Hydraulic fluorgypsum Cements: Effects of different additives and Portland cement on the hydration, water resistance and mechanical properties

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Abstract:

The hydration and hydraulic character of cheaper and enviromentally friendly cement pastes of fluorgypsum and fluorgypsum-Portland cement-Blast furnace slag, were investigated. Additives $Ca(OH)_2$, K_2SO_4, Na_2SO_4, $Al_2(SO_4)_3$, were used in different proportions and the water/solids ratios were ranged from 0.25-0.4. Fluorgypsum was used in level of 50-75%; PC was also used in levels up to 30 % and BFS replaced 40% of the PC in all cases. The activation of the reactions was examined through isothermal conduction calorimetry. The presence of PC and $Al_2(SO_4)_3$ increased the heat of hydration, this was less notorious with those systems only with K_2SO_4, Na_2SO_4. Samples cured under water developed compressive strength around 15 MPa for w/s=0.4 in 100%fluorgypsum systems; whereas 43MPa were reached for w/s=0.25. For composite pastes, ranged within 20-40 MPa for fluorgypsum contents from 50-75%. For pure fluorgypsum systems, SEM indicated larger gypsum crystals for additions of Na_2SO_4. For the composite systems ettringite, CSH and gypsum was found in the microstructures after 28 days of curing.

1 Introduction:

In many developing countries, there is an increasing need of construction materials due to the population growth. Considering that Portland cement is the most used binder in the construction industry, and that its production generates very high amounts of CO_2, our environmental awareness lead us to the search for alternative cemetitious systems to suit these demands under the premise of sustainable development. A most promising alternative cementing systems for general concrete applications at ambient temperatures currently appear to be those based al least in part of calcium sulphates [1]. Calcium sulphates are not only abundat in nature; many processes also generate them as by-products, such as fluorgyspum (from hydrofluoric acid production). Nearly 1200 ton/day are generated in Mexico en several plants for this residue [2]. This is a

problem of acumulation of wastes that can be turned into an opportunity of making materials with good cementitous properties at lower economical and environmental costs. It is known that fluorgypsum requires additives to accelerate its hydration process [3] since anhydrite $CaSO_4$-II (known as "insoluble anhydrite") is the main constituent. The cations in the additives affects physical characteristics like microstructure and size of crystals of gypsum, however the effects have not been studied extensively [4]; the cations also influence the kinetics of the hydration process.

The main problem associated to gypsum is its water solubility, which limits its applications to dry environments. In order to tackle this problem there have been approaches of composite cementitious systems in which commercial gypsum was combined with OPC and microsilica, such systems developed strength after curing under water for up to 200 days [5]. Various papers reported successful cementitious materials, in terms of water resistance and strength, based on fluorgypsum and phosphogypsum, blended with OPC and PFA or blast furnace slag [6,7]; while other workers reported studies on fluorgypsum blended with metakaolin and blast furnace slag [8]. This work presents results of an investigation on cementitious systems based on fluorgypsum as the main binder, admixed with CPC and Blast furnace slag as complementary cementitious materials. The aim was to determine the effect of the various sulphate additives on neat fluorgypsum and composite pastes hydration, as well as strength and microstructural development.

2   Experimental

2.1   Materials

Fluorgypsum (**Fy**-anhydrite) was obtained from Solvay Fluor de México (Cd. Juarez, Chihuahua, México); an excess of 3%wt. $Ca(OH)_2$ was added after neutralization. Portland cement **(PC)** CPC 30R [30MPa at 28 days, NMX-C-414-ONNCCE] with in-plant mineral admixtures of calcite and blast furnace slag **(BFS)** was used. Blast Furnace Salg **(BFS)** was supplied by Altos Hornos de Mexico S.A.de C.V. (Monclova, Coahuila, México). The chemical compositions of all materials is shown in Table 1. The additives used were $Ca(OH)_2$ **(CH)**, K_2SO_4 **(KŜ)**, Na_2SO_4 **(NŜ)** and $Al_2(SO_4)_3$ **(A₂Ŝ₃)**, all industrial grade, used from (1-3%wt.) relative to the binder. The selected additives are known to enhance the reactivity of the anhydrite of fluorgypsum[3]; however, combinations of them are not reported in the literature. The aim was to investigate the effect of various combinations on the reactivity and pastes

2.2 Sample preparation

The binders consisted of (%wt) **Fy** (50-100%) and **PC** (0-30%); while **BFS** replaced 40% of the **PC**. Pastes with a water/solids ratio (**w/s**) of 0.25-0.4, were prepared; a constant w/s=0.3 was chosen as best for composite systems **Fy**-**PC**-**BFS**. Distilled water was used in all cases. For w/s of 0.25-0.3 a superplasticiser Rheobuild-1000 was added up to 1.5% wt relative to the binder. Prior to the paste preparation, the additives were pre-dissolved with the mixing water together with the superplasticiser. The dry powders and **CH** were mixed in a planetary mixer for 5 minutes, 2 more minutes of mixing was allowed after the water addition. Cubic samples of 2.5 cm were cast and left 24 h at 20 °C for setting. After demoulding the cubes were cured under water for up to 90 days.

Table1
Chemical composition of raw materials (% wt).

Oxides	SiO_2	CaO	Al_2O_3	MgO	SO_3	K_2O	Na_2O	Fe_2O_3
BFS	37.21	37.24	11.63	9.27	2.69	0.92	0.71	0.67
PC	18.86	62.18	4.52	1.97	2.58	0.75	0.44	2.73
$CaSO_4$	0.04	29.70	1.98	0.024	68.03	------	------	0.04

2.3 Characterization:

The reported compressive strength values represent the average of 4 cubes tested. To arrest the hydration reactions some pieces from the crushed samples were dried with methanol for 24 h and further dried at 35 ºC in a vaccum oven for 24 h. Selected samples were chosen for fracture surface microstructure analysis with scanning electronic microscope (**SEM**, Phillips XL30 SEM). Selected samples were ball milled in a planetary ball mill, in batches of 10 g for 13 min at 300 RPM; such samples passed a 100 µm mesh for characterization by Differential thermal analysis (**DTA**, Perkin Elmer Pyris Dymond) and X-ray diffraction (**XRD**, Phillips X-Pert 3040) tests. Isothermal conduction calorimetry (**ICC**) was performed at 20 °C hydrating samples of 25 g for 40 h, the calorimeter was based on the Forrester Design [9].

3 Results

3.1 Compressive Strength

Fig. 1 shows the compressive strength for systems of 100% **Fy** modified with additives at diffrent w/s ratios. The increase of the w/s reduced the compressive strength of almost all systems after 90 days of curing. While

for a w/s= 0.25 the strengths reached up to 37 MPa, for w/s=0.3 and 0.4, the strengths were around of 25 and 22 MPa, respectively. At w/s=0.25, the system of **Fy** with $A_2\hat{S}_3$-**KŜ**-**CH** showed the lowest strength (0.7 MPa) at 1 day; nonetheless it was greater for higher w/s ratios.
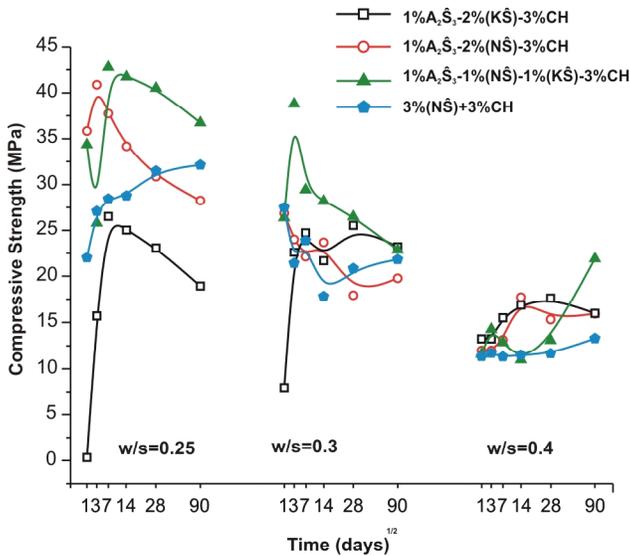

Fig 1. Compressive Stregth Vs time of fluorgypsum systems at different w/s ratios = 0.25, 0.3, 0.4 modified with additives NŜ, KŜ,CH and $A_2\hat{S}_3$

The pastes with $A_2\hat{S}_3$-**NŜ**-**CH** showed high strength (35 MPa, w/s =0.25) from the first day of curing wich is related to the amount of gypsum formed (as later discussed on ICC), but for w/s=0.25 and 0.3 after 3 to 7 days the strength decreased; only the system with w/s=0.4 remained stable at about 16 MPa (90 days). Pastes with **NŜ-CH** gradually developed strength for w/s=0.25, showed an strength reduction at w/s = 0.3 and remained stable for w/s=0.4. The addition of $A_2\hat{S}_3$ to **NŜ-CH** formulations favored gypsum hydration and strength development for w/s=0.25; however, for higher w/s ratios there was not a clear difference up to 28 days. The pastes with all additives (green lines in Fig 1.), showed in general the best compressive strengths of 35 MPa, w/s=0.25 at 1 day; however the strength of these pastes decreased at 90 days, only the paste of w/s=0.4 showed increasing strength up to 22MPa.

Even though it would be normally expected that a reduction of water increases strength, the concentration of the additives (relative to the amount of water) seems to have an effect on the hydration of fluorgypsum and strength development. At higher concentrations of sulfates in solution (w/s=0.25) the compressive strengths were higher for additives bearing **NŜ**, while at w/s=0.4 the strengths were closer regardless of the type of additive. Seems that the effect of the additives on the strength development depends of the amount of water, but there is not clear pattern.

Fig. 2 shows the results of compressive strength for various composite cementitious pastes of **Fy-PC-BFS**, a fixed w/s=0.3 was chosen. As previously noted for the 100% **Fy** pastes, the addition of $A_2\hat{S}_3$ in the additive mixes enhanced the strength of all composites more notably for pastes with **KŜ-CH** (lowest strengths)**,** increasing from 22-30 to 37-40

MPa. All composite cements show a trend to increase strength at longer curing periods. It was also noted that as amount of **Fy** increased, the strength decreased slightly but more markedly for pastes with **KŜ-CH.** The results indicate that the use of **NŜ** was better than **KŜ**, only without **A₂Ŝ₃**.
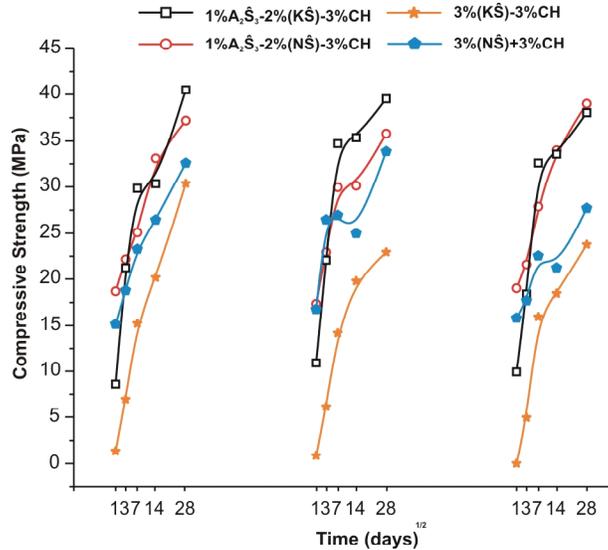

Fig 2. Compressive Stregth Vs time for various cementitious systems of fluorgypsum(Fy)-Portland cement (PC)-blast furnace salg(BFS), w/s = 0.3, modified with additives NŜ, KŜ,CH and A₂Ŝ₃

For a fixed additive type and regardless of the %Fy the pastes attained similar strengths, which indicates that the early strength depended upon Fy hydration. Strengths attained for Fy-PC-BFS were better than those described for 100% **Fy** pastes at 28 days. This is related to the hydration reactions of **PC** and **BFS**, that generate CSH and ettringite (shown in DTA and XRD results), which improve strength by enhancing the microstructure.

3.2 Calorimetry

Fig. 3 shows the results of ICC for various pastes. For the 100% **Fy** paste with **NŜ-CH** (Fig 3-a), the main peak appeared after about 8h, and appeared earlier and more intense relative to those of pastes with **A₂Ŝ₃-KŜ-CH** and **A₂Ŝ₃-NŜ-CH**, the latter showed broadened and less intense peaks at about 10-11 h. This indicates that the **NŜ-CH** favored a faster **Fy** hydration in the early stages of hydration. Respect to the compressive strength results, there is not a clear difference (Fig.1). This indicates that **A₂Ŝ₃** modify the process of gypsum formation. It is worth mentioning that the heat evolution of the paste 100% **Fy** with **KŜ-CH** showed similar features as other pastes,but it did not set completely after 24 h, that is why

the strength of such pastes was not reported above. Although some reports mention **KŜ** as an activator for anhydrite hydration [10], its combination with **CH** seems to retard setting compared to the other systems investigated.

Figs. 3 shows the heat evolution curves for composite pastes 50%**Fy**-30%**PC**-20%**BFS** (Fig. 3b) and 75%**Fy**-15%**PC**-10%**BFS** (Fig. 3c)**.** For pastes with **NŜ-CH** the main peak appeared at earlier times, about 5h, relative to 100% **Fy**. It seems that the presence of **PC** accelerated the hydration reactions. Two peaks appeared for pastes with **NŜ-CH.** The first is associated to **PC** and **Fy** hydration, it showed earlier at higher **PC** contents (5 vs. 7 hours); however it was more intense in at higher **Fy** contents. A second peak showed earlier (14 vs. 22 h) and more intense at higher **BFS** contents (and higher %**PC** too), this peak is most probably related to **BFS** activation as a higher pH (13 vs. 12.7 at the time of the second peak) was measured from the extracted pore solution from the paste with higher **PC** and **BFS** contents. The more favorable alkaline environment for **BFS** hydration in 50%**Fy** pastes resulted since the activator **CH** was added relative to the total weight of binder; and more **CH** was present for higher **PC** contents. The addition of **AŜ₃** to mixtures of **NŜ-CH** modified the reaction patterns; the two peaks disappeared for the pastes **50% Fy** but remained, although not very intense, for the pastes with **75% Fy** showing at 22 h (black line Figs 3c).

Systems 50% **Fy** with **KŜ-CH** presented only one peak whose maximum is attained at 16.5 h; the activation of the slag is not as clear as in the **NŜ-CH** system. However the paste 75% **Fy** showed two peaks at 11 h and 28 h, corresponding to the activation of **Fy-PC** phases and **BFS,** respectively (green line Fig 3-c). The inclusion of **A₂Ŝ₃** the peaks appeared at shorter times, and the first peak appeared at 10 h for both **Fy** content; moreover a second peak was noted at about 28 h only for the paste 75% **Fy.**

Although $CaSO_4$ and **CH** are typical activator of **BFS** [11], in the early stages of reaction, seems that the combination of **NŜ** with CH concentration, %**CH** enhanced by higher %**PC**, contents was more effective to promote the **BFS** hydration. However, the second peak was not always present for pastes 50% **Fy**, but was present for 75% **Fy** pastes; this indicates that the **BFS** is activated in later periods at higher ratios $CaSO_4$/**BFS**.
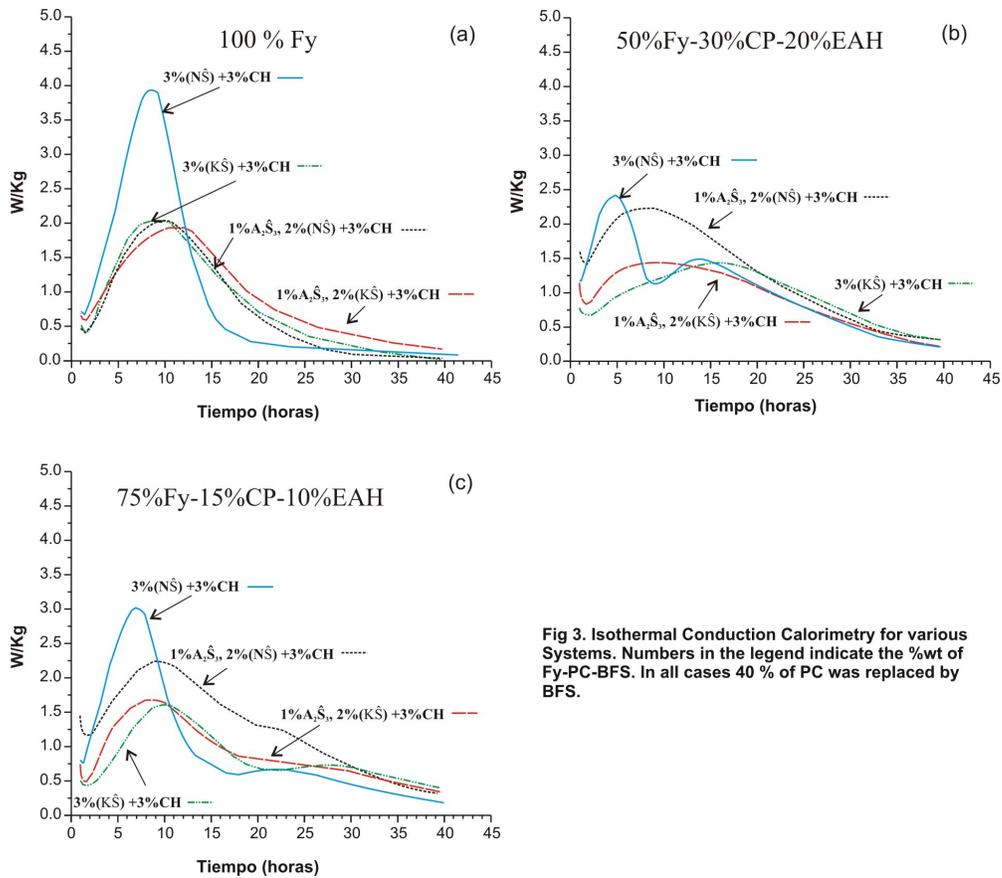
Fig 3. Isothermal Conduction Calorimetry for various Systems. Numbers in the legend indicate the %wt of Fy-PC-BFS. In all cases 40 % of PC was replaced by BFS.

Table 2. Shows the results of total heat liberated THL for **Fy** and **Fy-PC-BFS** pastes. A correlation was found between compressive strength and (THL) at the firsth day, higher THL corresponded to higher early strength; for example, THL for **NŜ** was always higher than for **KŜ**. The addition of **A₂Ŝ₃** increased the THL and the compressive stregth; except for the **Fy** pastes with **NŜ** for which the THL and strength were not modified. The total heat evolved from all pastes investigated was lower than that of the **PC**; moreover, the higher the **Fy** content the lower the heat evolved. This is due to the differences between the heat of **PC** (about 300 j/g [12] and $CaSO_4$ related phases (125-175 J/g [13]).

Table 2.
Total heat liberated data for **Fy** and **Fy-PC-BFS** systems

Additives	100 % Fy	Systems (Fy-PC-BFS)	
		50-30-20	75-15-10
Total Heat Liberated	**(J/g)**	**(J/g)**	**(J/g)**
1%A₂Ŝ₃,2%(NŜ)+3%CH	139.	208.	188.
1%A₂Ŝ₃,2%(KŜ)+3%CH	127.	162.	143.
3%(NŜ)+ 3%CH	139.	158.	149.
3%(KŜ)+ 3%CH	111.	144.	115.

3.3 XRD

Fig. 4 present X -ray diffraction patterns of systems of **Fy** (w/s=0.4). admixed with **A₂Ŝ₃-NŜ-CH** and **A₂Ŝ₃-KŜ-CH** after 28 days of curing. In both cases were noted peaks of gypsum and anhydrite, indicating that the gypsum formation was not complete despite the high w/s ratio.
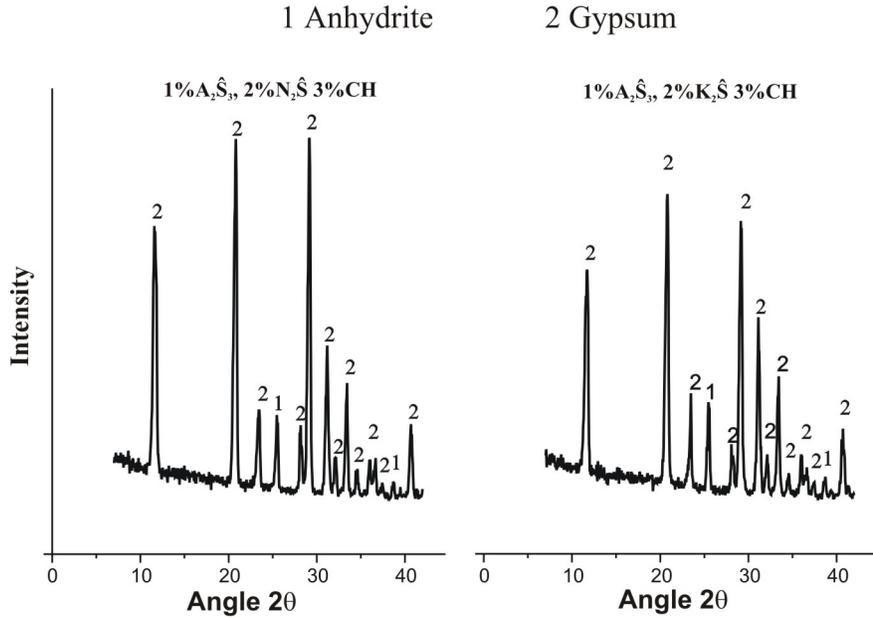

Fig 4. X-ray diffraction patterns of Fy systems at 28 days of curing with additives of NŜ, KŜ, CH, and A₂Ŝ₃.

Fig. 5 shows XRD results for composite pastes of 50, 65 and 70%**Fy**, comparing the effect of activators **A₂Ŝ₃-NŜ-CH** and **A₂Ŝ₃-KŜ-CH**. The main gypsum reflection (number 2) was higher for **A₂Ŝ₃-NŜ-CH** in general, only 65% **Fy** shows a different behavior. Anhydrite peaks were always slightly lower for **A₂Ŝ₃-KŜ-CH** systems, more intense gypsum peaks would be expected; however this was not observed and it is considered that gypsum was consumed by BFS more intensively in the presence **A₂Ŝ₃-KŜ-CH** as compared to **A₂Ŝ₃-NŜ-CH**. **CH** peaks show higher intensities at higher PC contents, these appear higher in the presence of **A₂Ŝ₃-KŜ-CH**. Ettringite peaks were present in both cases being slightly stronger in the presence of **A₂Ŝ₃-KŜ-CH.**
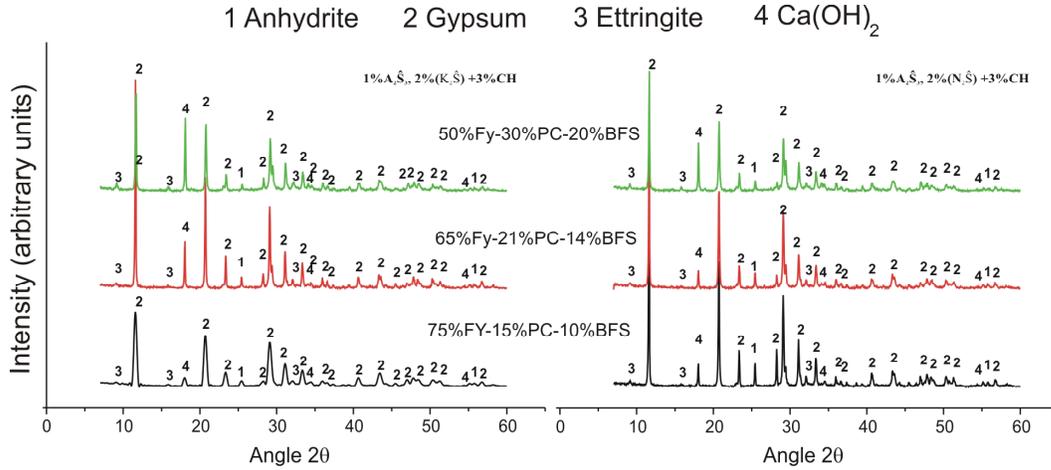
Fig 5. X-ray diffraction patterns of Fy-CP-BFS systems at 28 days of curing.
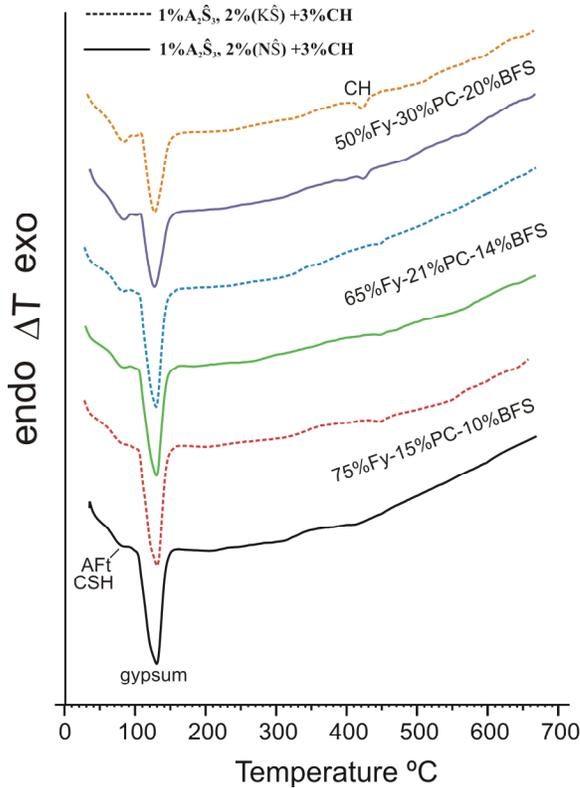
3.4 DTA

Fig 6. DTA of FyPCBFS systems at 28 days, at levels of Fy (50 to 75%), in presence of $A_2\hat{S}_3$

Fig. 6 presents DTA curves of the same systems previously described for XRD. 4 endothermic peaks were noted. C-S-H decomposition is noted at 80-90°C [8], its intensity decreased at higher %**Fy**. Probably peak of ettringite at 100°C follows the same behavior. The Gypsum dehydration was noted by only one peak at 130 °C [14,8], it was slightly higher for additions of **A$\hat{S}_3$-N$\hat{S}$-CH**. The decomposition peak of **CH** (420 -450 °C) was more intense for higher CPO contents.
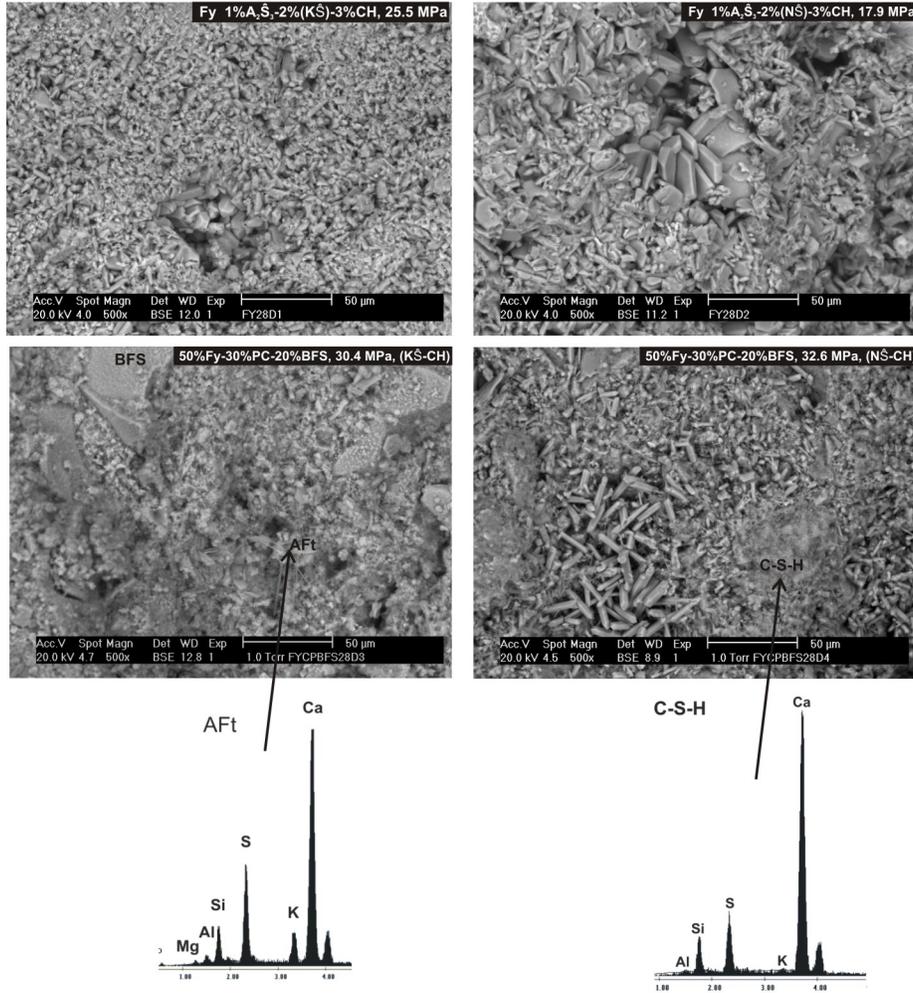
3.5 SEM

Fig 7. Scanning electron microscopy microstructures of fracture samples of Fy and Blended cements Fy-PC-BFS cured for 28 days.

Fig. 7 presents selected microstructures of samples of systems **Fy**, and **50%Fy-30%PC-20%BFS** cured for 28 days. **Fy-PC-BFS** systems of **A$_2$Ŝ$_3$-KŜ-CH** showed generally a more compact matrix and smaller gypsum crystal than **A$_2$Ŝ$_3$-NŜ-CH** (also noted by the broader XRD gypsum peaks); in the latter some gypsum crystals grew more and presented a more porous microstructure; this was in agreement with the strength reported. An enhanced growth of gypsum crystals was observed for **Fy** pastes relative to the composite pastes. The microstructure of blended pastes with **NŜ-CH** shows a variety of gypsum crystals sizes, some engulfed in part by CSH. On the other hand for **KŜ-CH** additions, the microstructures presented a more uniform matrix with gypsum crystals also engulfed by CSH products and the clear presence of AFt needles.

4   Conclusions

- Strength development and strength attained in **Fy** systems was influenced by the type and proportions of additives used, as well as the w/s ratio. At higher concentrations of sulfates in solution (w/s=0.25) the compressive strengths were favoured by those of **NŜ**, and the addition of **A₂Ŝ₃**.
- For composite systems **Fy-PC-BFS,** among highest strengths for pastes admixed with **A₂Ŝ₃**, were those of **NŜ-CH,** followed closely by the pastes added with **KŜ-CH**. Addition of **A₂Ŝ₃** resulted more favorable for pastes with **KŜ-CH.**
- Hydration reactions in **Fy** systems were accelerated by additions of with **NŜ-CH, Fy** reactions were also enhanced by the presence of **PC** in the composite systems. The presence of **A₂Ŝ₃** accelerated the early formation of gypsum, which corresponds with compressive strength.
- For high **PC** contents, the **BFS** activation was favored mainly by **CH** more than by the additives of alkali sulphates used; being inverse on higher **Fy** contents.
- Ettringite was reduced as the amount BFS reduced and that of **Fy** increased.
- Microstructures of **Fy** were more compact in presence of **A₂Ŝ₃-KŜ-CH,** with smaller and more uniform crystals relative to pastes added with **A₂Ŝ₃-NŜ-CH**.
- Microstructures in the composites **Fy-PC-BFS** were more compact and with a smaller crystal size than only **Fy** systems. For 50% **Fy** with **KŜ-CH** additions, a smaller particle size with AFt formation was detected.

5   References

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