



# Anhydrite/hemihydrate-blast furnace slag cementitious composites: Strength development and reactivity



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## HIGHLIGHTS

- We studied binders of CaSO<sub>4</sub> hemihydrate or waste anhydrite and blast-furnace slag.
- Initial strength is low but further gain was notable especially in anhydrite pastes.
- Reactions of anhydrite were notably slower and less exothermic than hemihydrate.
- Slag and pozzolanas hydration reactions were mainly promoted from 7 to 28 days.
- Fly ash or silica fume were beneficial for curing at 60 °C improving impermeability.

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## ABSTRACT

This paper reports on the hydration and properties of composite binders with 20–70% blastfurnace slag and 50–70% calcium sulphate (commercial hemihydrate or waste anhydrite) cured for up to 600 days; other small additions included silica fume or fly ash. Formulations of gypsum-based binders with good mechanical and hydraulic properties were obtained. Isothermal conduction calorimetry and non-evaporable water indicated that rapid initial gypsum formation is responsible for the initial strength: hemihydrate reacts intensively, whereas anhydrite reacted slower but resulted in better mechanical properties. Selective chemical dissolution demonstrated that slag hydration was slow but constant in the first 28 days.

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## 1. Introduction

Research on alternative cementitious materials is strongly focused in responding to the current ecological–economical challenges related to climate changes for which the Portland cement (PC) industry has an important share on the responsibility [1,2]. Environmental awareness and actions must be taken to develop and use alternative binders in new eco-friendly and preferably low cost construction materials. Among the promising alternatives are those based on gypsum, that have strongly attractive advantages such as: low costs, availability, aesthetics, fast hardening, low density, workability, insulating properties, relative easy processing with low energy demand and emissions, as well as its potential

recyclability. However, pure gypsum plasters are relative soft, suffer creep [3] and high water solubility. In order to tackle some of such deficiencies, many investigations have focused on combinations of gypsum with other complementary hydraulic binders such as Portland cement and pozzolanic materials, demonstrating the potential of such materials in common construction applications [4–11]. The matrix structuration of such binders corresponds to an initially formed network of gypsum crystals (CaSO<sub>4</sub>·2H<sub>2</sub>O) engulfed by C–S–H and other hydraulic phases formed from the slower hydration of the complementary binders, enhancing the mechanical properties and providing hydraulic character; however, an excessive formation of ettringite could represent expansive deleterious processes.

Early investigations for these “improved plasters” attempted to consolidate blends of hemihydrate–cement in proportions of 50% each, however these mixes disintegrated in less than a year due to the delayed formation of expansive phases [11]. Kovler et al. [4,5] studied composites of 75% hemihydrate and cement with

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silica fume additions (0–25%) cured for up to 200 days. They demonstrated that the use of the pozzolana meant an increase of 100% of compressive strength relative to pure gypsum–cement blend; however, the samples without silica fume disintegrated in less than 200 days due to the aforementioned cause, establishing that silica fume inhibits the ettringite formation. Colak [9] studied hemihydrate–cement–natural pozzolanas pastes where it was determined that the density of the specimens was relatively low between 1.34 and 1.42 g/cm<sup>3</sup> and depended on the binder compositions that worked well with additions of superplasticizers to improve the workability.

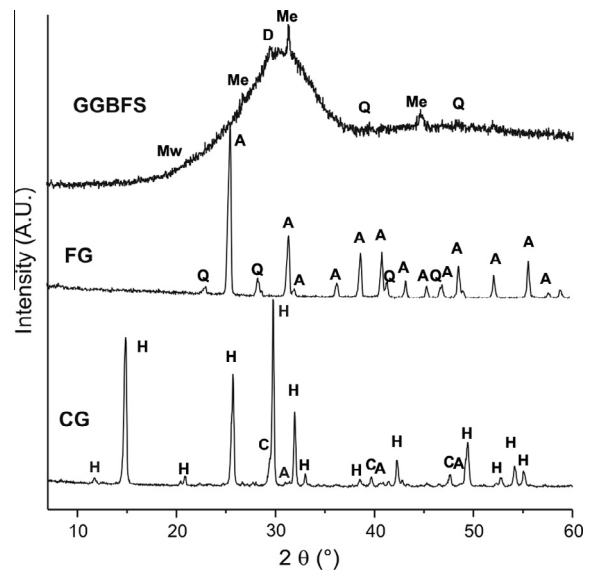
A well-studied variation of these compounds could be the supersulphated cements in which the main constituents are 70–90% ground granulated blast furnace slag, 10–20% calcium sulphate and <5% of PC or clinker. The alkaline environment from the PC hydration promotes the dissolution of Si, Al and Ca ions from the slag, which react with the calcium sulphate to form ettringite and C–S–H phases. More ettringite is formed in these cements than in PC, but it is not regarded as a deleterious phase and it contributes to the early strength development [12,13]. However, it can be considered that the small additions of the calcium sulphate in the supersulphated cements, act only as a “sulphatic activator” for the slag and do not form an initial gypsum matrix.

In Mexico, natural and waste gypsum sources are abundant:  $5.8 \times 10^6$  T of commercial gypsum in 2009 [2] and nearly 2000 T/day of fluorgypsum (FG) production [14] show the opportunity for these alternatives. This is confirmed by reports using materials of Mexican origin in which either hemihydrate or anhydrite wastes were used as the main constituents in composite construction materials. Studies on fluorgypsum–cement pastes cured at 20 °C and 60 °C [15,16] indicated that after 180 days of wet curing, those compositions with 10% of fly ash (70% FG –20% ordinary Portland cement) reached 32 MPa and 18 MPa. Chemically bound water for the pastes cured at 60 °C indicated that gypsum formation and strength were limited from the early ages. Martinez et al. [17] studied fluorgypsum binders with 20% silica fume, geothermal waste or fly ash, and found that the chemical nature and particle size of the pozzolanas had different effects on the strength development: siliceous pozzolanas were more advantageous than the silicoaluminate ones. Additionally, they noted by isothermal conduction calorimetry that geothermal waste accelerated the reactions over the other pozzolanas from early ages. Other reports on mortars of waste ceramic hemihydrate–blast furnace slag binders with granulated slag or silica sand as aggregates [18,19], indicated compressive strengths of  $20 \pm 2$  MPa after 120 days under water for mortars with aggregate:binder ratios of 2.3 and 3:1; the strength decreased with the use of silica sand in comparison with the reactive granulated slag aggregate.

In spite of the above, there exists limited information about the differences in the reaction mechanisms between hemihydrate and anhydrite from a direct comparison for a same mass of the reactive powders in composite cements with granulated blast furnace slag. This paper presents a study in that direction aiming to elucidate the differences during the early hydration processes for both calcium sulphates and to relate them to the reactivity of the other constituents in the binders, as well as to the strength development for later ages under different curing conditions. The aim was to understand the influence of the individual components on various formulations of composite binders.

## 2. Materials and fabrication

Two different sources of reactive calcium sulphate were used: commercial gypsum (CG) constituted mainly by  $\beta$ -hemihydrate with traces of calcite and anhydrite, and fluorgypsum waste (FG) composed of anhydrite with traces of quartz. Ground granulated blast furnace slag (GGBFS) was dried and ball milled to a Blaine fineness of 4300 cm<sup>2</sup>/g. The mineralogy of the main starting materials can be seen in Fig. 1,



**Fig. 1.** Phase compositions of the commercial gypsum (CG), fluorgypsum (FG) and the slag (GGBFS) used. Phases: H – hemihydrate, C – calcite, A – anhydrite, Q – quartz, D – diopside, Me – melilite, Mw – merwinite.

where a large fraction of amorphous material in the GGBFS denotes potential hydraulic reactivity. Two pozzolanas were used in some mixes as cementitious additives: densified silica fume by BASF (SF) that fulfill requirements of ASTM C 1240 was used manually dispersed, and a type F pulverized fly ash (PFA) from a local thermoelectric plant. Table 1 shows chemical composition of the raw materials in main oxides obtained by X-ray fluorescence.

Pastes of blended binders were formulated and cured for up to 600 days with the following proportions in weight percentage: commercial gypsum hemihydrate or fluorgypsum (30–70%), GGBFS (20–70%) and pozzolanas (0–10%). Pastes with commercial gypsum incorporated an additional of 10% of Portland cement (which had additions of calcite and slag in plant) as an alkaline activator referred to the weight of the GGBFS, and less than 0.5% of malic acid as a setting retarder [20]. The cements based on fluorgypsum were admixed for up to 3% with industrial grade reagents like  $Al_2(SO_4)_3$ ,  $K_2SO_4$ ,  $Ca(OH)_2$  to accelerate the anhydrite setting and activate the GGBFS hydration. The water/solids (w/s) ratio was fixed for good workability at 0.45 and 0.30 for commercial hemihydrate and fluorgypsum binders, respectively, some mixes with SF required additions of superplasticizer (Rheobuild-1000). A mixer with a 5 L bowl and planetary movement was used to process batches of ~1.5 kg of powdered starting materials, these were first manually homogenized and then added to the reaction water and mixed for a total of 2.25 min. Cubes of 2.54 cm were cast and left for 24 h to set isothermally at  $20 \pm 2$  °C. The cubes were afterwards demoulded and cured in air or under water at  $20 \pm 2$  °C in plastic containers until mechanical testing. Some specimens with 50–70% commercial gypsum or fluorgypsum with pozzolanic additions were also cured at 40 and 60 °C.

## 3. Characterization

Compressive strength (CS) was measured for ages up to 600 days and reported as the average of 4 samples, the tests were

**Table 1**

Chemical composition (wt%) and physical properties of raw materials: CG – commercial gypsum, FG – fluorgypsum, GGBFS – granulated blast furnace slag, PFA – 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. (cm <sup>2</sup> /g)	5100	5200	4300	9000	15,000
Density (g/cm <sup>3</sup> )	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

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