

# Effects of Calcium Sulfate and Aluminum Crystal Forms on the Kinetics of Ettringite Formation

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## ABSTRACT

The production of valuable cementitious materials from fluidized bed combustion (FBC) spent bed and fly ash has been hampered due to problems of dimensional stability, especially swelling. This is due to the uncontrolled production of ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ ), the primary cementitious mineral, and the delayed hydration of "dead burned" or beta-form anhydrous calcium sulfate ( $\beta\text{-CaSO}_4$ , anhydrite). This work is part of an ongoing effort to determine the factors controlling ettringite formation. Laboratory pastes were formed from naturally occurring anhydrite ( $\beta\text{-CaSO}_4$ ), heated (dehydrated) gypsum (mixed  $\gamma/\beta\text{-CaSO}_4$ ), Klein's compound (*i.e.*, the mineral yeelimite,  $\text{Ca}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ) in calcium aluminosulfate/belite cement, calcium aluminate cement, alumina and/or portlandite. The reaction of these materials to form ettringite was monitored by powder X-ray diffraction (XRD). Although natural anhydrite did not rapidly hydrate to gypsum, its presence did not appear to hamper the rate or extent of ettringite development in the pastes. The formation of ettringite in the hydration of the yeelimite paste appeared slower than that in the calcium aluminate/ $\text{CaSO}_4$  pastes.

## INTRODUCTION AND STATEMENT OF THE PROBLEM

Solid byproducts from fluidized bed combustion (FBC) contain large amounts of free lime and calcium sulfate. These calcium-bearing compounds impart a cementitious property to the FBC ashes when they are mixed with water and can potentially be utilized as a binder in "no-cement" concrete products (Bland et al., 1987; EPRI, 1991). Currently in the U.S., FBC ash is not commercially utilized in concrete or cement applications, but rather is used in various types of fills, and in waste and soil stabilization applications (ACAA, 2005).

A major impediment to higher-value use of FBC and other calcium sulfate-rich coal utilization byproducts (CUBs), such as spray dryer ash and conventional and forced oxidation wet flue gas desulfurization products (FGD), is their long-term dimensional stability. There are several phases in these materials that can contribute to dimensional changes during hydration, including calcium oxide (CaO, calcia or raw lime), which hydrates to calcium hydroxide (Ca(OH)<sub>2</sub>, portlandite, or slaked lime) and anhydrous calcium sulfate (CaSO<sub>4</sub>, including β-CaSO<sub>4</sub>, anhydrite), which hydrates to form gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O). If CaSO<sub>4</sub> hydration is delayed, it can cause destructive dimensional changes at later curing stages.

The occurrence of calcium hydroxide, calcium sulfate and a reactive aluminum phase (soluble at high pH) form the complex mineral ettringite (Ca<sub>6</sub>Al<sub>2</sub>[SO<sub>4</sub>]<sub>3</sub>[OH]<sub>12</sub>·26H<sub>2</sub>O). Ettringite is often implicated as the cause of expansion in hydrated FBC ash, spray dryer ash and ash-lime stabilized FGD materials. However, as noted above, delayed gypsum formation can also play a role. Conversely, in some types of cement, most notably those based on calcium aluminosulfate/belite (CASB), ettringite is the most important cementitious mineral and is crucial to strength development. Even in Portland cement, ettringite is a contributor to early strength (Cody et al., 2004).

Clearly, to develop high-value uses for calcium-rich CUBs, it is important to understand the factors controlling the rate of development and morphology of ettringite during the hydration of these materials. Ettringite-forming reactants and reactions during the early stages of curing are of particular interest, especially the influence of anhydrite and aluminum phases on the kinetics of ettringite formation.

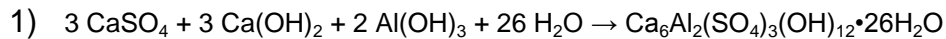
The polymorphs of anhydrous CaSO<sub>4</sub> represent a complex factor in ettringite formation. Anhydrous CaSO<sub>4</sub> has three crystal forms: 1) α-CaSO<sub>4</sub>, a very high temperature hexagonal form (Table 1) not of interest here; 2) anhydrite or β-CaSO<sub>4</sub>, which is an orthorhombic form that slowly reacts if its "dead burned" and 3) γ-CaSO<sub>4</sub>, also orthorhombic, which typically forms from the dehydration of gypsum and is the more readily soluble form of anhydrous CaSO<sub>4</sub>. Naturally occurring CaSO<sub>4</sub>, or anhydrite, is the beta-form, as is the anhydrous CaSO<sub>4</sub>

found in fluidized bed combustion ash. It should be noted that “reactive” is a kinetic phenomenon as the free energies of formation of the anhydrous  $\text{CaSO}_4$  forms differ only slightly (Dean, 1979, p. 9.15).

These tests are part of an ongoing series of experiments designed to help understand the factors controlling the formation of ettringite in calcium-rich CUBs. The specific objective for this work is to assess the effects of the crystal form of anhydrous  $\text{CaSO}_4$  and the reaction mechanisms on the formation of ettringite.

## MATERIALS AND METHODS

Powder X-ray diffraction (XRD) methods were used in this study to monitor the growth of ettringite in laboratory cementitious pastes during the first week (168 hours) of curing (Table 2). The growth of ettringite in cements requires the presence of reactive calcium, aluminum, and sulfate compounds. A number of laboratory test pastes were prepared that contain various proportions of an aluminum source, various crystalline forms of calcium sulfate, the possible addition of portlandite ( $\text{Ca}[\text{OH}]_2$ , Fisher reagent grade) and deionized water. For the pastes containing portlandite, the materials were mixed in stoichiometric quantities based on the following ideal reaction for ettringite:



To form  $\gamma\text{-CaSO}_4$ , samples of reagent grade (Fisher brand) gypsum and wet scrubber gypsum were heated to 300-350°C to dehydrate them. This range is well above the minimum temperature to dewater gypsum, but was used to assure that there was no bassanite ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ , or “hemi-hydrate”) present, as  $\gamma\text{-CaSO}_4$  is formed from the release of water from the bassanite crystalline structure and the XRD patterns of the two compounds are very similar and difficult to distinguish (International Centre for Diffraction Data [ICDD], 2004).

The dehydration products that formed were not pure  $\gamma\text{-CaSO}_4$ , but rather a mixture of  $\beta$ - and  $\gamma\text{-CaSO}_4$  (Table 3). We will refer to dehydrated gypsum and scrubber sludge as  $\beta/\gamma\text{-CaSO}_4$ . During the study, the  $\beta/\gamma\text{-CaSO}_4$  was stored at about 100°C to prevent the rehydration of the  $\text{CaSO}_4$ .

Naturally occurring anhydrite (obtained from the Wards Scientific Co.) was used for the  $\beta\text{-CaSO}_4$  form. This material was nearly pure  $\beta\text{-CaSO}_4$  with minor gypsum (Table 3).

Major aluminum sources for the pastes included calcium aluminate or CA cement (Secar® 80 from LaFarge Inc.), aluminum-refining waste collected from electrostatic precipitators, and a commercial calcium sulfoaluminate-belite (CSAB) cement from China. The compositions of the aluminum materials are shown in Tables 3-4. The primary cementitious hydraulic phase in the CSAB

cement is “Klein's Compound” ( $\text{Ca}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ), which is also known as the mineral yeelimite (Table 3).

Once the pastes were prepared, they were cured in a room with 100% humidity. Beginning at one-hour after mixing and periodically continuing for at least 168 hours, an aliquot of each paste was analyzed for ettringite and other crystalline compounds with a Philips powder XRD unit (model PW2404) operating at 45 kV and 40 mA (Figure 1).

The relative quantities of ettringite in the samples were estimated by measuring the height of the (100) peak at about  $9.09^\circ 2\theta$  (Figure 1). Peak heights are affected by many factors besides concentration, especially grain size from the grinding of the sample. As shown in the figures, the peak height measurements are often “noisy” and only provide qualitative results. Although peak area measurements were evaluated, they did not reduce the amount of noise. Table 5 shows the  $2\theta$  values that were used to estimate the relative quantities of various compounds in the samples.

## RESULTS AND DISCUSSION

### Hydration of Anhydrous $\text{CaSO}_4$ Forms.

The aluminum refining waste was found to be non-reactive and served as a good substrate to test the relative reaction rates of the  $\text{CaSO}_4$  forms. The  $\gamma\text{-CaSO}_4$  from the  $\beta/\gamma\text{-CaSO}_4$  mixtures (dehydrated reagent-grade gypsum and scrubber sludge) was not detected in any of the analyses of the aluminum waste pastes, which indicates that it entirely hydrated to gypsum within the first hour of curing or otherwise reacted. The conversion of the anhydrite ( $\beta\text{-CaSO}_4$ ) portion of the  $\beta/\gamma\text{-CaSO}_4$  mixtures to gypsum was slower. Anhydrite disappeared in the aluminum waste-dehydrated gypsum paste (Al-DG) within 24 hours (Figure 2) and within six hours for the aluminum waste-scrubber sludge (Al-SS) paste (Figure 3).

In contrast, the natural anhydrite ( $\beta\text{-CaSO}_4$ ) was much slower to react and persisted in the aluminum waste paste for the duration of the test, more than 200 hours (Al-NA; Figure 4). Unlike the artificial mixed-phase  $\text{CaSO}_4$ , natural anhydrite crystallized over a long period of time in the deep subsurface and probably under significant lithostatic pressure. Although the natural anhydrite has a similar surface area when compared with the dehydrated reagent-grade gypsum and scrubber sludge (Table 4), natural anhydrite is probably denser, better crystallized, and only forms gypsum on its surface. Unlike  $\gamma\text{-CaSO}_4$ , which can readily hydrate to bassanite and gypsum, the natural anhydrite ( $\beta\text{-CaSO}_4$ ) would have to dissolve and reprecipitate to fully convert to gypsum.

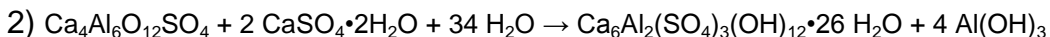
Although gypsum is plentiful in the aluminum waste pastes, the development of ettringite is very limited, with X-ray counts only slightly above the background. The major compound in the aluminum refining waste is  $\text{Al}_2\text{O}_3$  (corundum; Table 3), which is sparsely soluble in water and not favorable for the formation of ettringite. There were no detectable changes in the  $\text{Al}_2\text{O}_3$  concentrations of the pastes over 168 hours (one week). The relatively small amounts of ettringite that developed in the pastes may have resulted from the trace to minor amounts of sodium aluminum fluoride compounds in the aluminum wastes (Table 3). The sodium aluminum fluorides would dissolve in water. The released aluminum could then react with calcium sulfates to form ettringite and/or precipitate as  $\text{Al}(\text{OH})_3$ .

### Calcium Sulfoaluminate/Belite (CSAB) Cement Hydration Paste.

Yeelimite ( $\text{Ca}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ) is the major compound in the commercial CSAB cement (Table 3). Minor amounts of belite ( $\beta\text{-Ca}_2\text{SiO}_4$  or larnite), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), and anhydrite ( $\beta\text{-CaSO}_4$ ) are also present. In the CSAB-Water only (CSAB hydration) paste, 11.03 grams of the CSAB cement were mixed with 7.09 grams of deionized water (Table 2). Gypsum is normally added to CSAB cement to initiate the production of ettringite. However, an XRD analysis indicated that this cement was already interground with gypsum and no additional gypsum or other compounds were added to the paste.

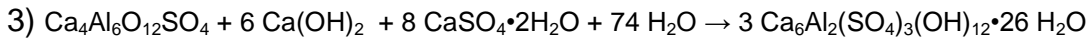
The initial pH of the CSAB-water paste was 10, which is alkaline enough for ettringite to precipitate (Cody *et al.* 2004, p. 870). Within 24 hours of storage in the curing room, the mixture had turned hard and mostly dry. The peak heights for yeelimite showed some variation between 4000 and 5000 units during the first six hours (Figure 5).

The gypsum in the CSAB cement was totally consumed within six hours of curing (Figure 5). Yeelimite concentrations also dramatically declined within 24 hours. At the same time, the ettringite peak heights increased. The disappearance of gypsum and yeelimite and the formation of ettringite in the paste can be explained by the following reaction:



The presence of  $\text{Al}(\text{OH})_3$  reaction products could not be confirmed by XRD. However, any  $\text{Al}(\text{OH})_3$  precipitates from the above reaction may be amorphous and undetectable.

Little or no portlandite ( $\text{Ca}[\text{OH}]_2$ ) was detected in the dry CSAB and its water-only paste, and the pH of the paste was only 10. If portlandite was present, the paste would have rapidly attained an equilibrium pH of  $\sim 12.5$ . In the presence of portlandite, the following reaction could occur:



Unlike reaction 2,  $\text{Al}(\text{OH})_3$  does not precipitate in reaction 3. In reaction 3,  $\text{Al}(\text{OH})_3$  would react with calcium from the portlandite to form additional ettringite.

The  $\beta$ - $\text{CaSO}_4$  concentrations did not appear to decline during the first 24 hours in the CSAB hydration paste. After 24 hours, ettringite peaks became intense enough to interfere with the main anhydrite peaks so that the reaction of anhydrite to form ettringite remained indeterminate. With only traces of yeelimite remaining after 24 hours, the ettringite concentration leveled off (Figure 5).

### CSAB-- $\text{CaSO}_4$ --Portlandite Pastes

Pastes were made from CSAB, portlandite, the two forms of anhydrous  $\text{CaSO}_4$ , and distilled and deionized water (Table 2; Figures 6 and 7). The growth of ettringite in the CSAB- $\text{Ca}(\text{OH})_2$ - $\text{CaSO}_4$  pastes showed some similarities with the CSAB hydration paste (Figures 5-7). Ettringite appears in the earliest XRD scans and increases in abundance during the first week of curing.

The natural  $\beta$ -anhydrite decreased rapidly between hours 6 and 24, during a time of increasing ettringite formation (Figure 6). The  $\beta/\gamma$ - $\text{CaSO}_4$  that formed from dehydrating scrubber gypsum rapidly disappeared within 72 hours probably by reconvertng to gypsum (Figure 7). The gypsum that formed from the  $\beta/\gamma$ - $\text{CaSO}_4$  mixture containing the heated scrubber sludge (CSAB-SS#2) then dropped in abundance during ettringite formation (notably between hours 168 and 504 [7 and 21 days]; Figure 7).

The yeelimite behaved much differently in the CSAB-- $\text{CaSO}_4$ --portlandite pastes than in the CSAB hydration test (Figures 5-7). Yeelimite persisted much longer and in the paste with the natural anhydrite (Figure 6) it remained throughout the test. In the paste with the mixed scrubber sludge  $\beta/\gamma$ - $\text{CaSO}_4$  (Figure 7), yeelimite did not significantly decline until after 168 hours (one week), which coincided with a sharp decline in the concentration of gypsum. The simultaneous decline of yeelimite and gypsum after 168 hours for CSAB-SS#2 (Figure 7) could be explained by reaction 2. However, since portlandite had been added to the paste (Table 2; Figure 7), reaction 3 is more likely.

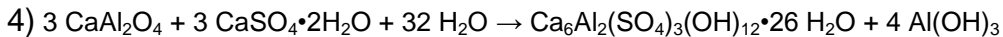
### Calcium Aluminate— $\text{CaSO}_4$ Pastes

The calcium aluminate cement used in these tests was primarily composed of calcium aluminate ( $\text{CaAl}_2\text{O}_4$ ) with minor grossite ( $\text{CaAl}_4\text{O}_7$ ) and alumina ( $\text{Al}_2\text{O}_3$ ) (Table 3). The most intense anhydrite and grossite XRD peaks have very close  $2\theta$  values (*i.e.*,  $25.3^\circ$   $2\theta$  for grossite and  $25.5^\circ$   $2\theta$  for anhydrite; ICDD, 2004; Table 5), which caused some difficulties and may add errors to the

measurements. The grossite appeared to be non-reactive and the alumina only sparingly so (Figures 8 and 9).

As in the tests described above, the rate of formation of ettringite did not appear to be greatly affected by the forms of  $\text{CaSO}_4$ , at least within the variability of the XRD method. Natural anhydrite persisted through the test (Figure 8) and, at least,  $\gamma\text{-CaSO}_4$  initially formed bassanite and then gypsum (Figure 9). The rate of ettringite formation was much different in these tests when compared with the yeelimite pastes. Ettringite developed very rapidly with most of it appearing within the first six hours of the tests. The development of ettringite in the CSAB tests was later, between 6 and 24 hours or more (Figures 5-7).

In the CA and scrubber sludge #2 paste (CA-SS#2), bassanite/ $\gamma\text{-CaSO}_4$  was detected during the first four hours of curing (Figure 9). The bassanite/ $\gamma\text{-CaSO}_4$  probably converted to gypsum, which can react with  $\text{CaAl}_2\text{O}_4$  to form ettringite through reaction 4:



## OBSERVATIONS AND DISCUSSION

The natural anhydrite ( $\beta\text{-CaSO}_4$ ) used in this study behaved similarly to the “dead burned”  $\beta\text{-CaSO}_4$  found in fluidized bed ashes. It persisted throughout most of the tests and only hydrated to gypsum very slowly. The mixed phase  $\gamma/\beta\text{-CaSO}_4$  readily and rapidly rehydrated to gypsum and completely disappeared in some of the tests. The form of  $\text{CaSO}_4$  did not appear to have a large, noticeable impact on the rate of ettringite formation. Thus, one possible route to reduce delayed gypsum formation is to eliminate the bulk of the  $\beta\text{-CaSO}_4$  through the early formation of ettringite.

This study also suggests that  $\text{CaSO}_4$  is not the rate limiting nutrient in the formation of ettringite in these systems. Comparing the data for ettringite formation in CSAB, CASB/ $\text{CaSO}_4$ /portlandite, and CA/ $\text{CaSO}_4$  pastes indicates that the availability of reactive alumina is the critical factor. The formation of ettringite is also faster from CA/ $\text{CaSO}_4$  than from yeelimite.

## ACKNOWLEDGEMENTS

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Table 1: Common calcium sulfate compounds.

Form	Temperature of Formation	Crystal Class	Crystal Space Group	References
CaSO <sub>4</sub> melt	> 1450	---	---	Lide (2005)
α-CaSO <sub>4</sub>	1210-1495	Hexagonal	P31c	PDF-26-0328 (International Centre for Diffraction Data, 2004)
β-CaSO <sub>4</sub> (anhydrite; insoluble form)	650 - ~1210, Often metastable at lower temperatures	Orthorhombic	Amma	Bezou et al. (1995)
γ-CaSO <sub>4</sub> (soluble form)	300 - 650	Orthorhombic	C222	Bezou et al. (1995)
CaSO <sub>4</sub> •0.5H <sub>2</sub> O (bassanite; plaster of Paris)	128 - 163	Monoclinic	I121	Bezou et al. (1995); Lide (2005)
CaSO <sub>4</sub> •2H <sub>2</sub> O (gypsum)	< 128	Monoclinic	I2/a	Bezou et al. (1995); Lide (2005)

Table 2: Compositions of the cementitious pastes.

Date and Sample ID	Mass (g) Secar® 80 CA cement heated ~100°C	Mass (g) Aluminum Refining Waste	Mass (g) CSAB cement	Mass (g) Natural Anhydrite ( $\beta$ -CaSO <sub>4</sub> )	Mass (g) Fisher Gypsum heated to 300°C	Mass (g) Scrubber Sludge heated to 300°C	Mass (g) Unheated Fisher Ca(OH) <sub>2</sub>	Mass (g) Distilled and Deionized Water
090606 (AI-SS)	0	1.3023	0	0	0	4.1435	2.2290	8.5
091106 (AI-NA)	0	1.1644	0	3.7301 (<38 $\mu$ m)	0	0	2.2024	10.3
111406 (AI-DG)	0	1.3192	0	0	4.0828	0	2.2254	6.9
031207 (CSAB-Water, Initial pH = 10)	0	0	11.03	0	0	0	0	7.09
092606 (CSAB-SS)	0	0	6.1060	0	0	1.4144	0.7440	6.9
013007 (CSAB-SS#2)	0	0	6.1051	0	0	1.3626	0.7441	6.86
110706 (CSAB-DG)	0	0	6.1064	0	1.3646	0	0.7445	6.9
112806 (CSAB-NA)	0	0	6.1036	1.3624 (<45 $\mu$ m)	0	0	0.7425	6.9
072606 (CA-SS)	2.6877	0	0	0	0	1.3751	0	2.4
080806 (CA-SS#2)	2.6870	0	0	0	0	1.3688	0	2.6
073106 (CA-DG)	2.6799	0	0	0	1.3617	0	0	2.1
080206 (CA-NA)	2.6906	0	0	1.3773 (<38 $\mu$ m)	0	0	0	2.4

Table 3: X-ray diffraction (XRD) results on components used in the cementitious pastes.

Material	Major Phases	Minor and Trace Phases
CSAB	Yeelimite ( $\text{Ca}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ )	Belite ( $\beta\text{-Ca}_2\text{SiO}_4$ ), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), anhydrite ( $\beta\text{-CaSO}_4$ )
Aluminum Waste	Corundum ( $\text{Al}_2\text{O}_3$ )	$\text{Al}(\text{OH},\text{F})_3$ , $\text{NaAlF}_4$ , $\text{Na}_3\text{AlF}_6$
Scrubber Sludge: Heated 300-350°C	Anhydrite ( $\beta\text{-CaSO}_4$ )	$\gamma\text{-CaSO}_4$
Dehydrated Gypsum: Heated 300-350°C	Anhydrite ( $\beta\text{-CaSO}_4$ )	$\gamma\text{-CaSO}_4$
Natural Anhydrite	Anhydrite ( $\beta\text{-CaSO}_4$ )	Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )
CA cement	$\text{CaAl}_2\text{O}_4$	Grossite ( $\text{CaAl}_4\text{O}_7$ ), $\text{Al}_2\text{O}_3$

Table 4. Major element oxides (X-ray fluorescence) and other properties of the aluminum and calcium sulfate materials.

Element (oxide) (wt%)	CSAB (China)	Scrubber Sludge	Natural Anhydrite	Aluminum Refining Waste	CA cement	Dehydrated Fisher Gypsum
$\text{SiO}_2$	11.12	3.72	4.29	3.84	0.19	---
$\text{Al}_2\text{O}_3$	26.94	0.67	1.01	83.15	77.65	---
$\text{Fe}_2\text{O}_3$	1.76	0.57	0.55	1.49	0.53	---
CaO	44.99	39.82	34.9	0.57	20.51	---
MgO	3.18	0.37	3.14	0.23	0.42	---
$\text{Na}_2\text{O}$	0.04	<0.01	0.02	6.27	0.74	---
$\text{K}_2\text{O}$	0.19	0.05	0.19	0.30	0.01	---
$\text{P}_2\text{O}_5$	0.11	0.05	0.04	0.05	0.10	---
$\text{TiO}_2$	0.79	0.06	0.06	0.09	0.07	---
$\text{SO}_3$	12.23	49.75	51.54	1.87	<0.01	---
F	---	0.03	0.02	1.72	---	---
Loss on Ignition	5.47	22.68	6.23	13.53	1.06	---
Surface Area ( $\text{m}^2/\text{g}$ )	---	4.9020	5.4670	---	---	4.7285

Table 5. 2θ values for determining the powder XRD peak heights of various compounds.

Al <sub>2</sub> O <sub>3</sub> (corundum)	35.1
Anhydrite (β-CaSO <sub>4</sub> )	25.5
Bassanite/γ-CaSO <sub>4</sub>	14.7
Belite (larnite) (β-Ca <sub>2</sub> SiO <sub>4</sub> )	32.0
Ca <sub>3</sub> Al <sub>2</sub> O <sub>6</sub>	33.2
Calcite (CaCO <sub>3</sub> )	29.4
Ettringite (Ca <sub>6</sub> Al <sub>2</sub> [SO <sub>4</sub> ] <sub>3</sub> [OH] <sub>12</sub> •26H <sub>2</sub> O)	9.09
Grossite (CaAl <sub>4</sub> O <sub>7</sub> )	25.3 and 19.9
Gypsum (CaSO <sub>4</sub> •2H <sub>2</sub> O)	11.6
Lime (CaO)	37.3
Portlandite (Ca[OH] <sub>2</sub> )	34.1
Yeelimite (Ca <sub>4</sub> Al <sub>6</sub> O <sub>12</sub> SO <sub>4</sub> )	23.6

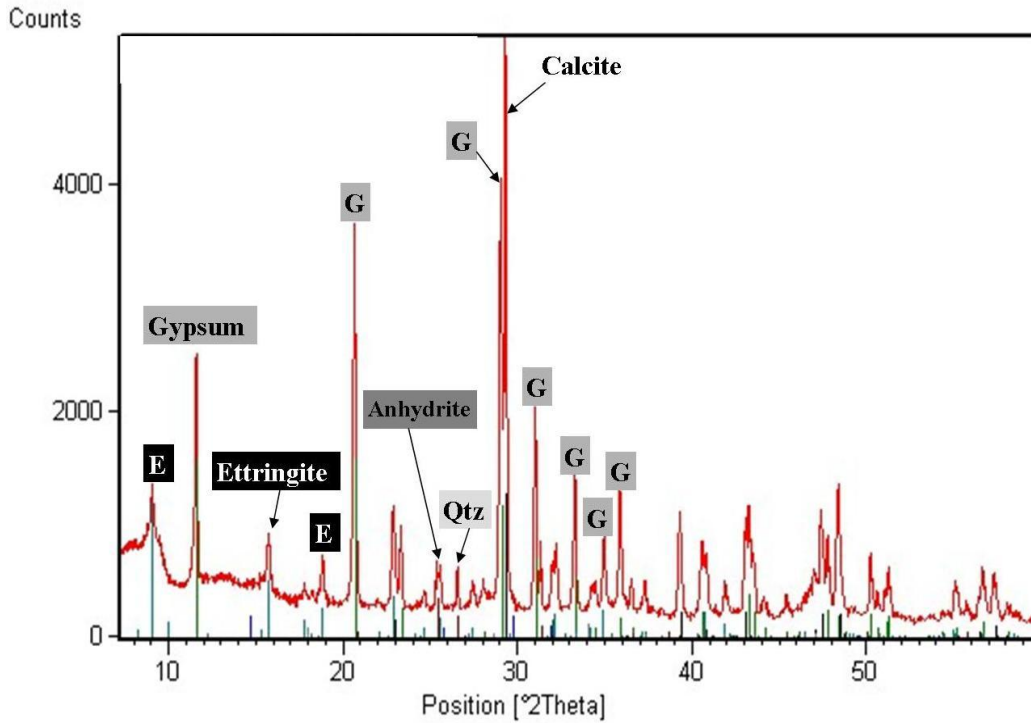


Figure 1. X-ray diffraction (XRD) pattern showing principal peaks of ettringite (E), gypsum (G), anhydrite (A), calcite (C) and quartz (Qtz).

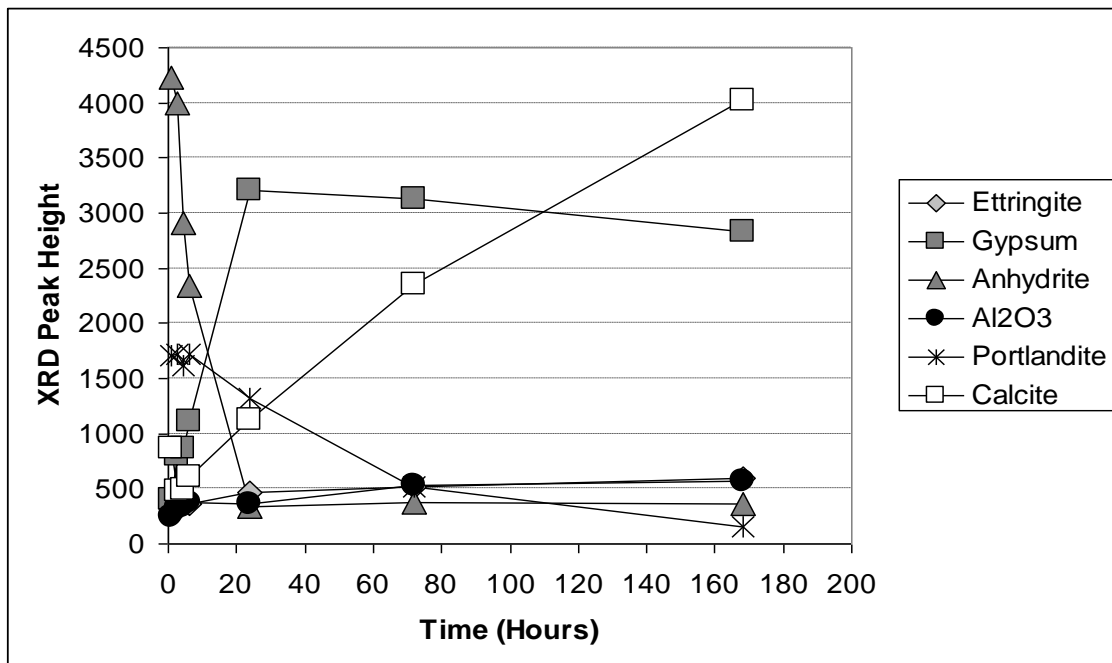


Figure 2. XRD data for the rehydration of  $\beta/\gamma$ -CaSO<sub>4</sub> from reagent grade gypsum (AI-DG).

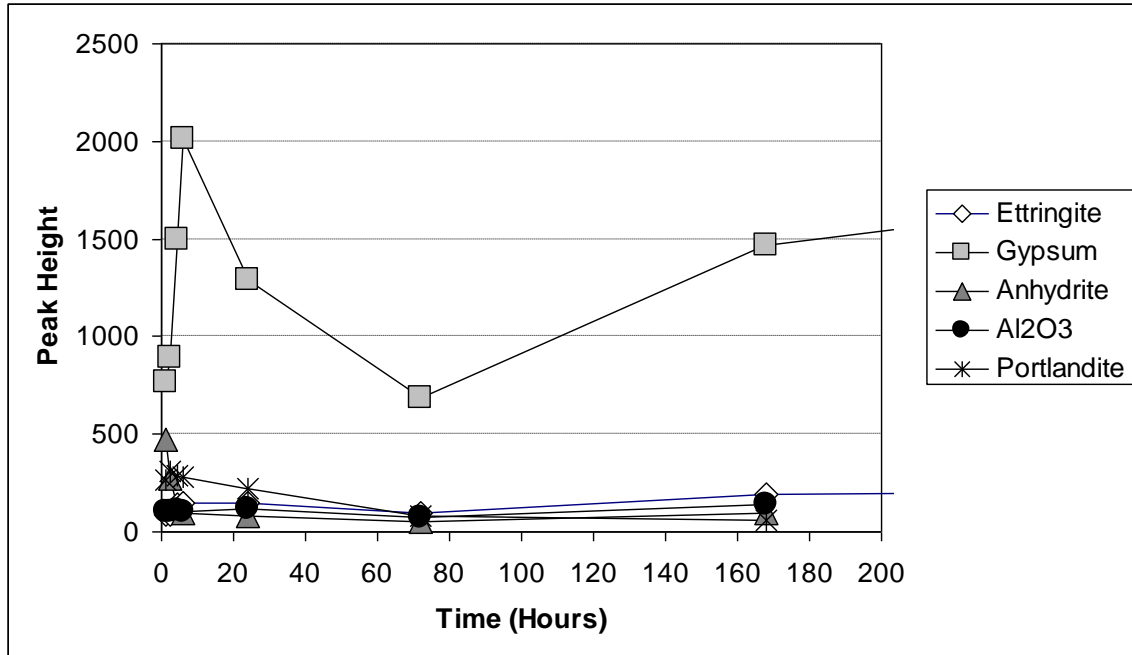


Figure 3. XRD data for the rehydration of  $\beta/\gamma$ -CaSO<sub>4</sub> from scrubber sludge (Al-SS).

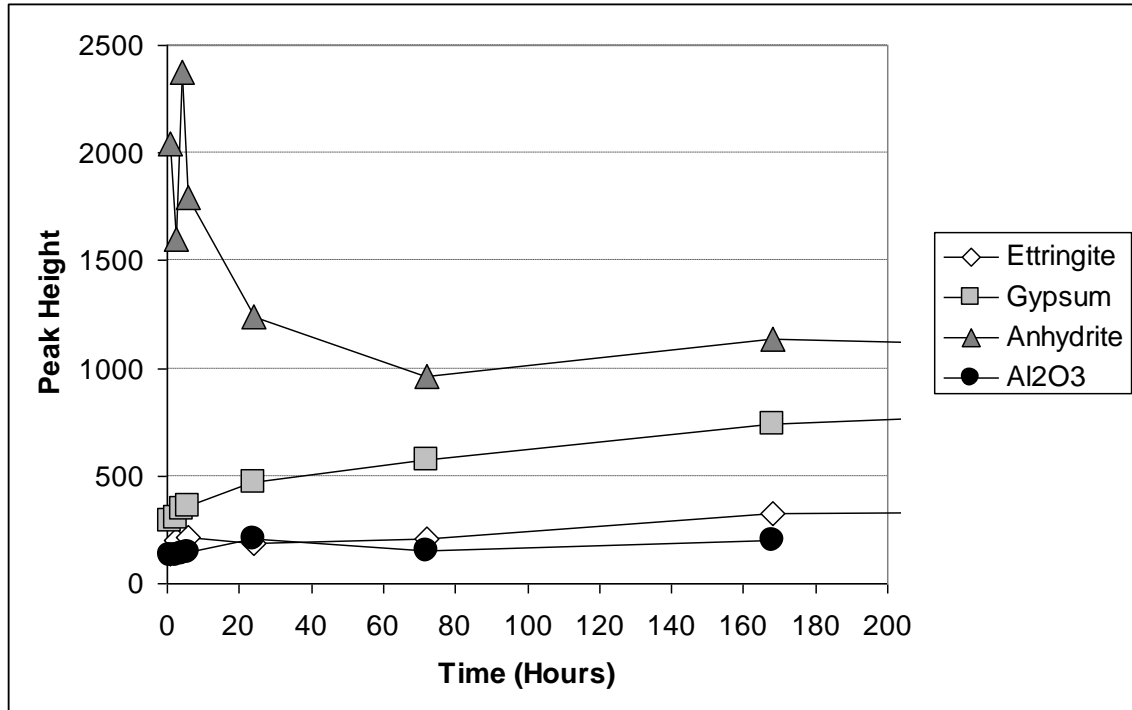


Figure 4. XRD data for the rehydration of  $\beta$ -CaSO<sub>4</sub> from natural anhydrite (Al-NA).

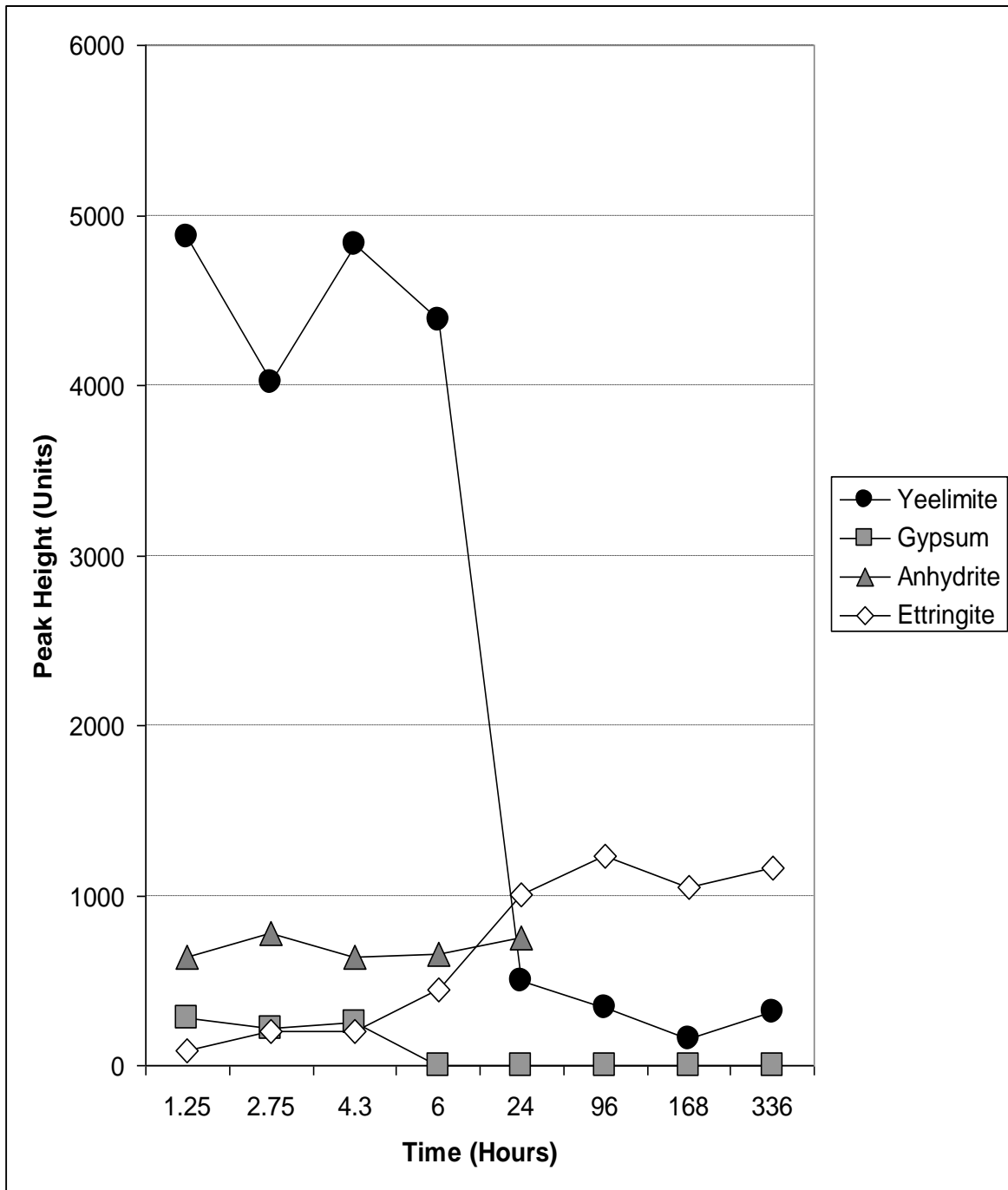


Figure 5. XRD data CSAB cement hydration products (CSAB-water only).

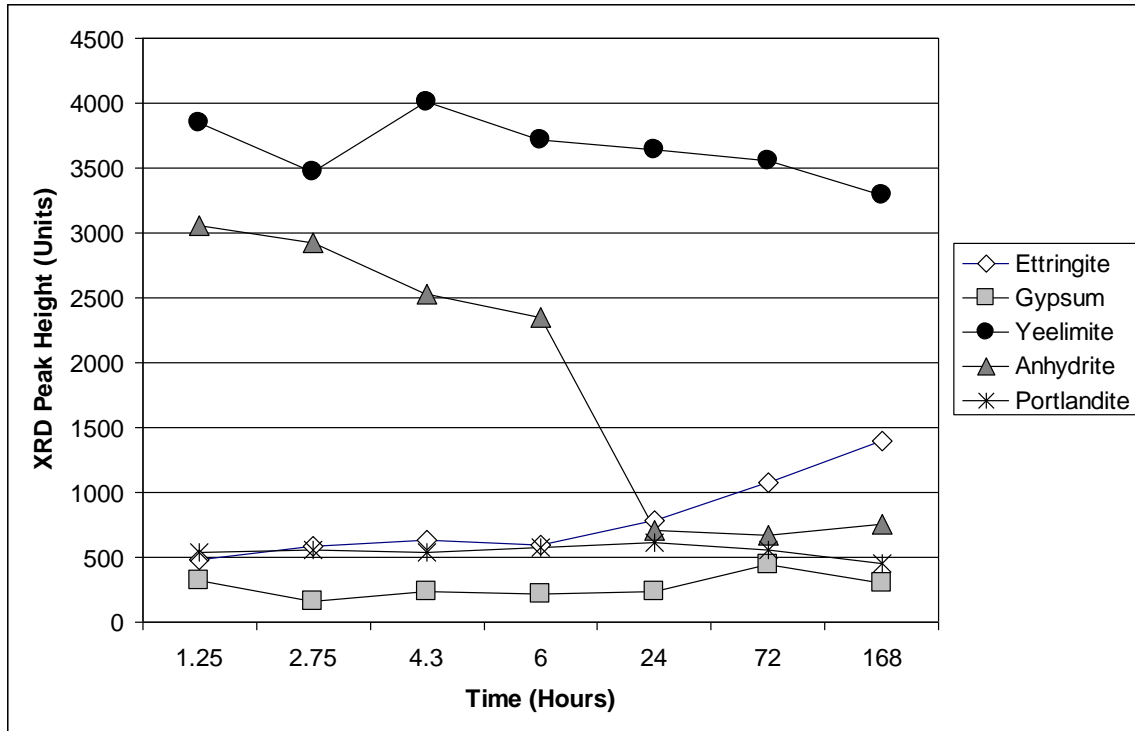


Figure 6. XRD data for the hydration of CSAB cement with  $\beta$ -CaSO<sub>4</sub> from natural anhydrite (CSAB-NA).

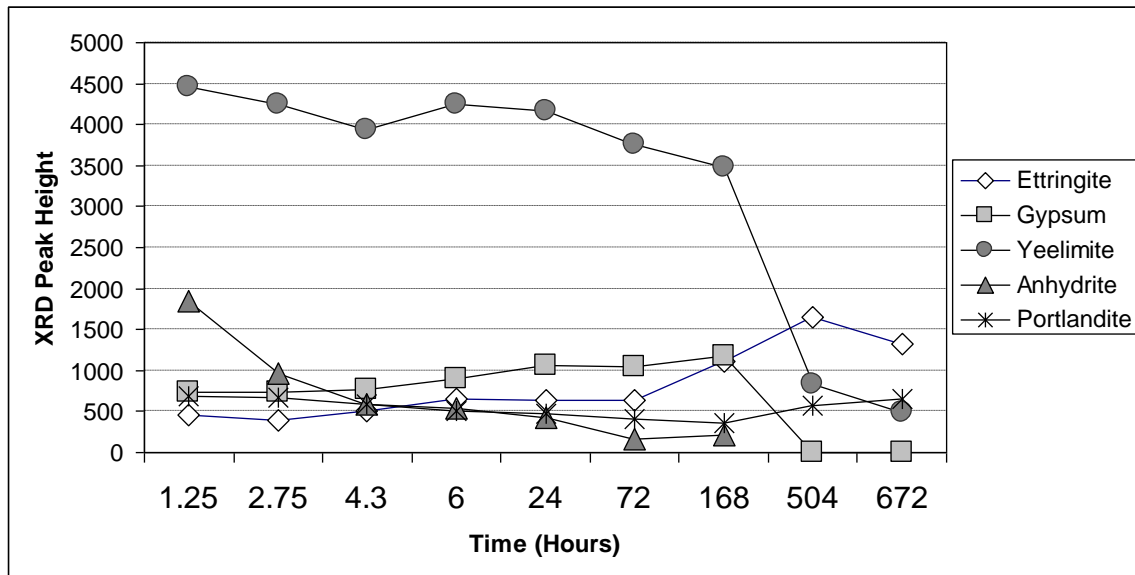


Figure 7. XRD data for hydration of a CSAB-Ca(OH)<sub>2</sub>- $\beta/\gamma$ -CaSO<sub>4</sub> paste (CSAB-SS#2).

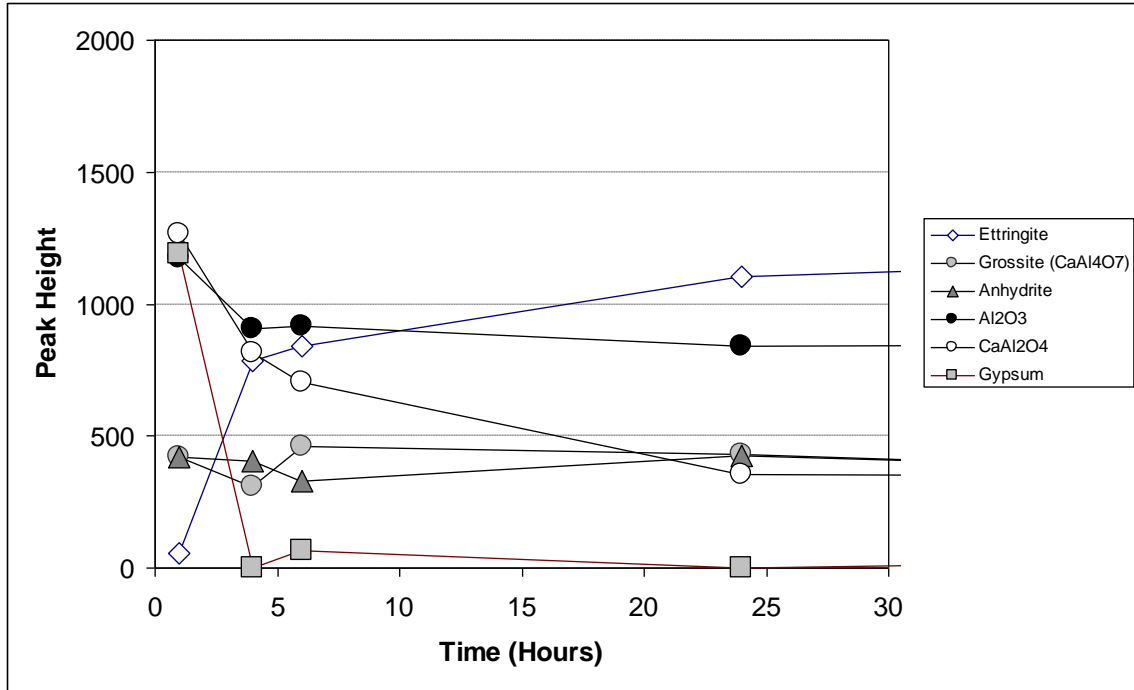


Figure 8. XRD data for the calcium aluminate and natural anhydrite paste (CA-NA).

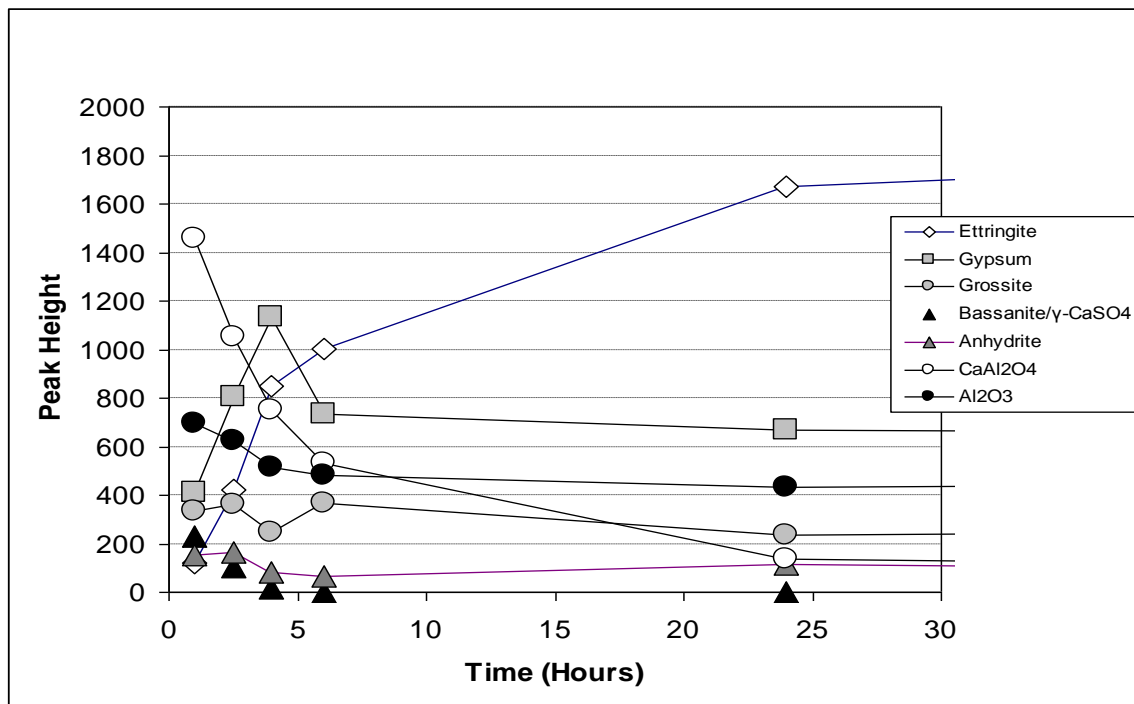


Figure 9. XRD data for a calcium aluminate and  $\beta/\gamma$ -CaSO<sub>4</sub> paste (CA-SS#2).