Effects of Different Calcium Sulphates on the Mechanical Properties of a Rapid Setting High Flow Anchoring Grout

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Abstract

High flow anchoring mortars (HFAM) are commonly employed both for new building constructions and concrete repairs. They are suitable to connect precast concrete elements, to fill rigid joints, to anchor metallic carpentry or to execute underpinnings. During winter or when rapid job execution is required, fast setting pre-packaged HFAM can also be employed. These products are mainly composed of Portland cement, high alumina cement and calcium sulphate. This combination of materials is an ettringite forming system. The anchoring mortar develops its holding capability through the pressure arising from the ettringite expansion. In this paper the effects of two different sulphates (gypsum and anhydrite) on the compressive strength development and the dimensional changes of a HFAM were studied. In order to elucidate the role of calcium sulphate on the material properties, some morphological (ESEM-FEG), crystal-chemical (XRD) and physical-chemical (hydration temperature profile) analyses on cement paste samples were also carried out.

1. Introduction

During the last years, rehabilitation and protection of urban infrastructure is becoming very important in construction practice. A quality repairing material requires rapid setting, early strength, good adhesion to the substrate, compatibility with the existing concrete and shrinkage compensation. High flow anchoring mortars (HFAM) are usually used when a rapid job execution is demanded, especially in repair situation where an early return to traffic is requested. These materials have a wide range of application [1]. For examples they are employed for connecting precast concrete elements, filling rigid joints, anchoring metallic carpentry, kerbstones and protection barriers, executing underpinnings, repairing airports runways or pedestrian concrete pavements. The hydraulic binder of a classical HFAM is based on variable combinations of three main ingredients: calcium aluminate cement (CAC), Portland cement (OPC) and calcium sulphate (CS). This combination is a system forming ettringite [2] whose formation is controlled to produce the desired performances (e.g. setting, hardening kinetics, dimensional changes). Today only few studies are available on this subject [3-6]. In this paper the influence of two different calcium sulphates (gypsum and anhydrite) on the mechanical properties of a HFAM was studied. In order to clarify the role of calcium

sulphate on the material properties, morphological (ESEM-FEG), crystal-chemical (XRD) and physical-chemical analyses on cement paste samples were also performed.

2. Experimental

2.1 Raw Materials
A Portland cement type I 52,5 R (according to ENV 197/1 [7]; Tab. 1), high alumina cement (Tab. 1), anhydrite (from Yesos Ibericos, Spain, μ: 8 µm; where μ is the weighted mean particle diameter) or gypsum (from Lages, Italy, μ: 19 µm) were employed for mortar (*Ref*, *Manhd*, *Mgyps)* and cement paste preparations (*Pref*, *Panhd*, *Pgyps*; Tab. 2). Silica sand ranging between 0 and 5 mm was also used.

2.2 Mechanical tests
Mortar specimens were prepared and stored according to ENV 196/1 [7] (40x40x160 mm; 23°C and 50% R.H.). Flow (EN 1015/3 [7]– each result is an average of three measurements) and unit weight (by picnometer – each result is an average of three measurements) were detected on fresh made mortar samples (Tab. 3). Compressive strengths were determined after 4 hours, 24 hours, 7 and 28 days (each result is an average of six measurements; Fig. 1). Shrinkage was evaluated according to UNI 6687 [7] by a digital length comparator Mitutoyo model IDC 112B: after 3 hours of curing, 40x40x160 mm samples were demoulded and conditioned in a dry environment (23 °C and 50% R.H.); the data were calculated with respect to the specimen length after demoulding and measured from 24 hours till 28 days after mixing (Fig. 2).
Dimensional variations on *Manhd* and *Mgyps* were also detected immediately after casting on 50x50x250 mm restrained mortar samples (UNI 8147 [7]). The data were collected till 8 hours of curing by a digital length comparator connected to a computer (Fig. 3).

2.3 Physical-Chemical Analyses
The following analyses were performed on the cement paste samples.
The hydration temperature profile was measured keeping the cement paste sample (30 g) in a thermostatic bath (20°C) and registering the temperature during the first 10 hours of hydration by a digital thermometer type Testo mod. 781 (Fig. 4).
Cement pastes were treated with acetone, in order to stop the hydration process. XRD patterns of the resulting powder were collected with 5° and 40° 2Θ runs at 1 second per step after 10 minutes, 40 minutes, 3 and 6 hours of hydration (Figs. 5-7). A Philips PW 1830 Diffractometer with Cu(Kα) radiation was used for pattern detection.

2.4 Morphological Analyses

An Environmental Scanning Electron Microscope (Philips mod. XL30 ESEM-FEG) was used to analyse the morphology of hydrating cement pastes which were hydrated outside the chamber using the amount of water reported in Table 2. The special instrumental configuration of the ESEM-FEG allowed to work in low vacuum setting (6 Torr), with a 10 kV voltage, at a temperature of 5°C. Therefore, the sample could be analysed in the presence of significant amounts of residual water. The study was performed carrying out the curing for 6 hours (Figs. 8-11). The reported micrographs are representative of the whole sample.

3. Results

3.1 Mechanical tests

The results in Tab. 3 show that fresh mortar properties are very similar.

Anhydrite favours the highest compressive strength development, in particular at early curing age (Fig. 1). Furthermore *Mgyps* has higher compressive strength than *Ref*. After 28 days, the mechanical strength order changes completely: *Ref>Mgyps>Manhd* (Fig. 1).

Figure 2 points out that the specimen containing gypsum shrinks less than the sample added with anhydrite. As expected [8], the reference (*Ref*) is characterised by the most pronounced volume contraction.

The dimensional variations (Fig. 3) detected through the continuous registration method point out different expansion times for the samples containing calcium sulphates. In particular, volume increase begins after 1 hour for *Manhd* and after 3 hours for *Mgyps*.

3.2 Physical-Chemical Analyses

According to the thermodynamics, at constant pressure, the hydration temperature profile can be related to the rate of heat release [9]. This is a qualitative technique which is performed on larger amount of sample respect to the typical conduction calorimetry. As all the samples were analysed according to the same experimental procedure, a significant comparative evaluation of the hydration profiles can be carried out.

Three exothermic peaks were observed during the first 6 hours of hydration (Fig. 4 - standard deviation: +/- 0.5 °C). The first peak (during the initial 10 minutes) could be related to initial cement hydration and hydrated aluminates formation [10]. The second peak (between 20 and 50 minutes) could be connected to ettringite formation [3]. The third signal (between 1 and 6 hours) could be mainly associated to C_3S hydration, which produces C-S-H and portlandite [11]. *Panhd* shows an anticipated third peak formation compared to the other samples.

After 10 minutes of hydration, no crystalline hydration phases are visible on the XRD patterns (Figs. 5-7).

Only after 45 minutes of curing, ettringite signals are evident in all the samples. A significant reduction of anhydrite and gypsum occurs as these phases are sources of sulphate anions for the ettringite formation.

After 3 hours, a pronounced ettringite growth is visible in both the calcium sulphate containing samples (*Pgyps* and *Panhd*). Ettringite signals in *Pref* seem to remain unchanged.

After 6 hours, a hydrated phase, likely hemicarbonate, is visible in *Pref* and *Pgyps* while it is absent in *Panhd*. Moreover, although gypsum is disappeared in *Pgyps*, anhydrite is still present in *Panhd*. Hemicarbonate could be formed from the reaction between ettringite and calcium aluminates of Portland and calcium aluminate cement, in the presence of carbon dioxide (coming from the environment) [12-14]. This reaction cannot take place in *Panhd* because of the presence of anhydrite which supplies sulphate anions available for the reaction with calcium aluminate to form further amounts of ettringite.

3.3 Morphological Analyses

After 10 minutes of hydration, hexagonal plates of hydrated calcium aluminates are visible in all the samples (for example Fig. 8).

At later curing times (40 minutes), crystals of ettringite are evident in all the specimens. The size of these crystals is variable in *Pgyps* (Fig. 9), nevertheless they appear longer and thinner compared to the ones detected in *Panhd* (Fig. 10).

After about 3 hours, C-S-H is clearly visible in *Panhd* (Fig.11). This phase is less evident in *Pgyps*. These findings confirm the mentioned hypothesis concerning the faster C_3S hydration of *Panhd* (hydration temperature profile). The micrographs of *Pref* were not reported as its morphology is very similar to *Panhd*.

4. Discussion

The results clearly indicate that the mechanical properties of a typical HFAM (high flow anchoring mortar) depend on calcium sulphate amount and type. In particular, at early curing age, the samples containing calcium sulphates show higher mechanical strengths compared to their reference (without calcium sulphate) and that anhydrite promotes the highest strength development (Fig. 1).

The mechanical strength of these materials is mainly connected to ettringite and C-S-H formation [2,5]. A low amount of ettringite is formed in the sample without calcium sulphates for the lower availability of calcium and sulphate ions. This effect is indicated by the small intensity of the second peak in the hydration temperature profile (that is associated to ettringite formation – Fig. 4) and by the XRD analyses (Figs. 5-7). This

lower ettringite formation could explain the reduced compressive strength development of *Mref* compared to *Manhd* and *Mgyps*. On the contrary, the highest compressive strength promoted by the use of anhydrite could arise from the anticipated C-S-H formation emphasised in *Panhd* (ESEM – Fig.11 – and hydration temperature profile – Fig. 4). Likely, anhydrite, which is characterised by a slower dissolution rate than gypsum [15], favours the formation of few nucleation germs of ettringite which can properly grow to give well crystallized thick needles (ESEM – Fig. 10). On the contrary, gypsum, being more soluble, could promote a massive formation of nucleation germs inducing the growth of a gelatinous ettringite layer. In the former case, cement grains are more exposed to water which can easily enters and correctly hydrate C_3S. The protective gelatinous ettringite layer in *Mgyps* could retard cement hydration.

The results of this study also point out that the sample without calcium sulphate has the highest volume contraction (*Mref*) and that gypsum favours the lowest shrinkage (*Mgyps*; Fig. 2).

The literature [16] shows that ettringite formation can compensate the material contraction. Therefore, the high shrinkage of the reference could be related to the low amount of formed ettringite (small initial expansion).

In order to clarify the highest dimensional stability of *Mgyps* resulting from the shrinkage/expansion measurements (Fig. 2; UNI 6687), the results of the continuous registration method should be considered. This technique shows that the expansion of the sample containing anhydrite occurs within the first 2 hours (Fig. 3). On the contrary *Mgyps* expands between 3 and 5 hours of hydration (Fig. 3). The expansion/shrinkage measurements were determined (UNI 6687) respect to the length of the specimens after three hours of curing. Therefore, a large part of ettringite expansion in *Manhd* is not enclosed in the calculation and its final shrinkage is apparently higher. This finding underlines that the continuous registration method is the best technique to evaluate the dimensional behaviour of these kinds of mortars. The faster initial expansion of *Manhd* could be connected to its higher mechanical strength: the expansive ettringite formation is likely more effective.

5. Conclusion

The mechanical properties of the studied fast setting HFAM are strictly depending on the calcium sulphate type and amount. In particular it was found that anhydrite promotes higher compressive strength development and faster expansion compared to gypsum. The main reason of these mechanical differences could arise from the anticipated C-S-H formation in the sample containing anhydrite.

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	Al$_2$O$_3$	CaO	Fe$_2$O$_3$	SiO$_2$	TiO$_2$	Na$_2$O Equivalent
High Alumina Cement	44.54	36.98	13.58	2.01	1.89	0.1
Portland Cement	5.80	61.20	2.70	21.50	/	0.7

Tab. 1 XRF elemental analysis

Components	Ref	Manhd	Mgyps	Pref	Panhd	Pgyps
Portland cement	23.6	23.6	23.6	23.6	23.6	23.6
High Alumina cement	11.8	11.8	11.8	11.8	11.8	11.8
Anhydrite	/	2.95	/	/	2.95	/
Gypsum	/	/	3.67	/	/	3.67
0-5 mm Silica sand	64.60	61.65	60.93	/	/	/
Water	13.0	13.0	13.0	13.0	13.0	13.0

Tab. 2 Sample compositions

	Ref	Manhd	Mgyps
Flow (%)	305	310	300
Unit weight (kg/m^3)	2281	2270	2275

Tab. 3 Physical properties of fresh prepared mortars
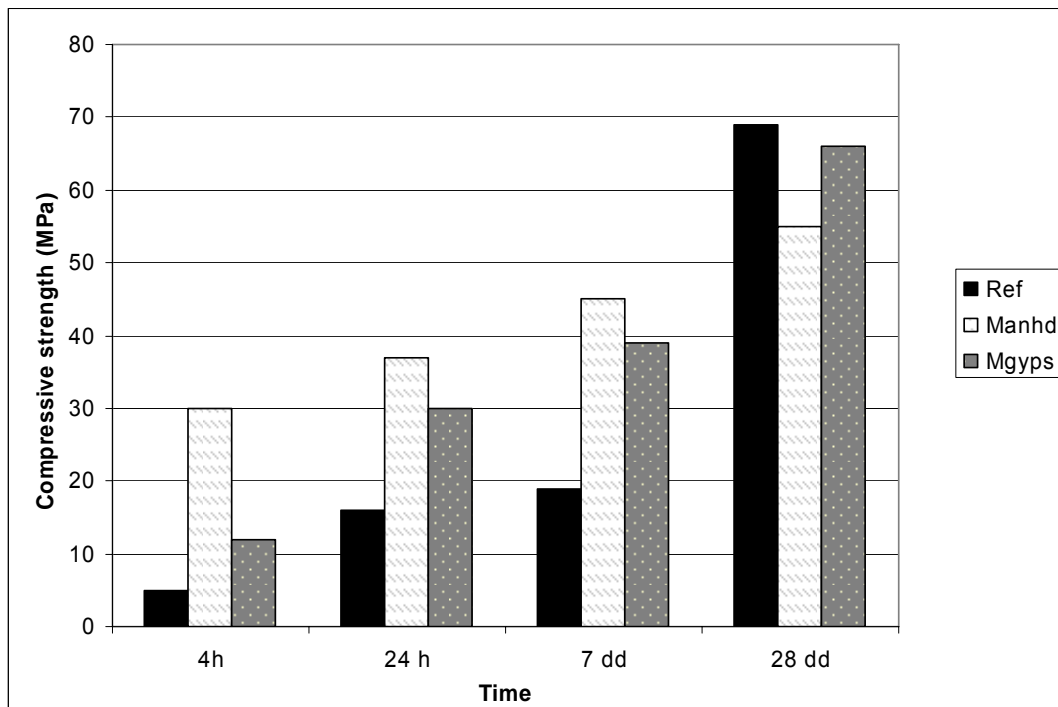
Fig. 1 Compressive strength development
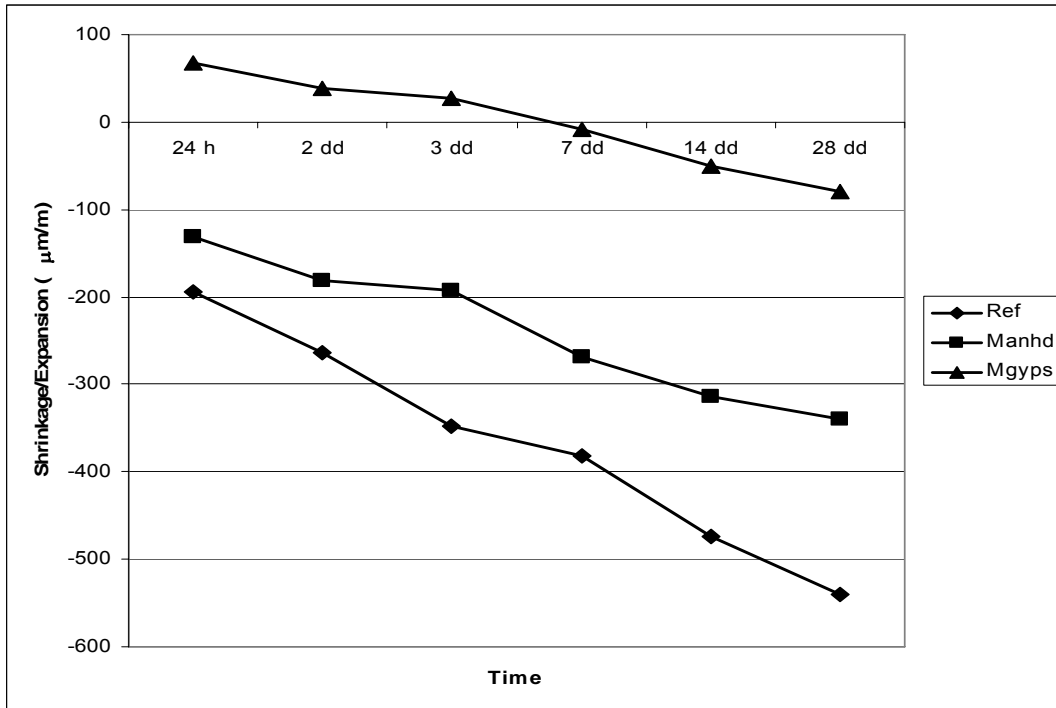
Fig. 2 Shrinkage/Expansion measurements (UNI 6687)
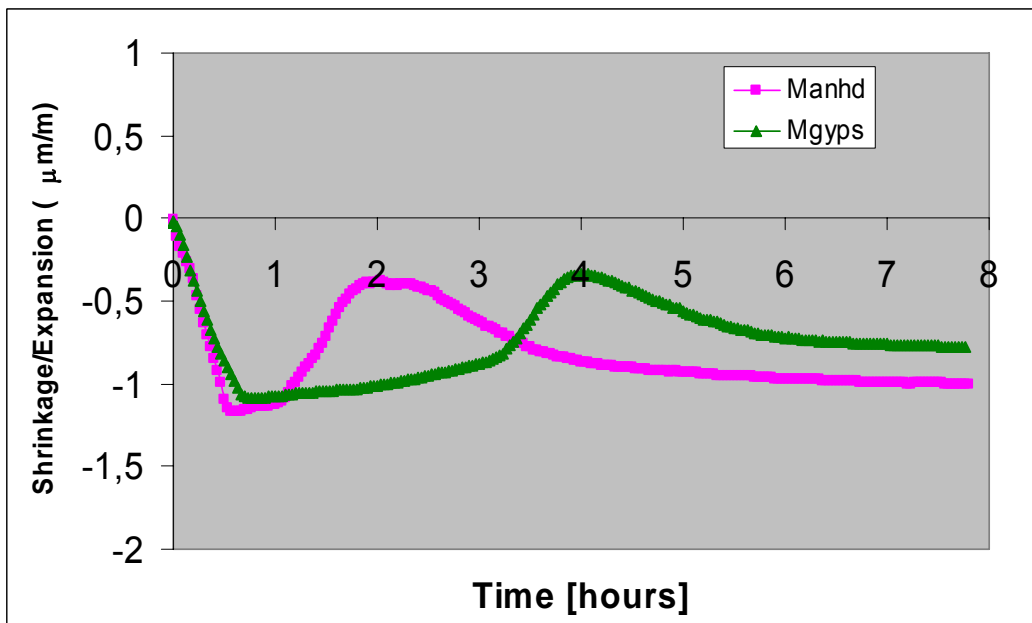
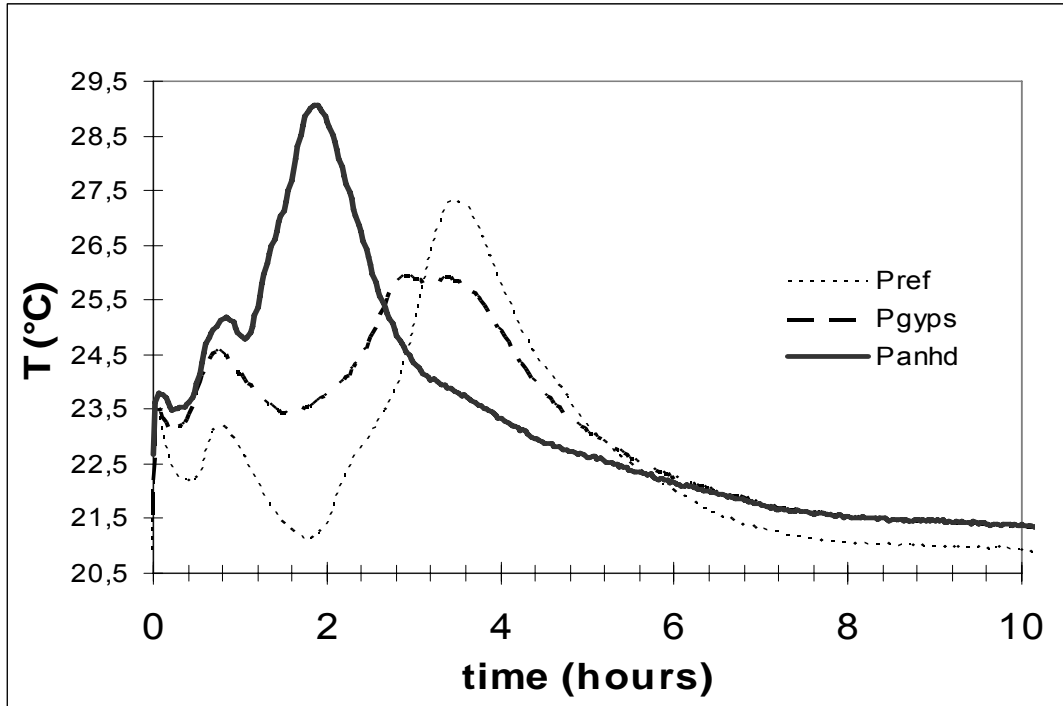Fig. 3 Shrinkage/Expansion measurements (continuous registration method)

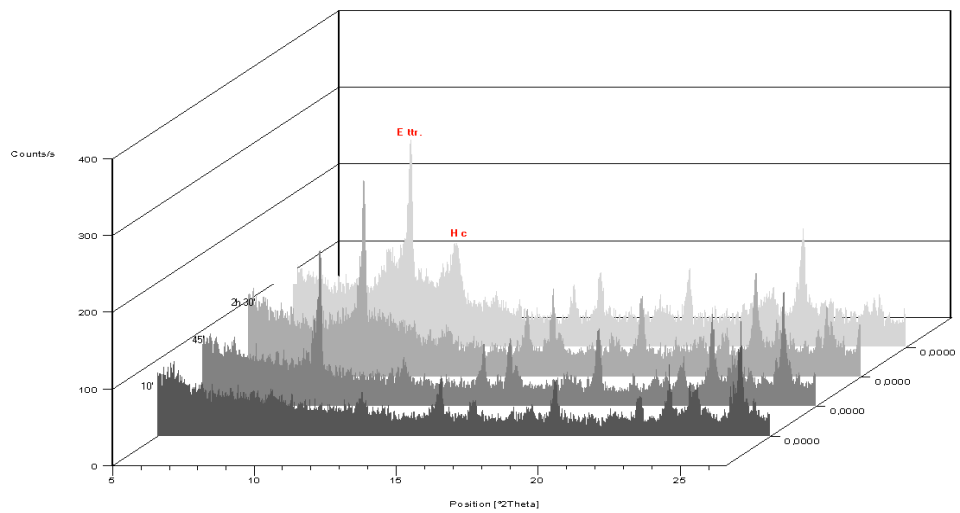Fig. 4 Hydration temperature profile

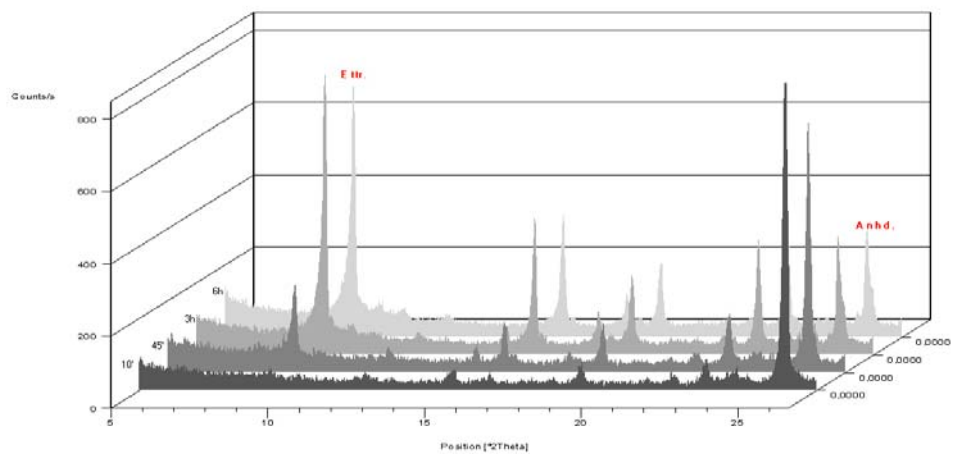Fig. 5 XRD of *Pref* at different curing times

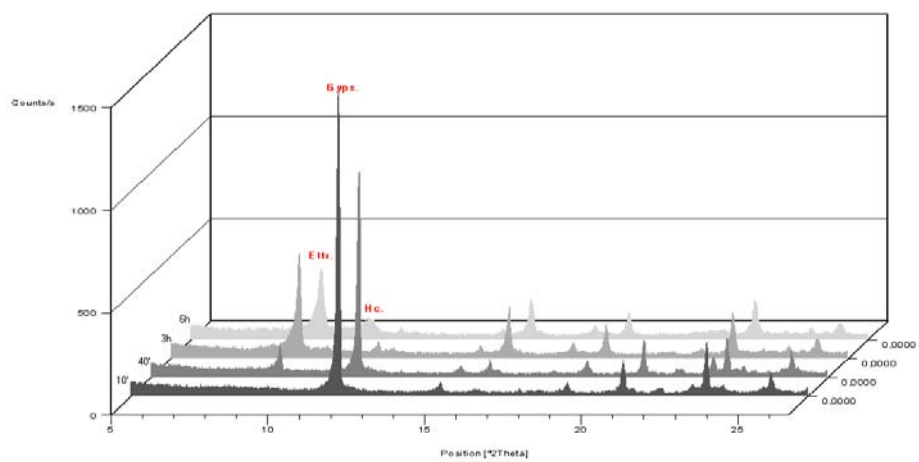Fig. 6 XRD of *Panhd* at different curing times
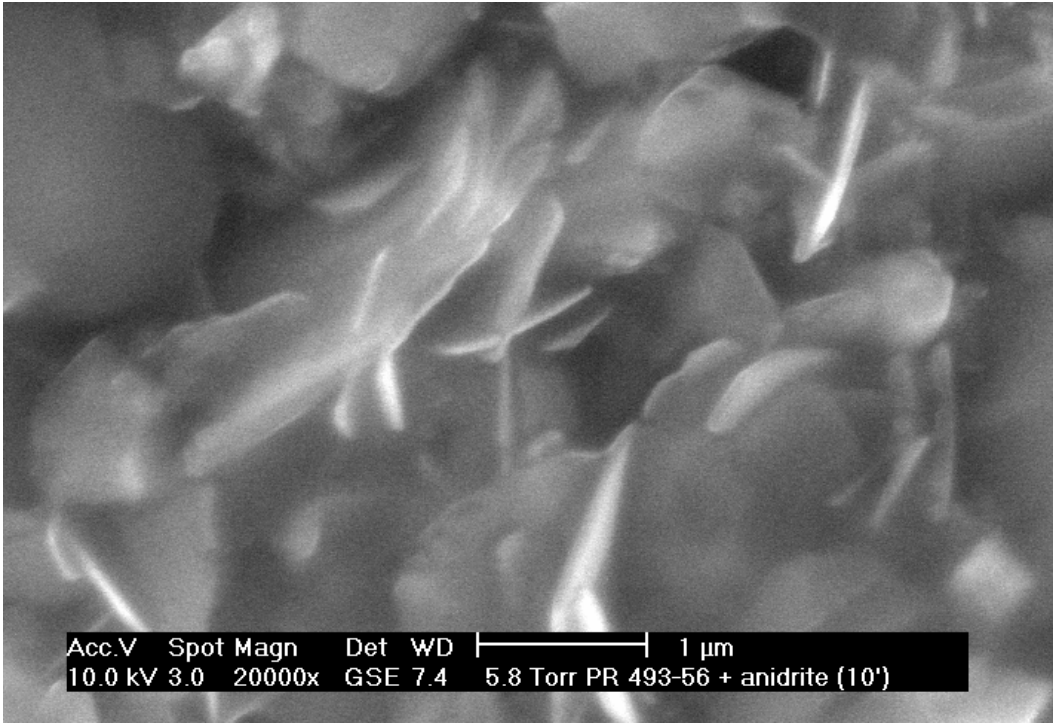

Fig. 7 XRD of *Pgyps* at different curing times

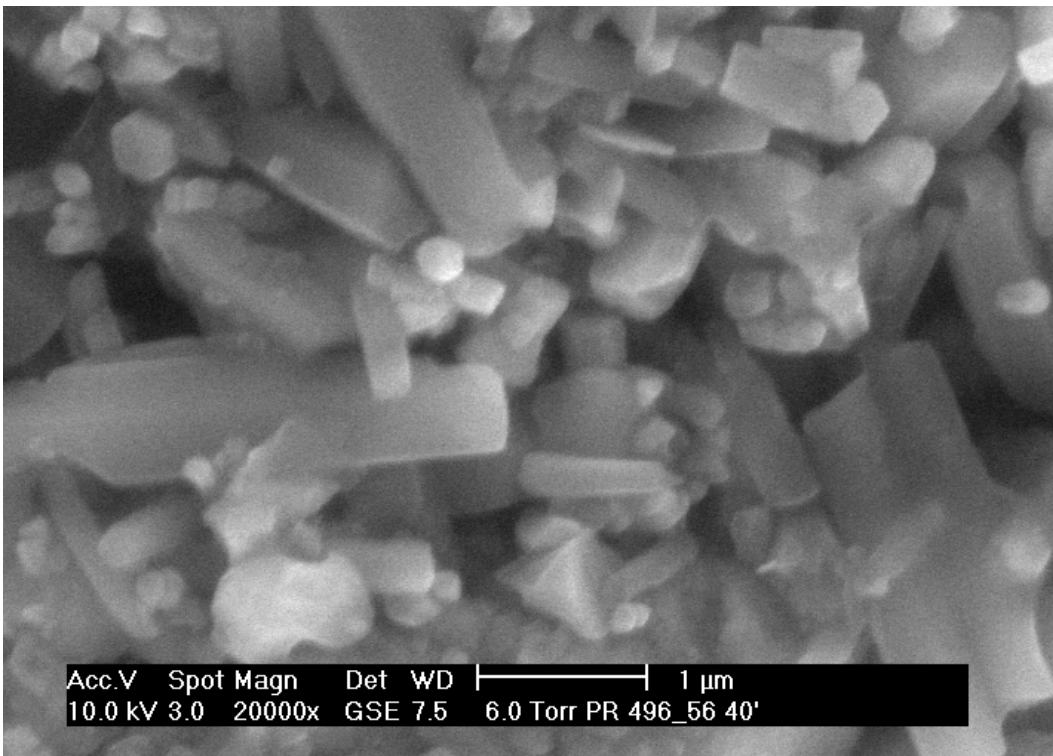Fig. 8 ESEM micrograph of *Panhd* after 10 minutes of hydration (unit length 1 μm)

Fig. 9 ESEM micrograph of *Pgyps* after 40 minutes of hydration (unit length 1 μm)

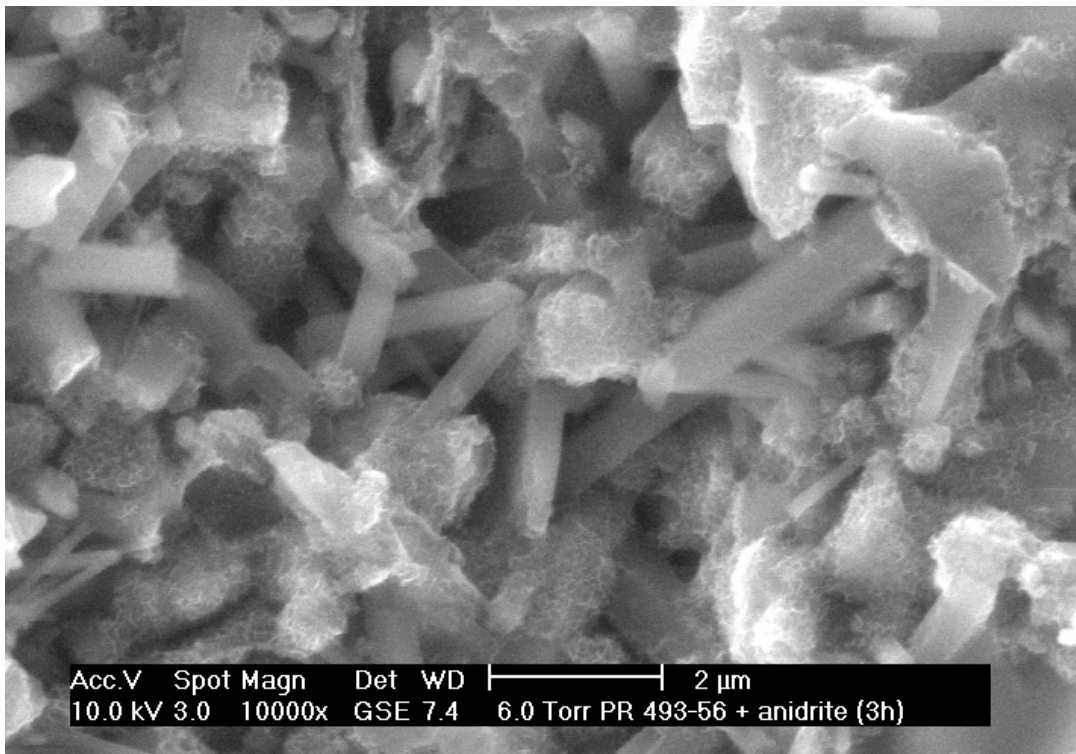Fig. 10 ESEM micrograph of *Panhd* after 40 minutes of hydration (unit length 1 μm)

Fig. 11 ESEM micrograph of *Panhd* after 3 hours of hydration (unit length 2 μm)