Chemistry and Materials Research, Vol.4 2013
Special Issue for International Congress on Materials & Structural Stability, Rabat, Morocco, 27-30 November 2013

Physico-chemical study of cementitious materials based on binary and ternary binders

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Abstract. This research aims to study the physico-chemical phenomena occurring during hydration process of binary and ternary cementitious matrices, combining Portland cement (PC), blast furnace slag(BFS) and limestone filler (LF). For this purpose, measurements of the reaction rate and mechanical performances were performed on 12 mineral binders prepared with the same water-to-cementitious materials ratio (w/cm = 0.32) and various dosages of PC, BFS and LF. Three parameters are quantified using thermo-gravimetric analysis: the advancement of hydration characterized by the degree of hydration, the evolution of the chemically bound water as well as the quantity of Portlandite produced. Results show clearly that the knowledge of these parameters allows predicting correctly the evolution of compressive strength and young modulus at early age. The synergistic effects of ternary binders, formulated with moderate additions of BFS and LF, manifested in the form of an increased amount of hydration products compared to predictions based on the individual effects of BFS and the LF in the binary systems.

1 INTRODUCTION

Cement is the main source of environmental impacts from the use of concrete material. To optimize this last one environmental perspective, it is necessary to reduce the cement content; this can be done by replacing part of the cement with mineral additions during manufacture such as blast furnace slag (BFS) and fly ash (FA). However in spite of the technical, economic and ecological advantages reported by the use of composed cements[1,2] the latter remain associated with disadvantages It is thus necessary to know if cements with several components (ternary) have synergistic effects so that their ingredients manage to compensate for their mutual weaknesses [3]. Ternary binders made with moderate amounts of limestone filler (LF) [4,5 and 6] can indeed provide better performances in terms of reactivity,mechanical strength at early age and durability[4,5] , compared to those prepared with binary binders. The beneficial effect of LF on the hydration rate of PC at early age has already been demonstrated in previous studies [7, 8, 9, and 10].

This research presents an experimental comparative study of the behavior of binary and ternary cementitious matrices, combining Portland cement (PC), blast furnace slag (BFS) and limestone filler (LF). The objective was to quantify the influence of various blended binders composition on their physico-chemical evolution at early and long age. For this purpose, measurements of the advancement of hydration characterized by the degree of hydration, the evolution of the chemically bound water, the quantity of portlandite produced water as well as mechanical performances were performed on 12 mineral binders prepared with the same water-to-cementitious materials and various dosages of PC, BFS and LF.

2 EXPERIMENTAL DETAILS

2.1 Materials

The portland cement used was a CEM I 52.5 N (Le Havre plant, Lafarge, France – French standard NF EN 197-1) with Bogue formulas, were 70% of C_3S; 9% of C_2S; 3% of C_3A and 13% of C_4AF. The granulated ground blast furnace slag was provided by the company ECOCEM (Aix-in-Provence plant, France). The limestone filler used (BETOCARB P2) was produced at Erbray's plant (France). It contained 97.7% of $CaCO_3$ and its density was 2714 kg/m^3.

The compositions of the various binder pastes are given in **Table 1.**

Table 1. Mass proportion (%) of binary and ternary binders

Labels	PC	BFS	LF
PC0S0F	100	0	0
PC30S0F	70	30	0
PC50S0F	50	50	0
PC80S0F	20	80	0
PC0S10F	90	0	10
PC20S10F	70	20	10
PC40S10F	50	40	10
PC70S10F	20	70	10
PC0S20F	80	0	20
PC10S20F	70	10	20
PC30S20F	50	30	20
PC60S20F	20	60	20

2.2 Testing methods

The compressive strength and the dynamic Young's modulus (Edyn) (apparatus used: Grindosonic® device) were measured on $4 \times 4 \times 16$ cm^3-specimens stored in autogenous conditions in an air-conditioned room at 20 ± 2 °C until the time of testing.

Thermo-gravimetric analysis was performed using a TGA/DSC of Mettler Toledo. The sample with a mass between 200 and 250 mg is subjected to a temperature of up to 1050 °C, this apparatus measures the evolution of the mass of the sample and that of its derivative versus temperature allows determining the material composition.

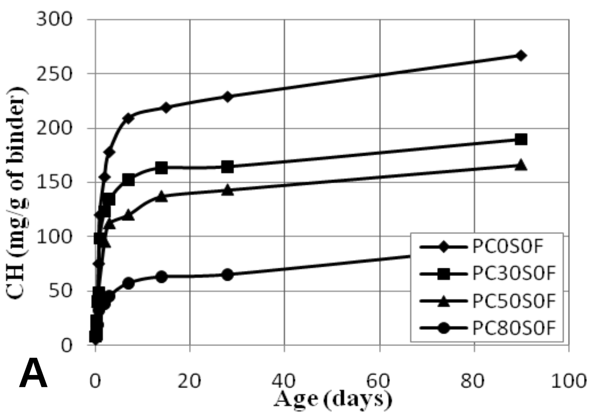
3 EXPERIMENTAL RESULTS AND DISCUSSION

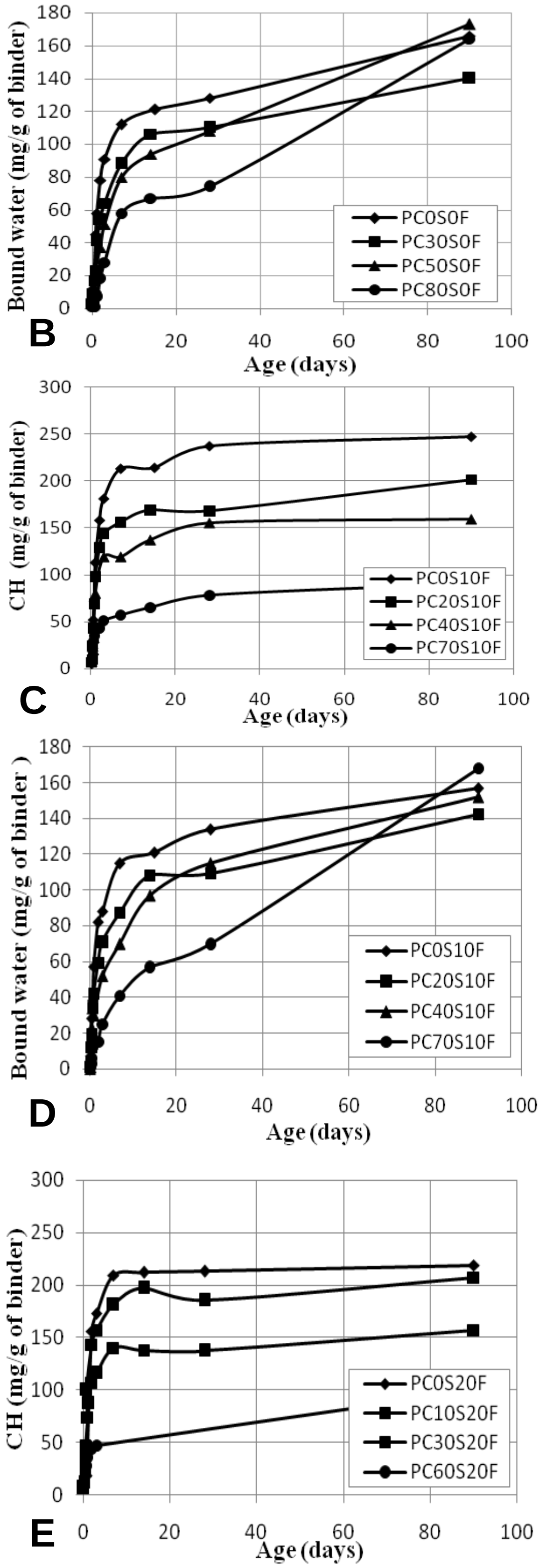
3.1 Thermogravimetric analysis

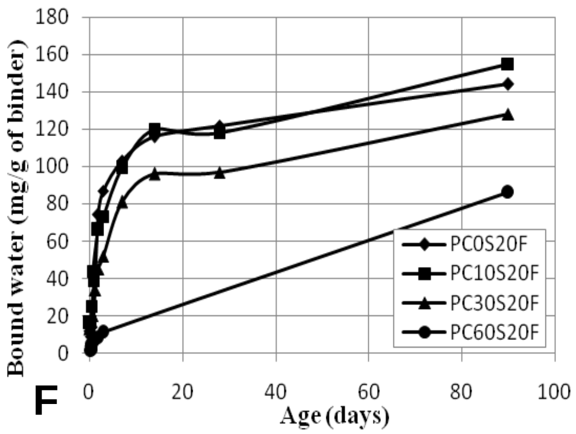
3.1.1 Formation of hydration products

In order to evaluate the chemical reactions of binders during hydration (at early and long term), thermo-gravimetric analysis of hydrated binders wasdone. Among the studied parameters, we have detected the variation in calcium hydroxide (CH), computed from the loss of mass at 400 °C and 500 °C, and the amount of chemically bound water (W)derived from the differences in sample mass at 145 °C and 1100 °C Figure 1.

Fig. 1. Evolutions of CH (left) and Bound water (right) of the binders; A and B: without LF; C and D: with 10% of LF; E and F: with 20% of LF.







The important initial increase in the amount of CH (up to three days) for all pastes is likely attributed to accelerated hydration of the Portland cement [11]. For cement-slag binders, it we seems that for low slag content, large amount of CH is produced by the hydration of the cement with a higher slag content the amount of CH is lower. This implies that, when the Portland cement hydration produces CH, a part of this formed CH is consumed by the slag reaction and this consumption is increased by the increasing slag content. In addition the decrease in CH content with increasing percentage of slag is associated with a delay in cement hydration [12, 13] and then all reactions related to clinker hydration are delayed. This low content of Portlandite is due to its consumption by the pozzolanic reaction of slag to product additional C–S–H. These results are consistent with those found by [1].

In the other hand, compared to binary binders with only blast furnace slag, binders containing only filler limestone have larger CH amounts. This can be explained by the acceleration of cement hydration at early age. This acceleration may be due to the dilution effect of limestone fillers in the ternary binders [9]. Moreover; this acceleration is due to the large amount of water available for cement hydration.

A significant reduction in CH content was observed for mixtures with 80% additions for both binary and ternary binders. A moderate decrease in CH content was held for the four ternary binders containing 30% and 50% additions fig.1 (C and E), this reflects synergy effect observed for these ternary systems that is attributed to an increase in the CH amounts and then the upsurge of hydration progress.

For the change in the total bound water content, we can see that during the first three days, the chemically bound water content evolves faster for all binders. During the first 28 days all reactions mixtures progress more slowly than in the ordinary cement mixture PC0S0F. Especially both binders PC20S10F and PC10S20F have a bound water amount comparable to that the reference binder, for these ternary mixtures the amount of non-evaporable water was only slightly less than for the OPC mixture while for the binary and ternary binders with high dosage (80% additions) the quantity of non-evaporable water was the smallest for the three types of binders.

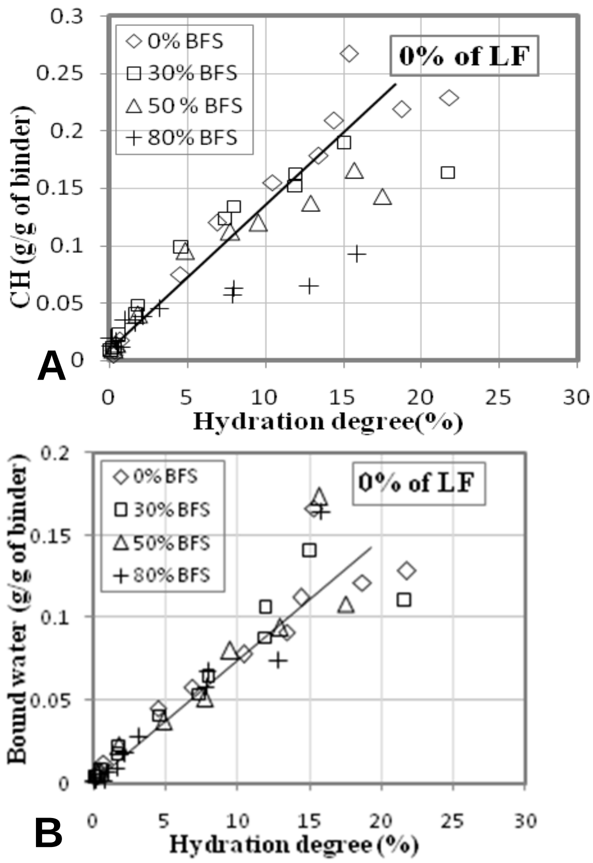
However, a substantial increase in the water was observed from 28 days for the same mixtures (80% additions), consequently their hydration seems well advanced from 28 and 90 days. At 90 days the non-evaporable water content of PC70L10F and PC60L20F is similar to that of the only cement mixture.

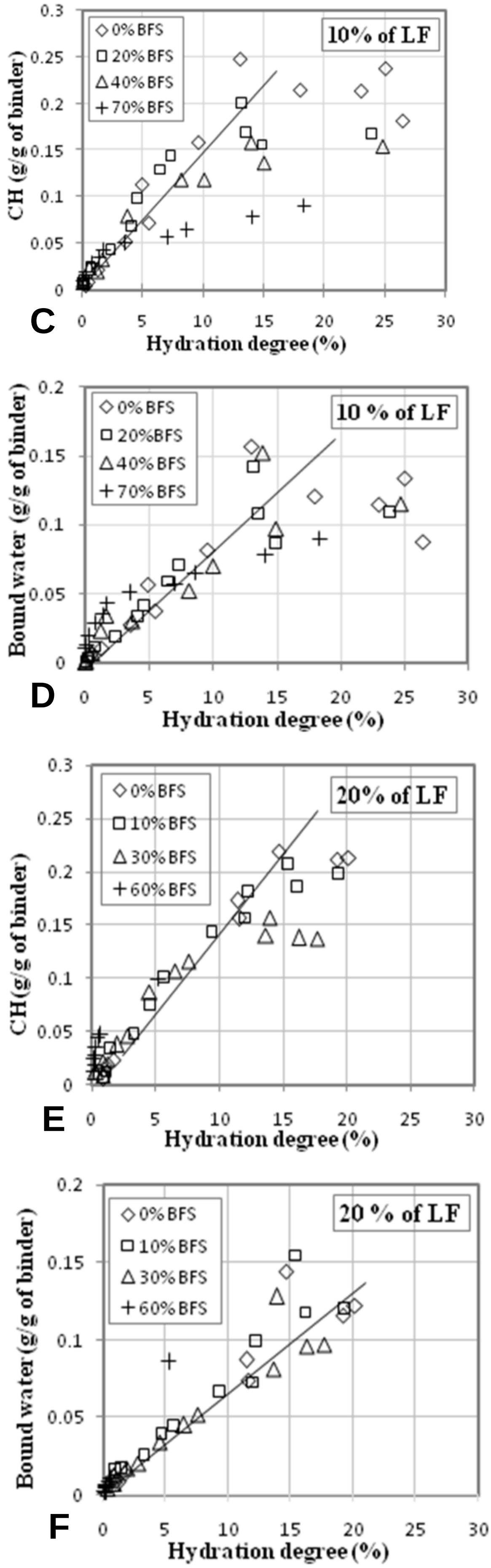
For the ternary mixture containing 20% L and 10% F, the synergistic effect was observed mostly at long-term (7 days later). This benefit effect observed was attributed to an increase in the chemically bound water (W) and consequently promote hydration products amount.

3.1.2 Degree of hydration

According to the previous experimental results, slag and limestone filler additions modify the hydration reaction evolution. To determine its effect on the evolution of the mechanical properties, it is important to quantify the hydration evolution by means of the hydration degree. From the evolution of the chemically bound water content, the evolution of the hydration degree can be estimated. To better define the type of relation between these parameters, the evolution of the portlandite quantity, the amount of bound water and the hydration degree for different studied binders have been developed Figure.2.

Fig. 2. CH content function of the degree of hydration (left) Bound water (W) content function of the degree of hydration (right) of the binders; A and B: without LF; C and D: with 10% of LF; E and F: with 20% of LF.





According to these figures, a quasi-linear correlation was observed between the degree of hydration of cement and the amount of CH produced. In fact up to about 5% of hydration degree, hydration rate and the content of Portlandite followed similar kinetics, since points are much closed to the linear line. Beyond this point (5%) of hydration the points are a little more scattered. This observation is available for only binary and ternary binders with respectively 0% LF and 10 % LF Fig.2 (A &C).

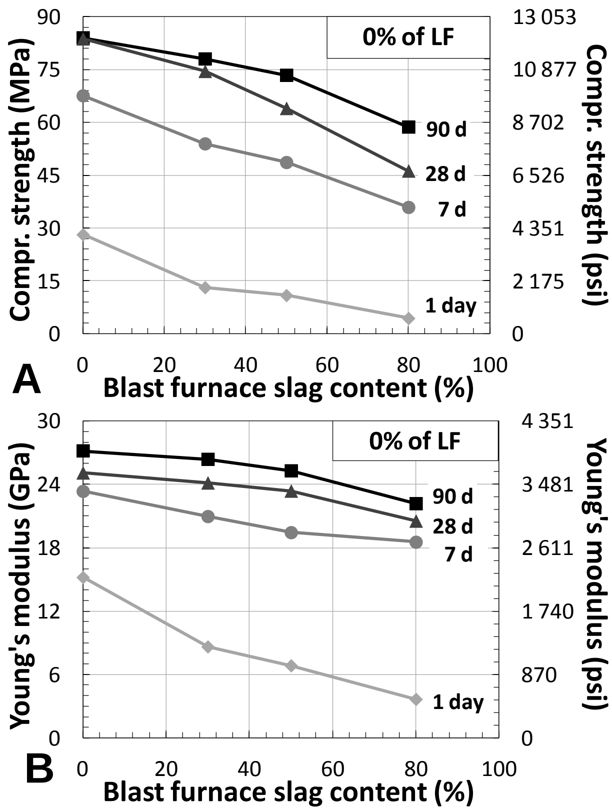
In addition, for binders with 20% LF this linear relation stops at 10% of hydration Fig.2 (E). In the other hand the evolution of total bound water (W) content, function of the degree of hydration, for all binders, follows a linear course below exactly 15% of hydration Fig.2 (B, D and F).

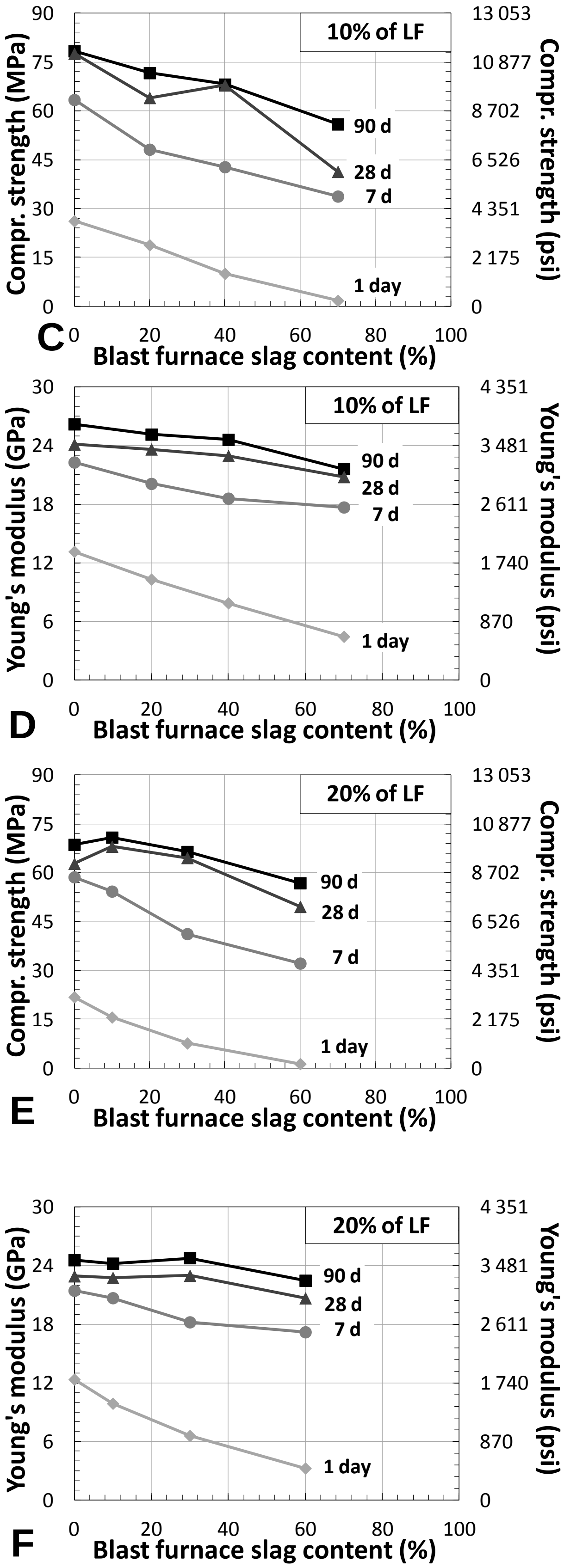
3.2 Mechanical performances

Once the impact of mineral fillers and blast furnace slag on the hydration products and process were highlighted, a deeper understanding about mechanical strength properties is presented in this section.

The evolution of compressive strength and dynamic Young's modulus of the different pastes as a function of blast furnace slag mass content are provided in Figure 3.

Fig 3. Compressive strength (left) and dynamic Young's modulus (right) of the binders; A and B: without LF; C and D: with 10% of LF; E and F: with 20% of LF.





The partial substitution of PC with BFS and/or LF caused a global reduction of the mechanical performances of the pastes, throughout the whole period of investigation (1 to 90 days).

As for chemical shrinkage, the strength development of the slag blended cement pastes was strongly dependent on the dosage of BFS. The compressive strength of pastes with a slag dosage of 0 and 30% became almost constant beyond 28 days. For the two other binary slag binders (PC50S0F and PC80S0F), the strength continued to significantly increase between 28 and 90 days. This increase reached 30% for the cement paste with 80% of slag. It was explained by the slag contribution in the later hydration reactions. The filler blended cement binders and the ternary binders (PC + BFS + LF) also showed systematically lower compressive strength and Young's modulus that those of the pure PC paste (Fig. 3.C to 3.F).

This reduction in mechanical performances was attributed to the dilution effect induced by the replacement of cement with slag and/or filler. Additionally, the water-to-cement (w/c) ratio increased in binary and ternary binders due to the reduction of the cement dosage: it was 0.32 for the control binder, and 0.46, 0.64 and 1.60 for the cement substitution rates of 30, 50 and 80%, respectively. Considering the very little contribution of filler to produce hydrates and the low reactivity of slag at early age, the increase of the w/c ratio may lead to a higher porosity volume in blended binder pastes, and therefore to a lower gain of strength.

In some cases, the addition of filler in slag-cement system enabled to enhance the early-age compressive strength of pastes: for example, at 30% of cement substitution, the paste with 20% of BFS and 10% of LF (PC20S10LF) and the one with 10% of BFS and 20% of LF (PC10S20LF) showed a 1-day compressive strength 43% and 19% higher than that of the corresponding binary binder paste (PC30S0LF), respectively. But this effect was only temporary since the compressive strength of PC20S10LF and PC10S20LF became 14% and 9% lower than that of PC30S0LF at 28 days.

TGA measurements confirm that the loss in mechanical strength of ternary binders that would be due to the substitution of cement with BFS less reactive, is compensated in part by firstly substituting cement by fillers and secondly by the accelerating effect of hydration by limestone fillers and, which act as nucleation sites of CSH, promoter strengths.

Conclusion

In this study, an experimental program is performed to investigate the advancement of the hydration reaction for ternary and binary binders formulated with: Portland cement, blast furnace slag and limestone filler. We have also examined the results of the various tests of thermal gravimetric analysis (TGA) performed on different studied binders in order to make correlations between these parameters: the hydration degree the evolution of the chemically bound water as well as the quantity of Portlandite produced.

The main result of this research allowed us to estimate that synergic effect of ternary binders, formulated with moderate additions of BFS and LF, manifested in the form of an increased amount of hydration products compared to predictions based on the individual effects of BFS and the LF in the binary systems. This has also improved the mechanical properties of these same binders.

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