Desalination and Water Treatment
www.deswater.com

7 (2000) 86–92

1944-3994 / 1944-3986 © 2009 Desalination Publications. All rights reserved.

Experimental investigation of scaling control by a non-phosphorous polymer: polyaspartic acid

A. Martinod[a], A. Neville[a], M. Euvrard[b*]

[a]*School of Mechanical Engineering, University of Leeds, Leeds, LS2 9JT, UK*
[b]*Institut UTINAM, UMR 6213, Université de Franche-Comté, 25030 Besançon, France*
Tel. +33 3 81 66 20 45; Fax +33 3 81 66 20 33; email: myriam.euvrard@univ-fcomte.fr

Received 3 October 2008; accepted in revised form 12 April 2009

ABSTRACT

Environmental issues lead to study the effect of environmentally-friendly additives without phosphorous to prevent scaling in desalination plants. In this way, the role of polyaspartic acid on the crystallization of calcium carbonate in seawater was investigated. An experimental procedure permitted to follow in situ and in real-time the growth of scale particles in the micrometric range and experimental results were fitted with a mathematical model based on a diffusion-controlled process that allows determining the kinetic parameters of crystallization. The results showed that polyaspartic acid may strongly influence the nucleation/growth process. At a concentration of 1 ppm, it reduces the surface coverage of deposits on the substrate by decreasing the micronic particles. At a concentration of 4 ppm added at the start of the experiment, it strongly inhibs the development of crystals, the lateral growth rate was almost zero and the effect of the additive was close to phosphino polycarboxylic acid. When the macromolecule was added after 10 min of experiment, it highly decreased the growth of crystals. The role of this additive in affecting the crystallization is discussed in relation to the principal mechanisms by which it acts in comparison with other additives.

Keywords: Green additive; Crystallization; Growth; Calcium carbonate; PASP

1. Introduction

The control of crystallization processes is one of the parameters to consider in desalination plants. Due to its low solubility, calcium carbonate is the major salt which may lead to the formation of scale in the pipes [1–3]. The appearance and persistence of the three crystalline polymorphs, calcite, aragonite and vaterite are highly dependent on the local condition of precipitation temperature, supersaturation and the presence of additives in water. Some phosphorous compounds are well-known to inhibit the development of crystals but they may cause severe damage to the environment such as eutrophication [4,5]. One of the current challenges is to understand how environmentally–friendly additives without phosphorous influence the crystallization process to prevent scaling in desalination plants. Previously, several studies were carried out on the effects of scaling inhibitors [6–8] but they did not visualize their effects *in situ* and in real time.

This research aims to improve the understanding of the role of green additive on scaling phenomena in seawater. The electrochemical and optical technique presented in this paper allows the follow-up of crystallization and the effects of inhibitors at the solid-liquid interface.

---

* Corresponding author.

Presented at EuroMed 2008, Desalination for Clean Water and Energy Cooperation among Mediterranean Countries of Europe and the MENA Region, 9–13 November 2008, King Hussein Bin Talal Convention Center, Dead Sea, Jordan.

The effects of polyaspartic acid, a carboxylated protein, were studied by this way; the role of this additive in affecting the crystallization will be discussed in relation to the principal mechanisms by which it acts in comparison with other additives.

2. Experimental conditions

2.1. Chemicals

Synthetic water ("reference water") was prepared as follows: two brines were prepared and mixed 50:50 just before the experiments with composition reported in Table 1. The reactants were purchased from Aldrich. The resulting composition was close to that of the North Sea.

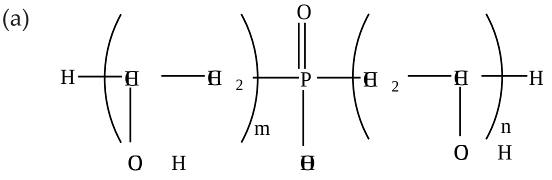
Polyaspartic acid (PASP) was investigated; it was obtained from the sodium salt. It is defined as green chemical additive because it enters in the PLONOR list (Pose Little or NO Risk) which is based on environmental tests to quantify toxicity, bioaccumulation and biodegradability [7].

In order to compare it to conventional additive, phosphino-polycarboxylic acid (PPCA) was studied too because it is often used in the anti-scale treatment of water [8,9]. The molecular structures of the additives are presented in Fig. 1 and their main characteristics and ecotoxicological properties are presented in Table 2 and 3.

Table 1
Composition of the brines

	Brine 1	Brine 2
NaCl, $g.L^{-1}$	64.10	63.00
KCl, $g.L^{-1}$	2.25	0
$MgCl_2$, $g.L^{-1}$	5.75	0
$CaCl_2$, $g.L^{-1}$	28.45	0
$NaHCO_3$, $g.L^{-1}$	0	1.55

(a)



PPCA, M.Wt.~3,600g/mol

(b)

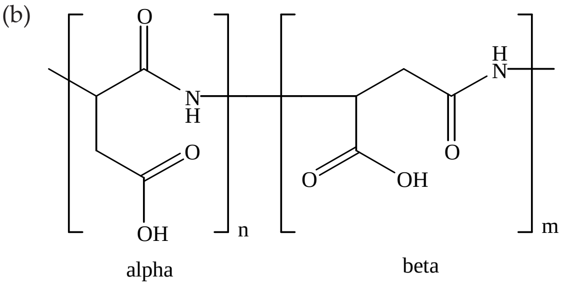


Fig. 1. Molecular structures of the additives: (a) phosphinopolycarboxylic acid (PPCA), (b) polyaspartic acid.

For the experiments, the chosen concentrations were 1 and 4 ppm; additives were added at the start of the experiment and after 10 min of crystallization in order to study their effects on the nucleation and growth of crystals.

3. Procedures

3.1. Crystallization and morphology of the calcium carbonate particles

In order to induce scaling and to accelerate the formation of crystals, we have used an electrochemical process which induces a supersaturation near the working elec-

Table 2
Characteristics of the additives

Additive description/ Reference	Details	Supplier	Active content (%)	Molecular weight
Non-green PPCA/ Bellasol S40	Phosphino polycarboxylic acid	BWA	42	~3600
PASP/T/1120	Poly-α-β-D,L-aspartic acid	Champion Technologies	39	Low

Table 3
Ecotoxicological properties of the additives

Additives	Toxicity	Bioaccumulation	Biodegradability
PPCA	$EC_{50\ 48\ h\ Daphnia} > 320$ mg/L $LC_{50\ 96\ h\ Fish} > 1000$ mg/L	$\log P_{ow} < 0$	Not readily biodegradable
PASP	$EC_{50\ 48\ h\ Daphnia}$: 1798 mg/L $LC_{50\ 96\ h\ Fish}$: 2117 mg/L	$\log P_{ow} < 0$	> 70% Inherent biodegradability testing OECD 301A-F (1992f)

trode. The procedure consists of polarizing an electrode to stimulate the reduction of oxygen. Due to the associated increase in pH, bicarbonate ions form carbonate species which in turn precipitate with calcium ions to produce scale at the surface of the electrode. The electrochemical cell fully described previously [10] integrates three electrodes: the working electrode is a removable plug comprising a circular stainless steel electrode, the counter electrode is a window that was made electrically conducting by deposition of tin oxide and the reference electrode is a silver wire that was pretreated with a diluted solution of hydrochloric acid (Ag/AgCl electrode).

The optical and measurement setup was already presented [10,11]; the crystals were imaged at different times and several parameters were determined: density number, surface and diameter, shape factor and surface coverage S (t) (%).From a nucleation-growth model described previously [11], the experimental data enable determination of the type of nucleation and the mean lateral growth rate of crystals. The calculation of the extended surface area *Sext(t),* the surface that would be covered by all the nuclei at time t without effects of overlap was done from the actual covered surface area *S(t)* as follows:

$$S(t) = 1 - \exp(-S\exp(t)) \tag{1}$$

$$Sext(t) = (M k_l N_0 / \rho)[t - 1/A + \exp(-At/A)] \tag{2}$$

A is the nucleation rate, k_l the lateral growth rate (mol/μm/s), M is the molar mass of $CaCO_3$ (100 g/mol) and ρ is the density of the crystals ($\rho = 2.71\times10^{-12}$ g/μm^3 for calcite).

The kinetic parameters can be evaluated for small or large nucleation rates.

In case of instantaneous nucleation, if $At >> 1$, i.e. for sufficiently long observation times, e.g. $t > 1$ s, Eq. (2) is simplified as follows:

$$Sext(t) = -\ln(1 - S(t)) = M k_l N_0 t / \rho \tag{3}$$

Sext(t) is a linear function of t and

$$k_k = -\ln(1 - S(t))\rho / M N_0 t \tag{4}$$

In the case of progressive nucleation**,** the value of *Sext* is quantified as follows:

$$Sext(t) = -\ln(1 - S(t)) = M k_l N_0 A t^2 / \rho \tag{5}$$

Sext(t) is a linear function of t^2.

4. Results

4.1. Reference water

In reference water, as soon as the electrical potential was applied, numerous small crystals appeared spontaneously at the surface of the electrode. Then, they grew homogeneously; SEM micrographs confirmed the homogeneity of the calcium carbonate particles composed of calcite (Fig. 2). Because growth in crystal size was very fast, after 40 min, the coalescence of crystals was too extensive to permit the characterization of individual crystals; only the surface coverage was quantified. The scaling power of the water was high because after 60 min the coverage surface was of 33% (Fig. 3); the number of crystals was 130 (±20) per 600 μm². As *Sext* is a linear function of time, it indicates that the nucleation was instantaneous (Fig. 4). The constant lateral growth rate was constant during the experiment: of about 1.4× 10^{-15} (mol/μm/s) (Table 4).

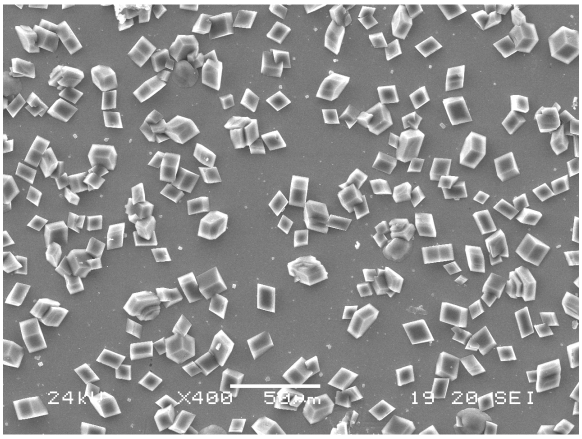


Fig. 2. Reference water: SEM photo of crystals after 60 min of polarization.

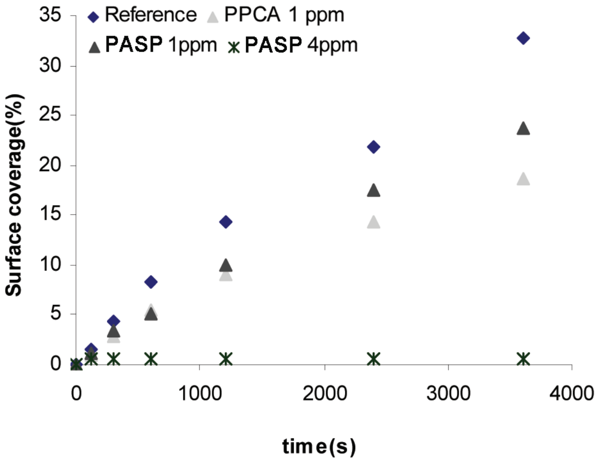


Fig. 3. Surface coverage by calcium carbonate during the experiment.

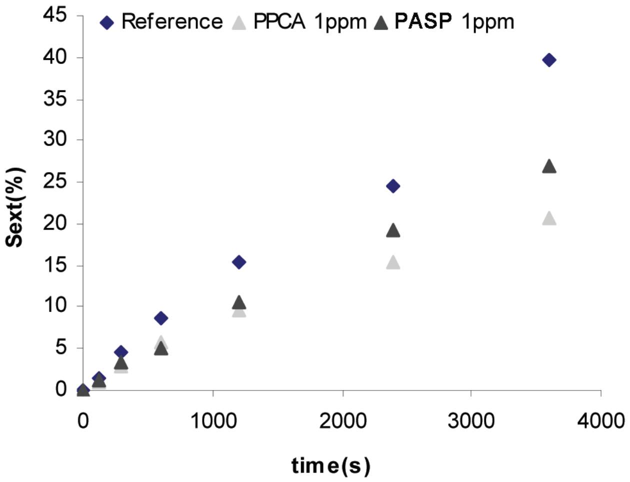


Fig. 4. *Sext* in function of time.

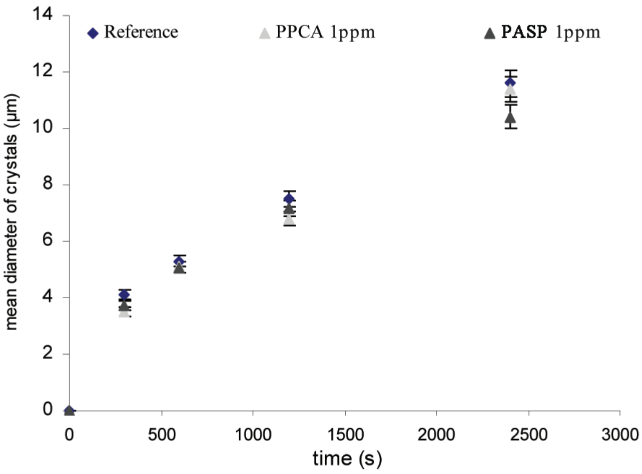


Fig. 5. Mean diameter of micronic crystals during the experiment (additives added at $t = 0$ min).

Table 4
Lateral growth rate (mol/µm/s) of the crystals of $CaCO_3$ with 1 ppm of PASP in function of time

Time (s)	No additive	PASP 1 ppm
120	1.4×10^{-15}	1.4×10^{-15}
300	1.6×10^{-15}	1.9×10^{-15}
600	1.6×10^{-15}	1.4×10^{-15}
1200	1.4×10^{-15}	1.5×10^{-15}
2400	1.1×10^{-15}	1.3×10^{-15}

4.2. Influence of polyaspartic acid added at the start of crystallization

Polyaspartic acid induces a modification of the crystallization of calcium carbonate.

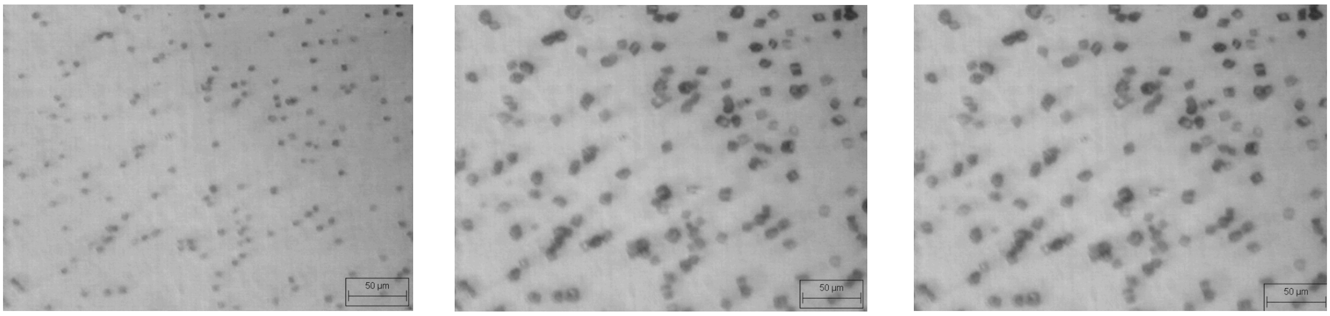
At a concentration of 1 ppm, it reduced the surface coverage: it was of 23.5% after 60 min of the experiment (Fig. 3) whereas it was of 33% in reference water. Fig. 5 indicates that the mean size of crystals is close to that of reference water but the number of detectable crystals decreased: it was 90 (±20) per 600 µm². It must be noted that the photos of the crystals obtained *in situ* by optical microscopy (Fig. 6) during the experiment show the formation of a film on the surface of the electrode. The pictures obtained by SEM (Fig. 7) indicate that the shape of crystals were similar to those present in reference water.

The calculation of *Sext* indicates that the nucleation was instantaneous (Fig. 4). The coverage *Sext* can be expressed as a linear function of time as follows:

- in reference water $Sext = 0.011\,t$
- in the presence of polyaspartic acid at a concentration of 1ppm: $Sext = 0.008\,t$
- in the presence of PPCA at a concentration of 1 ppm: $Sext = 0.006\,t$

The lateral growth rate was not significantly different to the value calculated for reference water (Table 4).

At a concentration of 4 ppm, the effect of PASP on calcium carbonate particles increased strongly. No more crystals were quantified by optical microscopy during the experiment indicating that the surface coverage



(a) (b) (c)

Fig. 6. Seawater with 1 ppm of PASP — optical photos of crystals from the visualization in situ (a) 5 min, (b) 20 min, (c) 60 min.

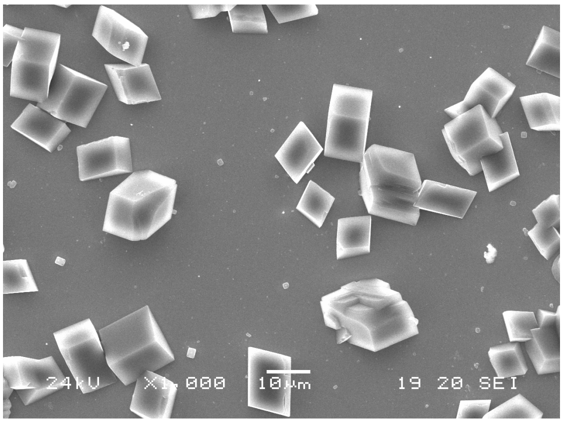


Fig. 7. Seawater with 1 ppm of PASP — SEM photo of crystals after 60 min of polarization.

detectable is less than 1%. SEM analysis revealed the presence of small crystals distorted with a mean size of about 0.5 µm (Fig. 8).

On the one hand, compared to PPCA, the reduction of the surface coverage was no so high in presence of 1 ppm of polyaspartic acid. On the other hand, at a concentration of 4 ppm, the effect of polyaspartic acid is close to PPCA; the surface coverage was less than 1%.

4.3. Influence of polyaspartic acid added after 10 min of crystallization

To study the effect of the macromolecule on the growth of crystals, 4 ppm of the additive was added to the aqueous solution after 10 min of crystallization. At this concentration polyaspartic acid affected to a great extent the morphology of the crystals (Fig. 9). Two kinds of crystals of calcium carbonate were observed:

- Small: with a size less than 10 µm
- Big: with a size more than 15 µm

Both categories of crystals were distorted. The big crystals had a really specific shape: the base of the crystals (in contact with the metal surface) seemed to be larger than the top of the crystal like a hat-shape. No additive film was detected with 4 ppm of PASP added after 10 min (contrary to what has been observed with 4 ppm of PASP added at $t = 0$).

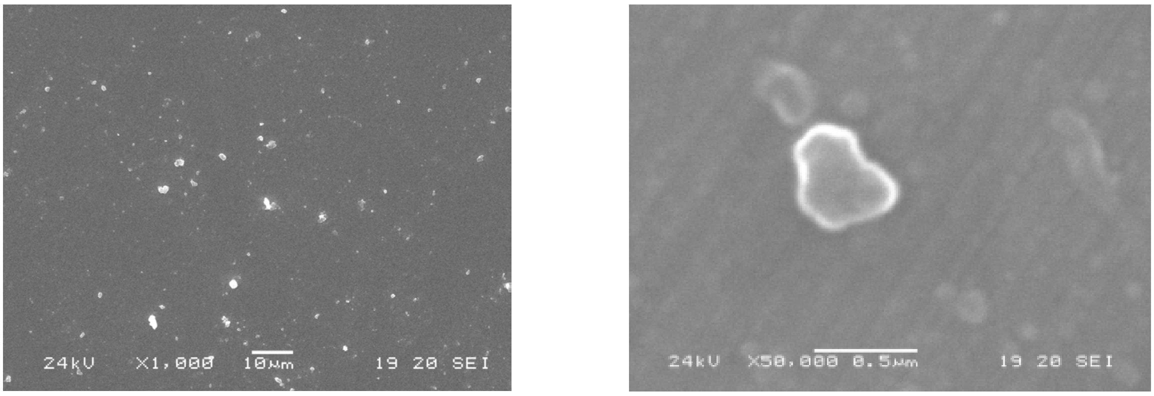
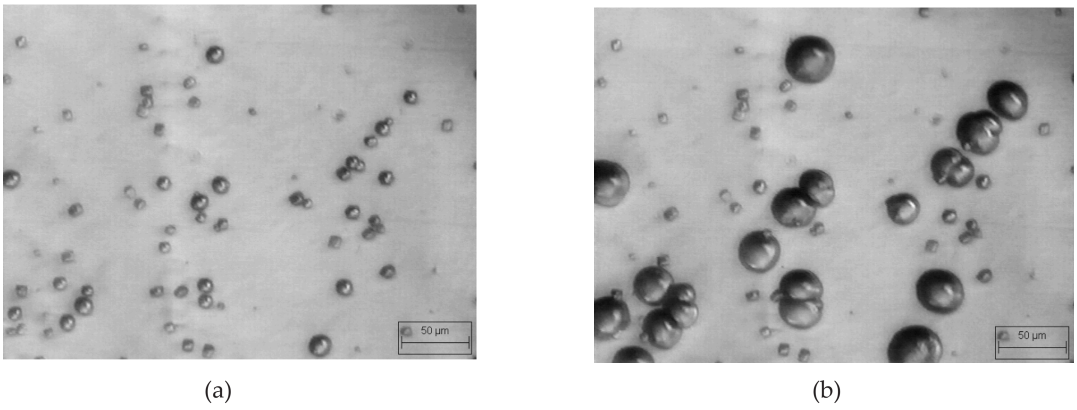


Fig. 8. Seawater with 4 ppm of polyaspartic acid added at the start of the experiment — SEM photo of crystals after 60 min of polarization.



(a) (b)

Fig. 9. Seawater with 4 ppm of PASP added after 10 min of crystallization — optical photos of crystals from the visualization in situ (a) 20 min, (b) 60 min.

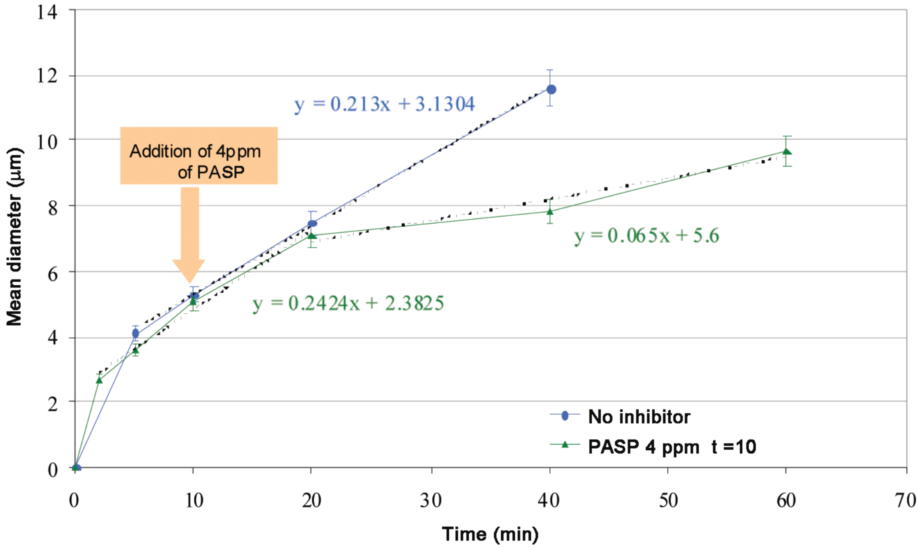


Fig. 10. Mean diameter of micronic crystals during the experiment (additives added at t = 10 min).

Quantitative analysis shows that the surface coverage is lower than in reference water and that the mean size of crystals was reduced (Fig. 10).

It must be noted that the slow down of the kinetics was greater with the addition after 10 min. of PPCA (the growth of the crystals were blocked after 10 min). In the case of PASP, no complete stop of the growth was observed.

5. Discussion

Compared to the crystallization that occurred in reference water, the presence of PASP may lead to a decrease of the crystallization of calcium carbonate.

The first experiments suggested that PASP may act by reducing the crystallization of the salt during the first step of crystallization The presence of the additive at a concentration of 1 ppm may quickly block the development of some submicronic crystals which were no more detectable. Nevertheless, the other crystals grew as in reference water. So, it must be noted that whereas the inhibition of PASP on the crystallization of calcite is not so high than this of PPCA, it may lead to a decrease of the surface covered by calcium carbonate. At concentration of 4 ppm, PASP was enough to limit highly the growth of all the crystals, only submicronic particles were observed.

The second experiments indicated that when PASP was added at a concentration of 4 ppm after 10 min, it may highly modify the growth of crystals.

So, this macromolecule interacts on the crystallization of calcium carbonate and can modify the ongoing processes. Different ways of action of the polymers can be viewed [12]:

- It can alter the shape of the primary nanoparticles by selective adsorption and/or enrichment onto specific crystal faces which leads to growth inhibition of these crystals faces
- By complexing the ions, PASP can block or retard the growth path of single ions making assembly effects more significant then the classical crystallization route
- It can colloidally stabilize metastable intermediates such as amorphous precursor structures.

Usually the added polymers adopt more than one role mentioned previously [12].

The results indicated that PASP induces a decrease of the number of micronic crystals and promotes a modification in the shape of crystals. From these results, it is demonstrated that PASP may act preferentially by selective adsorption on crystals. In agreement with this conclusion, previous studies had demonstrated PASP consists of carboxylated residues that favor a a-helicoidal structure in solution [13] and when adsorbed to calcite, PASP was suggested to adopt a b-strand conformation.

This study also shows that the adsorption of PASP is fast during the crystallization process; at a concentration of 1 ppm, the polymer may quickly block the growth of some crystals as the number of crystals detected showed it. Moreover the addition of PASP after 10 min of crystallization indicated that it quickly delayed the growth of a few crystals.

6. Conclusion

This study has demonstrated that it is possible to visualise *in situ* and in real time the effects induced by additives on the modification of crystallization on a metallic surface. It gives qualitative and quantitative pieces of information about the nucleation stage and the growth of crystals.

The results showed that polyaspartic acid may strongly influence the nucleation/growth process.

At a concentration of 1 ppm, it reduces the surface coverage of deposit on the substrate by a decrease of the micronic crystals. At a concentration of 4 ppm added at the start of the experiment, it strongly inhibits the development of crystals, the lateral growth rate was quasi nil and the effect of the additive was close to phosphino ploycarboxylic acid. SEM analysis had shown that this protein leads to the formation of submicronic distorted particles. When the macromolecule was added after 10 min of experiment, it decreased the growth of a few crystals.

The results suggest that PASP may act preferentially by selective adsorption on crystals; the kinetic of adsorption was fast.

Many further studies will be required in order to understand the effects of scaling treatments in relation with the structures and concentrations of macromolecules, with the physico-chemical conditions such as the composition of water and or the concentration of carbon dioxide.

Refrences

[1] K. Al-Anezi and N. Hilal, Desalination, 204 (2007) 385–402.
[2] B. Amor, D. Zgolli, M.M. Tlili and A.S. Manzola, Desalination, 166 (2004) 79–84.
[3] M. Jefferies and D. Comstock, Desalination, 139 (2001) 341–344.
[4] Commission, M.M.o.t.O., 2003 Strategies of the OSPAR Commission for the Protection of the Marine Environment of the North-East Atlantic. Bremen: 25 June 2003, ref. no. 2003-21.
[5] S. Lattemann and T. Höpner, Desalination, 220 (2008) 1–15.
[6] V. Tantayakom, T. Sreethawong, H. Scott Fogler, F.F. de Moraes and S. Chavadej, J. Colloid Interf. Sci., 284 (2005) 57–65.
[7] A. Ketsetzi, A. Stathoulopoulou and K. Demadis, Desalination, 223 (2008) 487–493.
[8] Y. Tang, W. Yang, X. Yin, Y. Liu, P. Yin and J. Wang, Desalination, 228 (2008) 55–60.
[9] E. Dalas, A. Chalias, D. Gatos and K. Barlos, J. Colloid Interf. Sci., 300 (2006) 536–542.
[10] M. Euvrard, C. Filiatre and E. Crausaz, J. Crystal Growth, 216 (2000) 466–474.
[11] M. Euvrard, F. Membrey, C. Filiatre, C. Pignolet and A. Foissy, J. Crystal Growth, 291 (2006) 428–435.
[12] H. Cölfen, Current Opinion Colloid Interf. Sci., 8 (2003) 23–31.
[13] E.M. Burke, Y. Guo, L. Colon, M. Rahima, A. Veis and G.H. Nancollas, Colloids Surfaces B: Biointerf., 17 (2000) 49–57.