

Waste gypsum-activated blast furnace slag composites: Effect of aggregate type on strength development

R. X. Magallanes-Rivera, J. I. Escalante-García, A. Gorokhovskiy
Centre for Research and Advanced Studies (Cinvestav), Saltillo, México

The comparative behavior of granulated blast-furnace slag (GBFS) and silica sand was investigated in hydraulic environmentally friendly cement mortars with a constant sand/binder ratio=3/1. Three binder compositions (wt%) of waste gypsum (50-70%) and blast-furnace slag (30-50%) were used, 10% OPC was added as chemical activator. The mortars were cured in air and under water. Compressive strength was low after 3 days but reached up to 20 MPa for high slag contents (even under water), better than traditional gypsum plasters. After 90 days the strength was higher with GBFS aggregates relative to silica sand. The interfaces of hydration products with both aggregates were dense and continuous; the chemical reaction of the slag promoted a chemical bonding, which increased the strength. Dense microstructures of gypsum crystals engulfed by C-S-H products from slag hydration explained water resistance. Non evaporable water results indicated that early strength values were related to gypsum formation.

1. Introduction

The considerable population growth in recent years has conduced to a higher demand for infrastructure and housing. In developing countries, this problem must lead to the search of alternatives to answer the economical and ecological challenges that this carries along; one excellent option lies in the use of industrial wastes to elaborate construction materials. Considering that Portland cement is an expensive commodity in Mexico, and also that its manufacture generates large amounts of CO₂ [1,2], there is a great interest in developing environmentally friendly alternative cementitious systems of good properties at low costs. 2.1 millions tons of blast-furnace slag are generated in Mexico annually [3], together with by-product gypsum resources (such as ceramic processing plants), there is a latent opportunity to combine both wastes materials into composite binders and turn them in useful materials.

The hydraulic behavior and excellent strength of alkali activated blast-furnace slag cements are well documented in the literature; they represent a cement of low CO₂ emissions. On the other hand, gypsum cements are widely used in construction due to its aesthetics, low density, fast hardening, fire resistance and other characteristics. Gypsum is the most

abundant sulphate on earth, is cheap and its fabrication process involves very low CO₂ emissions. It is important to recognize that gypsum based cements would become an excellent alternative for many applications as international ecological restrictions dictate difficult to reach parameters for construction industry. Nevertheless, Plaster of Paris applications are restricted to interiors due to their relatively low strength and high water solubility (2g/litre).

The above leads the interest towards investigations of cements based on calcium sulphates of hydraulic character, which could be attained by means of combinations with hydraulic binders like Portland cement, activated blast-furnace slag and pozzolanas. The properties of such cements are early hardening, water resistance and low expansion normally associated to the sulfate reactions [4,5,6,7].

Mixes of 50:50 gypsum and Portland cement were studied in early investigations [1], however these cements disintegrated in less of a year due to delayed formation of expansive phases. Kovler et al. [8,9] worked on 65-85% commercial gypsum pastes mixed with OPC and silica fume as cementitious additive, they showed that incorporation of the pozzolana doubled the strength even under water for up to 200 days of curing. Other reports [10,11,12,13] established the viability of using anhydrite by-products in composite cements. However, these reports have been oriented to pastes or to mortars in which attention has not been focused to elucidate aspects of the interaction binder-aggregate.

Since about 75% of the volume in concretes corresponds to aggregates it is important to know the characteristics and chemical interactions of the aggregates with the binder. According to their chemical properties, granulated blast-furnace slag can be regarded as non deleterious reactive sand with the potential of physical-chemical union with the mass of hydration products surrounding the grain aggregates. In this work the aims were: (1) to develop a water-resistant cement based on waste calcium sulphate and blast furnace slag, with improved strength relative to traditional plasters; and (2) to evaluate strength development and interfacial interactions after the incorporation of a reactive aggregate in forming construction materials like hydraulic mortars.

2. Experimental details

The hydraulic binder were mixes of (wt.%): 50, 60 and 70% of calcium sulphate β -hemihydrate obtained from wasted ceramic gypsum moulds (**WG**); the mix was complemented with blast-furnace slag (**BFS**). All blends were added with an excess of 10% Portland cement relative to the **BFS** weight. Citric acid was used as a setting retarder at 0.07% of the total weight of binder; 2% of superplasticizer Rheobuild-1000 was incorporated

to improve the workability. Mortars systems were investigated in which the aggregates were Granulated blast-furnace slag (**GBFS**) and silica sand graded within the sieves number 20 and 30.

Spent molds from a jiggering process were provided by Ceramica Santa Anita (Saltillo, Mexico); the molds were crushed and pulverized to a blaine of 5,000 cm²/g and the **WG** was fired at 160°C for 24 hours in a chamber oven. The **BFS** was ball milled to a blaine of 4,000 cm²/g and the **GBFS** used as aggregate required only drying before usage. The Portland cement (**PC**) was donated by Cementos Holcim-Apasco (Ramos Arizpe, Mexico), it had calcite and **BFS** additions. Table 1 shows the properties and compositions of raw materials.

Table 1. Composition of binder constituents in main oxides and grading of aggregates

Oxide	Binder			Sand		
	WG	BFS	PC	US Mesh #	GBFS	Silica
SiO ₂	-----	37.21	18.86			
CaO	38.88	37.24	62.18	18	28.2	
Al ₂ O ₃	-----	11.63	4.52	20	51.9	0
Fe ₂ O ₃	-----	-----	2.73	30	74.3	100.0
MgO	-----	9.27	1.97	40	90.2	
SO ₃	55.52	2.69	2.58	50	100.0	
Blaine (cm ² /g)	5,000	4,000	4,100			
Density (g/cm ³)	2.55	2.91	2.90			

Cubic mortar samples of 50 mm were prepared, the dry solids were homogenized for 5 minutes in a portable bucket concrete mixer; the reaction water and additives were added and the mortar was mixed for 2 minutes. The mortars were cast into the molds and vibrated for 2 minutes; the samples were left to set at 20°C for 24 h. The specimens were demolded and then cured in air or submerged in water for curing up to 90 days. Setting times of the mortars were initial 34 and final 45 minutes. Compressive strength (**CS**) was measured on 4 specimens after 1, 7, 28 and 90 days of curing. After such test, pieces of crushed cubes were dried at 35°C for 24 hrs in a vacuum oven in order to stop hydration by eliminating the free water. The dried pieces were characterized by for non evaporable water (**NEW**), X-Ray diffraction (**XRD**) and scanning electronic microscopy (**SEM**) analysis.

3. Results and discussion

3.1 Strength Development

Table 2 presents the arrangement of the mortars investigated and the results of CS and NEW, it also shows the water/binder (w/b) ratios used to attain a fluidity of 110±5 [14]. One paste system of 60% **WG** was also prepared for reference purposes.

Table 2. Properties of hydraulic mortars

A:B	WG	BFS	Curing	w/b	Sand	CS (MPa) - (NEW [%])			
						1d	7d	28d	90d
3:1	50	50	Air	0.7	GBFS	0.7 (3.3)	5.6 (4.8)	15.0 (5.9)	21.2 (7.4)
			Water			0.7 (3.3)	5.3 (5.4)	16.4 (6.3)	19.1 (8.0)
	60	40	Air	0.7	GBFS	0.9 (3.8)	4.0 (5.3)	13.5 (6.3)	15.8 (7.4)
			Water			0.9 (3.8)	4.1 (5.4)	11.0 (6.8)	17.5 (7.9)
	70	30	Air	0.7	GBFS	1.4 (5.1)	4.1 (6.3)	11.4 (7.7)	16.4 (8.1)
			Water			1.4 (5.1)	4.5 (6.6)	11.3 (7.8)	19.2 (8.3)
	50	50	Air	0.5	Silica	0.9 (3.5)	6.5 (5.5)	12.2 (6.3)	11.3 (6.5)
			Water			0.9 (3.5)	5.1 (5.4)	9.9 (6.4)	10.7 (6.3)
	60	40	Air	0.5	Silica	1.7 (4.3)	9.4 (6.0)	12.6 (6.8)	15.4 (7.0)
			Water			1.7 (4.3)	7.0 (6.1)	12.2 (6.9)	12.0 (7.0)
	70	30	Air	0.5	Silica	1.7 (4.6)	6.5 (6.9)	11.9 (6.9)	11.6 (7.1)
			Water			1.7 (4.6)	6.9 (5.4)	10.1 (6.0)	10.5 (7.0)
Paste	60	40	Air	0.43	-----	4.9 (16.1)	12.9 (19.6)	18.6 (22.1)	22.6 (24.9)
			Water			4.9 (16.1)	10.1 (20.7)	19.5 (28.2)	20.6 (30.6)

Notes: A:B-Aggregate:Binder ratio, w/b-water/binder ratio. CS=compressive strength, NEW non evaporable water

It was noted that the early strength for all mortars after 1 day of curing was low and under 2 MPa, in contrast the paste developed about 5 MPa after 1 day. After 7 days, the strengths of some mortars were still low at about 4-7 MPa whereas the paste reached of about 10-12MPa. Moreover, for the first 7 days, the strengths of the mortars with **GBFS** were lower than those made with silica sand.

Initial strength was related to both w/b ratio and **WG** content in the binder; some aspects are worth considering. **GBFS** is obtained by water quenching of the slag, the final granulated product presents high intrinsic porosity capable of absorbing high amounts of water, more than regular aggregates like silica or limestone. Such **GBFS** water absorption greatly increased the w/b ratio in the mortars for the fluidity selected, i.e 0.7 as shown in Table 2, whereas for silica sand the required w/b was only 0.5. Hence, increasing w/b corresponds to lower CS values in early ages for mortars with **GBFS**.

With respect to the composition of the binder, it was noted that higher contents of **WG** resulted in higher initial strength; nevertheless, the trend was inverted after 28 days and higher strengths were noted for lower **WG** contents, especially for the mortars with **GBFS** sand. This indicates that the initial mechanical development is attributable to gypsum hardening and hydration of **BFS** is takes place slowly; it is only in the later stages that the **BFS** reactions contribute to strength development.

Alkali chemical activation of **BFS** has proven to be a good choice to obtain high performance cements; however, the nature of the commonly used reagents like sodium hydroxide or waterglass cannot be used in blends with hemihydrates since the rheology is affected and the setting greatly accelerated, complicating the mixing and cast stages. In this work **PC** was selected as a secondary chemical activator for the **BFS**; although its

activating action effect is slower than traditional alkalis, it allowed to manipulate the setting times by means of citric acid additions.

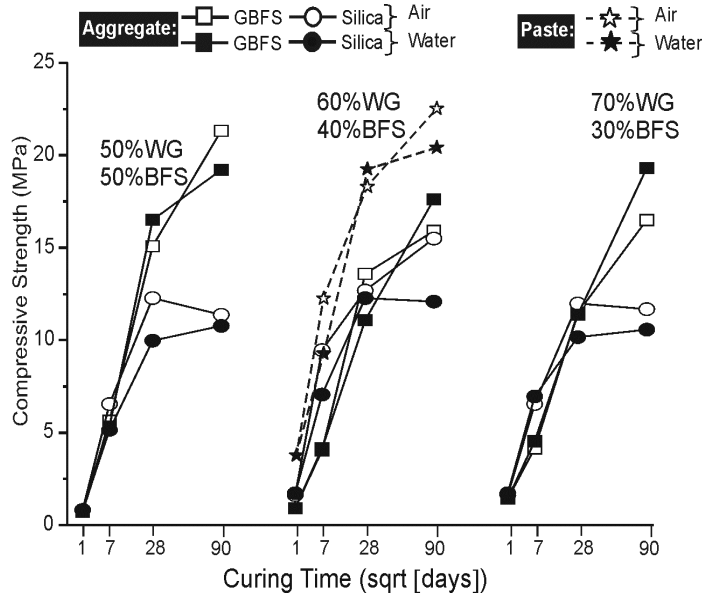


Fig. 1 Compressive strength vs Time for studied mortars

It is well known that in Portland cement based mortars and concretes; the replacement of **PC** by **BFS** shows its advantages in strength after 14-28 days [15]. Fig. 1 shows CS evolution of the mortars up to 90 days it can be seen that the **GBFS** sand mortars with 50% **BFS** reached higher CS values than those with lower **BFS** contents after 28 days of curing. It is considered that the

hydration of Portland cement also contributes to strength development. On the other hand the contribution of the **BFS** to strength is considered as a result of the activation by the Ca(OH)_2 and the sulphates. The **BFS** activation results in the liberation of Ca, Si and Al, which can lead to the formation of C-S-H and ettringite; higher **BFS** contents (50%) would form larger amounts of the latter, thus improving the strength over cements with lower **BFS** contents.

Table 2 shows that during the first 7 days of curing, **GBFS** mortars exhibited lower compressive strength values than those made with silica sand for a given binder composition. However, after 28 days **GBFS** samples reversed this tendency, and at 90 days silica sand systems were inferior, regardless of the binder composition. Such trend was noted at earlier stages for binders of low high **BFS** content (50%), which indicates that the **BFS** and **GBFS** hydration makes an important contribution to strength before the 28 days of curing and it is responsible for the long term strength. Nonetheless, when comparing the strengths of mortars with the two types of sand, it is clear that the strength enhancement results from aggregate interactions with the hydrated phases which resulted in stronger bonding aggregate-matrix.

Strength differences between air and water curing could not be appreciated for **GBFS** samples, the only clear tendency correspond to silica sand mortars for total binder compositions were curves for air curing (Fig 1.) maintain above the water curing ones from 28 to 90 days.

It is also interesting to note that the **GBFS** mortars with 50% **BFS** showed similar strengths to those of the paste of 60% **BFS**; such mortars are cheaper and lighter than the paste, which makes them potentially attractive as strong thermally insulating materials.

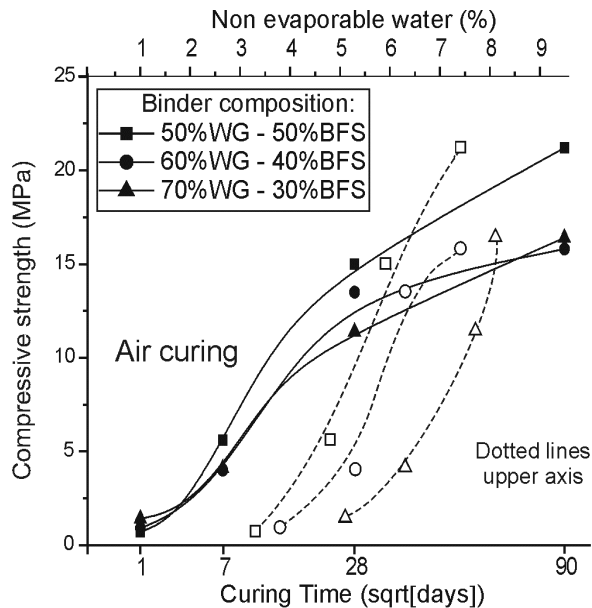


Fig. 2 CS vs Time vs NEW for GBFS mortars

Fig. 2 shows a combination of results of NEW and CS vs time for **GBFS** mortars, dotted lines belong to the upper X-axis. NEW values were higher for **GBFS** mortars compared to silica sand mortars (only shown in Table 2). It can be noted that the NEW-CS curve for the mortar 70%**WG** is shifted to the right relative to the other **WG** contents, this indicates that at the very early curing stages, the cements with higher **WG** contents reached higher NEW values for a given CS. This corroborates that gypsum is responsible of early

hardening, increasing the NEW values but with low strength development. For example after 1 day, the **GBFS** mortar with 70%**WG** (cured in air) showed NEW=5.1 and 1.4 MPa (see Table 2); whereas the mortar with 50% **WG** showed NEW=3.3 and 0.7MPa.

However, as time curing progressed, the **BFS** contributed markedly to the strength and in lesser grade to NEW values. Table 2 shows that after 28 days NEW values increased in lesser proportion (note sharp slopes in Fig. 2) than CS data; for example the mortar with 50%**WG** had NEW=5.9 (44% increase) and 5.0 MPa (95% improvement).

3.2 Microstructures and reaction products

Fig. 3 and Fig. 4 shows SEM results for graphite coated polished mortar samples of both aggregates with a binder of 50% **WG**-50% **BFS**; the images were obtained at 500 and 1000 magnifications in backscattered electron image mode. The microstructures of both mortars seem dense and compact; it is also clearly noted that the gypsum crystals appeared engulfed by C-S-H products that resulted from the **PC** and **BFS** hydration (arrowed in the micrographs). The C-S-H appeared homogeneously dispersed throughout the microstructure and a few partially hydrated **BFS**

grains appeared with rims of reaction products around them; this indicates that the **BFS** hydration occurred by a mechanism dissolution-precipitation process and in lesser proportion by a solid state diffusion mechanism. In **GFBS** mortars (Fig. 3 *b*) a continuous bonding between the mass of hydrated products and **GBFS** grains was observed, such chemical interaction between the **GBFS** with the $\text{Ca}(\text{OH})_2$ and sulphates (similar to that of the **BFS**) enhanced the CS in mortars at later curing ages. In contrast, the interface binder-aggregate in silica sand mortars (Fig. 4 *a*) does not show a chemical interaction nor a strong bonding. These observations are in agreement with the strength differences mentioned above.

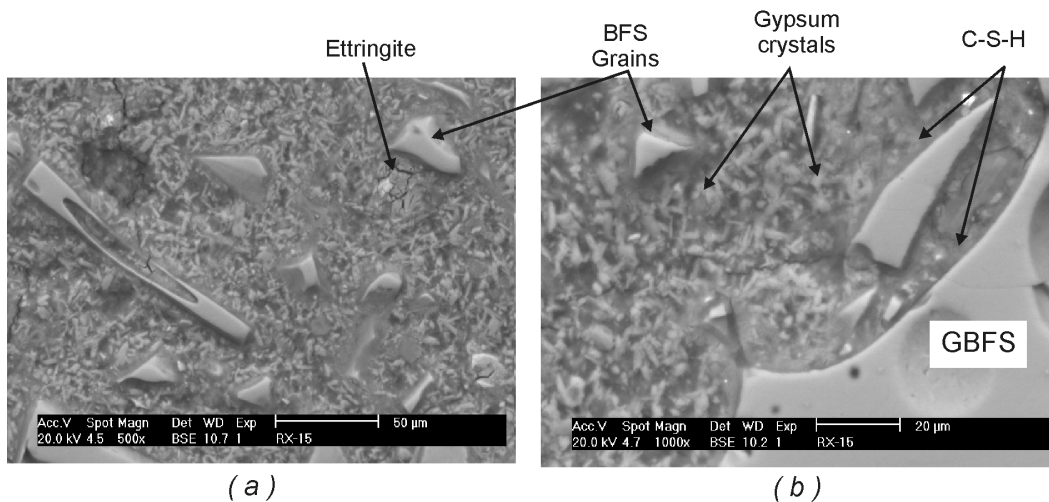


Fig. 3 SEM results for mortar with GBFS aggregate; 50%WG-50%BFS cured under water for 90 days: (a) 500x, (b) 1000x

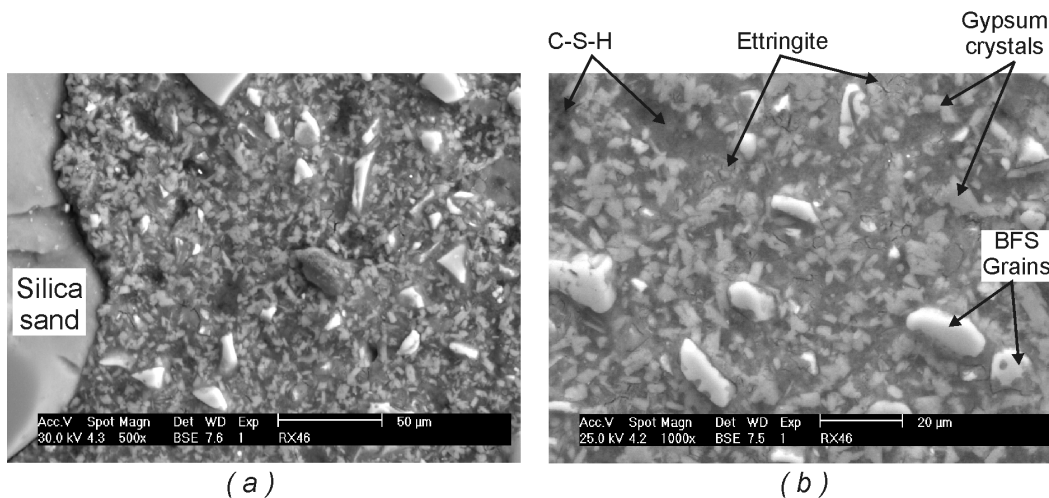


Fig. 4 SEM results for mortar with silica sand; 50%WG-50%BFS cured under water for 90 days: (a) 500x, (b) 1000x

The gypsum crystals formed were of about 5 μm instead of the typical fine needle sharp crystals, this can be associated to effects of the citric acid used as a setting retarder, which not only acts as a retarder, but also as a

modifier of the crystal morphology [16,17,18]. The adsorption of citrate from the organic acid on the surface of hemihydrate crystals hinders the dissolution and delays the formation of gypsum. However once the latter is formed, subsequent adsorption promotes growing of crystals in shapes different to those of plasters without additives, producing thicker and more compact crystals. The gypsum crystals appeared well dispersed in the matrix of hydrated products in Fig. 3 and Fig. 4, they formed in the initial stages constituting the starting structure and promoting the growing of C-S-H around them; the latter consolidated the microstructure and protected the gypsum crystals against dissolution.

Fig. 5 presents X-Ray diffraction patterns for paste samples (a), **GBFS** mortars (b) and silica sand specimens (c). Fig. 5 (b) showed a large fraction of amorphous **GBFS** aggregate; in the same manner Fig. 5 (c) exhibits strong quartz reflections. All graphs showed that after 1 day gypsum was present and that hemihydrate was absent; moreover, the peak around $12^\circ 2\theta$ decreased in intensity with the curing time. Ettringite appeared in the pastes and GBFS mortars after 28 days as a result of the slag involvement in the reactions; ettringite peaks were not seen in the silica mortars, it is possible that these were overshadowed by the quartz reflections. A small fraction of anhydrite resulted from the firing of **WG**, it was present even 90 days, showing that there are not favorable conditions for its hydration or that the setting retarder probably inhibited its reactions and it can be considered in the mixes only as an inert "space occupier". C-S-H products could not be identified by X-ray diffraction. The **BFS** peaks remained unchanged.

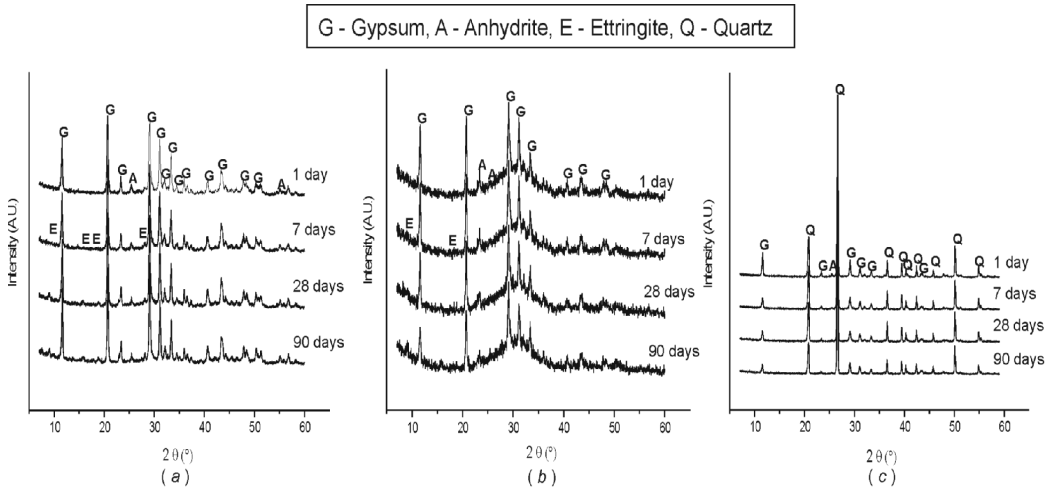


Fig. 5 DRX patterns for 60%WG-40%BFS binder composition cured under water samples; (a) Paste, (b) GBFS mortar, (c) Silica sand mortar

Fig. 6 shows results for differential thermal analysis (DTA) obtained for a paste 60% **WG** cured under water. In agreement with XRD data, gypsum was present from 24 hours as indicated by the endotherms at $120-180^\circ\text{C}$;

no peaks of hemihydrate decomposition were observed. The area of the gypsum peak reduced after 90 days as shown by the insert in the graphic. After 7 days of curing time ettringite and C-S-H appeared well distinguished in the overlapping endotherms at 90-110°C. DTA results were in agreement with XRD data regarding the presence of gypsum and ettringite, and also evidenced the formation of C-S-H.

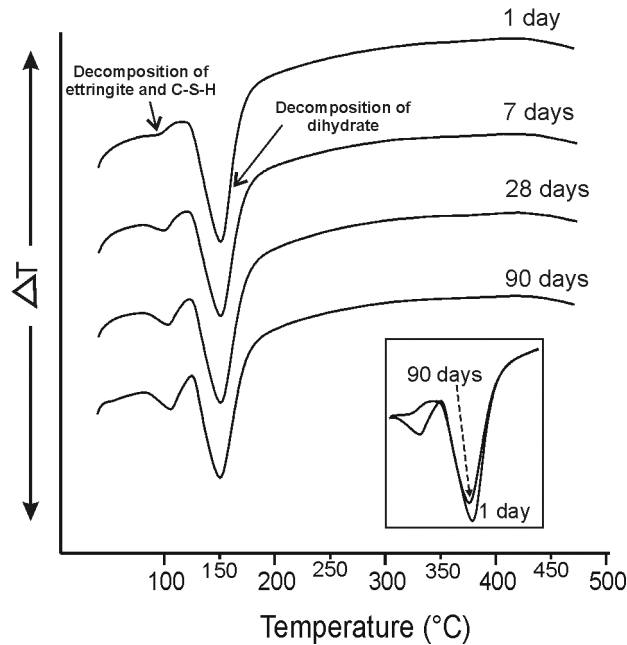


Fig. 6 DTA for 60% WG paste system

3.3 Suggested reaction mechanisms

The analysis of all results allows proposing a mechanism of reactions for the mortars divided in three stages as follows. In the first period, hemihydrate reacted rapidly during the first 24 hours forming a framework of gypsum crystals; this increased the NEW values but contributed little to compressive strength development. In a second stage (7-28 days) **PC BFS** hydration reactions formed C-S-H, markedly increasing the strength. **BFS** reacted mostly by a dissolution-precipitation mechanism liberating aluminum ions from the vitreous network, this lead to the formation of ettringite after the reactions with the sulphates. After the second stage, gypsum crystals are embedded in the C-S-H which protects them against solubility in water. It is important to note that ettringite formed without an expansive process, and far from becoming a deleterious factor, it seemed to contribute to strength development from 28 to 90 days of curing.

DRX and DTA indicated that a fast hemihydrate complete reaction; moreover both techniques indicated that the amounts of dihydrate reduced from 7 days onwards while DTA showed that the amounts of C-S-H and

ettringite increased (favoring strength); these observations indicate that that gypsum reacted with the **BFS**. On a third period of reactions from 28 to 90 days strength improvement was less significant, where larger **BFS** grains continued hydration by a diffusion mechanism, sulphate and aluminum ions combined to form more ettringite; also **GBFS** aggregates bridged chemically with the matrix of hydrated products enhancing even more the strength when compared to silica mortars.

It is known that lower w/b ratios favor higher compressive strengths in cementitious systems. In this case, the **GBFS** mortars required more water than those of silica sand; in agreement with this, the initial strengths were actually better for the silica sand mortars. Nonetheless, after 28 days of curing, the strengths of the **GBFS** mortars were the highest considering better aggregate-binder union owing to **GBFS** reactions. This suggests that the excess of water had probably been used to continue the hydration reactions without a negative effect of a high w/b ratio in the late periods.

4. Conclusions

Composite materials of hydraulic character can be obtained by combining by industrial wastes such gypsum and blast-furnace slag , with better mechanical properties than traditional plasters.

The replacement of standard silica sand by granulated blast-furnace slag resulted advantageous in terms of compressive strength. Reactive slag aggregates bonded chemically with the hydrated products from slag and Portland cement reactions.

Portland cement acted as a good chemical activator for blast-furnace slag in composites with waste gypsum. Although its alkaline activation is relatively slow, this is necessary to allow adequate setting times.

All mixes studied exhibited low initial strengths attributed to high water/binder ratios and slow reaction from blast-furnace slag. Initial strength gain is related to hardening by gypsum formation; intermediate and final strengths depended on factors: hydration of slag to form CSH and ettringite and the chemical bonding between aggregate and binder.

The microstructures consisted of a mixture of hydrated phases such as gypsum, ettringite and C-S-H. Gypsum crystals were embedded in C-S-H products preventing solubility.

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