

OPTIMIZATION OF AN ANTISCALE TREATMENT TO PREVENT SCALING OF A SOLAR DESALINATION UNIT USING EVAPORATION-CONDENSATION PRINCIPLE

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The main purpose of this investigation was to optimise an antiscaling treatment to prevent scaling of a solar desalination plant using brackish water. Scales were identified by XRD as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. To prevent its formation, laboratory study was performed. Three antiscalants (STP, Flocon and RPI 2000) were tested at different conditions to stop or delay gypsum crystallisation in supersaturated solutions prepared by mixing CaCl_2 and Na_2SO_4 solutions. Kinetics, XRD and SEM data showed that the RPI 2000 was the most efficient.

Keywords: solar energy, alternative energy and ecology



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Introduction

Tunisia (North Africa) is currently confronted to the crucial problem of the public, agricultural and industrial feed water supply, in particular in the center and south areas. Production of fresh water by seawater and brackish water desalination has proved to be an alternative for these regions. Water desalination stations that use conventional methods such as reverse osmosis (RO), multi-stage flash (MSF) and multiple effect (ME) distillation are large and non- autonomous. In addition, they consume high energy and have a heavy structure. The use of solar-powered water desalination plants seems to offer an attractive alternative, given the availability of this free energy source in the arid regions, the low cost infrastructure, and the low maintenance [1-2]. However, all the desalination processes are based on the concentration principle of waters already presented higher salinity. So, scale problem can occurs by the accumulation of minerals such as CaCO_3 and CaSO_4 . These salts form hard and strongly adhering deposits on the surfaces and their formation is favoured by the decrease of their solubility with increasing temperature [3]. Calcium carbonate scale can be prevented by several methods e.g. antiscalants and acid treatments. On the other hand, calcium sulphate crystallisation cannot be controlled easily. The only method that is always applied to control its formation is the use of scaling inhibitors at very low concentration (mg/L). Studies have shown that these inhibitors performance strongly depend on their structure such as the functional groups, the chemical composition and the molecular weight [4-5]. Therefore, the choice and the optimization of the antiscalant are important to reduce the cost of product water. The effectiveness of a number of additives such as aminophosphate polymers, organic phosphate, mineral phosphates, and polyacrylate in preventing or reducing the crystallization of calcium sulphate from supersaturated solution has been the subject of numerous investigations [6-10]. El Dahan and Hegazy [7] studied the effect of organic phosphate ester on gypsum precipitation at temperature ranging from 40-90 °C and showed that the dose required for inhibition increases with temperature. Linnikov and Podbereznyi [6] showed that, for the same aminophosphate antiscalant dose (20 mg/L), the growth rate of gypsum scale in seawater is 6 times more important at 82 °C than 70 °C. Jasbir [8] has examined the influence of a polyamine Phosphonate. It was found that this inhibitor was very effective for controlling all salts that can be precipitated in sea water desalination.

The main objective of this study was to optimise an antiscalant treatment to elude scaling problem in a solar desalination unit hosted in the south of Tunisia and using the solar multiple condensation evaporation cycle principle (SMCEC). For this purpose, a characterisation of the scale and feed water was performed. The effect of three antiscalants on scale crystallisation, from thermodynamics, kinetics and crystallographic point of view, were developed at laboratory scale.

Problematic and unit characterisation

The unit has three major components: solar collectors, evaporation tower and condensation tower. Fig. 1 shows a representative schema of this unit. The structure of the evaporation and condensation towers is completely made of polypropylene tubes. The principle of this installation consists of heating brackish water by solar collectors via a heat plate-exchanger. The temperature varies between 50 and 90 °C with season. Then the hot water is injected to the top of the evaporation tower (via the polypropylene tubes). The latter is equipped with a packed bed (a polypropylene vertical tissue) which has as role to increase the surface of contact water/air and therefore to improve the humidification rate. The saturated humid air migrates towards the condensation tower by natural or forced convection. This vapour is finally condensed in contact with the cold condensation plates. The distilled water is collected in a basin at the bottom of the condensation tower. The basin is made of polypropylene material. Pumps are installed to facilitate water circulation in different parts of the desalination unit. Water which may not be evaporated is collected in a basin at the bottom of the evaporation tower and then recycled. This concentrated water is thereafter discarded generally after 24 hours. After some weeks, scale deposits were observed on the heat exchanger surfaces, on the polypropylene tubes and on the packed bed tissue which require frequent stoppage of the unit. Fig. 2 shows a photo of a polypropylene conducts completely encrusted.

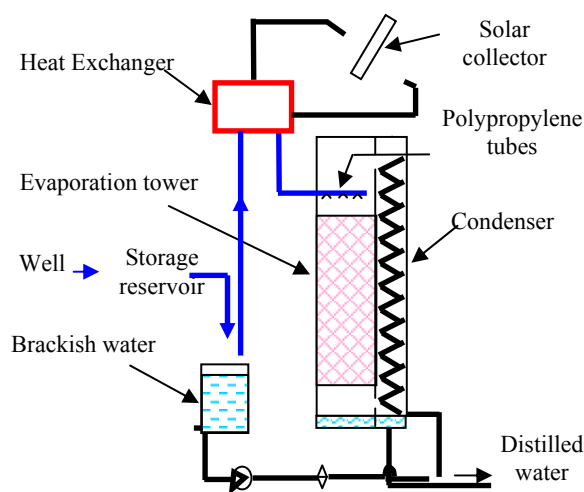


Fig. 1. A representative schema of the desalination unit [1]



Fig. 2. Scale formation on the polypropylene conducts

Water analyses (Table 1) show that the feed water is brackish water (salinity < 10 g/L). It is rich in calcium (520 mg/L) and sulphate ions (2430 mg/L) for only 51 mg/L of bicarbonate ions. The calcium sulphate precipitation is thus more probable than calcium carbonate one. In addition, it should be noted that the scaling tendency of the desalination unit increases with work time by increasing ions concentration responsible to form scale: Ca^{2+} , SO_4^{2-} and HCO_3^- (Fig. 4) [11].

XRD analyses (Fig. 3) show that the formed scales were only gypsum.

Table 1

Physicochemical analyses of well water

Water characteristics	
pH	8.1
Conductivity, $\mu\text{S}/\text{cm}$	6510
Dry residual, g/L	5.6
Calcium, mg/L	520
Magnesium, mg/L	146
Sodium, mg/L	1310
Bicarbonates, mg/L	51.24
Sulphates, mg/L	2430.5
Chlorides, mg/L	803.4
Potassium, mg/L	9
$\Omega_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}$ (supersaturation) at 30 °C	1.35
$\Omega_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}$ (supersaturation) at 90 °C	2.6
Ω_{CaCO_3} (supersaturation / calcite)	3.15

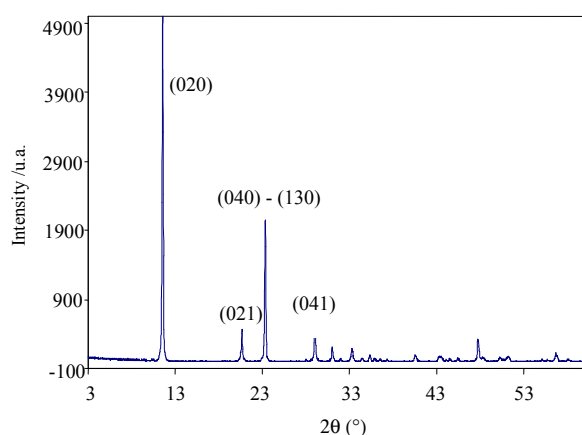


Fig. 3. X-ray diffraction patterns of deposit scale

This threat of scaling is more serious when the temperature increases; indeed, these two salts, CaCO_3 and CaSO_4 , present the particularity to have an inverse solubility phenomenon.

The precipitation of each salt can not occurs only if the ion activities product exceeds the solubility constant.

Knowing the water characteristics, the supersaturation ratios, Ω , of gypsum and calcite were calculated considering the liquid – solid equilibrium between Ca^{2+} and SO_4^{2-} and solid $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ for gypsum (1) and Ca^{2+} and CO_3^{2-} and solid CaCO_3 for calcite (2):

$$\Omega_{\text{gypsum}} = \frac{a_{\text{Ca}^{2+}} a_{\text{SO}_4^{2-}}}{Ks_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}}, \quad (1)$$

$$\Omega_{\text{calcite}} = \frac{a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}}}{Ks_{\text{CaCO}_3(\text{calcite})}}, \quad (2)$$

where a – the ion activity and Ks – the solubility constant of gypsum ($Ks = 3.3 \cdot 10^{-5}$ at 30 °C and $Ks = 3.5 \cdot 10^{-5}$ at 90 °C) [12–13] or calcite ($Ks = 3.09 \cdot 10^{-9}$ at 30 °C) most stable varieties of calcium sulphate and calcium carbonate, respectively.

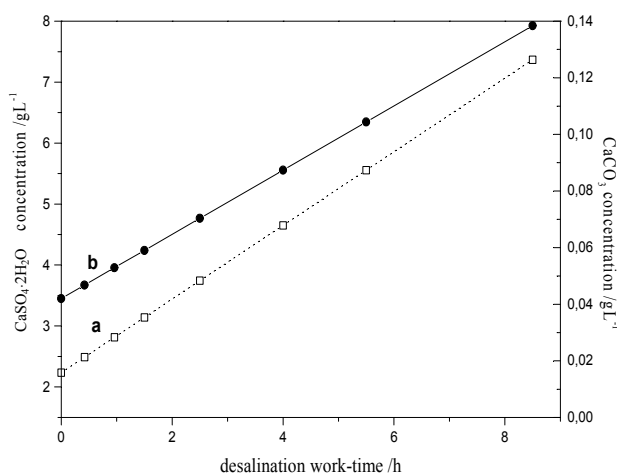


Fig. 4. Effect of water evaporation on (a) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and (b) CaCO_3 concentrations [11]

It can be concluded that well water is initially supersaturated on both calcium sulphate and calcium carbonate: $\Omega_{\text{gypsum}} = 1.35$ and $\Omega_{\text{calcite}} = 3.15$; and therefore susceptible to form scale. When the temperature and the working time of the unit increase, the evaporation rate increases and therefore the supersaturation coefficient of gypsum and the one of calcite increase also. This explains, theoretically, the fastest scale formation in this unit. In these conditions, considering that gypsum and calcium carbonate precipitate together, calcium carbonate constitutes about 1.7 wt % of the mixture [11]. Gypsum is thus the only scale deposits. This confirms the XRD analyses.

In the following, the effect of three antiscalant inhibitors, with different chemical composition, were tested at laboratory scale.

Experimental methods

All crystallization tests were carried out in a 0.350 dm^3 double-walled Pyrex vessel thermostated by water circulation through a constant-temperature bath at the

desired temperature. To avoid the effect of evaporation, especially for high temperatures, the system was fitted with a water-cooled condenser. The total volume of the working solution was 0.200 dm³ and the stable supersaturated solutions employed were prepared by mixing equal volume of equimolar CaCl₂ and Na₂SO₄ solutions previously kept at the work temperature. Chemicals were of analytical grade. The solutions-stirring was performed at constant speed using a magnetic stirrer. The onset of gypsum precipitation was accompanied by the drop of free Ca²⁺ ions, measured by EDTA complexometry titration of small water samples. The experiment was stopped after the concentration of free calcium ion had no more significant change.

Fig. 5 shows the temporal evolution of free calcium ion concentration after mixture of Na₂SO₄ and CaCl₂ solutions in absence of any additives. Three parts can be distinguished on this curve. The first, within $t = 0$ and $t = t_N$ (nucleation time), corresponds to the nucleation step where the concentration of free Ca²⁺ remains constant. From t_N , the crystalline growth stage begins. The free calcium ions concentration decreases gradually until t_S , scaling time, (part II). From t_S , the precipitation rate becomes infinitely slow.

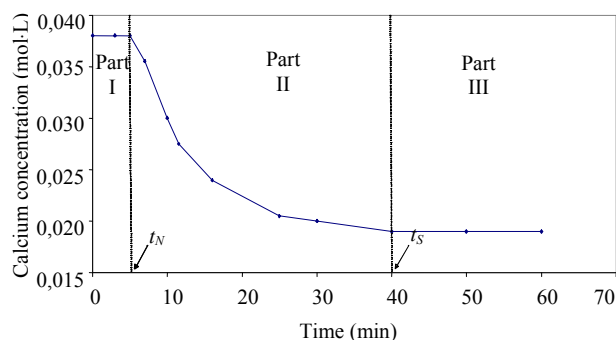


Fig. 5. Evolution of calcium concentration vs time in absence of additives

From this precipitation curve, the supersaturation coefficient Ω at $t = t_S$ and the crystalline growth rate V can be determined as:

$$\Omega_{\text{gypsum}} = \frac{a_{\text{Ca}^{2+}} a_{\text{SO}_4^{2-}}}{Ks_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}} \quad (3)$$

$$V = \frac{d[\text{Ca}]}{dt} \quad (4)$$

Crystallisation tests were done in presence of three antiscalant inhibitors used in the Tunisian industry:

- The STP, Sodium TriPolyPhosphate, mineral with chemical formula Na₅P₃O₁₀, marketed as a powder. It represented 100 % of active matter.
- The Flocon 260, a mixture of polycarboxylate and phosphonate. The active phase represents 35 % of which 79 % of sodium CIS (poly-2-carboxyethyl) phosphinate.
- The RPI 2000, sodium polyacrylate, has an active phase representing 30 %.

Two addition modes of these inhibitors solutions to the system were studied. In the first mode, the inhibitor solution was added to the CaCl₂ solution before mixing. This addition mode is referred below to as mode A in the text for simplicity. The second mode (mode B) consists of adding the inhibitor in the Na₂SO₄ solution.

Throughout this study, the crystallisation temperature was fixed at 70 °C, which is the fluently reached temperature in the desalination plant. The supersaturation was fixed at 6. It corresponds to the one reached before a working time of 4 hours [11].

At the end of each experiment, precipitate was recovered by filtering the precipitating solution through a 0.45 µm filter. The samples were dried at room temperature before analysis by XRD and SEM (Philips Quanta 200). XRD was carried out at room temperature with a Philips X'PERT PRO diffractometer in step scanning mode using Co K α radiation. The XRD patterns were recorded in the scanning range $2\theta = 10-55^\circ$. The d spacing and the normalized intensity of each peak were determined using "X'Pert HighScore Plus" software.

Results and discussion

In Table 2 are recapitulated the kinetic (t_N , t_S , V) and the thermodynamic (supersaturation coefficient Ω) parameters determined for each crystallisation test in absence and in presence of inhibitors.

It can be seen that either the addition mode (A or B), the presence of the inhibitors delay the nucleation time t_N and prolongs the scaling one t_S . The effect on nucleation time depends on the scale inhibitor types: t_N passes from 5 minutes in absence of inhibitors to 10, 14 and 35 minutes in presence of only 1 mg/L of STP, Flocon and RPI respectively. The same effect is observed for t_S . An increase in inhibitors concentrations increases the t_N and decreases the crystalline growth rate V . For example, the presence of 1 mg/L of Flocon slowed down the crystalline growth rate by a factor 4 compared to the base line (precipitation in absence of inhibitors). This factor becomes 21 and 583 when the Flocon concentration increases to 2 and 3 mg/L respectively. It is interesting to note that the addition mode of the inhibitors has an important effect on the kinetics parameters. When it is added in the calcium solution, the inhibitors prolong the nucleation time and the scaling one and decrease the growth rate.

From Table 2, it is also remarkable that, either the antiscalant type, the nucleation time t_N and the scaling time t_S determined in mode B are less significant than those registered when the inhibitors are added following mode A. , in the presence of 1 mg/L of RPI t_N is about 20 minutes according to the mode B and it is 35 minutes according to the mode A. In the same way for t_S : it is about 130 and 145 minutes respectively according to whether the RPI 2000 is added in the solution of sulphate or calcium. Moreover, the crystalline growth rate V of gypsum was also affected. It was slowed down by a factor 4 in presence of 3 mg/L of RPI: it passes from

$2.1 \cdot 10^{-3} \text{ mmol} \cdot \text{l}^{-1} \cdot \text{min}^{-1}$ to $8 \cdot 10^{-3} \text{ mmol} \cdot \text{l}^{-1} \cdot \text{min}^{-1}$ if it was added according to mode B or A, respectively.

At the end of the precipitation, marked by a constant free Ca^{2+} concentration value vs time, the calculated supersaturation values Ω were about 2. Therefore, it can be concluded that, at the contrary to their effect on kinetics parameters, the presence of the inhibitors did not

influence the thermodynamic condition of the solution at the end of precipitation. In spite of elevated operate temperatures, the Ω values remain sharply superior to 1 (thermodynamics equilibrium). This metastable state can be explained by the presence of foreign ions in the $\text{CaSO}_4\text{-H}_2\text{O}$ system [11].

Table 2

Effect of the addition mode of the tested inhibitors on t_N , t_S , V and Ω

	C , mg/L	Inhibitors added in calcium solution MODE A				Inhibitors added in sulphate solution MODE B			
		t_N , min	t_S , min	Ω	V , $\text{mmol} \cdot \text{l}^{-1} \cdot \text{min}^{-1}$	t_N , min	t_S , min	Ω	V , $\text{mmol} \cdot \text{l}^{-1} \cdot \text{min}^{-1}$
STP	0	5	30	1.88	3.5	5	30	1.88	3.5
	1	10	42	1.96	2	5	35	2.04	2.5
	2	15	90	2.04	1.2	10	60	2.04	0.9
	3	20	120	2.04	0.3	15	106	2.04	0.2
Flocon	0	5	30	1.88	3.5	5	30	1.88	3.5
	1	14	40	1.96	0.8	7	30	1.96	0.6
	2	38	300	2.04	0.2	30	230	2.04	0.2
	3	55	400	2.25	$6 \cdot 10^{-3}$	45	260	2.12	$3.6 \cdot 10^{-2}$
RPI	0	5	30	1.88	3.5	5	30	1.88	3.5
	1	35	145	1.96	0.3	20	130	1.96	0.2
	2	45	395	2.04	$2.8 \cdot 10^{-2}$	40	385	2.04	$2.4 \cdot 10^{-2}$
	3	65	590	2.16	$8 \cdot 10^{-3}$	50	520	2.16	$2.1 \cdot 10^{-3}$

The fact that the tested inhibitors are more effective when they are added in the calcium solution can be interpreted by the affinity of the calcium ion to the functional groups ($-\text{PO}_3^{2-}$) of STP, ($-\text{COO}-$) of RPI and ($-\text{PO}_3^{2-}$, $-\text{COO}-$) of Flocon. Indeed, the calcium ion has the possibility to react with SO_4^{2-} or these functional groups. Because of its affinity to these groups, Ca^{2+} spends more time in their neighbour than of the sulphates ion [14]. According to the mode A, the possibility of forming a germ is thus more probable than in the case of mode B.

Fig. 6 and 7 show that, by comparing the kinetics parameters, the RPI 2000 antiscalant is the most efficient. It delays more the nucleation step and the crystalline growth one of gypsum crystallisation. It can be also concluded that the STP is the least effective inhibitor. Indeed, it should be noted that for temperature superior to 70°C , the polyphosphate STP molecules are hydrolysed in shorter chains to lead finally to the orthophosphate form which does not inhibit any more [7].

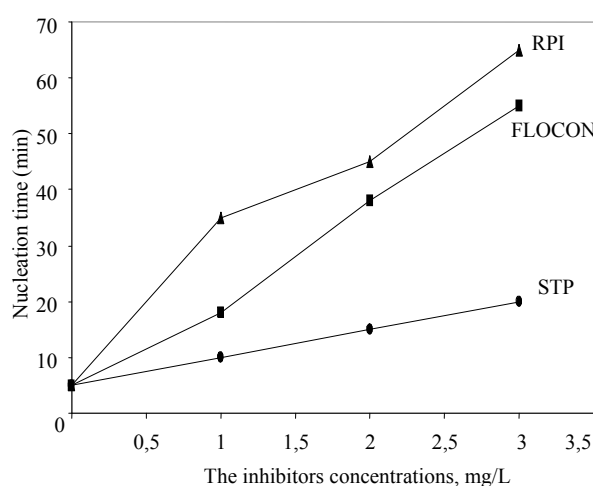


Fig. 6. Effect of the tested inhibitors concentrations on the nucleation time t_N

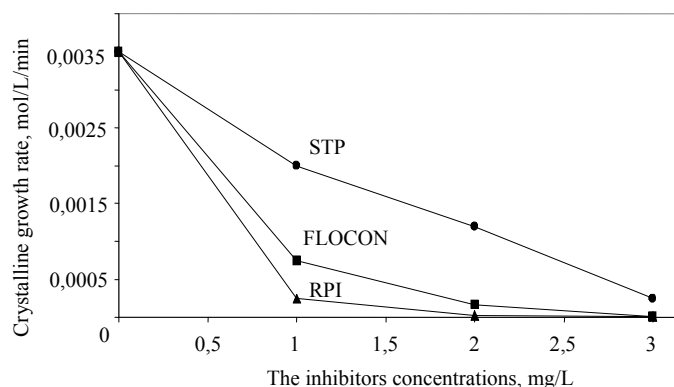
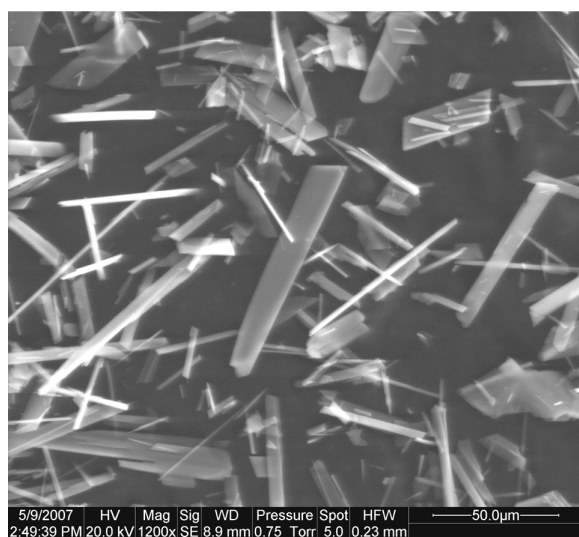


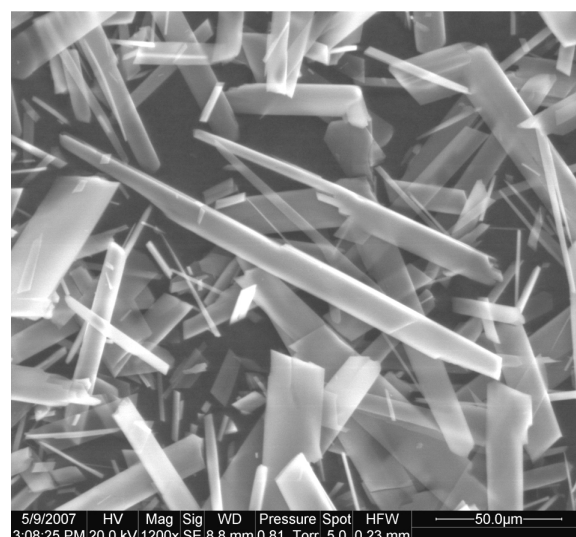
Fig. 7. Effect of the tested inhibitors concentrations on the crystalline growth rate V

In the goal to better understand the effect of the tested antiscalant on gypsum crystallisation, SEM analyses were done. Fig. 8

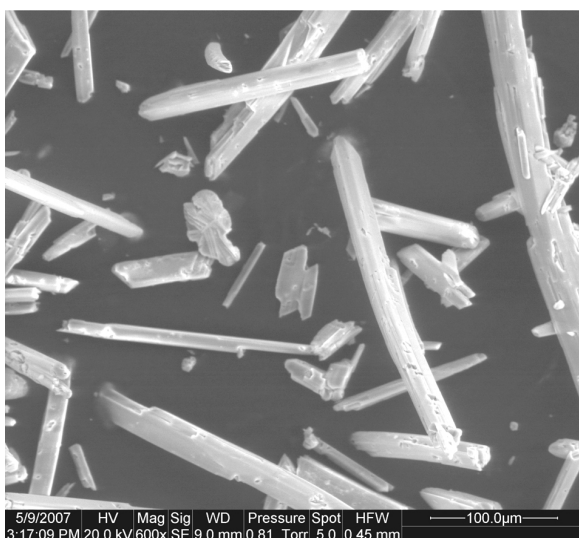
shows the photos of the recuperated precipitates, at the end of experiments, in presence of 3 mg/L of STP, Flocon, RPI and in absence of inhibitors. In absence of inhibitors, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystallized in a needle form (Fig. 8, *a*) with an average size of 100 μm . The presence of inhibitors did not affect the gypsum morphology in the same way. The addition of STP influences only the needles size (Fig. 8, *b*). The presence of Flocon alters the gypsum morphology (Fig. 8, *c*). This influence is even more remarkable when the added inhibitor is RPI 2000 (Fig. 8, *d*) where the laminated structure is completely destroyed by the adsorption of the additive molecules on the gypsum crystalline surface. X-ray diffraction analysis shows that the addition of the tested inhibitors did not change the precipitates variety which remain $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.



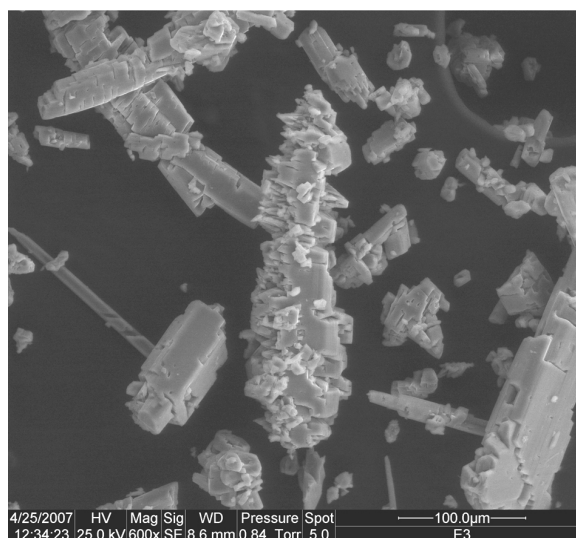
a



b



c



d

Fig. 8. SEM photos of gypsum precipitated at 70 °C (a) in absence of inhibitors and in presence of 3 mg/L of (b) STP, (c) Flocon and (d) RPI 2000

Conclusion

The scale deposit in the studied desalination unit was identified as gypsum. Three chemical antiscalants were tested at laboratory scale and in conditions reported those encountered in the desalination plant. It was shown that the tested inhibitors are more efficient when they are added in the calcium solution. From kinetics data analyses, it can be concluded that the RPI 2000 is the most effective inhibitor. SEM analysis shows that the RPI influences gypsum crystallisation by adsorption on crystal growth sites. The X-ray diffraction analysis showed that the addition of the inhibitors did not affect the deposits scale structure.

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