CHANGES IN THE GROWTH MORPHOLOGY OF GYPSUM DUE TO ORGANIC ADDITIVES OF INDUSTRIAL INTEREST

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INTRODUCTION

The purpose of this research is to study the growth morphology of gypsum in aqueous solution and in the presence of organic matter added to the environment of crystallization, with the aim to assess the morphological changes characterizing the final habit of gypsum. Several experiments of crystallization by evaporation were carried out, leading to the formation of many gypsum crystals, observed by optical and scanning electron microscopy.

The observations made it possible to identify the phosphonates EDTMP (Ethylene Diamin TetraMethylene Phoshonic acid) and DTPMP (Diethylene Triamine PentaMethylene Phoshonic acid) and copolymers SP1, SP3 and SR3, as the substances more appropriate to change significantly the final morphology of gypsum, and to determine the disappearance of its characteristic elongated and acicular habit.

STUDY OF GYPSUM

Calcium sulfate dihydrate ($CaSO_4{\cdot}2H_2O$, space group $A2/a$, $a = 5.630$, $b = 15.150$, $c = 6.230$ Å, $\beta = 113.80°$ (de Jong & Bouman, 1939; Follner *et al.*, 2002) is the most abundant natural sulphate and is frequently formed during the early stages of evaporitic formation. It also occurs in massive calcium sulphate deposits in association with limestone and shales. Due to its high solubility, gypsum significantly influences the geochemical distribution of Ca^{2+} and SO_4^{2-}.

This mineral is widely used in various industrial sectors as a lubricant during drilling of oil wells, in the preparation of the paper, plaster of Paris, as fertilizer in agricultural field and especially as a retardant for commissioning during the hydration of a concrete paste.

In industrial applications gypsum is the source-rock for wallboard plaster manufacturing and it plays an important role in gypsum-based building materials (Livingston *et al.*, 1991; Middendorf & Budelmann, 1955; Bosbach *et al.*, 1996). Gypsum also is known to be subject to crystal growth inhibition by some substances which act as cement set retarders. Gypsum is arguably the most important of all cement additives, being universally added to commercial Portland cements to suppress the rapid hydration reaction to calcium aluminate. Dissolving gypsum flushes calcium and sulphate ions into solution within seconds of first wetting the cement (Hall & Cullen, 1996).

Gypsum is an important mineral from both geological and industrial point of view. For this reason its nucleation, growth and morphology were widely investigated. Variety of technologies requires developing procedures that allow a controlled crystallization and morphology of crystals.

Some authors attempted to reproduce natural solutions in order to study the influence of supersaturation and impurities on growth kinetics and morphology (Cody & Shanks, 1974; Austin *et al.*, 1975; Kushnir, 1980; Rinaudo *et al.*, 1988).

For industrial aims, such as scale prevention or improvement of plaster properties, many inorganic and organic additives were tested (Liu & Nancollas, 1973; Liu & Nancollas, 1975; Murat & Foucault, 1977; van Rosmalen, 1981; Amathieu, 1985; Rinaudo *et al.*, 1988).

In the present work the crystallization of gypsum in aqueous solution was carried out to assess what {*hkl*} forms characterize the final morphologies, in the presence of specific habit modifiers. The aim of this investigation is to study the inhibiting effects of phosphonates and copolymers. New generations of organic polymers (sulphonates, phosphonates, acrylates and other polymers) nowadays find a widespread use as plasticizers in the cement mixtures. We have tested as well the habit-modifying effects of the phosphonic ethylenediamine-tetra-methylene phosphonic acid (EDTMP) and diethylene-triammino-pentamethylene-phosphonic acid (DTPMP) and copolymers SP1, SP3, SR3.

MATERIALS AND METHODS

The gypsum crystals were obtained by mixing two equimolar solutions ($2.5 \cdot 10^{-2}$ M) of calcium chloride ($CaCl_2 \cdot 2H_2O$) and sodium sulphate (Na_2SO_4). For each experiment we used a volume of aqueous solution of 200 ml, placed in an oven to evaporate at a constant temperature of 35°C. The evaporation of the solution is dictated by the need of increasing the concentration of ionic species that is the progressive increasing of the supersaturation of the solution, in order to reach the nucleation and the subsequent growth of crystals.

In addition to the experiments carried out in neutral environment experiments in alkaline environment were also performed by adding sodium hydroxide (0.1 M of NaOH).

Many experiments were carried out using two different types of additives. Initially we used two phosphonates such the EDTMP and the DTPMP (Table 1), and subsequently we used three copolymers consisting of acrylic polymers of monomeric composition with different molecular weight, indicated by the letters of reference SP1, SP3 and SR3 (Fig. 1).

Concentrations (from $1 \cdot 10^{-6}$ M to $1 \cdot 10^{-2}$ M) of phosphonates and copolymers in the growth solution have been used to assess how the change affects the final morphology of gypsum. Further, amounts between 0.0004 and 0.4% were used, comparable with those employed in cement.

Table 1 - Molecular characteristic of the employed phosphonate molecules.

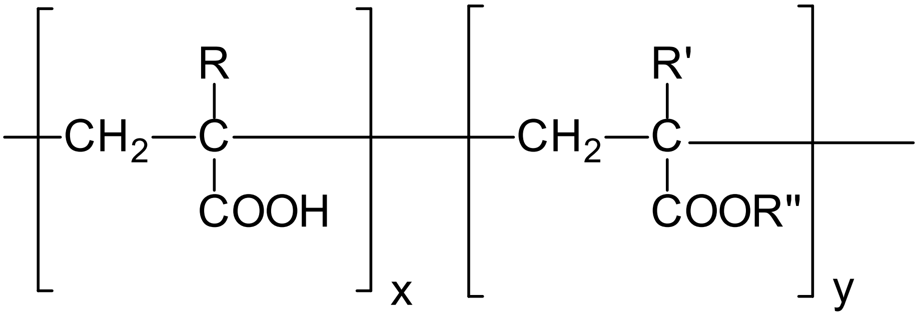
	Chain length (linear approx.) [Å]	Molecular weight [g/mol]	N° Active anionic group (PO_3^{2-})
EDTMP	16	436	4
DTPMP	20	573	5

RESULTS

Phosphonates

The experiments carried in the presence of phosphonates revealed significant changes in the characteristic acicular habit of gypsum, especially on {120} and {$\bar{1}$11} forms.

The use of EDTMP resulted in a decrease in the crystal size, especially concerning the elongation along the [001] direction which appears to be significantly reduced. When the concentration in solution



$$\left[-CH_2-\overset{\displaystyle R}{\underset{\displaystyle COOH}{C}}- \right]_x \left[-CH_2-\overset{\displaystyle R'}{\underset{\displaystyle COOR''}{C}}- \right]_y$$

Fig. 1 - General structure of the copolymers used.

reaches $1 \cdot 10^{-3}$ M it was possible to observe a very significant transformation of the habit of gypsum: the forms {010} and {120}, which usually are the most important, are either absent or poorly developed, and the forms $\{\bar{1}11\}$ and $\{0\bar{1}1\}$ are not detectable in crystals. Further, there is the appearance of the form {001}, usually not present, which becomes the most developed and able to give the quite flattened look of gypsum crystals (Fig. 2).

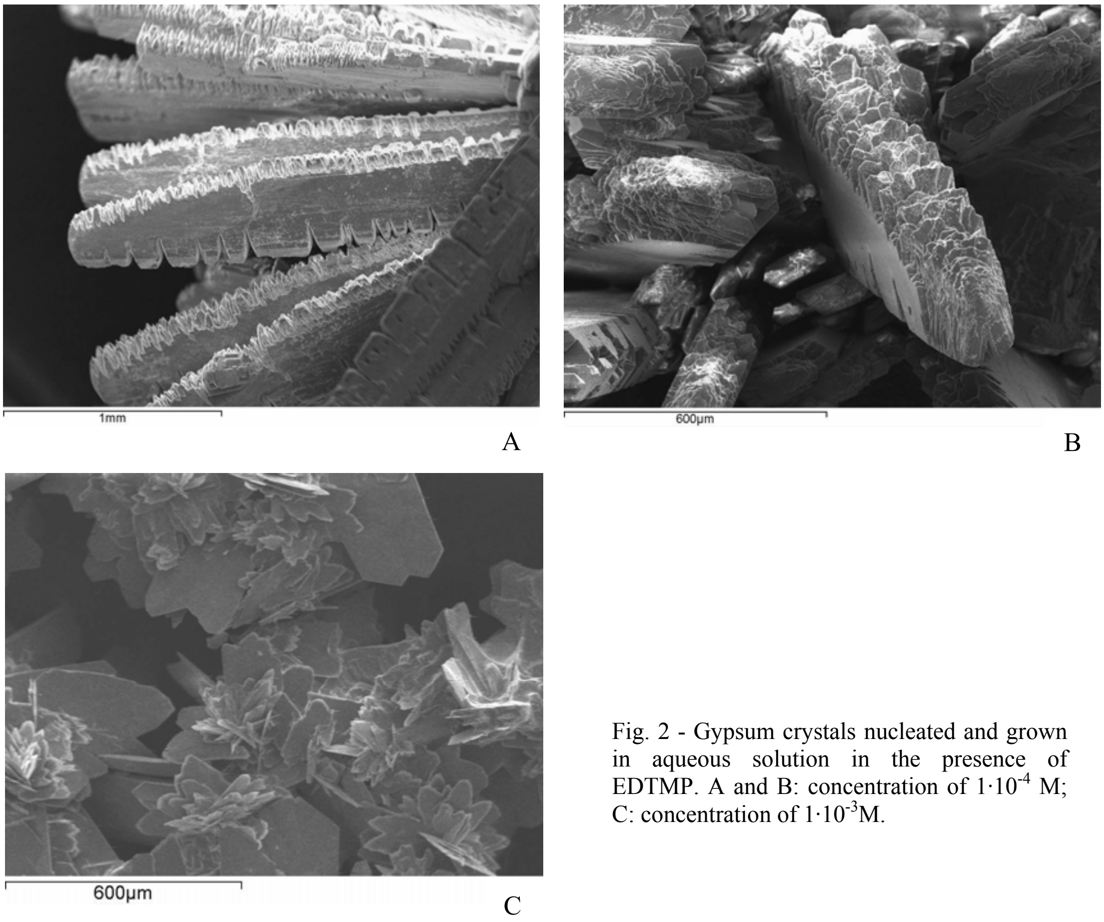


Fig. 2 - Gypsum crystals nucleated and grown in aqueous solution in the presence of EDTMP. A and B: concentration of $1 \cdot 10^{-4}$ M; C: concentration of $1 \cdot 10^{-3}$M.

Also DTPMP originated a significant decrease in the [001] crystal elongation. Fig. 3a shows the crystalline morphology of gypsum grown in the presence of DTPMP ($3.5 \cdot 10^{-4}$ M), and we can see the skeletal appearance of the crystal, especially in correspondence of the forms {120} and {010}. The use of higher concentrations of $1 \cdot 10^{-4}$ M (Fig. 3b) and $5 \cdot 10^{-3}$ M (Fig. 3c), triggers the formation of "jagged" crystals with a fairly regular repeated indentations, as was found when using EDTMP in concentration of $1 \cdot 10^{-4}$ M.

$1 \cdot 10^{-3}$ M of DTPMP (Fig. 3d) caused more significant changes, in such a way that it was not possible to identify the characteristics growth forms such as {010}, {120}, $\{\bar{1}11\}$ and $\{0\bar{1}1\}$. Instead, the form {001} appears to be significantly developed, which gives the crystals a flattened morphology, similar to that found when using the EDTMP (at the same concentrations).

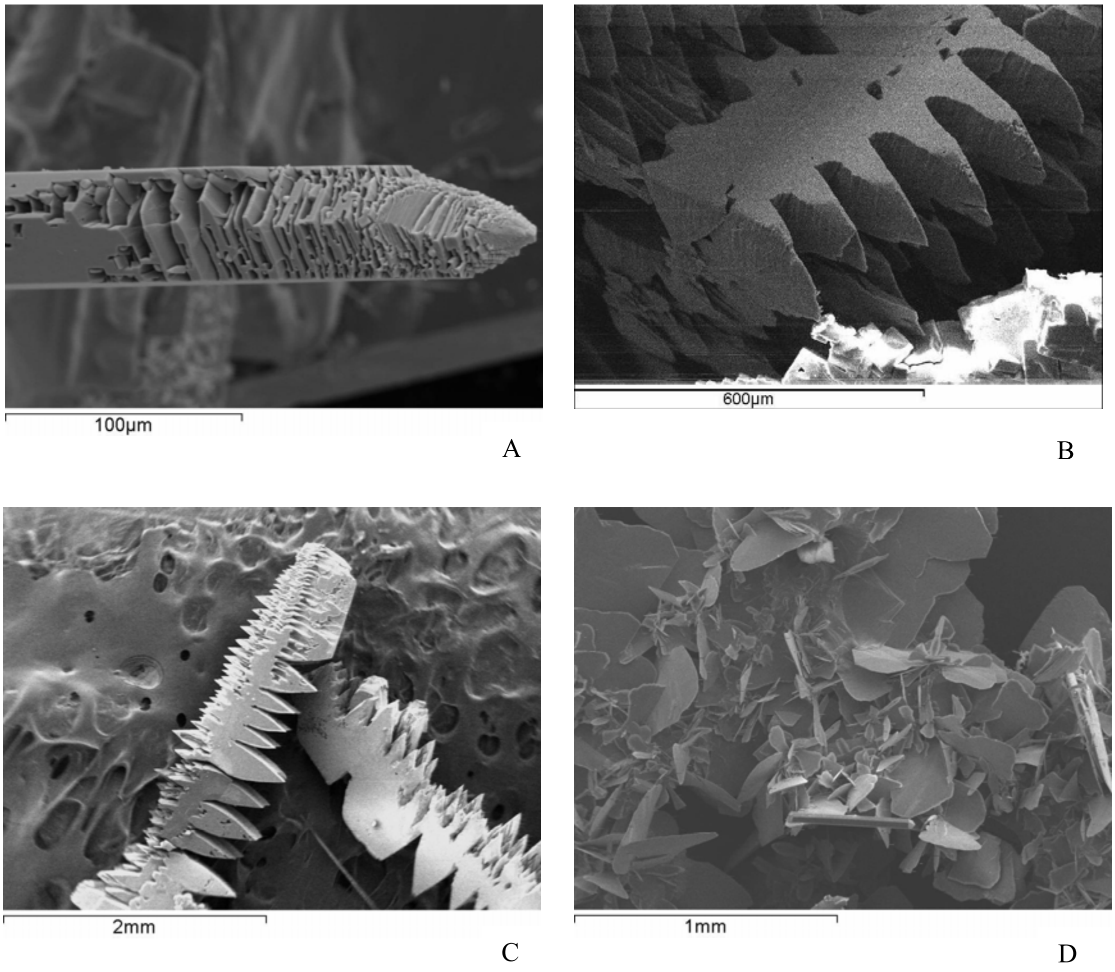


Fig. 3 - Gypsum crystals nucleated and grown in aqueous solution in the presence of DTPMP. A: concentration of $3.5 \cdot 10^{-4}$ M; B: concentration of $1 \cdot 10^{-4}$ M; C: concentration of $5 \cdot 10^{-3}$ M; D: concentration of $1 \cdot 10^{-3}$ M.

Copolymers

The amount of copolymers we used (in between 0.0004% and 0.4%) is lower compared with that usually used in cement industry, although the experimental conditions are different. In the cement industry they are generally added to the cement powder before adding water, whereas in our experiments copolymers were added to the solution.

The copolymers showed an important interaction with {$\bar{1}11$} and {$0\bar{1}1$} forms, resulting in significantly altered morphology: in some cases, the final crystalline geometry is completely different from the characteristic acicular habit of the gypsum.

Copolymer SP1 caused a general decrease in the mean size of crystals and the appearance of {$\bar{1}11$} and {$0\bar{1}1$} forms, showing a large quantity of growth "hillocks" (Fig. 4a). If the percentage of SP1 reaches 0.4% (the highest in this study), the most significant morphological changes occur (Fig. 4b). As it can be seen in Fig 4c, the crystals show a rather compact habit. The use of this copolymer in this amount gave rise to more significant changes in alkaline and in neutral conditions, further confirming its greater effectiveness at higher *p*H values, similar to those found in industrial applications.

SP3 copolymer, (used under the same conditions as for SP1) also changed the final habit of gypsum. Individuals smaller than those usually found in pure solutions showed forms such as {$\bar{1}11$} and

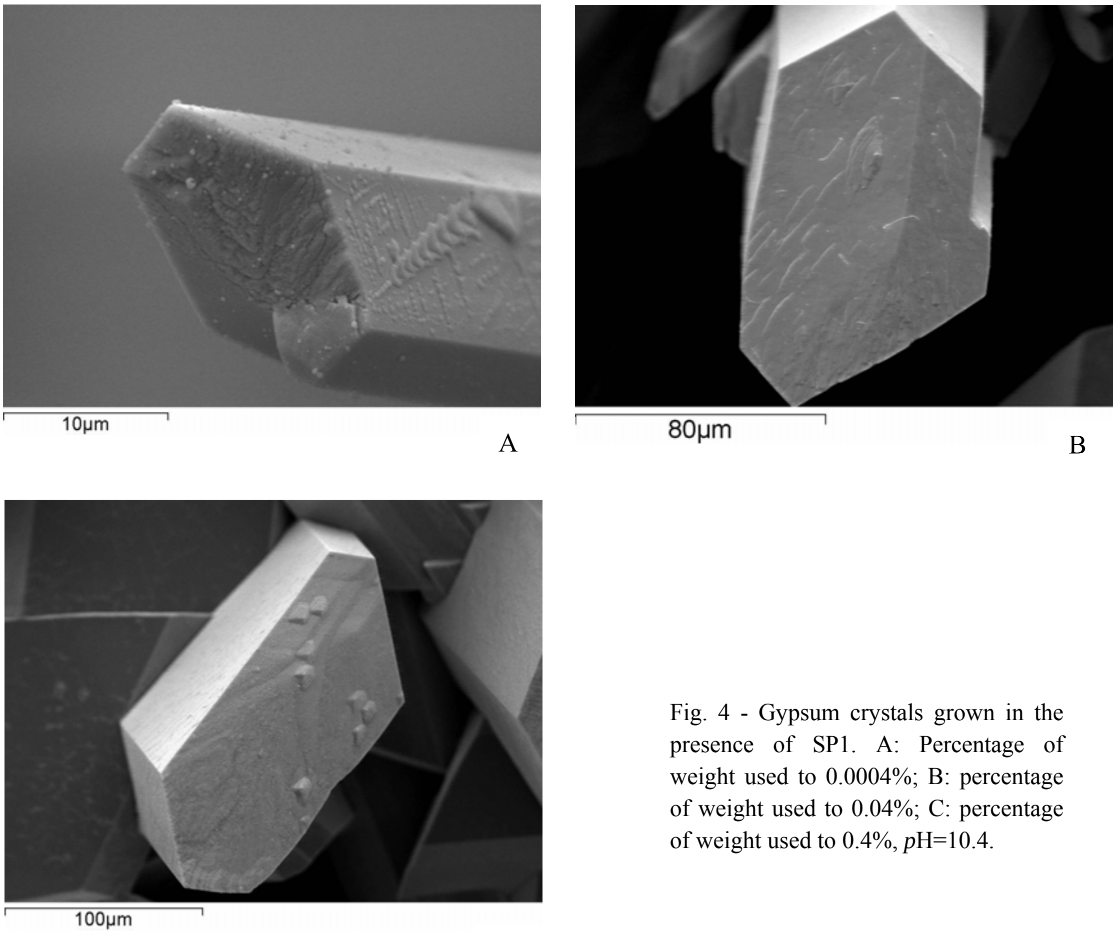
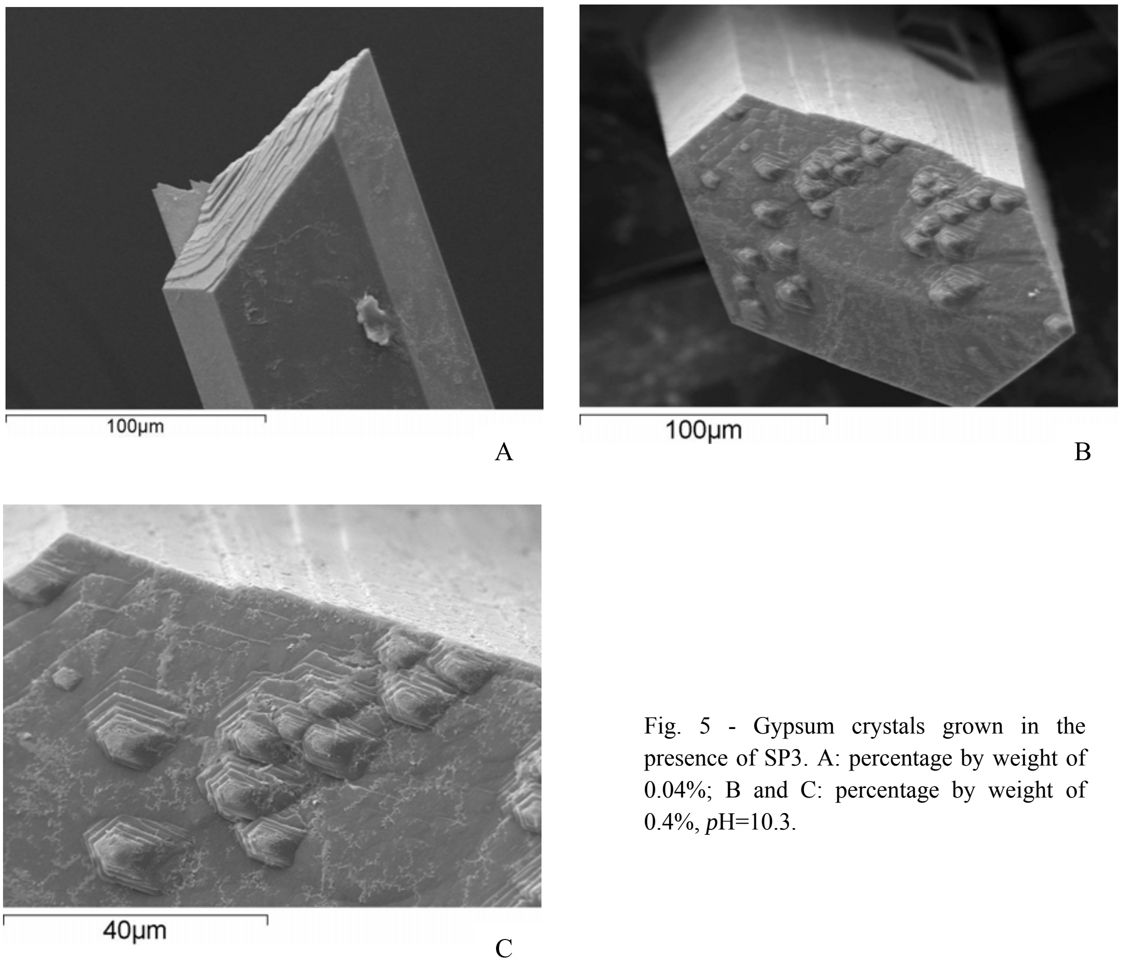


Fig. 4 - Gypsum crystals grown in the presence of SP1. A: Percentage of weight used to 0.0004%; B: percentage of weight used to 0.04%; C: percentage of weight used to 0.4%, *p*H=10.4.

$\{0\bar{1}1\}$ where one can observe the presence of growth macrosteps (Fig. 5a).

When experiments were performed in alkaline environment and with amounts equal to 0.4% the terminal forms of the crystals showed numerous and well developed “hillocks” (Fig. 5b and detailed in Fig 5c) due to the spiral mechanism responsible for their growth.

SR3 copolymer caused less significant morphological changes with respect to those generated by the other two copolymers.



A

B

C

Fig. 5 - Gypsum crystals grown in the presence of SP3. A: percentage by weight of 0.04%; B and C: percentage by weight of 0.4%, *p*H=10.3.

DISCUSSION

Phosphonates caused significant morphological changes in the gypsum crystals, either by varying their concentrations, or by changing the neutral conditions of the crystallization environment. The variation of *p*H was dictated in order to test these additives in conditions close to those employed in the cement industry.

The gypsum crystals grown in the presence of phosphonates are generally elongated along the direction [001], although this elongation appears to be slightly less than that observed in crystal grown from pure solutions. These crystals, however, show significant variations in their final shape.

The phosphonates DTPMP and EDTMP determined the disappearance of {010}, {120}, {$\bar{1}$11} and {0$\bar{1}$1} forms and the corresponding appearance of the {001} form which usually does not occur. When using concentrations of $1\cdot10^{-3}$ M this form appears to be well developed, being the only detectable form, since the final morphology is extremely flattened.

The effect of phosphonates increases with their concentration, and often this feature turns out to be independent on the neutral or the basic state of the growth solution.

Concerning the effects due to the copolymers, the morphological changes increase with the quantity introduced at the initial stages of evaporation of the mother solution.

The use of SP1 which caused the most significant transformations, significantly lowered the elongation of the crystals along the *z* axis causing the formation of numerous “hillocks” on the terminal forms of crystals; these “hillocks” are not found in other experiments and are due to the growth spiral of terminal forms of gypsum.

The use of the SP3 showed no significant changes on the final habit of gypsum, especially in alkaline environment, thereby decreasing the average lengths of the crystals and, as was observed in the case of SP1, resulting in the formation of “hillocks” on the terminal forms of crystals.

The additive SR3 seems to show less interaction with gypsum, since the morphological changes observed appear to be lower than those found when copolymers SP1 and SP3 are used.

CONCLUSIONS

This study was carried out in order to test some additives (phosphonates and copolymers) that can act as morphological modifiers of gypsum in aqueous solution.

The phosphonates DTPMP and EDTMP, used at concentrations $1\cdot10^{-4}$ M, caused a decrease of the crystals elongation, the presence of a skeletal appearance and “indentations” on the forms {010} and {120}. Higher concentrations ($1\cdot10^{-3}$ M) involve a deep transformation of the crystal habit; the skeletal appearance disappears and the elongation along the direction [001] is further reduced. The characteristics forms of gypsum like {010}, {120}, {$\bar{1}$11} and {0$\bar{1}$1} are no recognizable, and the form {001} appears to be considerably developed, so the crystals take on a lamellar shape, very similar to that of natural aggregates known as desert roses.

The increase in concentration and molecular size (from EDTMP to DTPMP) appears to cooperate in changing the morphology of crystals. Furthermore, the greater effects occurred more in neutral than in alkaline environment, contrary to what one would expect, since these additives are widely used in alkaline environment.

The copolymers SP1, SP3 and SR3 have been used in different quantities and conditions with respect to those usually used in industrial cements. These organic molecules are usually mixed during the preparation of dried powdered cement, while we used them in strongly hydrated environment.

The copolymers used in percentage ranging from 0.0004% to 0.4% caused a strong decrease of crystal growth along the [001] direction, leading to the formation of crystals with a rather compact habit. Their effects were more significant when used at higher concentrations and in alkaline environment.

The experiments carried out in neutral environments showed a decrease of the average length of crystals and the formation of steps of growth on the terminal forms of crystals, while the study performed in alkaline environment showed a greater reduction in the elongation and the formation of “hillocks” on the terminal forms such as {$\bar{1}$11} and {0$\bar{1}$1}, due to their layer growth.

SP1 and SP3 copolymers generated significant morphological changes while the SR3 copolymer was less effective.

In conclusion, we can say that:

- the phosphonates significantly changed both the final size of crystals and their growth habit, in some cases leading to the transformation from an acicular habit to the flattened morphology;
- the copolymers induced a significant reduction in the size of the crystals, giving rise to rather compact individuals retaining the typical {*hkl*} forms of gypsum;
- the increase of both the concentration and molecular weight of additives acted together to change the habit of gypsum;
- the neutral *p*H conditions favored the action of phosphonates, while higher *p*H values (alkaline environment) enhanced the effects of the copolymers on the modifications of gypsum morphology.

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