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Cement & Concrete Composites 30 (2008) 88–96

Cement & Concrete Composites

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Fluorgypsum binders with OPC and PFA additions, strength and reactivity as a function of component proportioning and temperature

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Received 20 October 2006; received in revised form 4 May 2007; accepted 30 May 2007
Available online 24 June 2007

Abstract

Cementitious composites based on 50–80% fluorgypsum, 15–50% OPC and 0–15% PFA, were wet and dry cured for up to 180 days at 20 and 60 °C. All pastes developed and maintained strength up to 32 MPa, even under water. Characterization by thermal analysis and X-ray diffraction indicated that gypsum formed intensively in the first days, providing the initial strength jointly with a partial hydration of OPC, incomplete fluorgypsum reactions were observed. Wet curing at 20 °C gradually increased the strength and the nonevaporable water. At 60 °C, wet curing limited the gypsum formation and affected strength development, whereas dry curing resulted in the decomposition of the already formed gypsum and reduced the compressive strength. PFA additions were beneficial in some formulations in late periods, and its reactions were enhanced at 60 °C. The microstructure consisted of gypsum crystals surrounded by calcium silicates, and with localized areas of gypsum surrounding unreacted fluorgypsum.

Keywords: Alternative cement; Fluorgypsum; Hydration; Composite cements

1. Introduction

Calcium sulphates compounds (CS) exist in three levels of hydration, i.e. anhydrite ($CaSO_4$), hemihydrate ($CaSO_4 \cdot 1/2H_2O$) or gypsum ($CaSO_4 \cdot 2H_2O$). Among them, mineral gypsum is a widely available and utilized material in the construction industry, it is a binder of an environmental impact lower than Portland cement; however, its applications are limited due to its poor mechanical properties and water solubility. CS are also a problem of waste generation for various chemical industries, for example, fluorgypsum is the by-product of the hydrofluoric acid production, where CaF_2 and H_2SO_4 are the raw materials; anionic interchange leads to formation of the main product and HF and by-products of $CaSO_4$ or $CaSO_4 \cdot 2H_2O$.

It is widely accepted that the utilization of waste products as cementitious material is to be encouraged to reduce the environmental impacts of waste accumulation and CO_2 emissions from the production of portland cement. The ideal wastes are those able to be used with as little as possible further treatment other than milling. Those wastes with potential to replace portland cement in various applications should be investigated to take advantage of the economical and environmental advantages involved.

The use of CS as cementitious materials is indicated in various reports in the literature, using commercial and waste sources, in the development of water stable composite cements. Most of the reports deal with cementitious mixtures involving CS contents lower than 50%, only a few reported cements contain 75% CS. Kovler [1,2] reported blends of 75% gypsum, 20% OPC and 5% microsilica as cements that developed strengths of up to 17 MPa after curing for 200 days under water. Colak [3] investigated blends

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doi:10.1016/j.cemconcomp.2007.05.015

of 41% gypsum: 41% OPC: 18% natural pozzolana, the blends set and gained 4 MPa after 1 h and reached about 22 MPa after 95 days under water. Singh and Garg [4] investigated on the properties of blends of 40% hemihydrate phosphogypsum with 40% pulverised fuel ash and 10–20% calcium hydroxide and 0–10% OPC; they found strengths of 8–23 MPa after 90 days, and that curing at 50 °C was favourable compared to 27 °C. The same authors also studied cements of 50–75% phosphogypsum anhydrite with blast furnace slag [5] similar properties as above were found. Yan and Yang [6], Yan and You [7] and Yan et al. [8] studied systems of 31–50% fluorgypsum, 12–20% OPC and 34–57% PFA; they concluded that the fluorgypsum content needed to be under 40% and that of PFA greater than fluorgypsum. Strengths of up to 59 MPa were obtained for samples of low water/binder ratios of 0.22 cured under water. Fraire-Luna et al. [9] investigated water resistant paste systems of 75% fluorgypsum with blast furnace slag and metakaolin, samples were cured under water and showed water stability for up to a year, reaching up to 14 MPa.

The above quoted references reported cementitious systems of various compositions, using different sources of CS and complementary cementitious materials, which developed and maintained strength after curing under water; for some cases, very high strengths were reported after using relatively low water/cement ratios. Not many studies report the properties evolution for relatively long periods of curing under water of cementitious materials bearing calcium sulphates. For some of the references, PFA is used as the main cementitious component in the systems described [6,7], or those of 60% PFA with CH and up to 30% phosphogypsum or pure gypsum [10]; in other reports where anhydrite is the main constituents, it is used with secondary materials such as blast furnace slag and OPC.

The objective of this research was to investigate the mechanical properties and hydration characteristics of composite cementitious mixtures, where fluorgypsum (anhydrite) was the main cementitious component, with contents above 50% and up to 80%, with complementary materials of OPC and PFA; combinations of such proportions were not found in the literature.

2. Experimental and materials

2.1. Materials

Fluorgypsum (F) from the company IQM (San Luis Potosi, SLP) was ground to a Blaine of 4000 cm^2/g, the X-ray diffraction pattern indicated only $CaSO_4$ peaks and the chemical analysis indicated 99.1% anhydrite. The traces of acids required neutralization with CH. Pulverised fuel ash (PFA) was obtained from the power station Termoeléctrica Lopez Portillo (Nava, COAH), quantitative X-ray diffraction showed quartz and mullite and about 60% of amorphous fraction. An ordinary portland cement 30R complying with NMX C-414-ONNCCE [11], with calcite additions, was used. Table 1 presents the chemical composition of starting materials.

2.2. Paste preparation

The compositions of the binder were of F 50–80%, OPC 20–50% and PFA 5–15%, the nomenclature used in the document for the various mixes is described as: e.g. 70–20–10, indicating the weight percentage of F–OPC–PFA. Industrial grade $Ca(OH)_2$ (CH) and Na_2SO_4 were used as activating agents. The water/solids ratio was kept at 0.4 for all pastes in order to provide the same amount of water while having workable pastes. The cementitious powders materials were weighed and homogenized before adding the mixing water. Batches of about 8 kg of pastes were mixed for 2 min in a planetary mixer, and cast in cubic moulds of 50 mm, the moulds were vibrated for about 1 min to eliminate air bubbles. The specimens were covered with a damp cloth, to avoid water evaporation, and left to set for 24 h at 20 ± 2 or 60 ± 3 °C. After demoulding, the cubes were randomly placed in plastic containers and cured isothermally at 20 ± 2 and 60 ± 3 °C in air and also under water. The high temperature was selected since the fluorgypsum waste is generated in regions that are quite hot and dry in summer.

2.3. Characterisation

The compressive strength was measured from 1 to 180 days from 4 cubes randomly selected, the average was reported. Fragments of the crushed samples were hand ground to particles of about 1–4 mm and dried in a vacuum oven at 35 °C for 24 h. This procedure ensured rapid dehydration of the free water without accelerating the reactions. Dried samples were further ground in a planetary ball mill in agate containers, the powders were characterised by the following techniques. X-ray diffraction (XRD) (Philips X'Pert 3040), the diffractometer was operated at 30 kV and 40 mA, step of 0.02 2θ with 2 s per step. NonEvaporable Water (NEW) was estimated after calcination at

Table 1
Chemical composition of the cementitious materials

	Oxide weight (%)									
	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	TiO_2	Na_2O	K_2O	SO_3	LOI
Fluorgypsum		33.02							66.04	
OPC	18.86	62.18	4.52	2.73	1.97	–	0.44	0.75	2.58	5.9
PFA	55.82	1.93	25.33	3.47	0.37	0.84	.08	1.06	1.4	9

950 °C, the values are referred to the ignited weight. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were simultaneously carried out in an air atmosphere, powder aliquots of 15 mg were heated at 10 °C/min using alumina crucibles (Pyris Diamond TGA/DTA, Perkin–Elmer). Additionally, solids fragments of crushed specimens were mounted in resin, ground and polished down to a 1/4 μm using a water free lubricant and carbon coated for analysis under the scanning electron microscope (Philips ESEM Philips XL30ESEM), operated at 20 kV.

3. Results

3.1. Compressive strength

Figs. 1 and 2 show the evolution of compressive strength vs time for various cementitious systems cured in air and under water, respectively. In general, the pastes developed strength at relatively high rates, and the values reached registered are useful for many applications. In the absence of PFA, the increments in the F contents up to 80%, at the expenses of the OPC, reduced the initial strength; the lowest 1 day strength was 8.4 MPa of corresponding to 80% F, whereas the highest was 13.6 for 50% F. The presence of the PFA in the pastes with 50% F, wet or dry cured, reduced the strength during the 180 days of the investigation. On the other hand, for 70% F in wet conditions the PFA had a positive effect after 90 days. The strengths registered by the pastes with 80–20–0 and 80–15–5, were relatively close to those of lower F contents (high CPO contents); and, in view of the low amounts of OPC used, they are the cheapest and most environmentally friendly among all of the investigated cements.

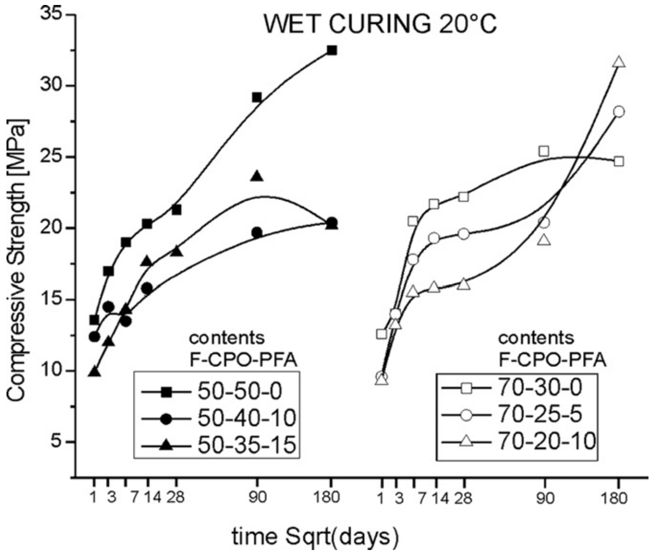

Fig. 2. Compressive strength vs. time for systems of fluorgypsum–portland cement–PFA wet cured at 20 °C.

Fig. 3 presents a comparison of strength development after curing at 20 and 60 °C for wet and dry conditions. For the systems with 50–70% F and 0% PFA, curing at 60 °C resulted in lower strengths when compared to curing at 20 °C; similar findings were noted in the presence of PFA (system 70–20–10). Steam curing at 60 °C for 6 h was reported as favourable [6] for strength of mortars with cements of 30–50% fluorgypsum, 30–50% PFA and 16–20% OPC; on the other for blends of 40% hemihydrate phosphogypsum with 40% PFA, curing at 50 °C was favourable compared to 27 °C. The cements of this investigation had F contents above 50% and much lower PFA contents, so the noted strength reduction, possibly originated from an effect of the longer periods of curing at higher temperature on the gypsum formation, as revised below.

3.2. Nonevaporable water (NEW)

Fig. 4 presents the correlation of strength vs. nonevaporable water for the systems cured at 20 °C, corresponding

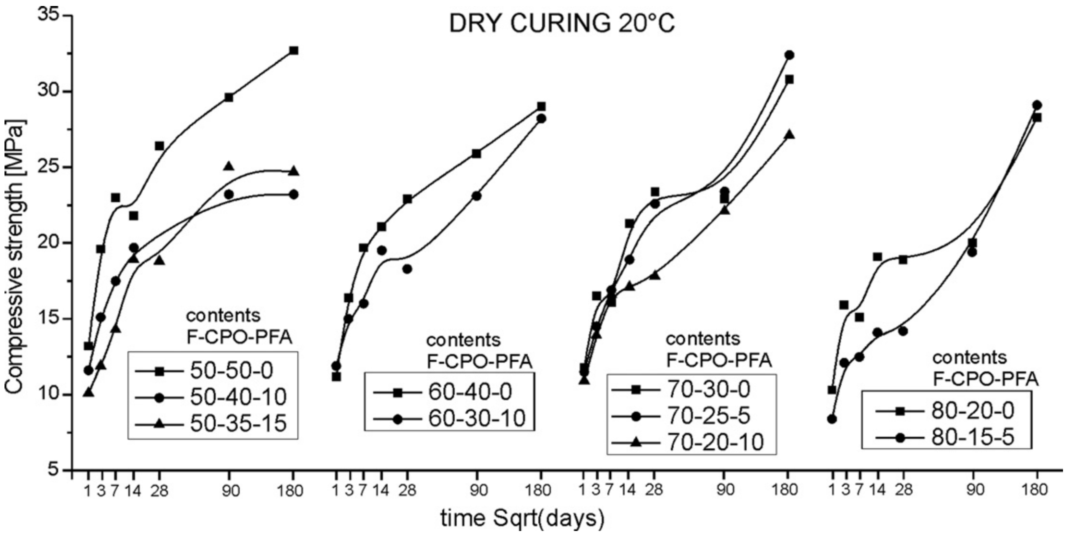

Fig. 1. Compressive strength vs. time for systems of fluorgypsum–portland cement–PFA dry cured at 20 °C.

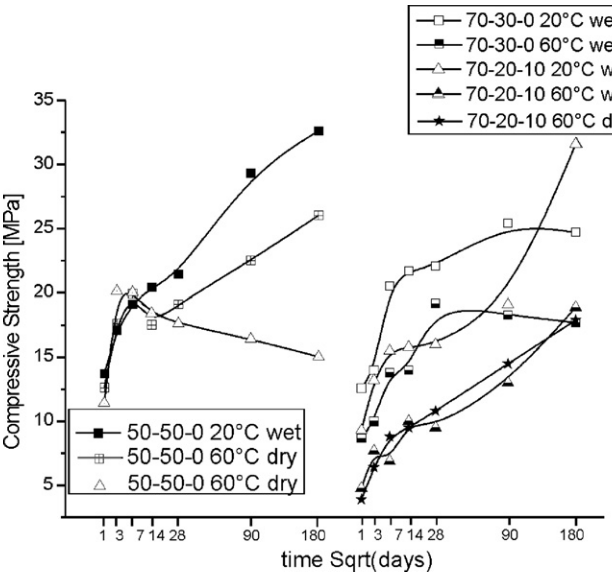

Fig. 3. Compressive strength vs. time for systems of fluorgypsum–portland cement–PFA wet and dry cured at 20 and 60 °C.

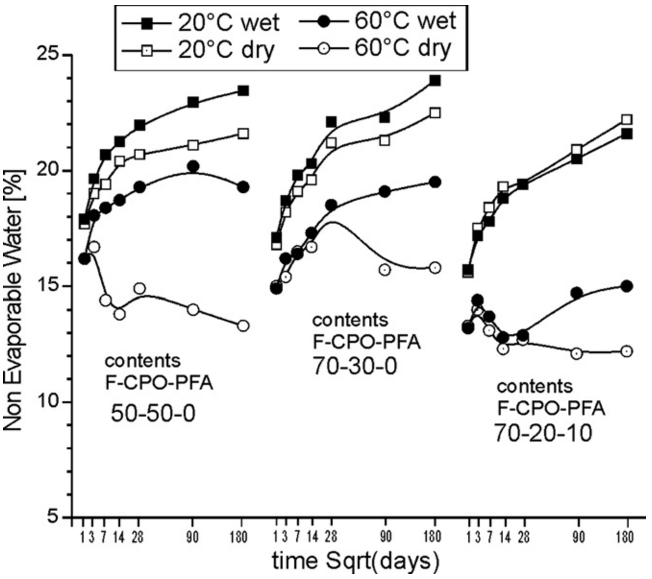

Fig. 5. Nonevaporable water vs. time for pastes cured at 20 and 60 °C and under dry and wet conditions.

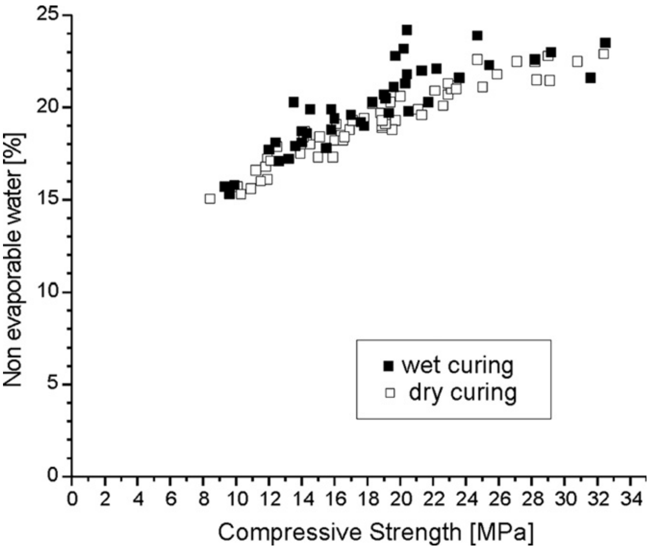

Fig. 4. Nonevaporable water vs. compressive strength for dry and under water samples cured at 20 °C.

to those pastes described in Figs. 1 and 2; open squares represent dry curing and solid squares wet curing. After 1 day, the range of both data sets started at ~8–10 MPa and 15% NEW, and followed a similar linear trend afterwards in which higher strength corresponded to increased amounts of bound water; data from wet curing showed slightly higher NEW for any given strength. For complete hydration anhydrite takes in about 26% of its weight in water to form gypsum, whereas OPC takes 23% [12], the obtained NEW results were within such limits. Considering that the calcium sulphates react potentially faster than OPC, it is reasonable to say that the 1 day high NEW, combined with a relatively high strength (lower than pure OPC), was the result of the initial fast reaction of the fluorgypsum, and to some extent of the portland cement.

Fig. 5 shows the evolution of NEW vs. time for various pastes cured at 20 and 60 °C under dry and wet conditions. Increasing the temperature reduced the NEW values, also for both temperatures the NEW values of dry cured specimens commonly reached lower values. After curing at 60 °C the systems 50–50–0 (dry) and 70–30–0 (wet), the NEW values were lower than those obtained at 20 °C, this pattern was in agreement with the lower strengths observed in Fig. 3. On the other hand, wet curing of paste 70–20–10 at 60 °C caused lower strengths (compared to 20 °C), nonetheless strength increased with time; however, the NEW values did not increase in the same proportions; the formation of new hydration products possibly combined with gypsum dehydration could be the cause of this. Considering that the 1 day NEW values for the various temperature conditions described are not too different (13–17%), this suggests that in first 24 h (pastes in the moulds), part of the OPC and a large fraction of the fluorgypsum rapidly react binding water. The subsequent dry curing limited the availability of water for the reactions and for some cases the strength development; moreover, subsequent curing at 60 °C could have delayed further gypsum formation or caused its dehydration reducing the NEW values, this effect is discussed with the data of thermal analysis.

3.3. Thermal analysis

Considering the high level of fluorgypsum utilization and the favourable strength development of the pastes with 75% F, these were selected for thermal analysis; the effects of the PFA and temperature are analyzed. Fig. 6 presents the results of thermal analysis for the systems 70–30–0 at 20 °C (upper), 70–20–10 at 20 °C (middle) and 70–20–10

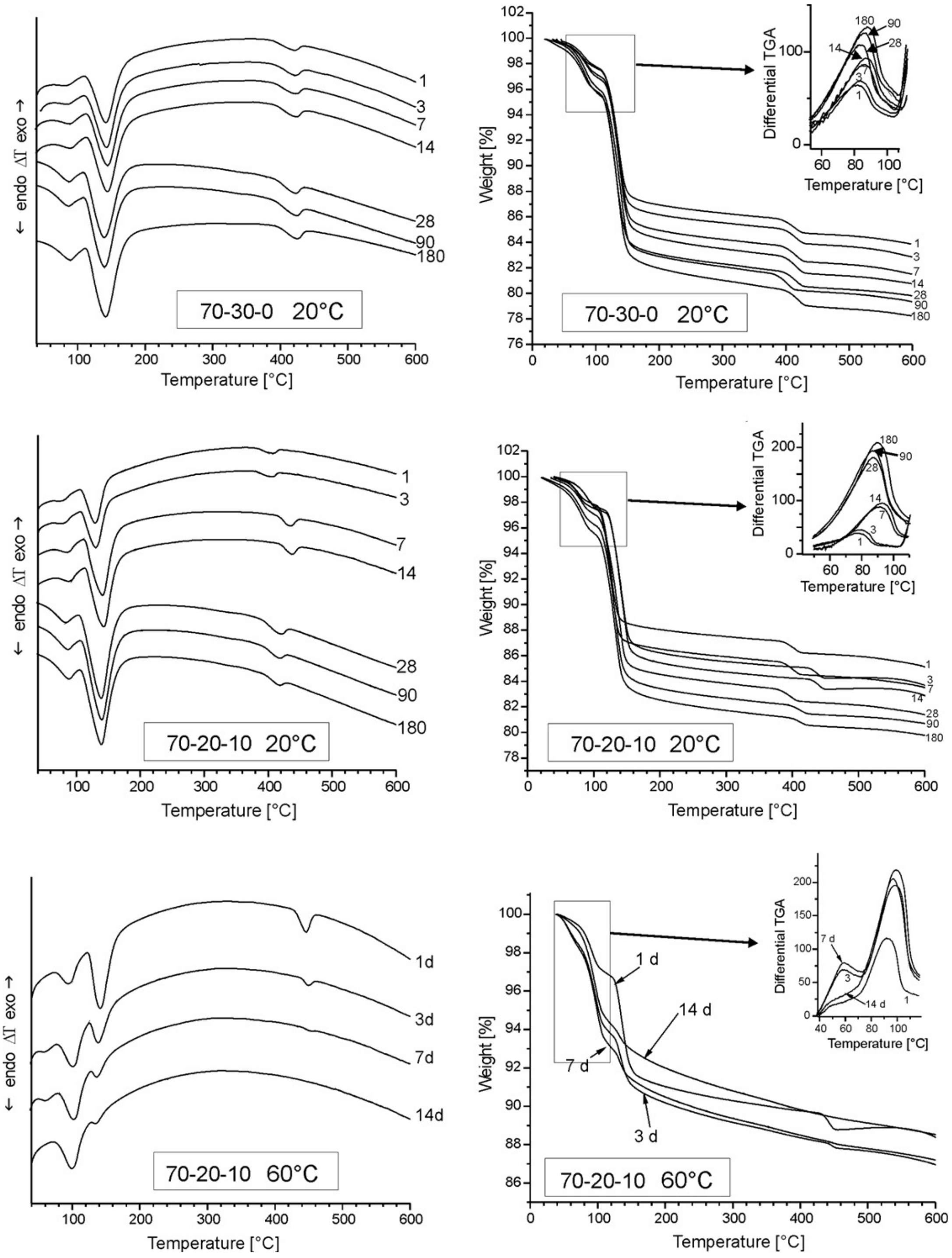

Fig. 6. Differential thermal analysis and thermogravimetrical analysis for the systems 70% F-30% OPC and 70% F-20% OPC-10% PFA cured at 20 and 60 °C under water.

at 60 °C (lower). DTA and TGA show three main features, namely the C–S–H and ettringite overlapping at about 90 °C, the peak of gypsum decomposition at about 130 °C and the calcium hydroxide dehydroxylation at about 420 °C [10,13–15].

For the system 70–30–0, the peak of gypsum decomposition appears relative intense after 1 day of curing, it grew rapidly during the first 28 days, then remained fairly unchanged afterwards, indicating that most of the gypsum was formed in this period. The peak from the contributions of C–S–H and ettringite increased slowly in the first 14 days and it became larger as time progressed, the overlapping makes complicated the separation of each phase. The amount of CH also increased with time confirming C–S–H formation from OPC hydration. For the system 70–20–10 (middle set) cured at 20 °C, the features were basically the same as for 70–30–0; the CH produced seems less as the cement was partially replaced, and such peak reduced with time as it was consumed by the PFA to form more C–S–H.

For the system 70–20–10 wet cured at 60 °C (lower set), the peak of C–S–H and ettringite was more intense than at 20 °C and grew markedly during the first 14 days, indicating faster reactions. A rapid consumption of CH was noted after 14 days of curing indicating a reaction with the PFA. After 1 day, the presence of gypsum was noted; however, after the subsequent curing the intensity of the gypsum thermal feature decreased with time, suggesting that (a) there was no further anhydrite hydration or (b) gypsum was decomposed and/or reacted with the PFA to form new hydration products. Thermal analysis experiments were not run after 14 days at 60 °C since the thermal features of gypsum and CH disappeared and no other significant changes were noted.

The TGA curves show various weight loss steps, associated to C–S–H, ettringite, gypsum and CH, at the temperatures described before for the DTA curves. The inserts on the TGA curves correspond to the derivative of the weight loss curve up to ∼110 °C. For the pastes cured at 20 and 60 °C, the weight loss in the near 100 °C increased with time, more clearly than as shown by DTA; this was confirmed by the derivative curves. The weight losses at about 100 °C were stronger after curing at 60 °C, indicating more intensive reactions for C–S–H and AFt formation. The weight losses from CH decomposition describe the cement hydration and pozzolanic reaction, for the pastes 70–20–10 cured at 20 °C the step of CH gradually reduced; whereas at 60 °C such step was absent after 14 days of curing, as it was consumed by the PFA. At 20 °C weight losses from gypsum decomposition increased with time in both pastes; however, at 60 °C such step gradually reduced due to the reasons already mentioned for DTA results.

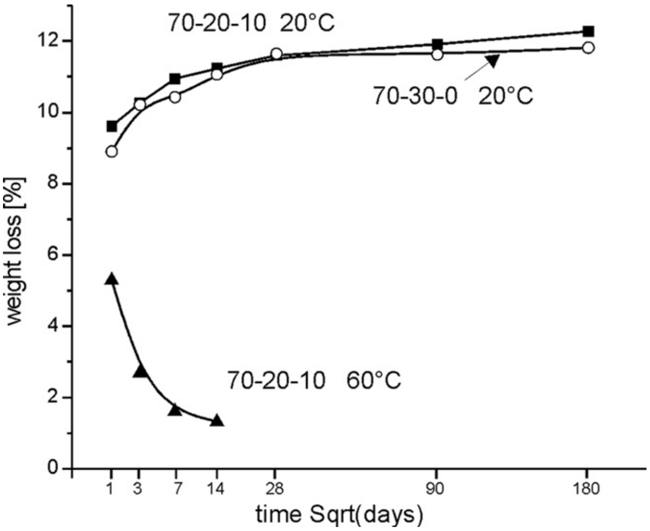

Fig. 7. Water losses in the range of approximately 110–150 °C, estimated graphically.

Fig. 7 shows the weight losses in the range of approximately 110–150 °C (gypsum decomposition) measured graphically (similarly as the method used for CH determination [12]). At 20 °C, the results indicate an intensive gypsum formation in the first day, further formation for up to 28 days, and from that time onwards the weight losses increased marginally. In contrast, at 60 °C the weight losses due to gypsum reduced, and the step disappeared after 14 days (see Fig. 6), in agreement with the DTA curves.

3.4. X-ray diffraction (XRD)

Fig. 8 presents the XRD data corresponding to those systems characterized by TGA/DTA. For curing at 20 °C there was an intensive formation of gypsum after 1 day; however, the F peaks diminished little after 14 days, and remained after 180 days. Similar results were reported by other authors for up to 28 days [6,8]. This indicates that gypsum formed intensively during the first 14–28 days, and then its formation is slowed down and not all of the fluorgypsum reacted after 180 days. It seems that the presence of PFA did not affect the kinetics of fluorgypsum hydration. The peaks of CH from OPC hydration increased with time; however, they reduced in the presence of PFA after the pozzolanic reaction. The peaks of anhydrous OPC were too weak and overshadowed by the crystalline gypsum and fluorgypsum. Weak peaks of ettringite were noted from day one in the systems 70–30–0 and 70–20–10, with no clear difference regarding the presence of the PFA.

Curing at 60 °C showed a different picture, the peaks of gypsum were very weak after 1 day of curing, and disappeared after 14 days, whereas the peaks of anhydrite were strong at all curing times. This indicates that during the initial 24 h (in the covered moulds) the formation of some gypsum took place at 60 °C. However, as the curing time progressed there was (a) limited further anhydrite hydration, (b) dehydration of the already formed gypsum and/or (c) gypsum consumption by reaction with the PFA; in agreement with NEW and TGA results. The pozzolanic reaction was accelerated as the peaks of CH disappeared rapidly; also the peaks of ettringite were stronger than in the case of curing at 20 °C.

3.5. Scanning electron microscopy

Microstructures of fracture surfaces of gypsum-based cements are widely available in the literature and no reports were found presenting microstructures of polished samples, which offer a completely different perspective. Fig. 9 presents a typical microstructure of the pastes 70–30–0 and 70–20–10 after 90 days of curing under water. The elemental maps for the paste 70–20–10 help identifying the distribution of the reactants and hydration products in the matrix. The PFA particles are easily recognized by their typical rounded morphology and their prominence in the Al and Si maps. Other features noted in the Al map are

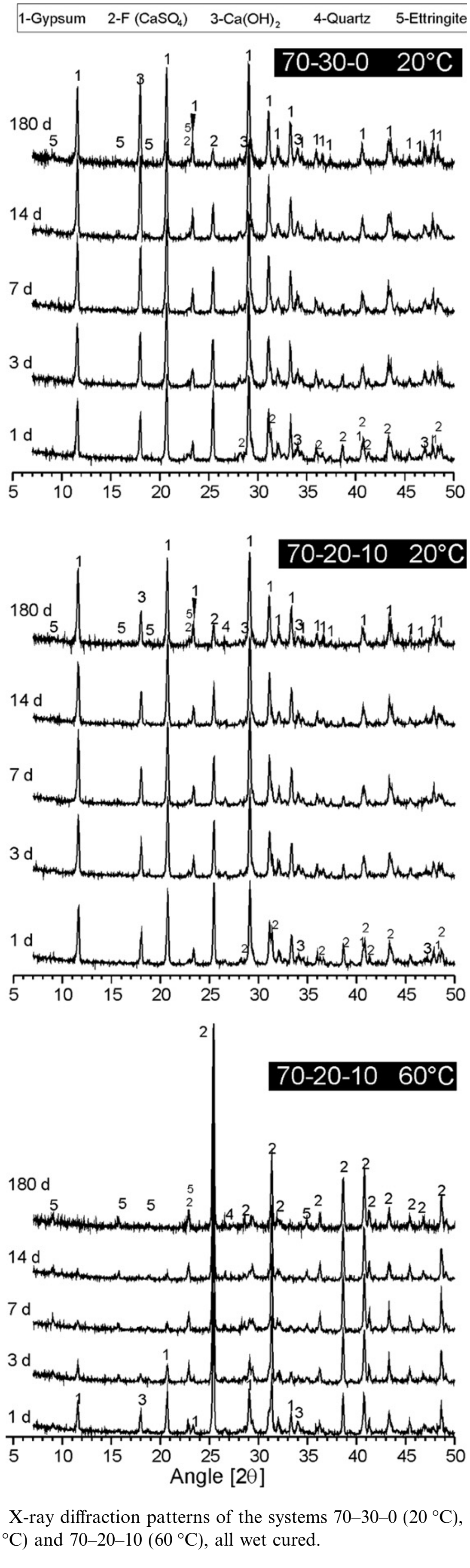

Fig. 8. X-ray diffraction patterns of the systems 70–30–0 (20 °C), 70–30–10 (20 °C) and 70–20–10 (60 °C), all wet cured.

particles of unreacted OPC. Zones of ettringite were not clearly identified in the microstructures, as it was in small amounts and intimately mixed with the C–S–H or finely distributed throughout the microstructure.

The maps show that Ca distributed throughout the microstructure in the hydration products. In the upper left hand side of the microstructure of paste 70–20–10 the area consists of gray hydration products with spots of a brighter phase, S and Ca were the only elements present. Considering that the intensity of the backscattered electrons is proportional to the average atomic number of the irradiated zone, the brighter spots correspond to F (anhydrite) which are surrounded by gypsum that appeared of a darker shade (lower average atomic number due to the presence of water). The rest of the microstructure (right hand side) shows a distribution of S, Si and Ca, except where PFA particles were present; the silicon concentrates where S is absent, indicating a mixture of C–S–H and gypsum products.

The microstructure of the paste 70–30–0, at a higher magnification, shows a grain of partially reacted CPO and gypsum crystals embedded in other hydration products such as C–S–H; some F particles are also noted. The microstructures seem relative dense and compact, in agreement with the strengths reached of nearly 25 MPa.

4. Discussion

The investigated cementitious fluorgypsum-based cements, showed high reactivity of the anhydrite under the alkaline environment created by the OPC and additives. A fast formation of gypsum in the first days was evidenced by high NEW values, TGA/DTA and XRD results. It is reasonable to say that the 1 day strength resulted from the initial reaction of part of the OPC and the intensive hydration of F, the latter resulted in the configuration of a framework of gypsum crystals. Nonetheless, incomplete reaction of F was noted even after 180 days of curing; even though sufficient water was provided. It is possible that the densification of the matrix, after further hydration of F and OPC, limited the complete F reaction after 28 days; as evidenced by TGA/DTA, XRD and by the zones of gypsum surrounding anhydrite crystals observed by SEM. The strength increased up to 32 MPa during the 180 days of the study, due to the densification after continuous formation of CSH (OPC and pozzolanic reaction) surrounding the gypsum crystals, which enhanced the water durability.

After curing at 60 °C, the presence of gypsum was less evident by TGA/DTA and XRD data; the compressive strength and NEW values were also reduced. Dry curing at 60 °C led to a faster water evaporation, which limited the hydration reactions of the cement and gypsum; moreover, gypsum decomposition was possible since the dehydration can start at about 45 °C [16].

During the first 24 h the specimens were covered in the moulds, which could have favoured all reactions; however,

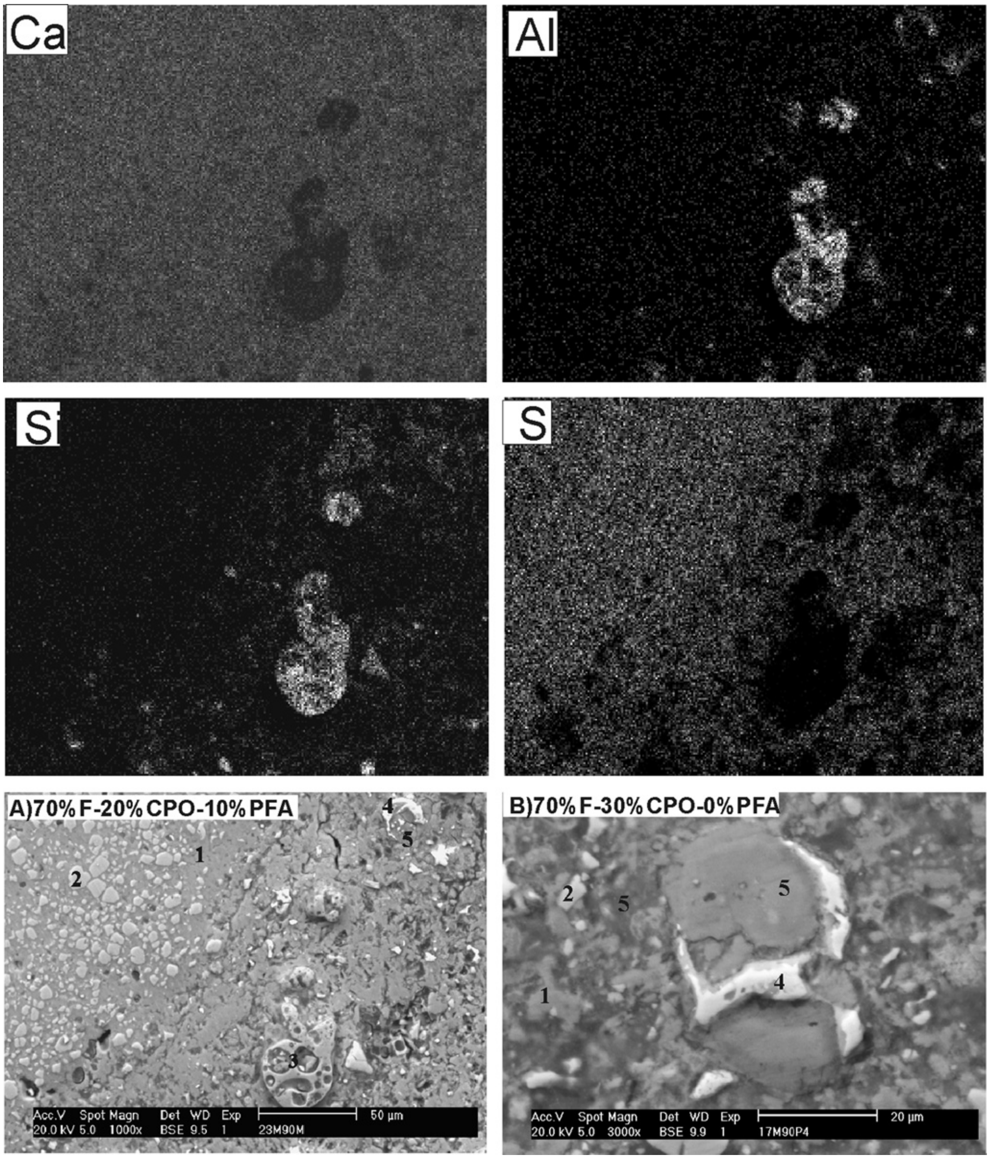

Fig. 9. Backscattered electron images for pastes 70–20–10 and 70–30–0, and elemental mappings of Ca, Al, Si and S for the system 70–20–10. All cured at 20 °C under water.

the effects of the increased temperature and curing conditions manifested once the cubes were transferred to the subsequent curing conditions. Dry curing resulted in lower NEW relative to wet curing, more markedly at 60 °C (Fig. 5); however, lower strengths were noted only at 60 °C (Figs. 1–3). The XRD of paste 70–30–0 wet cured at 60 °C (not shown) displayed very weak gypsum peaks that remained fairly constant during the 180 days, indicating that some of the gypsum formed during the 24 h of setting remained. The NEW values from wet curing of paste 70–30–0 at 20 and 60 °C increased with time, such increment at 60 °C is therefore attributable only to the continued cement hydration since no additional gypsum appeared to be formed, whereas NEW increments at 20 °C included the formation of additional gypsum. On the other hand, for paste 70–20–10 wet cured at 60 °C the gypsum peaks disappeared as probably dehydrated or reacted with the PFA forming ettringite (noted by XRD Fig. 8). The evidence indicates that wet curing at 60 °C limits only the progress of the F hydration, affecting the strength to some extent; whereas dry curing at 60 °C leads to actual gypsum dehydration with an even more negative effect on the strength.

5. Conclusions

1. Cementitious systems with 50–80% fluorgypsum developed and maintained strength even after curing under water for 180 days. The strength reached for the fluorgypsum rich pastes is acceptable for various applications.
2. Partial replacement of the OPC by PFA was beneficial in the late stages since the latter also participated in the hydration reactions, consuming CH and gypsum to

form C–S–H and ettringite. However, it must be considered that PFA free pastes made also cements acceptable for when PFA is not available.

3. Anhydrite reactions were intensive during the first 28 days of curing, a fraction of anhydrite remained unreacted even after 180 days.
4. Curing at 60 °C accelerated the reactions of ettringite and CH consumption; however, gypsum formation was affected, which in turn affected the strength. Wet curing at 60 °C limited the amount of gypsum formed, the presence of PFA consumed gypsum and formed ettringite. Dry curing at 60 °C resulted in gypsum decomposition and strength losses.
5. The microstructures of polished samples (supported by X-ray elemental maps) indicated that the microstructure consisted of gypsum crystals surrounded by C–S–H, which provided water resistance. Some zones of gypsum surrounding unreacted anhydrite were also observed.

Acknowledgement

Research funded by Project FOMIX Conacyt-FMSLP-2002-3954, Scholarship to Escobar-Rios provided by Conacyt.

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