



# Hemihydrate or waste anhydrite in composite binders with blast-furnace slag: Hydration products, microstructures and dimensional stability



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## HIGHLIGHTS

- We studied composite binders of hemihydrate or anhydrite and blast-furnace slag.
- The main hydration products are gypsum, amorphous C–S–H and ettringite.
- Gypsum from anhydrite is less porous than the gypsum matrix from the hemihydrate.
- Excellent dimensional stability is observed when silica fume and fly ash are used.
- C–S–H with Ca/Si composition from 1.08 to 1.78 was intimately mixed with the gypsum.

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## ABSTRACT

This paper presents results of an investigation of calcium sulphate-blast furnace slag binders cured for up to 600 days with small additions of fly-ash or silica fume. Hemihydrate and fluorgypsum were used as the calcium sulphate sources. The binders showed good mechanical and hydraulic properties; the water resistance was attributed to the formation of C–S–H with Ca/Si ratio between 1.08 and 1.78 finely inter-mixed with the gypsum initially formed. Ettringite was formed after the reaction between gypsum and aluminum from the slag and fly ash; however, its formation was hindered in the presence of silica fume, which improved the dimensional stability.

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## 1. Introduction

Recent investigations on calcium sulphate-based composite binders reveal a general perspective of actual feasibility to obtain alternative eco-friendly cements that, in addition to the intrinsic properties of the gypsum such as workability, aesthetics and low density, could be reliable upon their mechanical properties for outdoor applications without the risk of dissolution, or in other words, binders with hydraulic character. The above offers an area of opportunity to contribute in the search for sustainable construc-

tion materials; however, calcium sulphate may come from diverse sources and in different hydration states such as gypsum and hemihydrate from mineral or waste calcined gypsum, anhydrite by-products of several chemical industries, or by-products from the scrubbing of combustion gases (flue-gas desulfurization).

A practical way to group such cements would be according to the mineralogy of the calcium sulphate source used. Thus, hydraulic composite binders based on reactive anhydrite [1–5] or hemihydrate [6–10], can be considered as cements that lead to the formation of a gypsum framework interacting with water insoluble hydrated phases of the type C–S–H and ettringite formed from the reactions of the “supplementary cementitious materials”, such as granulated blast-furnace slag (GGBFS), Portland cement, sulphoaluminate clinker or pozzolanic materials. On the other hand, other composites could be elaborated with calcium sulfate dihydrate,

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where the main role of calcium sulphate is to perform as a buffer of sulphatic activator for the supplementary cementitious materials, rather than as a reactive material to form gypsum [11–13].

Nevertheless, the information available about such cementitious materials is limited in terms of direct comparisons of properties and reactions mechanisms for binders of the same mass formulations fabricated with different sources of calcium sulphate. This study presents the results of a comparison of the chemical and morphological nature of the hydration products among composite binders formulated with anhydrite or hemihydrate with blast furnace slag and pozzolans cured under different conditions for long periods. The aim was to widen the understanding of the influence of the individual components and their interactions towards the integration of the microstructural configuration of the composites, emphasizing the characterization of the chemical composition of the hydration products of the type C–S–H that impart the hydraulic character, providing a new perspective about these composites throughout X-ray energy dispersive spectroscopic studies. In addition, there exists limited information on dimensional stability on gypsum-slag composites that could be potentially expansive by excessive ettringite formation; therefore, this study intends to relate the dimensional changes with the hydrated phases and their structuration.

This work is a complement of a previous contribution that deals with the strength development and reactivity of the same composite binders, in which a detailed description of the state of the art and characterization of the raw materials was presented [14]. Some of the conclusions of such work highlighted the marked differences in compressive strength between both types of calcium sulphate binders: the use of anhydrite was better over the use of hemihydrate in terms of strength; however, a notable gain in the rate of heat evolution was registered by the former during the initial minutes of curing. This behavior indicated that a rapid dissolution of the hemihydrate takes place from the early stages of curing, but lead to a gypsum structure of lower strength relative to that of the gypsum formed from the anhydrite. On the other hand, experiments of a selective dissolution technique showed that the reaction of the slag is slower than both calcium sulphate sources; however, it was effective for later stages of curing.

## 2. Experimental details

Table 1 shows the chemical composition obtained by X-ray fluorescence spectroscopy and physical properties for the materials used. Commercial  $\beta$ -hemihydrate Plaster of Paris (CG) from USG Mexico and anhydrite from a fluorgypsum waste (FG) were used as calcium sulphate sources. Ground granulated blastfurnace slag from Altos Hornos de Mexico (GGBFS) was ball milled to a Blaine fineness of 4300  $\text{cm}^2/\text{g}$ . Two pozzolanic materials were used as complements to the binders: type-F pulverized fly-ash (PFA) from a local thermoelectric plant and a silica fume (SF) from

**Table 1**  
Chemical composition (wt%), physical properties of raw materials and mixing design of the pastes. Abrev. CG – Commercial hemihydrate, FG – fluorgypsum, GGBFS – granulated blastfurnace slag, PFA – type F fly ash, SF – silica fume.

OXIDE	CG	FG	GGBFS	PFA	SF
SiO <sub>2</sub>	1.9	0.1	32.7	60.6	97.3
CaO	41.0	40.7	39.2	2.1	0.9
Al <sub>2</sub> O <sub>3</sub>	0.4	0.1	11.3	27.9	0.3
Fe <sub>2</sub> O <sub>3</sub>	0.4	0.1	0.5	3.8	1.0
MgO	0.3	0.04	8.6	0.4	0.2
SO <sub>3</sub>	55.0	58.2	3.5	–	0.1
K <sub>2</sub> O	0.1	0.01	0.9	1.1	0.2
Na <sub>2</sub> O	–	0.03	0.5	0.1	–
Blaine Fin. ( $\text{cm}^2/\text{g}$ )	5100	5200	4300	9000	15,000
Density ( $\text{g}/\text{cm}^3$ )	2.6	3.0	2.9	1.9	1.1
Wt% used in the formulations	30–70	30–70	30–70	10–20	10–20

BASF. Details of the mineralogical composition of the raw materials was reported previously [14], where the main phases of CG and FG were hemihydrate and anhydrite, respectively, while traces of calcite and anhydrite were detected for the latter and quartz for the former. The GGBFS denoted a large fraction of vitreous network with crystalline phases such as melilite, merwinite and diopside.

Pastes were prepared according national standard [15] and cast as cubic samples of 2.54 cm on polystyrene molds. The pastes were left to set isothermally at 20 °C for 24 h and further cured in air or under distilled water for up to 600 days until the predetermined dates for mechanical testing; some samples were cured at 60 °C. Table 1 shows the compositional ranges (wt%) of the composite binders. The commercial gypsum pastes were added with 10% of Portland cement, as chemical activator, referred to the weight of the GGBFS + pozzolans, and 0.2% of malic acid as setting retarder as reported elsewhere [16]. The fluorgypsum pastes were added with 1–3% of Ca(OH)<sub>2</sub> and aluminum and potassium sulphates as chemical activators for anhydrite and GGBFS + pozzolans based on laboratory experience from the authors and as reported elsewhere [3,17]. The water/binder ratios were established for good workability at 0.43 for commercial gypsum and 0.3 for fluorgypsum binders. Compressive strength was measured for up to 600 days and reported as the average of 4 samples tested in a 25 T hydraulic press (Sercomp 7/50-C7022, Controls). For measurements of the dimensional changes, four prismatic bars for each selected formulation were made and tested after different ages of curing based on the Mexican standard NMX-C-418-ONNCE-2001 [18].

Pieces of crushed cubes were immersed in methanol for 24 h to stop the hydration and then dried in a vacuum oven at 35 °C. A fraction of those was ball milled to ~105  $\mu\text{m}$  for characterization by X-ray diffraction (XRD, Philips Xpert and Bruker D8 Advance) using Cu K $\alpha$  radiation, operating the equipment at 40 kV and 30 mA, within the range of 7–60° 2 $\theta$ , with a step of 0.03° 2 $\theta$  every 3 s. Some solid specimens were carbon coated to make them conductive for characterization by Scanning Electron Microscopy (SEM, Philips XL30 ESEM,) with X-ray energy dispersive spectroscopy (EDS) capabilities (EDAX). Samples were observed in fracture surfaces using secondary electron imaging, as well as in polished surfaces using backscattered electron imaging with offers chemical contrast. Series of microanalyses from selected polished samples were taken from phases clearly outside GGBFS grains in the spaces initially occupied by water (outer products). Backscattered electron images were used to select the areas for analysis, care was taken to locate the electron spot at a distance of at least 3  $\mu\text{m}$  from any visible anhydrous material and gypsum crystals. The microscope was operated at 20–30 kV and the time of analysis was 70 s, ZAF corrections were performed using the software of the equipment. Some samples were tested for Non-evaporable water measurements (NEW) as the weight losses of samples of ~5 g calcined at 950 °C for 1 h.

## 3. Results and discussion

### 3.1. X-ray diffraction and dimensional stability

Fig. 1 shows XRD results for 30% commercial gypsum pastes cured for up to 600 days where hemihydrate (HH) reflections were absent at all the studied ages, and readily identifiable gypsum peaks (20.8, 11.7 and 29.3° 2 $\theta$ ) were noted from one day of curing. This indicated complete hydration of HH after 24 h, in agreement with [6]. Small peaks of anhydrite and calcite as remnants after the commercial gypsum manufacture are noted after 600 days, while quartz (SiO<sub>2</sub>) was similarly present for the pastes with PFA. The pastes with 20%PFA and 0% pozzolan denoted peaks of portlandite after 24 h as result of the Portland cement hydration, such peaks disappeared after 7 days after its consumption by the pozzolanic reaction to form C–S–H, and possibly ettringite as the PFA can dissolve Al<sub>2</sub>O<sub>3</sub> under the activating environment, which in turn favored the initial strength development. This can be seen in Table 2 with the representative results of strength and non-evaporable water (NEW) of the binders of this study from a previous report [14]. The main reflection of ettringite at 9.65° 2 $\theta$  was observed from 7 days onwards in the composites with PFA and 0% pozzolan; the intensity grew slightly with time indicating increased ettringite contents from early ages, similar to reports on supersulphated cements [19]. It is noteworthy that the paste with SF did not show peaks of ettringite nor portlandite during the studied time span. This suggests that the formation of ettringite is influenced by the chemical nature of the pozzolans: the PFA has a silicoaluminous reactive phase able to provide Al<sub>2</sub>O<sub>3</sub> for the precipitation of ettringite, while the SF is purely siliceous. Additionally, according the results in Table 2, it seems that the SF hindered the initial reactivity of the GGBFS, therefore

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