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Composite systems fluorgypsum–blastfurnance slag–metakaolin, strength and microstructures

P.E. Fraire-Luna, J.I. Escalante-Garcia *, A. Gorokhovsky

Center for Research and Advanced Studies (Cinvestav-Saltillo), Carretera Saltillo-Monterrey Km. 13, Saltillo, Coahuila, CP 25000, México

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Abstract

The hydration and properties of composite cementitious pastes with 75% fluorgypsum were investigated; blastfurnace slag and metakaolin were the complementary cementitious materials. The pastes were cured under water at 20 °C for 360 days. All pastes developed and maintained strength under water, except those of commercial gypsum. The addition of metakaolin had a positive effect, after 360 days compressive strengths of 13.4, 13.8 and 14.6 MPa were registered for systems with 0%, 5% and 10% of metakaolin, respectively. The microstructure of the composite pastes was formed of a framework of gypsum crystals, which formed in the initial stages; the matrix was later densified by the formation of C–S–H and ettringite, as a result of the slag and metakaolin reactions. The fluorgypsum reacted rapidly in the first days, however it was still present after one year; the slag reacted in a slower fashion, and the metakaolin was very reactive and contributed with the ettringite since the early ages, which enhanced the strength.

Keywords: Fluorgypsum; Blastfurnace slag; Metakaolin; Ettringite; Characterization

1. Introduction

Gypsum plasters offer fast setting and fine finishing and are used mostly for aesthetic works, rapid construction or fire retarding purposes for indoor applications. Its use in outdoors and construction is limited due to the inconveniences of low mechanical strength and poor water resistance; nonetheless, gypsum is a material intensively used worldwide.

In order to reduce the environmental impact of construction materials, the incorporation of alternative materials is becoming an important option in the construction industry. For the case of gypsum materials, many industries generate gypsum byproducts and the associated waste accumulation represents ecological and social problems. Such is the case in various industrial plants in Mexico, where fluorgypsum (Anhydrite) is produced as a byproduct of the fabrication of hydrofluoric acid.

Various papers in the literature investigated cementitious systems based on gypsum from various sources. Investigations on the mixtures of phosphogypsum anhydrite and blastfurnace slag [1] reported that mixtures 70%–24% with admixtures of Ca$(OH)_2$ and $Na_2SO_4 \cdot 10H_2O$ and $FeSO_4 \cdot 7H_2O$ reached mechanical strengths of around 23 MPa after 28 days of curing at 27 °C and 90% RH; thermal analysis indicated the presence of ettringite and C–S–H as responsible for the mechanical strength. Another work reported that mixes of 75% commercial gypsum with silica fume/OPC ratio of 1/4 [2], developed up to 16 MPa after 200 days of curing in wet conditions; the presence of gypsum, hemihydrate, and small quantities of ettringite were noted by thermal analysis. For composite cements of fluorgypsum–fly ash–CPO [3], compressive strengths of 45 MPa were reported after 180 days of curing under water, for the composition 40%–40%–20% and a water/binder ratio of 0.41.

The incorporation of metakaolin in gypsum plasters has also been studied [4], the replacement of 5% and 10% of the plaster resulted in higher or similar strengths relative to pure gypsum plaster, substitution with metakaolin and CH resulted in lower strengths; and the replacement of gypsum by metakaolin and CPO improved the strength, the enhancement was due to the reduction in the open porosity. The work of Martínez-Aguilar [5] reported that mixtures of fluorgypsum–CPO–geothermal

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* Corresponding author.
E-mail address: ivan.escalante@cinvestav.edu.mx (J.I. Escalante-Garcia).

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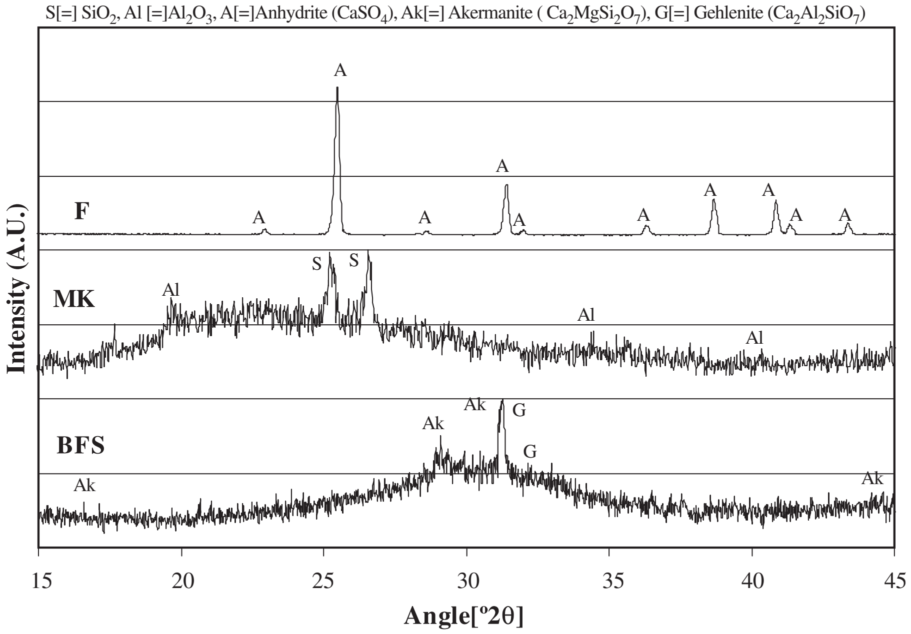

Fig. 1. XRD patterns of the starting materials.

waste registered strengths similar to neat OPC pastes; however the pastes fluorgypsum–CPO–metakaolin collapsed by the formation of ettringite [6].

Blastfurnace slag and metakaolin are commonly used cementitious materials that require activating agents in order to undergo hydration reactions. When mixed with OPC they react with the CH that results from the OPC hydration; they can also be activated by chemicals such as $Ca(OH)_2$ and Na_2SO_4. The resulting cementitious products are C–S–H, ettringite and other compounds can be formed. [7–9] as detected by XRD and SEM.

Many of the previous reports on gypsum, waste or mineral, deal with cementitious systems in which the gypsum is not the main component. Additionally, research on systems incorporating fluorgypsum, blastfurnace slag and metakaolin are not common. This report presents the results of an investigation of composite cementitious systems based on 75% fluorgypsum; the complementary cementitious materials were blastfurnace slag and metakaolin. The objective was to investigate the potential of these waste based environmentally friendly cements; analysing the reaction mechanisms associated to strength development, microstructure configurations and durability under water. A comparison is also made relative to commercial gypsum plaster.

2. Experimental

2.1. Materials

Fluorgypsum (**F**) from hydrofluoric acid production (Industria Quimica de Mexico S.A., S.L.P, Mexico.) was obtained in the form of a mixture of powder/pellets, it required neutralization and was conditioned to Blaine of 4000 cm^2/g, XRD showed only the presence of anhydrite (Fig. 1). Granulated Blastfurnance Slag (**BFS**) (AHMSA, Monclova, Mexico) was ball milled to a Blaine of 4000 cm^2/g, XRD indicated that it was predominantly amorphous with a small crystalline fraction of gehlenite ($Ca_2Al_2SiO_7$) and akermanite ($Ca_2MgSi_2O_7$) (Fig. 1). A commercially available Metakaolin (**MK**) Power Pozz™ was used, it had a surface area of 9000 cm^2/g, XRD showed an amorphous phase with small quantities of SiO_2 and Al_2O_3 (Fig. 1). Commercial gypsum Maximo™ of mineral origin ($CaSO_4 \cdot 1/2H_2O$) was also used as a

Table 1
Chemical oxide composition of the starting materials (in weight %)

Fluorgypsum		Blastfurnace slag		Metakaolin[a]	
$CaSO_4$	99.06	CaO	39.52	Kaolinite	96–98
CaF_2	0.64	SiO_2	38.08	Quartz	Max = 2
(H_2SO_4, HF)	0.28	Al_2O_3	9.36	TiO_2	1.90
–	–	MgO	7.65	Fe_2O_3	1.40
–	–	Fe_2O_3	0.41	K_2O	0.18
–	–	MnO_2	0.40	MgO	0.15
–	–	SO_4	4.67	CaO	0.11
–	–	–	–	Na_2O	0.05
–	–	–	–	Loss on ignition	13

[a] Data as indicated by the supplier.

Table 2
Mechanical strength of the pastes (MPa)

Time (Days)	Commercial gypsum	100% F	75% F–25% BFS	75% F–20% BFS–5% MK	75% F–15% BFS–10% MK
1	3.1	4.1	2.6	3.8	3.4
3	3.1	5.0	2.5	4.2	5.3
7	2.7	5.7	4.4	6.5	6.0
14	2.9	5.0	7.1	7.3	9.2
28	2.7	4.6	9.4	9.3	8.6
90	2.4	3.9	9.2	11.3	13.7
120	2.2	4.3	10.6	13.9	14.7
240	1.9	4.7	11.6	14.7	14.1
360	1.7	4.8	13.4	13.8	14.6

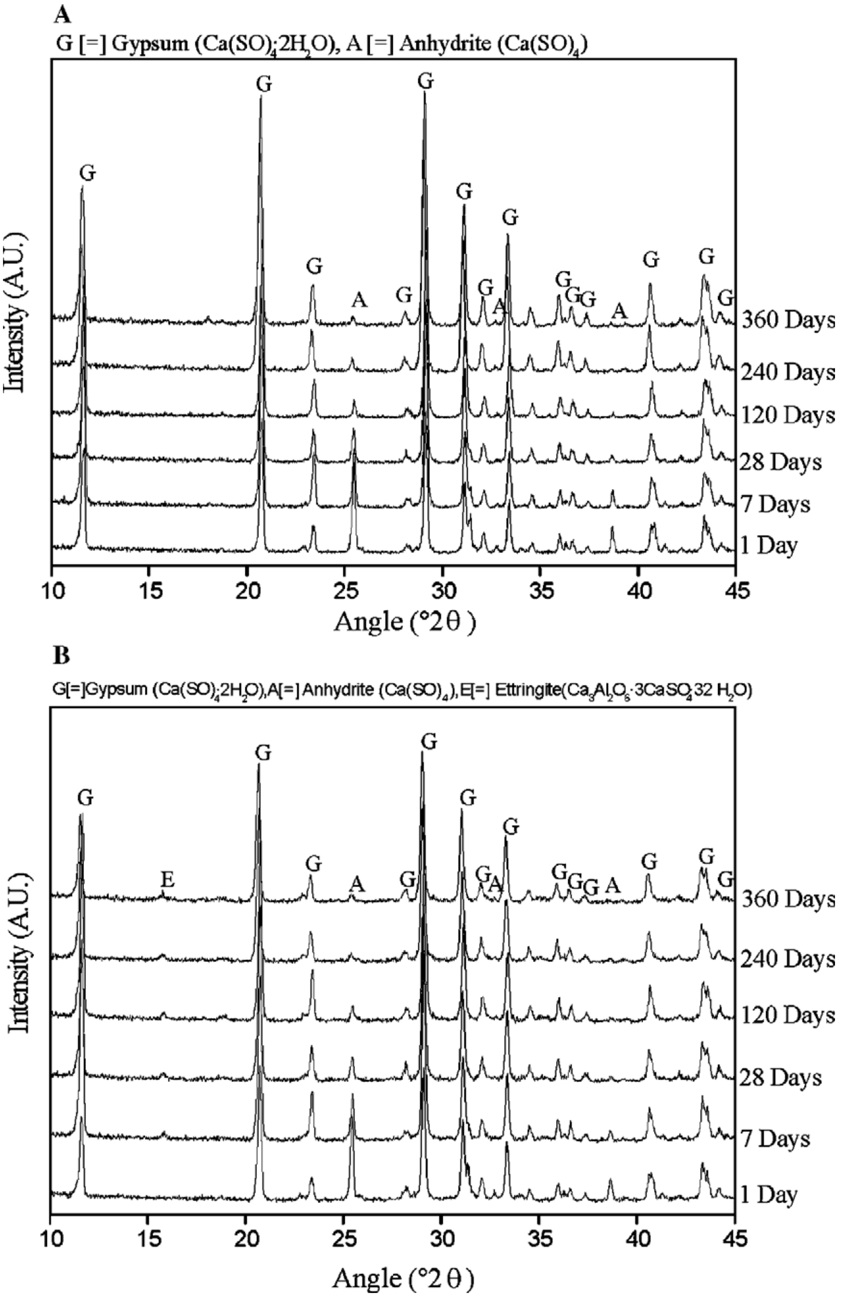

Fig. 2. XRD patterns of F (A) and F–BFS (B).

reference material. The chemical composition of the starting materials is presented in Table 1.

2.2. Sample preparation

Pastes were cast in cubes of 5 cm per side in polymeric molds (Nylacero™). Various compositions were prepared in which the F content was fixed at 75% (weight %) in order to maximize its use. The BFS was used in 25%, 20% and 15%, the rest was complemented with MK at 0%, 5%, and 10%. The water/solids ratio was fixed at 0.5. Technical grade $Ca(OH)_2$, Na_2SO_4 and $CaSO_4 \cdot 1/2H_20$ (commercial hemihydrate) were added, in proportion of 3 wt.%, as neutralizing and activating agents, except for commercial gypsum. The cementitious powders were dry mixed in batches of about 8 kg, the water with the additives, was then added and the paste was mixed for 3 min. The mold cavities were filled and left to set for 24 h at 20 °C, the cubes were demolded and randomly placed for curing under water at 20 °C for up to 360 days.

2.3. Characterization

Mechanical strength was measured as the average of 4 cubes after 1, 3, 7, 14, 28, 90, 120, 240, and 360 days. Some of the fragmented pieces were ground with a mortar and pestle and then dried in a vacuum oven at 35 °C for 12 h. This procedure was found adequate to quickly eliminate the free water without the use of solvents and without affecting the already formed gypsum

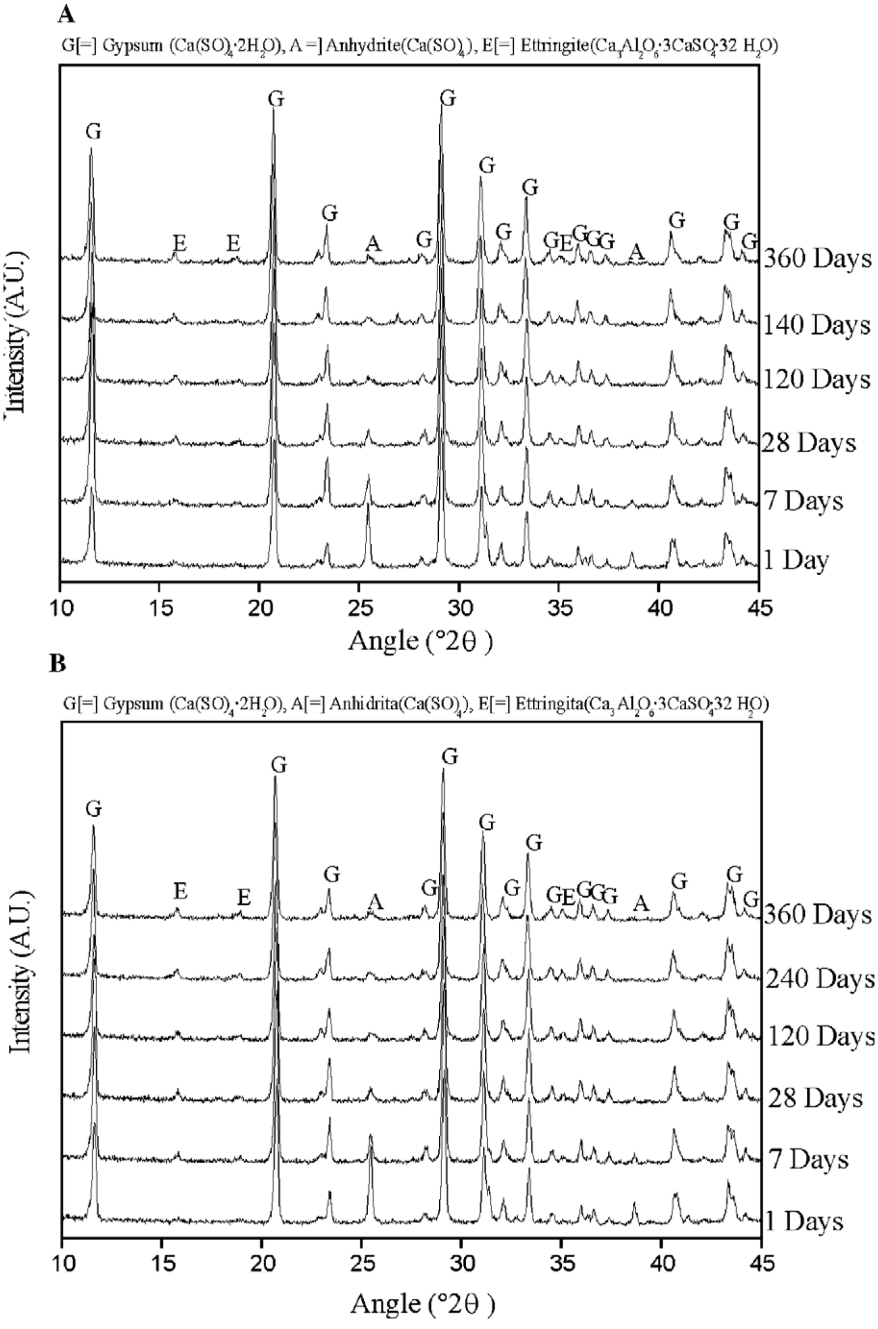

Fig. 3. XRD patterns of the systems F–BFS–5% MK (A) and F–BFS–10% MK (B).

crystals at any curing period. The dried powders were ground to pass a mesh of 150 μm, they were used for thermal analysis (Pyris Diamond TGA/DTA, Perkin Elmer) heating up to 500 °C at 10 °C/min in air; and also for X-ray diffraction (X´Pert 3040, Phillips) in the range of 10–45°2θ, with 2 s every 0.05°2θ. Selected samples were also used for fracture surface analysis using a scanning electron microscope (XL 30 ESM, Philips).

3. Results

The mechanical strength results are presented in Table 2. Commercial gypsum was included for reference purposes, its initial strength was 3 MPa and sustained gradual strength losses down to 1.7 MPa due to lixiviation (this effect is known as the commercial gypsum in wet conditions). In contrast the pure fluorgypsum samples presented a slightly superior strength, registering initial values of 4.1 MPa and staying in the range of 4–5 MPa; the specimens did not show signs of lixiviation (breakup) after one year of curing under water. The composite cementitious systems showed strength development over the 360 days of curing. During the first 28 days the strength attained was 60–70% of the 360 days strength level on each system, for the rest of the period the gain rate was slower. The addition of MK resulted in improved mechanical properties, with increases of at least 30% in the first 3 days, relative to the 0% MK paste; the highest properties found for those of the system F–BFS–10% MK with 14.6 MPa

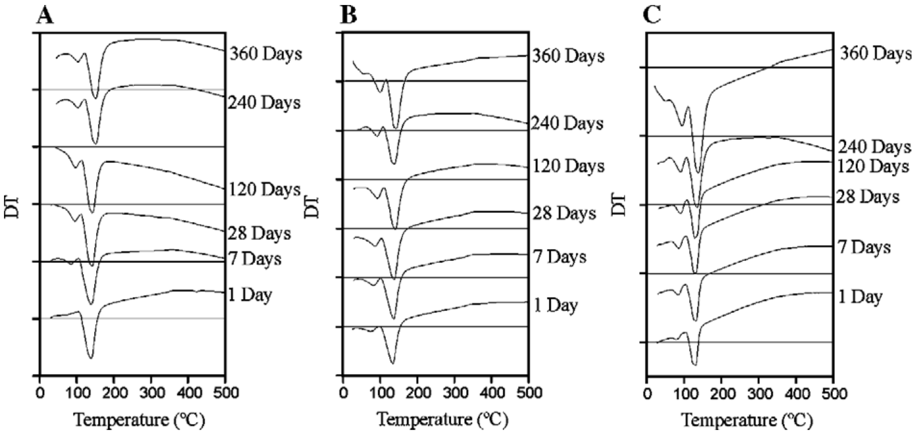

Fig. 4. Differential thermal analysis F–BFS (A), F–BFS–5% MK (B), F–BFS–10% MK (C).

after 360 days of curing under water. All pastes showed improved strength over the commercial gypsum.

Figs. 2 and 3 show the XRD results for the fluorgypsum paste (Fig. 2A) and composite pastes (Figs. 2B, 3A, and B). For the neat fluorgypsum pastes, the peaks of anhydrite were noted after 1 day of curing and gradually faded with time as it hydrated to form gypsum, no other peaks were identified. For the composite pastes, a similar pattern was noted regarding the formation of gypsum. The reaction of the anhydrite was not as fast as the hemihydrate present in commercial gypsum plasters, anhydrite peaks were relatively strong after 28 days, and were present even after one year of curing. However, in the presence of MK, the anhydrite showed faster hydration as the peaks were clearly weaker after 7 days when compared to the pastes of neat F and F–BFS pastes.

The XRD of the composite pastes, F–BFS and F–BFS–MK, showed ettringite peaks, which resulted as a reaction product of the MK and BFS in the calcium sulphate environment. In the F–BFS–MK composites, the peaks of ettringite were stronger and appeared since the first day of curing, whereas for the composites F–BFS they were observed until after 7 days. This indicates that the MK participates in the hydration reactions since the beginning and is more reactive than the BFS. The amorphous hump of the BFS or peaks of C–S–H were not observed, perhaps as overshadowed by the intensity of the gypsum and anhydrite peaks.

Fig. 4 shows the DTA results for pastes of F–BFS and F–BFS–MK for curing times from 1 to 360 days. Two main endothermic features were noted, one peak at ≈90 °C corresponding to the overlapped decomposition of the phases C–S–H and ettringite [10,11] and another at ≈130 °C attributable to gypsum [10–13]. The peak of gypsum increased gradually with the curing time, in agreement with the XRD results. On the other hand, the first peak was more intense in the presence of MK (compare Fig. 4A–C), indicating a faster formation of ettringite and C–S–H. The peak of CH, normally showing at about 450 °C, was absent as it probably reacted after one day with the BFS or MK.

Fig. 5 presents the results of the TGA analysis, where two main weight loss steps were noted. One at ≈ 90 °C, corresponding at the decomposition of the C–S–H and ettringite and a second step starting at ≈ 130 °C due to the decomposition of gypsum. On this basis, Fig. 6 shows the evolution of the graphically measured weight losses in two ranges, range 1 of approximately 35–100 °C and range 2 of 100–300 °C. The weight losses in the range 1 increased with the curing time, and were more marked for composite pastes of F–BFS–MK; this indicates the progressive

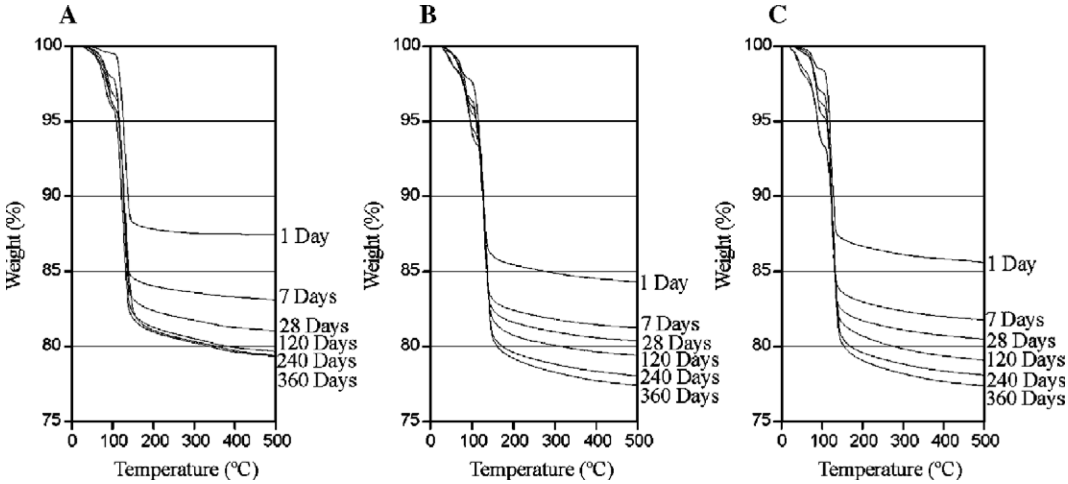

Fig. 5. Thermal gravimetric analysis F–BFS (A), F–BFS–5% MK (B), F–BFS–10% MK (C).

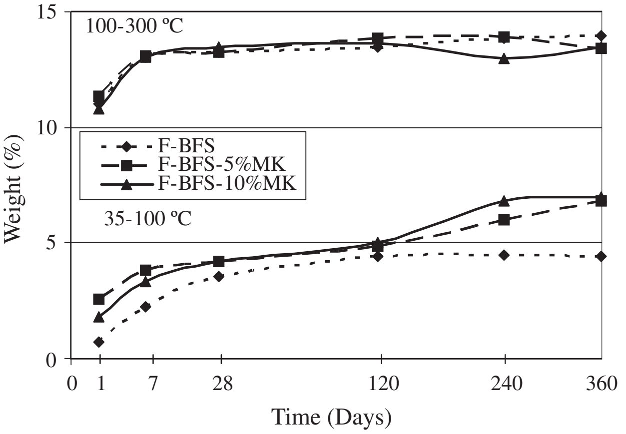

Fig. 6. Weight losses of the studied systems in the ranges 35–100 °C and 100–300 °C.

water intake by the formation of C–S–H and ettringite. The weight losses in range 2 were larger than those in range 1, and also increased with time but more intensively during the first 7 days; this was in agreement with the fast initial hydration of F. These results are consistent with the gypsum being the main hydration product, and the increases in the total weight losses (Fig. 5), indicated that in the later stages, the systems were binding water due to the hydration of anhydrite but mostly due to the formation of C–S–H and ettringite.

Fig. 7 shows the fracture surface microstructure of the paste of neat F after 120 days of curing under water. The morphology of the gypsum crystals is of canes and irregular shapes; the microstructure is porous since it is only formed by the framework of gypsum crystals. Fig. 8 presents the topographic microstructures after 120 and 240 days of curing for the composite pastes investigated. After 120 days, the paste F–BFS (Fig. 8A) was conformed by gypsum crystals with a cane-like morphology and irregular forms [14], such as that of fluorgypsum (Fig. 7), the gypsum crystals were surrounded by a more compact phase of C–S–H, as identified by X-ray microanalysis. As time progressed, the amount of C–S–H increased, making the microstructure more compact.

The microstructure of the composite F–BFS–5% MK (Fig. 8B) also showed a framework of gypsum crystals surrounded by C–S–H and ettringite after 120 days; the ettringite crystals showed the characteristic needle shape [7,15], and the amount of such needles increased with the curing time. For the system F–BFS–10% MK (Fig. 8C) the C–S–H and the ettringite needles were readily observed, more than in the microstructures of the paste F–BFS (Fig. 8B).

Evidence of BFS and MK particles was not observed in the images of fracture samples. A polished sample of the composite F–BFS–10% MK cured for 120 days, observed by backscattered electron imaging, is presented in Fig. 9. The differences among the fracture and polished surfaces are remarkable. In the fracture surfaces the ettringite and C–S–H are clearly noted, whereas the BFS or MK was not identified due to the relative small amounts present and the possible advance of their reactions. On the other hand, on the polished surface, the gypsum crystals are clearly seen surrounded by the C–S–H; however the ettringite crystals are not easily observed since they were very fine and distributed throughout the microstructure, as seen in Fig. 8. The very small BFS grains showed signs of a rim of hydration products. MK grains were not identified as they probably already reacted due to their small particle size and very high reactivity.

4. Discussion

The number of reported systems in which the $CaSO_4$ (or $CaSO_4 \cdot 1/2H_2O$), from various sources, as the main component in composite hydraulic cementitious materials is reduced; some of such previous works are described as follows. Singh and Garg [1] reported strength of about 23 MPa after 28 days at 27 °C and 90% RH, for mixtures of 70% phosphogypsum anhydrite with slag. Kovler [2] reported up to 16 MPa after 200 days of curing in wet conditions for pastes of 75% commercial gypsum with OPC and microsilica; the incorporation of CPO provided a lightly superior mechanical strength. Murat and Attari [4] studied pastes of neat gypsum plaster and its composites with CH, MK and Portland cement; after 180 days under water the neat plaster reached 12.7 MPa, the addition CH and MK reduced the strength, whereas the presence of CPO and MK resulted in similar strengths.

For F–BFS pastes we reported 9.4 and 11.6 after 28 and 180 days, respectively, of curing at 20 °C under water; moreover, the addition of MK enhanced the strength to 14.7 MPa after 120 days of curing under water. The strengths here reported for the composite cements were: lower than those reported for phosphogypsum [1], similar to those of gypsum plaster with OPC and microsilica [2], and higher than plaster with CPO and MK. The composite cementitious systems reported in this document showed water resistance and reached fairly acceptable mechanical strength. However, when comparing with other reported cements, various factors must be considered as they have strong effects on strength development, such as different $CaSO_4$ (or $CaSO_4 \cdot 1/2H_2O$) proportions and sources, the presence of additives (CH or sulfates) that influence the hydration of $CaSO_4$ (or $CaSO_4 \cdot 1/2H_2O$), the initial particle size (not commonly reported), curing conditions, the water/cement ratio and the presence of secondary cementitious materials such as OPC or puzzolanas. Investigations of the specific composite system F–BFS–MK have not been

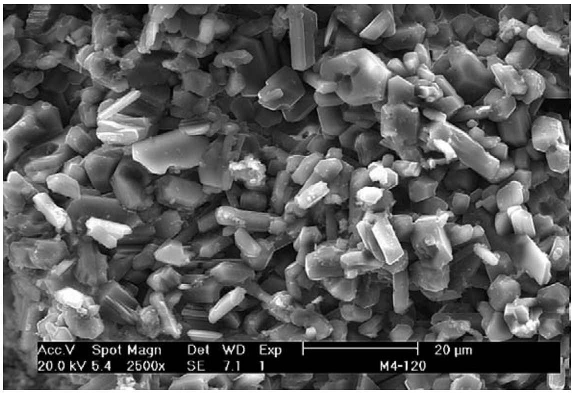

Fig. 7. Scanning electron microscopy micrograph of the hydrated fluorgypsum after 120 days.

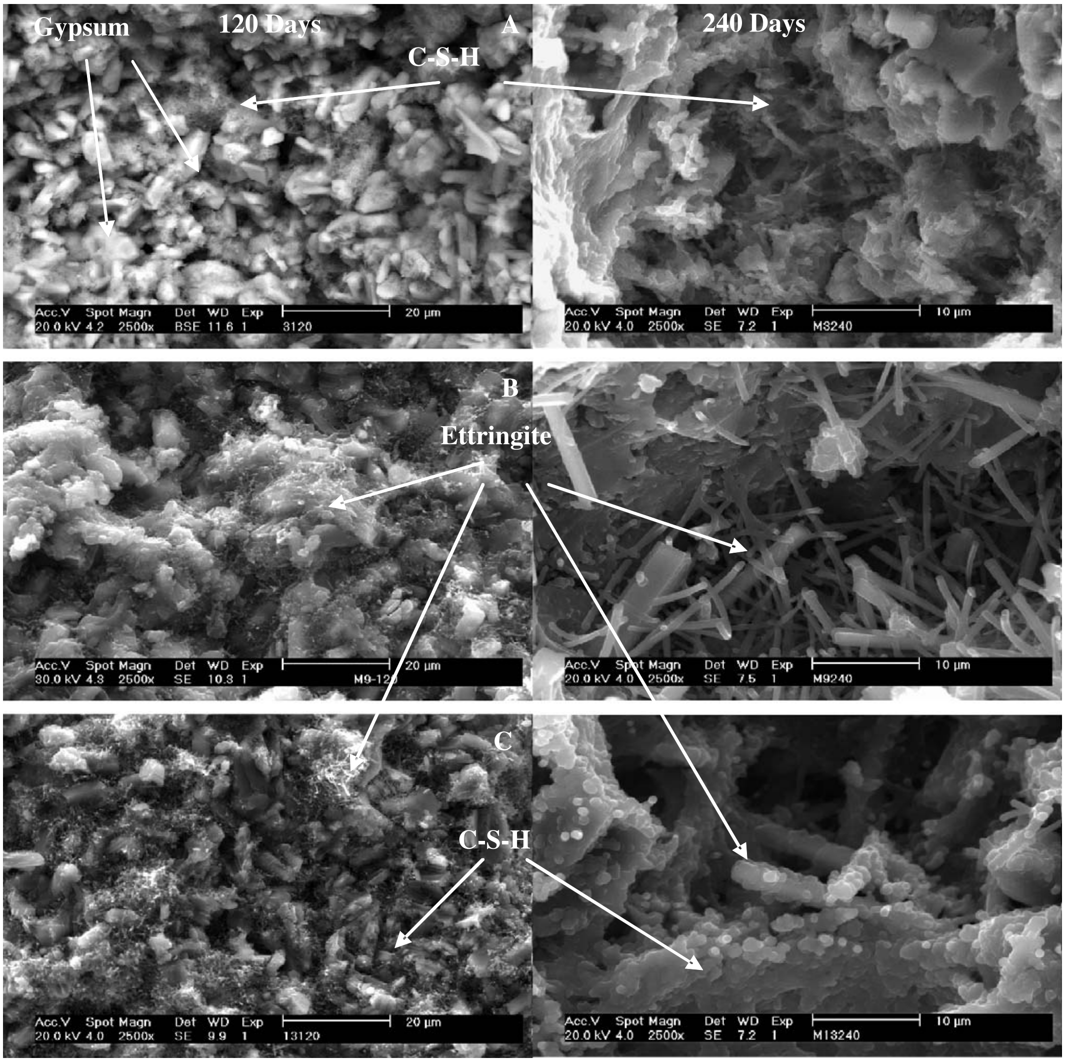

Fig. 8. Scanning electron microscopy micrographs of the systems F–BFS (A), F–BFS–5% MK (B), F–BFS–10% MK (C).

reported in the proportions here investigated; some relevant features that describe its hydration and properties are worth considering.

The F based cements reproduced and retained the smooth surface of the moulds and resisted water lixiviation due to the incorporation of activating agents, the strength maintained levels above 4 MPa after 360 days of curing. The incorporation of BFS, to F based cements, diminished the mechanical strength in early ages; however, after 7 days the mechanical strength increased due to the formation of C–S–H and ettringite, identified by XRD and DTA. Such phases result from the BFS reactions and contributed to the densification of the microstructure and provided water resistance.

Similar to the incorporation of MK to gypsum plaster with OPC [4], the addition of MK to the F–BFS composites had some positive effects. The strength was favored as the MK reduced the early open porosity shown by the microstructure of F and F–BFS cements. The presence of MK also accelerated the hydration of gypsum, possibly working as nucleating centers for the precipitation of gypsum crystals; this was observed with the quick reduction of the peak of the anhydrite in XRD patterns. Additionally the MK reacted providing additional C–S–H and ettringite, faster than the BFS due to the smaller particle size, as noted by the more intense DTA peak at ≈90 °C. The additional

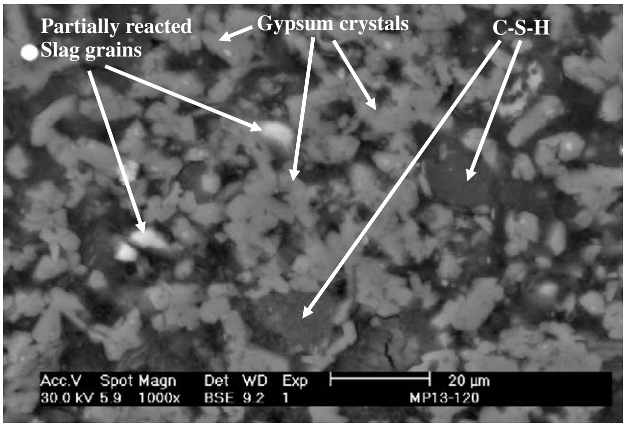

Fig. 9. Scanning electron microscopy micrograph obtained by the backscattered electron imaging of a polished sample of the composite F–BFS–10% MK cured for 120 days.

C–S–H and ettringite increased even further the mechanical properties in the late periods.

In the microstructures ettringite was observed since BFS and MK are very reactive sources of Al, and the Ca was provided by the BFS and the additives. It was noted that the ettringite needles grew throughout the microstructure and filled out the spaces left by the framework of gypsum crystals formed in the very early ages. Ettringite formation within dense microstructures such as CPO and composites of F–CPO–MK develops cracks and has a deleterious effect [6]. Under the investigated conditions for the composite cements F–BFS–MK, the effect of ettringite, earlier in the presence of MK, was positive since it densified the microstructure and enhanced the mechanical strength and the water resistance significantly.

The incorporation of BFS, MK and activating agents to fluorgypsum based cements, resulted in improved mechanical strength and water resistance, these attributes are not characteristic of the commercial gypsum plasters. The composites F–BFS–MK are promising for uses were the commercial plasters cannot be applied, for example, in external uses exposed to moist conditions. These composites are cheap and environmentally friendly since they are based on waste materials; additionally, the properties of stability and attained compressive strength, make them usable for construction applications, other than those of common gypsum plaster, such as bricks, blocks, panels, etc. More research is required to extend the possibilities of applications.

5. Conclusions

The composite cement pastes of fluorgypsum, blastfurnace slag and metakaolin developed and maintained strength even under water, showing improved properties over commercial gypsum. The compressive strength after one year under water was of 14.6 MPa for the composite F–BFS–10% MK.

The reactivity of the blending components was different. Fluorgypsum reacted mostly during the first days, although its presence was noted even after a year of curing. The BFS reacted in a slower fashion, forming ettringite and C–S–H. The MK was very reactive forming ettringite and C–S–H since the first days of curing, which enhanced the early strength.

In agreement with the reactivity of the components, the microstructures were conformed of a framework of gypsum crystals, which provided the initial strength. The matrix of hydration products was further densified and strengthened by the reactions of the BFS and MK, which according to XRD and TGA/DTA formed C–S–H and ettringite. The latter precipitated engulfing the gypsum crystals as shown by backscattered electron images. Secondary electron images showed that the amount of ettringite increased with the MK contents and the curing time. The formation of ettringite in the empty spaces left by the gypsum crystals formation, resulted in a positive effect without the expansion and cracking typically observed when ettringite forms in consolidated cementitious microstructures.

The incorporation of the reaction products of BFS and MK in the microstructure of the structure of the gypsum provides an acceptable mechanical strength and water resistance, obtaining a material that can be used under conditions where commercial plaster is not advisable, and also for other construction uses.

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