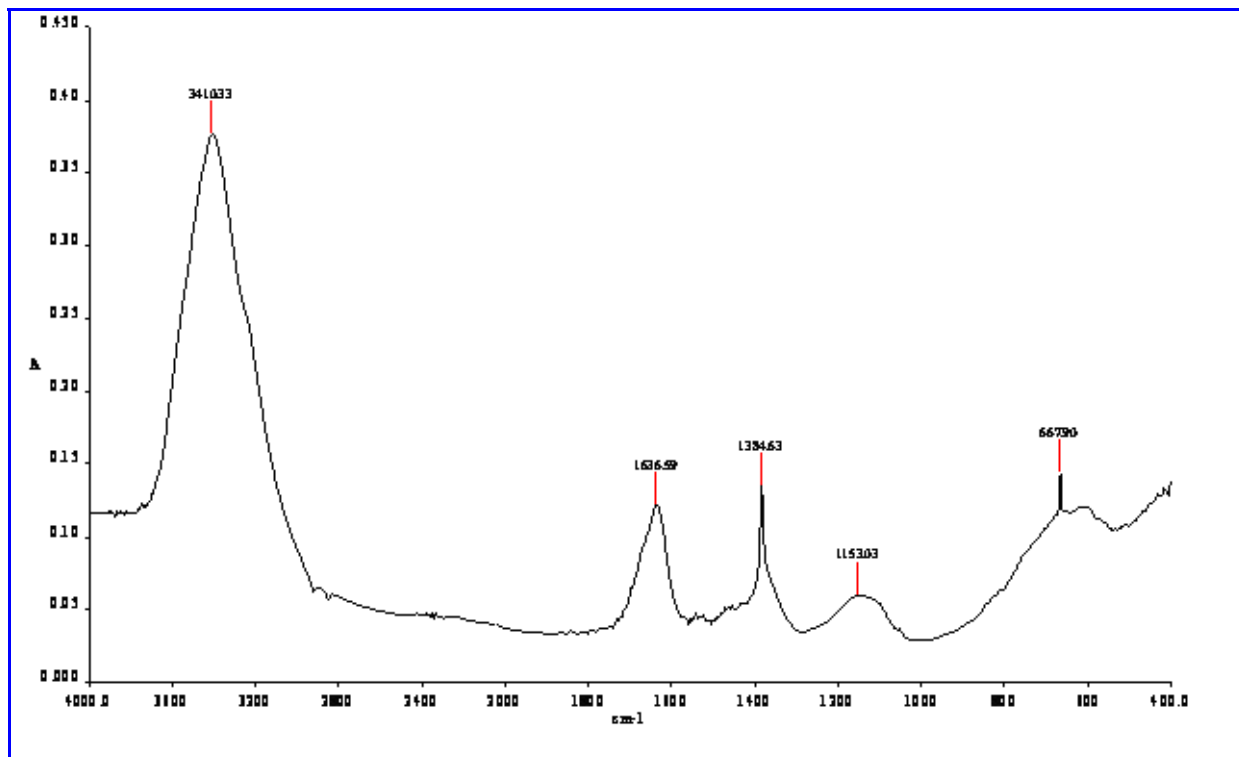


Figure 3: FTIR spectrum of raw water sample at 120°C (1).

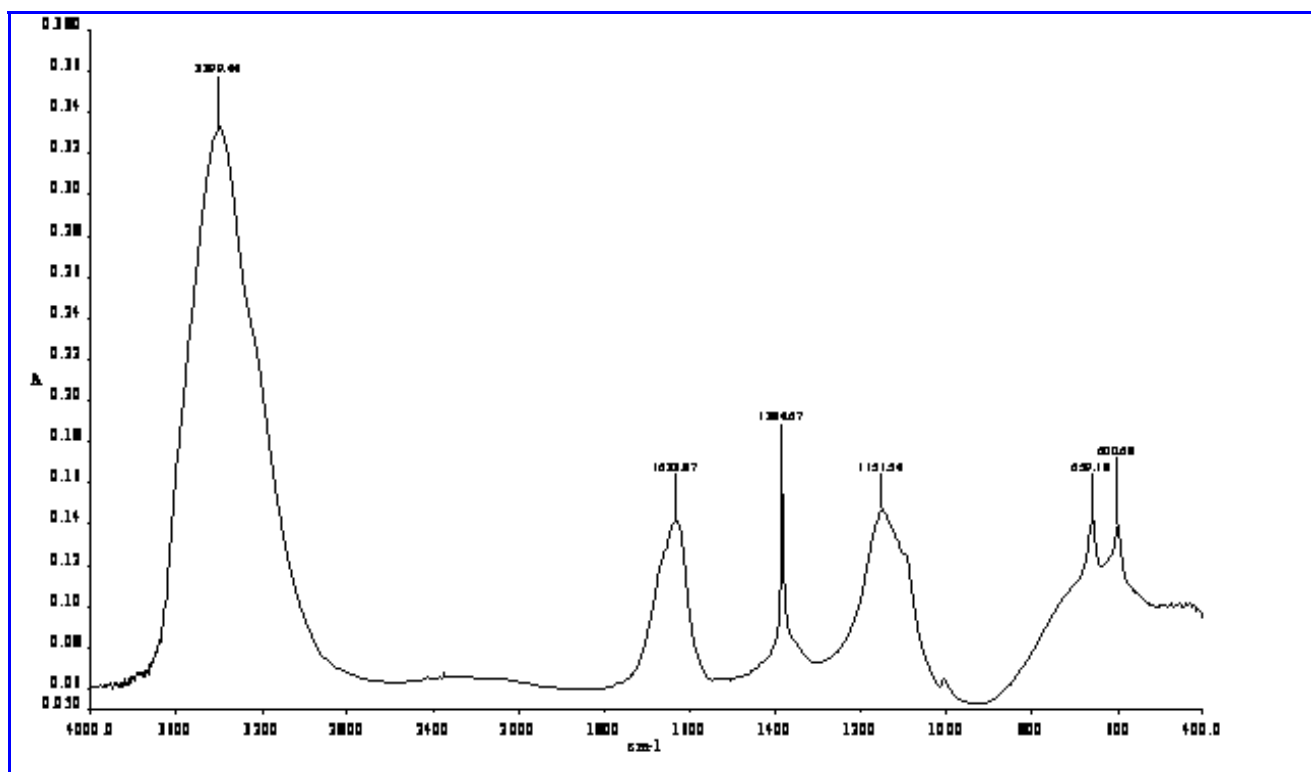


Figure 4: FTIR spectrum of EFS sample (2).

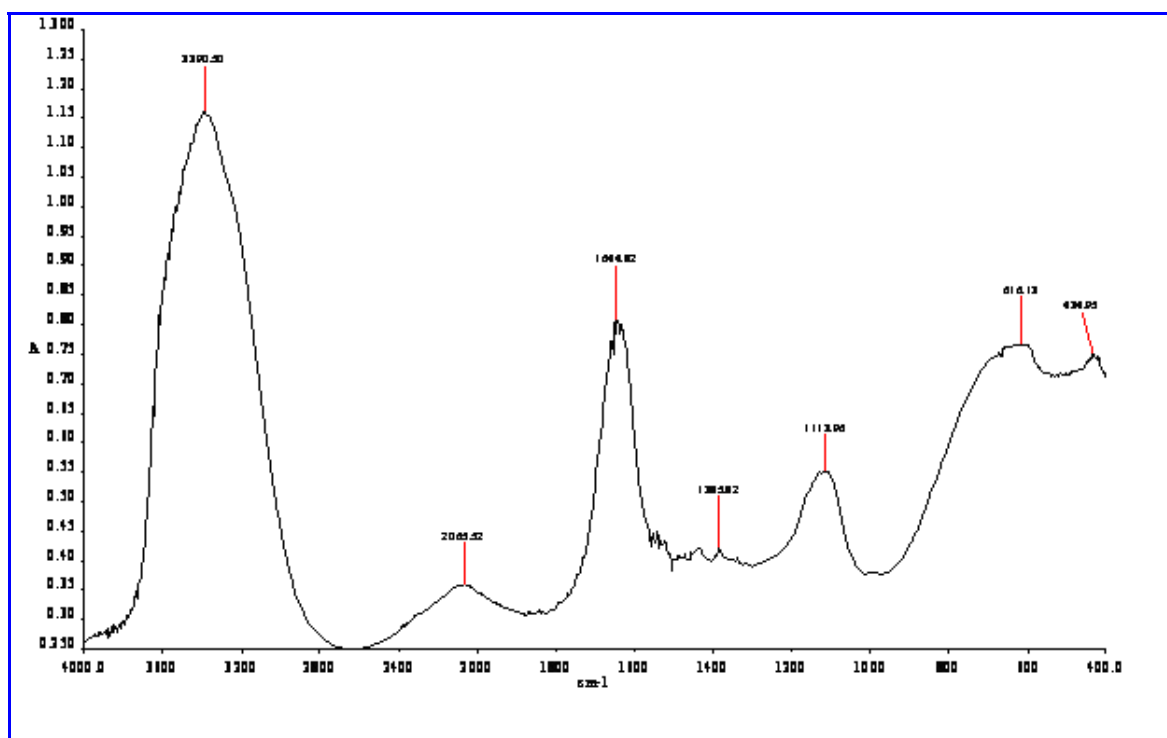


Figure 5: FTIR spectrum of ERO sample (3).



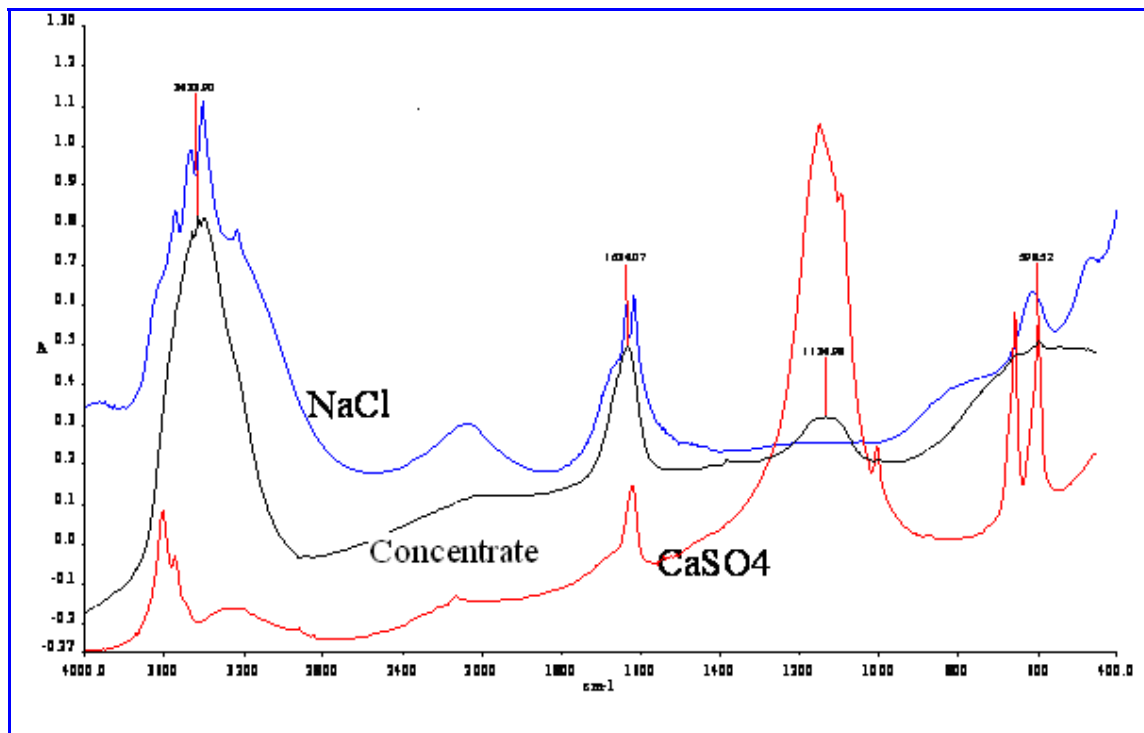


Figure 6: FTIR spectra of R, NaCl and CaSO<sub>4</sub> samples.

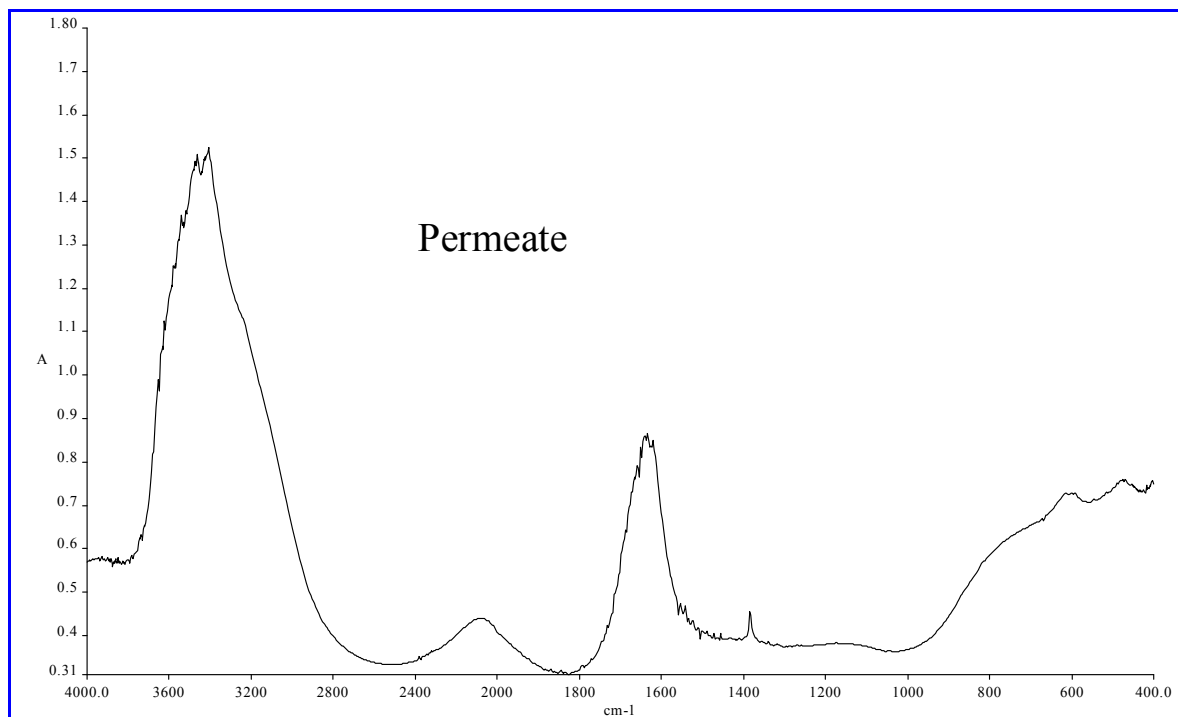


Figure7: FTIR spectrum of permeate sample at 120°C.

The presence of nitrate salts in the samples was also demonstrated by the presence of the nitrate band at  $1384\text{ cm}^{-1}$  with an intensity decrease starting from the raw water to the R samples: so nitrate salts are at quite different quantities at the entrance of the osmosis block, permeate and rejection samples compared to those of raw water and sand filter entrance.

The presence of sodium chloride in our samples was also characterized by comparing the infrared spectrum of sodium chloride and that of our samples. Likewise, we note that the threshold of the presence of nitrate salts, which are mostly magnesium and sodium nitrates, is characterized by a nitrates band at  $1384.67\text{ cm}^{-1}$  in raw water and the entrance of sand filter samples. The concentration in the entrance of the osmosis block and permeate are less important.

The IR bands characteristic of sodium chloride, located at  $3400\text{ cm}^{-1}$ ,  $2089\text{ cm}^{-1}$  and  $1634\text{ cm}^{-1}$  appear more clearly in the permeate (Figure 6). This is due to the presence threshold of sodium chloride in this sample, because actually there are more minerals in solution (Christensen, 2001; Fleming et al., 2001; Dudley, 2003; Kenedy et al., 2006; Rahadiarnato, 2006). This result is quite apparent in the discharge (Fig.6) where there are very large percentages of minerals. From this, the membrane used allows the passage of a certain amount of sodium chloride.

The desalination process of Brédéah plant built in four lines (A, B, C, D) with two floors each one. Each floor contains pressure tubes, comprising each one, seven cartridges spiral membranes. It should be noted that the four compartments do not work at the same time during production and maintenance.

In order to confirm the contribution of sulphate salts in clogging phenomenon, we determined the threshold scaling caused by the salts.

Figure 8 showing the flow evolution in the first two stages of permeate production during eight months period show a decrease in the flow and therefore in membrane permeability of the RO process.

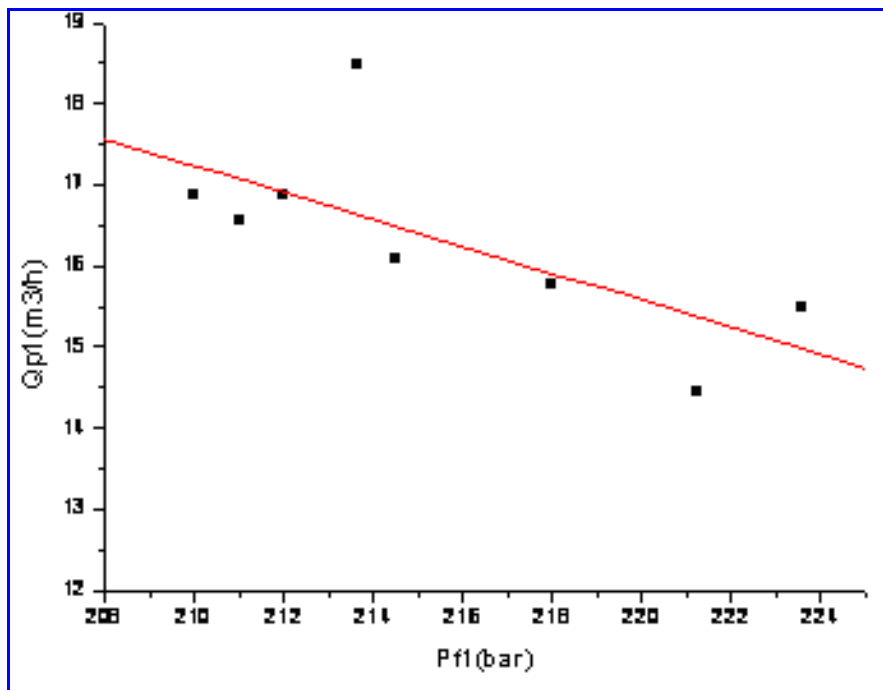


Figure 8: Variation of the permeate flow according to the supply pressure.

Table 3: Results of calculations by the program fortran.

Date 2006	raw water flow (m <sup>3</sup> /h)	permeate flow (bar)	Loss of charge (bar)	$\Psi$	R (m <sup>-1</sup> )	Risk of clogging
01/01	341	241	2,12	27,71	53,23	BaSO <sub>4</sub>
15/01	338	245	1,89		54,84	
01/02	339	245	1,98		55,32	
16/02	332	244	1,89		56,52	
01/03	328	223	1,90		56,64	
16/03	345	241	1,98		56,70	
31/03	348	249	1,91		56,89	
14/04	348	249	1,75		57,07	
29/04	339	247	1,97		57,08	
13/05	340	235	1,75		57,10	
28/05	338	245	1,89		57,20	
13/06	339	247	1,95		57,44	
28/06	341	249	1,94		57,56	
13/07	344	254	1,92		58,36	

This decrease in permeability is confirmed by the value of the polarization factor (27,7) and increasing the overall resistance of membranes (Fig.9).

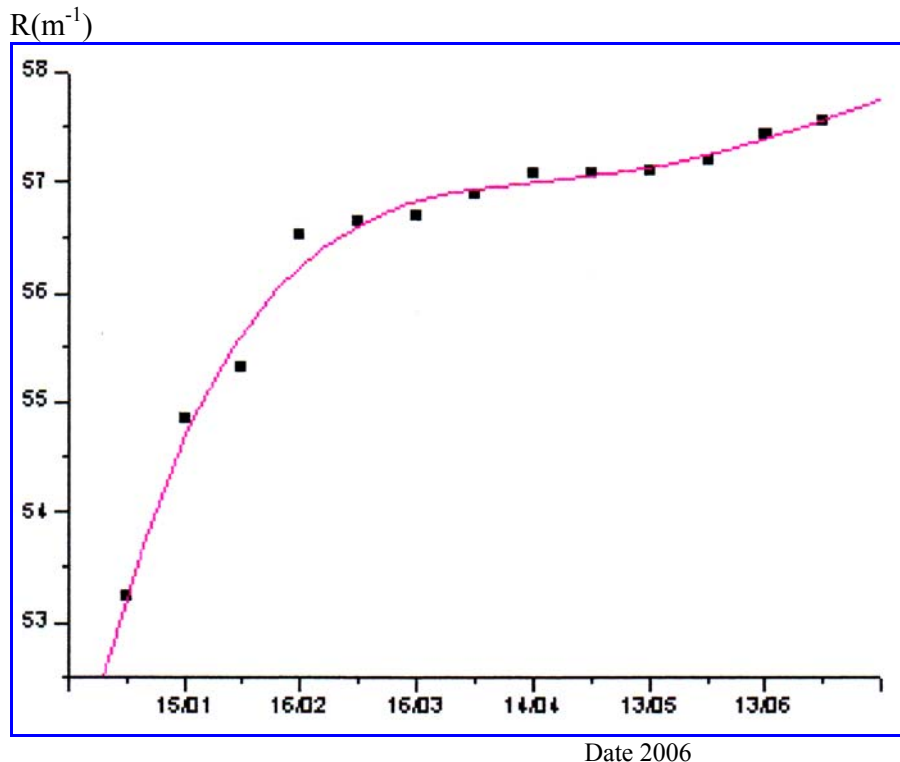


Fig. 9: Evolution of the overall resistance of the membranes over time.

The results show a progression of the growing resistance of the membrane that is defined by a function of the form

$$R(t) = 51,22 + 2,28t - 0,379t^2 + 0,0279t^3 - 8,65 \cdot 10^{-4} t^4 + 7,91 \cdot 10^{-6} t^5$$

It also notes that the coefficient of polarization  $\Psi$  is constant, and a strong contribution of barium sulphate in the phenomenon of scaling what was confirmed by FTIR spectroscopy.

### Conclusions

Information, gained by the spectrometry FTIR analysis, enabled us to do a non-destructive autopsy of membranes and to understand the mechanisms of precipitation and salts reactivity. This diagnosis is of great importance since it allows the prediction of the intensity of membranes fouling and will permit us to take necessary measures at the pre-treatment, quantity of added sulphuric acid, efficiency of the scaling inhibitor, products of washing of the reverse osmosis membranes. In addition, this method does not require analytical reagents and allows the simultaneous analysis of several soluble inorganic compounds in water samples, in an optimal time, after dehydration.

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