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Effect of malic and citric acid on the crystallisation of gypsum investigated by coupled acoustic emission and electrical conductivity techniques

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Abstract Plaster or gypsum ($CaSO_4 \cdot 2H_2O$) is obtained from a suspension of β calcium hemihydrate ($CaSO_4 \cdot 1/2H_2O$). The effect of two additives, known to retard setting, namely citric and malic acids, on the electrical conductivity and on the acoustic emission (AE) has been studied. This work presents the correlation obtained between these two techniques and their ability to differentiate between the crystallisation of a plaster with or without an organic additive. In particular, the surface adsorption of these carboxylic acids on solid surfaces has been evidenced by a specific acoustic emission activity.

Introduction

Gypsum or calcium sulphate dihydrate ($CaSO_4 \cdot 2H_2O$) is obtained from the reaction of calcium sulphate hemihydrate with water. The mechanism, which is currently recognised to be responsible for gypsum or plaster setting, is dissolution followed by precipitation [1, 2]. In the presence of some carboxylic acids [3], setting can be retarded. One explanation is the possible adsorption of the additive at the surface of either hemihydrate or gypsum. A conventional method to follow plaster setting is to carry out electrical measurements on dilute suspensions. When plaster starts setting, the conductivity drops. This sudden evolution of the conductivity is closely related to some physico–chemical changes in the medium leading to energy relaxation which can induce the generation and the propagation of an elastic wave.

To investigate such phenomenon, acoustic measurement is potentially a very useful monitoring tool. Direct contact with a process is not required allowing real-time, on-line monitoring with little or no intrusion. There are two methods of monitoring a process acoustically:

- active acoustics, which measure the effect of a process on a transmitted acoustic wave (usually low powered ultrasound);
- passive acoustics, focussed on the measurement of the acoustic emission activity (AE) created by the process itself.

Recent works have shown that ultrasonic methods, and more precisely acoustic emission, applied to cement setting and drying monitoring, can be sensitive to physical and chemical processes [4–9]. The results obtained from these studies underline the ability of this passive acoustic technique to characterise, with a quite good reliability, and either in a quantitative or in a qualitative manner, the mechanisms and their chronology.

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The present work is devoted to the study of gypsum setting, without and with two additives known for their retarding effect, namely citric and malic acids. A comparison will be done between electrical conductivity results and the acoustic emission signature.

Experimental

Material

Two lots of 50 g of β hemihydrate (MOLDA 3 NORMAL, BPB, England) mixed with 1 L of distilled water or 1 L of distilled water containing either malic acid, $C_4H_6O_5$ (0.005 mol L^{-1}; PROLABO, France; purity: 99.9%), or citric acid, $C_6H_8O_7$ (0.005 mol L^{-1}; ALDRICH, France; purity: 99%) were prepared. This acid content is sufficient to change both the setting time and the plaster morphology [10]. Figure 1 shows the three-dimensional representation of the two acids. Malic acid has two acid groups and one hydroxyl group. Citric acid shows three acid groups and one hydroxyl group. In the present pH range ($\approx$7), the acid functions are ionised since the acid constants are equal to $10^{-2.8}$, $10^{-4.2}$, and $10^{-4.7}$ for citric acid, $10^{-3.1}$ and $10^{-4.46}$ for malic acid [11]. The interatomic distances between the oxygen atoms taken from ref. [9] are also reported in Fig. 1. These distances were calculated assuming that the acid functions were ionised into carboxylate functions. Lastly, citric acid can complex calcium ions [11].

One lot was used for conductivity measurements as a function of time (Conductivity cell TETRACON 325, WTW, Germany). The other lot was used for acoustic emission characterisation. Calcium and sulphur concentrations were measured by Inductive Coupled Plasma, ICP (IRIS device from THERMOELECTRON, France) in solutions extracted by centrifugation at different times. Scanning Electron Microscopy, SEM, (HITACHI SC 2500, Japan) was carried out on the solid collected after centrifugation. Hydration was stopped by washing with alcohol and ketone. The solid was dried for 24 h at 40°C and grounded with a mortar and a pestle. Prior to observation, the powder was coated with a gold–palladium film. The working voltage was between 15 and 30 kV.

Acoustic emission technique

Acoustic emission (AE) is defined as “the class of phenomena whereby transient elastic waves are generated by the rapid release of energy from localised sources within a material (or structure)”. It also refers to the transient waves so generated [12]. This technique is a well-known non-destructive evaluation technique to monitor flaw formation and failures in structural materials. It has been used either on both the laboratory level and the industrial scale. This method is mainly used to monitor the onset of cracking processes in materials and components essentially submitted to external loading (mechanical or thermal). When a material is submitted to stresses, acoustic emission can be generated by a variety of sources, including crack nucleation and propagation, multiple dislocation slip, twinning, grain boundary sliding, Barkhausen effect (realignment or growth of magnetic domains), phase transformations in alloys, debonding of fibres in

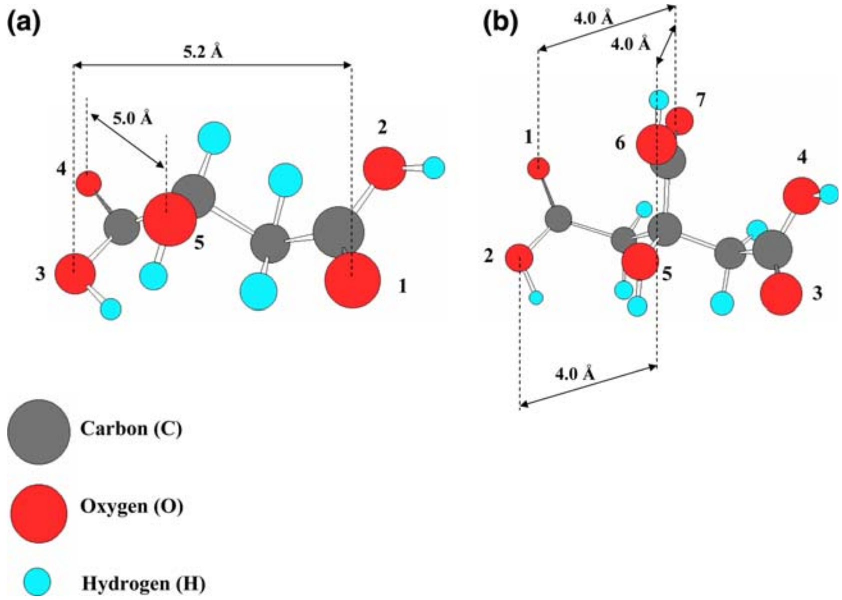

Fig. 1 3D schematic representation of (**a**) malic and (**b**) citric acids

composite materials, fracture of inclusions in metals [13–16]. In the present work, the technique will be used to record the elastic waves emitted during the chemical reactions and physical changes that occur during the setting of gypsum.

The AE experimental set-up consists of an AEDSP–32/16 MISTRAS digital system from Physical Acoustics Corporation. This system makes it possible to record the waveform and the main AE parameters (Fig. 2) such as count, hit, rise time, duration of hit, count to peak and amplitude (in dB).

The sampling rate was 8 MHz. Two sensors (PAC MICROPHONE R15), one test sensor and one reference sensor, were connected through 40 dB preamplifiers (EPA 1220A). The reference sensor was used in order to record noises due to the electromagnetic environment so that these parasite signals could be eventually subtracted from the ones recorded on the test sensor. A coupling fluid (Dough 428 Rhodorsil Silicone) was used to have an airless and flawless contact between the transducer and the specimen. The AE experimental set-up used in this work is presented in Fig. 3.

Results and discussion

Hydration of β hemihydrate

Figure 3 shows the conductivity measurements as a function of time. During the first 5 min, the conductivity increases rapidly to reach 5.7 μS cm^{-1}. It is associated with the dissolution of β hemihydrate where a little volume of solid is concerned, since the volume of the hemihydrate grains does not change significantly, but where the ionic concentration varies considerably to reach sursaturation with respect to gypsum [17]. An equilibrium is then established between hemihydrate dissolution and gypsum nucleation, which leads to little variation in terms of conductivity. Until 1.5 h, the conductivity stays between 5.7 and 5.6 μS cm^{-1} (zone 1, Fig. 4). Once gypsum crystals start growing, the conductivity drops down to 3.6 μS cm^{-1} at 6 h (end of zone 2) until no hemihydrate is available. Gypsum is then crystallised from the remaining sursaturation with respect to gypsum (zone 3).

With respect to the cumulative hits (Fig. 4), there little acoustic activity in zone 1. It means that the phenomena associated to hemihydrate dissolution and gypsum nucleation present an amplitude which is too low for detection or that the mechanical energy released by these phenomena is attenuated by the liquid medium. In zone 2, there is a marked increase of the acoustic activity linked to the formation of gypsum crystals; the hit rate has increased from 0.6 h^{-1} in zone 1 to 27.7 h^{-1} from 1.5 to 4.16 h in zone 2. In the same time range, the conductivity rate is the highest (0.59 μS cm^{-1} s^{-1}). Beyond 4.16 h, these two rates start decreasing, which can be associated to the beginning of gypsum precipitation from the remaining sursaturation. Figure 5 shows the amplitude (Fig. 5a) and hit duration (Fig. 5b) as a function of time. Before 6 h, the signals are short and exhibit high amplitude while there are long with a low amplitude after 6 h. Concerning the absolute energy variation ($E = \int V^2 dt$:V = amplitude of signal in volts) as a function of time (Fig. 6), different regimes can be distinguished. From about 1.16–2 h, the recorded hits present a high energy level (up to nearly 1,800 attoJoules) compared to the next period from 2 to about 6 h where the energy level decreases considerably to become low after 8 h. Two phenomena can explain this burst of acoustic activity just after 1.5 h: effective contacts (sudden hits) between the different crystals, and rubbing (fretting) between crystals as their quantity and size increase with time. A direct observation of the typical signals recorded within the first two hours and after 6 h confirms that these two mechanisms are present during the precipitation and the growth of hydrates.

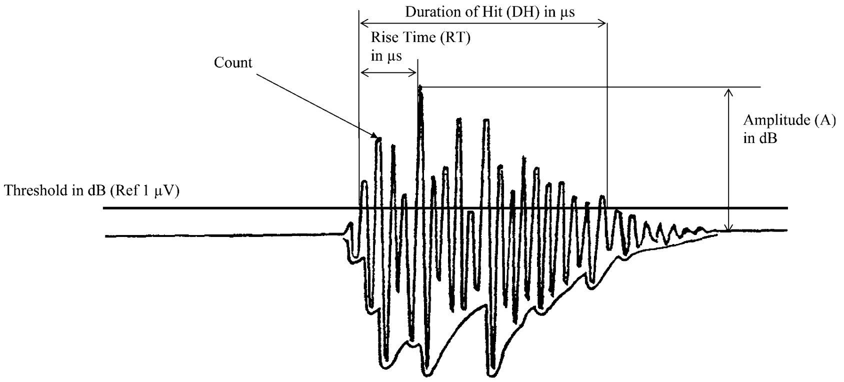

Fig. 2 Typical AE signal recorded with its associated characteristics

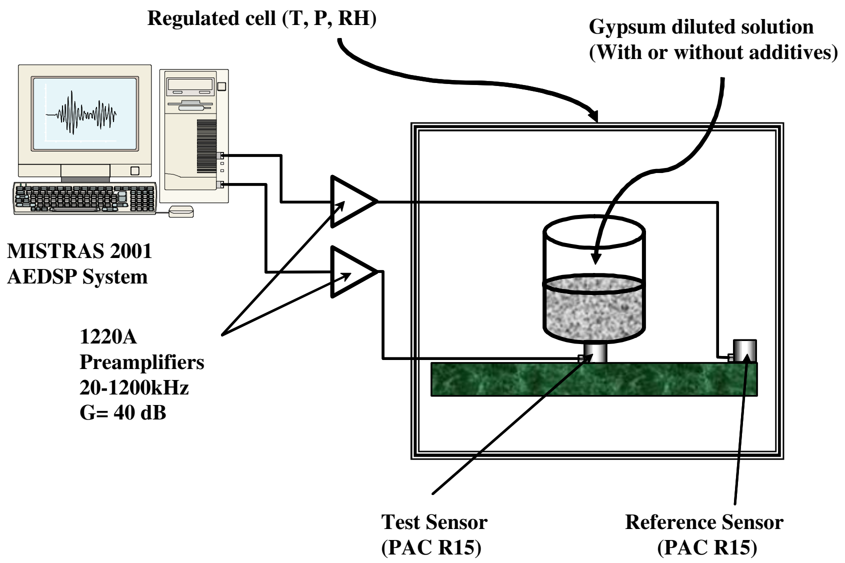

Fig. 3 Experimental set-up for AE measurements. (T = Temperature, P = Pressure, RH = Relative Humidity)

Hydration of β hemihydrate in the presence of carboxylic acid

Figure 7 shows the conductivity variations for β hemihydrate hydration in the presence of malic or citric acid. Both have a retarding effect; a significant drop in conductivity is observed after 4 and 5.75 h in the presence of malic and citric acid, respectively, instead of 1.5 h for β hemihydrate alone. Figure 8 presents the compared variations of the acoustic activity for the three situations. First of all, the activity level is very high for the solutions containing an acid, especially in the time range where there is no significant variation of the conductivity; Table 1 summarizes the hit rates for the solutions with the two acids and in different time ranges. Secondly, the hit rate is quite different for the hemihydrate without or with acid. For instance, if we chose to examine the situation at 2.5 h, the hit rate is respectively equal to 22, 434 and 565 hits h^{-1} for β hemihydrate alone and in the presence of malic or citric acid. Thirdly, the start of the acoustic activity occurs within the first minutes when an additive is present and only after 1.5 h without additive (Table 2).

The massive acoustic activity recorded in the presence of additive is not due to hemihydrate dissolution, as shown previously, but to another mechanism. These two acids are known to have a retarding effect on gypsum crystallisation and this has been explained by their adsorption at the surface of gypsum nuclei [3]. In citrate, the distance between two oxygen atoms in two neighbouring carboxylate groups, is equal to 4.0 Å. Since in the (120) and $(\bar{1}11)$ planes, which are two

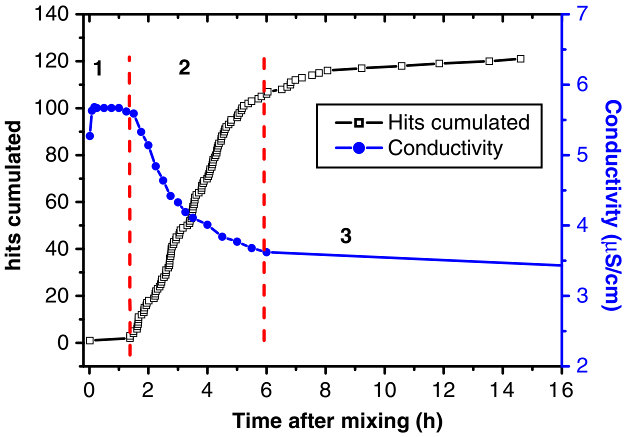

Fig. 4 Variations of electrical conductivity and cumulated number of hits as a function of time during hydration of β hemihydrate

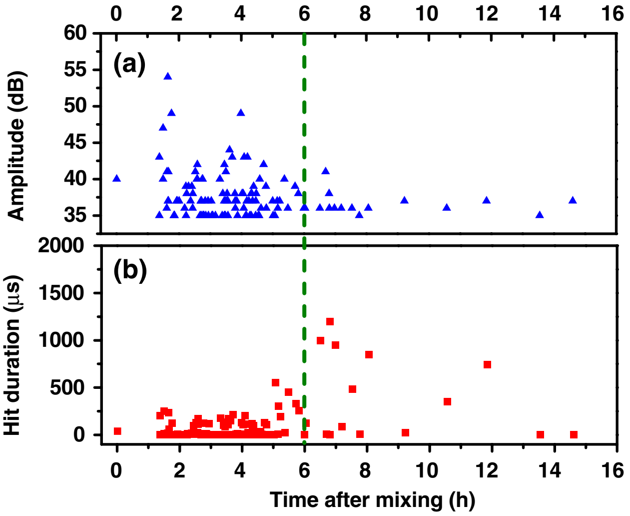

Fig. 5 (**a**) Amplitude and (**b**) hit duration as a function of time. Case of hydration of β hemihydrate

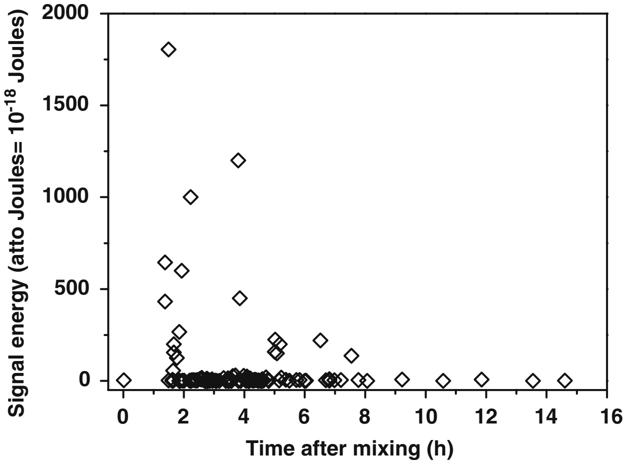

Fig. 6 Variation of AE signal energy as a function of time. Case of hydration of β hemihydrate

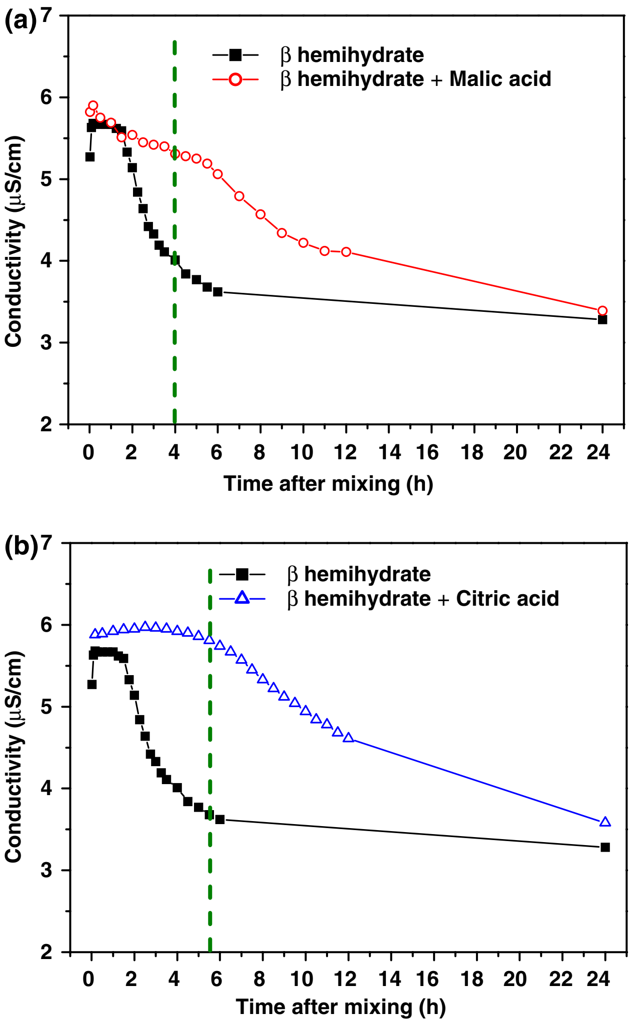

Fig. 7 Variations of electrical conductivity as a function of time during hydration of β hemihydrate with (**a**) malic and (**b**) citric acid. (acid concentration = 0.005 mol L^{-1})

Table 1 Hit and conductivity rates deduced from figure 4. Case of hydration of β hemihydrate

	from 0.16 to 1.5 h	from 1.5 to 4.16 h	from 4.16 to 6 h	beyond 6 h
$\frac{\partial(\mathrm{Nb\ salves})}{\partial t}$ (h^{-1})	0.6	27.7	6.4	0.7
$\frac{\partial\sigma}{\partial t}$ ($\mu S\, m^{-1}\, s^{-1}$)	0	–0.59	–0.16	–0.02

Table 2 Hit and conductivity rates deduced from Figs. 7 and 8. Case of hydration of β hemihydrate with malic or citric acid. (Hit rate = $\frac{\partial(\mathrm{Nb\ Hit})}{\partial t}$ in h^{-1} and Conductivity rate $\frac{\partial\sigma}{\partial t}$ in $\mu S\ cm^{-1}\ s^{-1}$

	Hit rate	Conductivity rate	
β hemihydrate+ Malic acid	Before 4 h	416	–0.10
	After 4 h	2	–0.18
β hemihydrate+ Citric acid	Before 5.75 h	420	≈ 0
	After 5.75 h	23	–0.19

possible faces for a gypsum crystal, the distance between two calcium atoms are equal to 4.0 Å, citrate molecules can adsorb at the surface via the oxygen of the carboxylate groups to form a complex. The adsorption can stabilize small gypsum nuclei and thus hinder their growth. In solution, calcium and citrate can form complex molecules too [3]. Figure 9 presents calcium and sulphate concentrations as a function of time, deduced from ICP measurements, for hemihydrate without and with citric acid. Without additive, the calcium and sulphate concentrations are of the same order of magnitude and follow with time the conductivity variations. With citric acid, the calcium concentration is higher than the sulphate one. A possible competition between different mechanisms can explain this result: formation of complex between calcium and citrate in the solution, adsorption of citrate at the solid surface, delayed hemihydrate dissolution and gypsum nucleation. Concerning malic acid, its adsorption at the solid surface is probably less easy than citrate because the atomic distances between oxygen atoms in carboxylate groups are of the order of 5.0 Å (Fig. 1); this value is 20% greater than the distance between two calcium ions. This hypothesis can be correlated with the lower level of cumulative hits compared to the case of citric acid.

On Fig. 10a and b are given the energy levels for the two situations with an additive. The highest energy levels for these two situations are lower than in the case of hemihydrate alone (Fig. 6) since the order of magnitude are 100 attoJoules with any additive and 1,000 attoJoules without additive. This shows that we have two distinct mechanisms in terms of energy, namely adsorption and precipitation. Concerning the

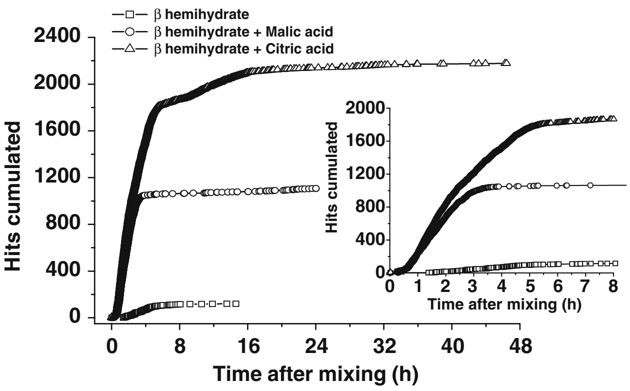

Fig. 8 Cumulative hits as a function of time for the hydration of *β* hemihydrate alone or in the presence of malic acid and citric acid. Magnification on the first eight hours. (acid concentration = 0.005 mol L^{-1})

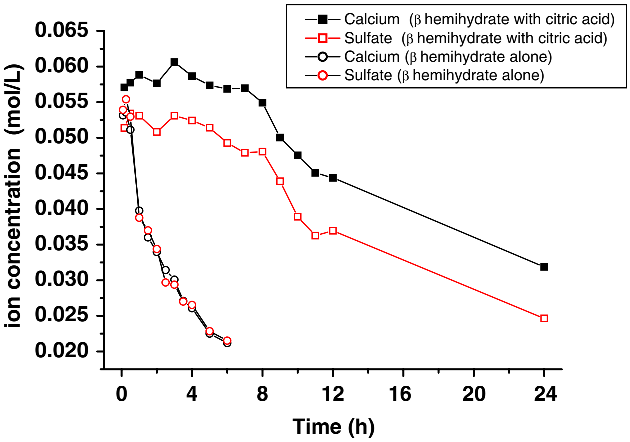

Fig. 9 Calcium and sulphate concentrations deduced from ICP measurements. Case of hydration of *β* hemihydrate alone and with citric acid

chronology with additive, the hits with the greatest energy correspond to the beginning of the experiment (zone A, Fig. 10a and b) and the energy drops considerably at 4 and 5.75 h for malic and citric acid, respectively. This low energy is concomitant with the beginning of the decrease in the electrical conductivity (Fig. 6). In zone B, the signal energy is different for the two additives. With malic acid, the energy is low between 4 and about 10 h and increases thereafter without reaching values as high as in zone A. In the presence of citric acid, a low energy level is observed just after 5.75 h but the energy values that are reached in zone B, when the energy re-increases, are higher than values in zone A. A possible interpretation of such behaviour is the following:

- zone A: it is the time range when the surface adsorption of the additive is quite active. Both hemihydrate dissolution and gypsum precipitation are retarded.
- zone B: gypsum crystals precipitate and generate less hits compared to zone A with an associated energy that is either lower (case of malic acid) or greater (case of citric acid) than in zone A.

Two hypotheses can be proposed: (i) acoustic emission is still associated to surface adsorption. In this case, a diminution of acoustic activity means that adsorption is less effective. Equivalently, the amount of available acid to cover all the gypsum faces is too low; (ii) acoustic emission corresponds to the development of gypsum crystals whose morphology is different from the case of gypsum without additive. Figure 12 presents the micrographs for the three situations. Gypsum alone exhibits needle like crystals while the presence of additives gives crystals with prismatic shapes. This difference in morphology could also

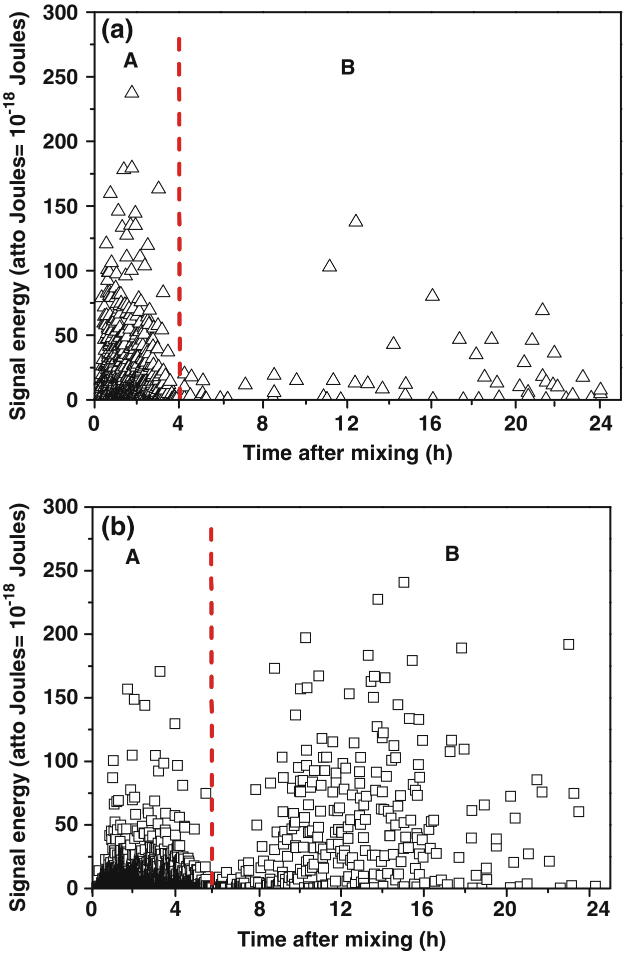

Fig. 10 Variation of AE signal energy as a function of time. As a function of time during hydration of *β* hemihydrate with (**a**) malic and (**b**) citric acid (acid concentration = 0.005 mol L^{-1})

account for differences in hit rate and energy level compared to gypsum.

Conclusion

The use of coupled AE technique and conductivity measurement to investigate the changes in crystallisation process in gypsum, with or without additive, has been shown to be successful. A strategy, based both on the analysis of the recorded signals characteristics and on the correlation obtained with the conductivity measurements, has lead to the identification of phenomena taking place sometimes at a very small scale (for example: surface adsorption of molecules on solid grains). From the work undertaken, the following conclusions can be drawn:

- Concerning the hydration of gypsum, three principal periods have been emphasised by both AE and conductivity measurements. The first one, at a very early stage (0–1.5 h), exhibits a constant value of the conductivity associated with a very low AE activity. This period can be related to the dissolution of plaster and to the heterogeneous nucleation of the first crystals of gypsum. The second period (from 1.5 to 6 h) is characterised by an opposite variation of the two parameters. As a notable decrease of the conductivity value is observed, in the same time, an important increase of the AE activity is quoted. This phase is related to the massive crystallisation (or precipitation) of gypsum. During the third stage, (over 6 h), the same kind of variation of the parameters (AE and conductivity) as the first period is observed (constant value of the conductivity and low AE activity), which traduces a slow ending of the process. A global analysis of the recorded AE signals (amplitude and frequency) (Fig. 11) mainly carried out during the second period, has revealed the existence of two distinct types of signal which can be related to two different mechanisms taking part during massive crystallisation: short signals with high amplitude associated to sudden hits between crystals and long signals with lower amplitude more likely to be linked to a rubbing process between crystals during the tangling of hydrates.
- When a carboxylic acid (malic or citric) is added to the gypsum, several effects of this addition can be successfully characterised by both AE and conductivity techniques. Firstly, an important delay on the fall of the conductivity and an intense AE activity in the first minutes are observed on acid added solution. This can be interpreted by the surface adsorption of the acid molecules which retards the dissolution process. This adsorption process can induce locally, a release of energy which can transform into acoustic waves. Finally, energetically speaking, the corresponding AE signal energy level recorded during the test on acid added gypsum is notably lower than for the one without acid. This can be explained by the difference in crystal morphology between the gypsum prepared with or without additive (Fig. 12).

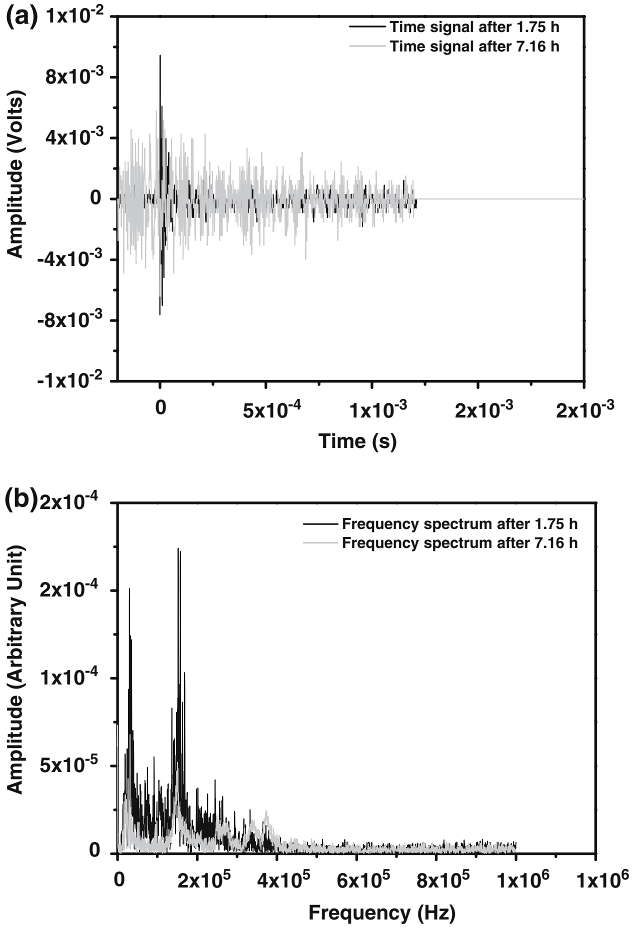

Fig. 11 AE hits recorded during hydration of β hemihydrate at specific times: (**a**) Time signals, (**b**) Frequency spectra

This work demonstrates the potential of the AE technique in detecting and analysing physical changes acting at a very small scale within a chemical process. Although this technique can be self-sufficient in few cases (damage characterisation), it is also important to note that, for an optimum efficiency in a process investigation approach, this method must be associated with another (here conductivity measurements). However, the research is extensive in time and effort,

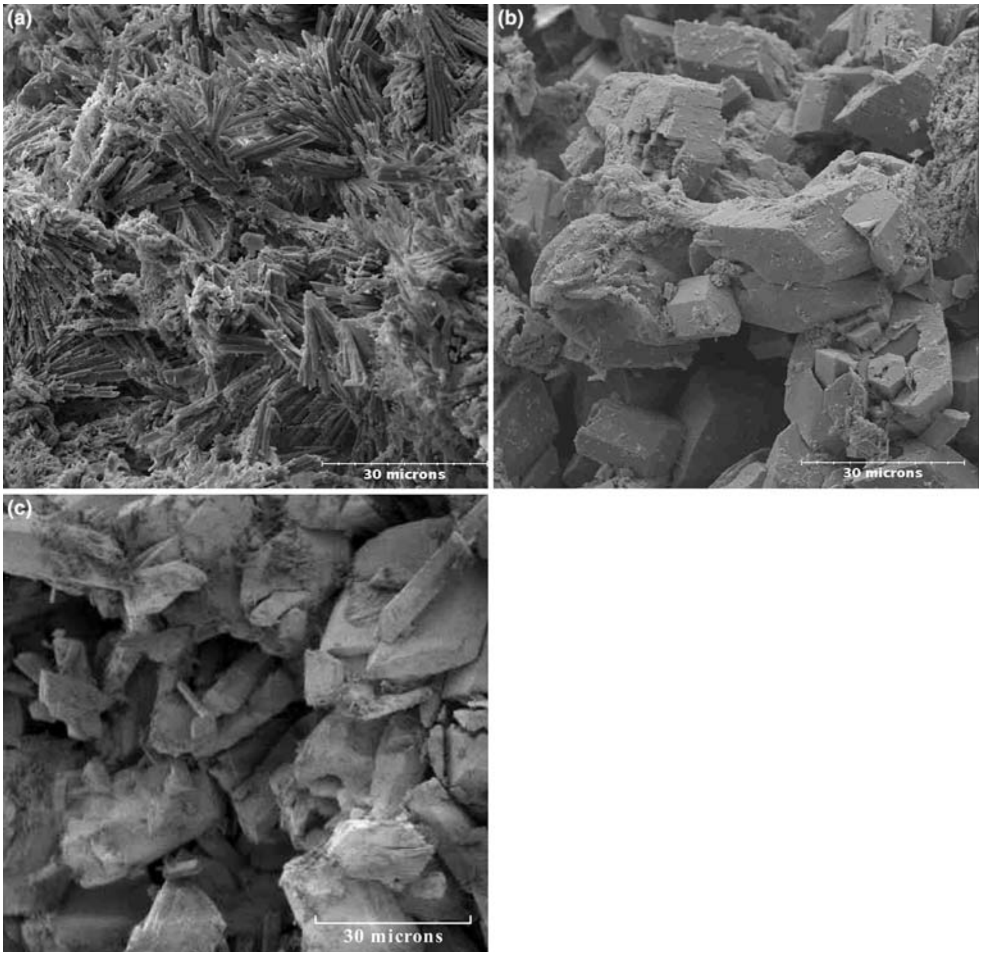

Fig. 12 Scanning Electron Micrographs of gypsum. (**a**) no additive, (**b**) addition of malic or (**c**) citric acid (acid concentration = 0.005 mol L^{-1})

although it is believed that within the data presented, interesting results have been observed in an area where there is too little published data.

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References

1. Bosbach D, Junta-Rosso LJ, Becker U, Hochella FM (1996) Geochim Cosmochim Acta 60:3295
2. Ludwig U, Singh NB (1978) Cement Concrete Res 8:291
3. Boisvert JP, Domenech M, Foissy A, Persello J, Mutin JC (2000) J Cryst Growth 220:579
4. Chotard T, Barthelemy J, Smith A, Gimet-Breart N, Huger M, Fargeot D, Gault C (2001) J Mat Sci Lett 20:667
5. Chotard T, Smith A, Codet N, de Baillencourt M, Fargeot D, Gault C (2002) J Mat Sci Lett 21:1261
6. Smith A, Chotard T, Bonnet JP, Louvet F, Gault C (2002) J Mat Sci 37:3847
7. Chotard T, Smith A, Rotureau D, Fargeot D, Gault C (2003) J Eur Ceram Soc 23:387
8. Chotard T, Rotureau D, Smith A (2005) J Eur Ceram Soc 25:3523
9. Chotard T, Ersen A, Smith A (2005) *in press.* J Eur Ceram Soc
10. Badens E, Vessler S, Boistelle R (1999) J Cryst Growth 198/199:704
11. Douglas D, Perrin E (1983) Stability constants of metal-ion complexes, Part B, organic ligands, Pergamon, Paris, p 316
12. Standard terminology for non-destructive examination. E1316–96, Non-destructive testing, (annual book of ASTM standards, Volume **03.03**, 1996), p 609
13. Bakuckas JG, Prosser WH, Johnson WS (1994) J Comp Mat 28:305
14. Barré S, Benzeggagh ML (1994) Comp Sci Tech 52:369
15. Berkovits A, Fang D (1995) Eng Fract Mech 51:401
16. Havlicek F, Crha J (1999) J Acous Emis 17:3
17. Amathieu L, Boistelle R (1988) J Cryst Growth 88:183