Ternary Blended Cement with Limestone Filler and Kaolinitic Calcined Clay

Alejandra Tironi, Alberto N. Scian and Edgardo F. Irassar

Abstract The use of calcined clays providing from low grade kaolinitic clays combined with the limestone filler in ternary blended cement formulation has received considerable attention in recent years. This paper describes the results of a research project to study the behavior of kaolinitic calcined clays (CC) in combination with limestone filler (F). Blended cements were obtaining replacing CC (0–30 %) and F (0–10 %) by mass by Portland cement (PC). The pozzolanicity of blended cement was assessed by the Frattini tests at 2, 7 and 28 days. The response of the system was evaluated in terms of flow, and the compressive strength at 2, 7 and 28 days. The hydration progress was determined by the type and amount of hydration compounds at 2, 7 and 28 days using the Rietveld method. The change in pore size distribution was determined by mercury intrusion porosimetry (MIP). Hydrated phases obtained correspond to the pozzolanic reaction (contribution CC) and phase stabilization (contribution F) modifying the pore structure and all factors contribute to develop acceptable mechanical properties with a large reduction of energy consumption and CO_2 emission.

1 Introduction

The use of calcined clays providing from low grade kaolinitic clays combined with the limestone filler in ternary blended cement formulation has received considerable attention in recent years [1]. The metakoalinite (MK) containing in calcined clays is the pozzolanic material [2], quartz is the main impurity of calcined clay [3] and the limestone filler provides the carbonate to form the AFm phases [4]. Calcium carbonate reacts with alumina from MK, forming additional AFm phases and stabilizing

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ettringite [5]. The aim of this paper is to investigate the use of calcined clay providing from low grade kaolinitic clay in combination with limestone filler as partial cement replacement in binary and ternary cements.

2 Materials and Methods

2.1 Blended Cements

Blended cements (bc) were obtained replacing calcined clay (0 to 30 % by mass) and limestone filler (0 to 10 %) by Portland cement (PC). The PC used is a normal Portland cement with a Blaine fineness of 315 m^2/kg, and its Bogue´s potential composition is 60 % C_3S, 16.4 % C_2S, 3.8 % C_3A and 11.5 % C_4AF by mass. For this PC, limestone is added as minor component (<°3 %). Kaolinitic clay was calcined at 750 °C and during 4 h to produce calcined kaolinitic clay (CC) with 44 % of metakaolinite (MK). Quartz is the main impurity in CC and it could be considered as filler due to its small particle size. The CC has a Blaine fineness of 623 m^2/kg, and limestone filler (F) of 515 m^2/kg. Blended cements were denominated as 10F, 30CC, 5F15CC, and 10F30CC according to the level of replacement of each addition.

2.2 Pozzolanic Activity

The pozzolanicity of blended cements was assessed by the Frattini test at 2, 7 and 28 days. The water demand of ternary system was evaluated in terms of mortar flow and the mechanical performance in terms of compressive strength at 2, 7 and 28 days.

In Frattini test [6], 20 g of blended cement was mixed with 100 ml of boiled distilled water. After preparation, samples were left in a sealed plastic container at 40 °C. At test time, samples were vacuum filtered through paper and cooled at ambient temperature in sealed Buchner funnels. The filtrate was analyzed for $[OH^-]$ by titration against dilute HCl with methyl orange indicator and for $[Ca^{2+}]$ by pH adjustment to 13, followed by titration with 0.025 M EDTA solution using Murexide indicator. This test compares the $[Ca^{2+}]$ and $[OH^-]$ contained in an aqueous solution that covers the hydrated sample with the solubility curve for CH in an alkaline solution at the same temperature.

Flow and compressive strength tests were assessed on standard mortars (1:3 and w/bc = 0.50) made with standard European sand (EN 196-1). The mortar was mixed in planetary mixer, the specimens were cast and compacted by vibration and cured 24 h in the molds in a moist cabinet. Then, they were removed from the mold and immersed in lime-saturated water until test age at 20 ± 1°C. Compressive strength was measured on mortars cubes (25 x 25 x 25 mm) [3] and the report values correspond to the average of five specimens.

2.3 Hydration

The hydrated phases were studied in pastes prepared with w/bc of 0.50. At 2, 7 and 28 days the hydration was stopped using acetone, dried and ground. The crystalline phases were identified by X-ray diffraction (XRD) (Philips X'Pert PW 3710, CuKα radiation with graphite monochromator operating at 40 kV and 20 mA). To quantify the crystalline and amorphous phases the Rietveld method with internal standard (TiO_2) [7] and PANalytical HighScore Plus [8] software were used. These values were checked by thermogravimetric analysis (TG) at 7 days.

2.4 Porosity

The pore size distribution in dried pastes at 2 and 28 days was determined using a mercury intrusion porosimeter (MIP-ThermoFisher Sc PA440) for the pore size diameters from 7.3 to 14000 nm.

3 Results and Discussion

3.1 Pozzolanic Activity

Figure 1 shows the results of Frattini test for blended cements. At all ages, PC and 10F cements do not have pozzolanic activity and the points representing the results are above the saturation curve. At 2 days, the combined effect of dilution and pozzolanic reaction decreases the [CaO] in the supernatant solution of blended cement with 30 % of CC. After 7 days, all bc prepared with CC showed evidence of

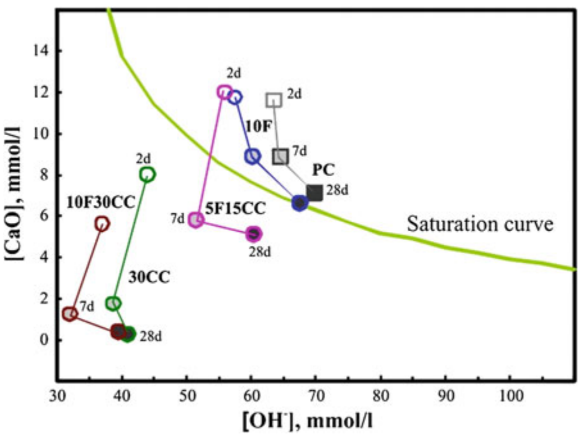

Fig. 1 Frattini test results at 2, 7 and 28 days

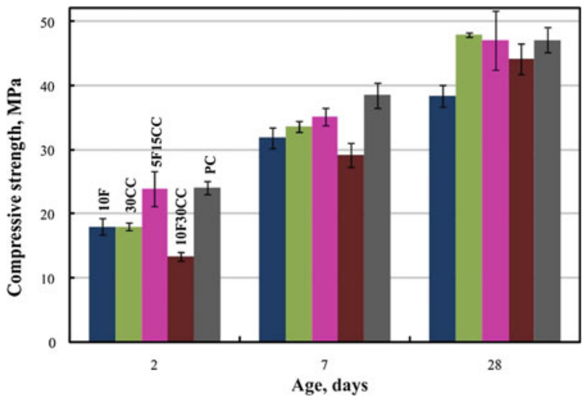

Fig. 2 Compressive strength of mortars at 2, 7 and 28 days

pozzolanic reaction. The [CaO] and [OH^-] reduction was greater when the CC replacement level increases. For 10F30CC and 5F15CC, the presence of limestone filler stimulates the pozzolanic reaction at 7 days, but it has less influence at advanced hydration ages (i.e., points of 10F30CC is overlapping the 30CC point).

The flow measured in standard mortars was 129, 129, 66, 150 and 68 % for PC, 10F, 30CC, 5F15CC and 10F30CC, respectively. Both additions have contrary effect on the workability: the CC decreases this property while the limestone filler improves it. The best result is obtained for 5F15CC cement.

Figure 2 shows the compressive strength (CS) at 2, 7 and 28 days. At 2 days, CS of 5F15CC (20 % of total addition) is comparable with that PC. The CS decreases when increasing the total replacement level (30CC and 10F30CC). For this case, the expected reduction of CS due to the dilution effect exceeds the contribution to the CS made by the proper pozzolanic reaction and/or the stimulation of PC hydration. At 7 days, 5F15CC remains as the highest CS blended cement, but the 30AC improves its contribution to CS compared with 2 days performance. At 28 days, the maximum value of CS was for 30CC showing the significant contribution of the pozzolanic reaction of calcined clay, this was followed by 5F15CC and then by 10F30CC. The last blended cement (10F30CC) with 40 % replacement of PC has CS greater than 40 MPa at 28 days, indicating an acceptable mechanical performance with a large reduction of gas emission by MPa obtained.

3.2 Hydration

Figure 3 shows the amount of CH determined from quantification by XRD analysis and Rietveld method in hydrated pastes at 2, 7 and 28 days. At 2 days, 10F contains the greatest amount of CH due to the stimulation caused by limestone filler. For bc with CC, the CH decrease in paste due to the dilution effect and the consumption by the pozzolanic reaction. In 5F15CC paste, the CH consumption was higher than expected by dilution and amount of reactive MK (6.6 % in 5F15CC and 13.2 % in

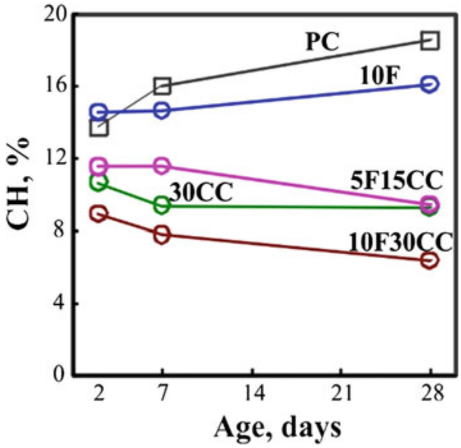

Fig. 3 CH content in hydrated pastes at 2, 7 and 28 days

30CC) showing the favorable stimulation caused by limestone filler. These results are in agreement with the CS-value at the same age (Fig. 2). At 7 days, the CH content in paste is reduced for all bc containing CC due to either dilution effect and pozzolanic reaction. Finally, the pastes made with ternary cement (5F15CC and 10F30CC) show a high CH consumption that expected by the replacement level.

Figure 4 shows the XRD patterns corresponding to hydrated pastes at 28 days. Two types of AFm phases are detected: hemicarboaluminate (HC) and

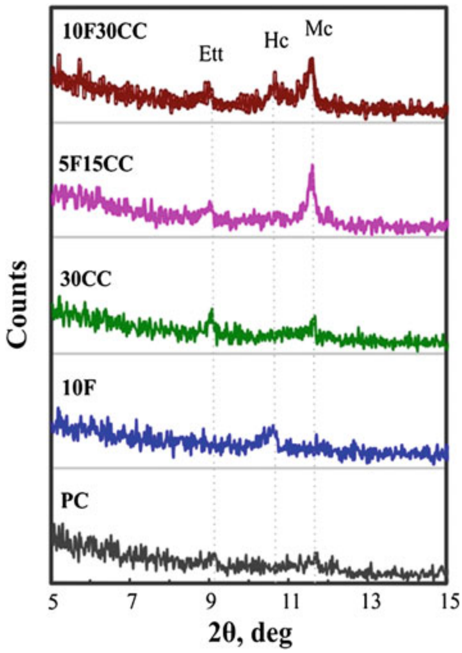

Fig. 4 XRD pattern for hydrated pastes at 28 days

Table 1 Pore size distribution of pastes at 2 and 28 days

Paste	Volume accumulated of pores, (mm^3/g)		Volume of pores between 10 to 50 nm, (mm^3/g)		Volume of pores diameters > 50 nm, (mm^3/g)	
	2 days	28 days	2 days	28 days	2 days	28 days
PC	194	112	55	41	133	62
10F	237	163	52	63	183	96
30CC	277	171	65	79	203	75
5F15CC	260	177	60	87	194	84
10F30CC	285	162	65	102	211	39

monocarboaluminate (MC). For ternary blended cements (5F15CC and 10F30CC), the intensity of peak assigned to MC increases considerably in accordance with previous results reported by Antoni et al. [5]. For blended cements with CC, the amount of CH decreases with time (Fig. 3) and the progress of pozzolanic reaction release a large amount of reactive alumina. In presence of limestone filler, the AFm phase is stabilized as MC and it could stimulate the pozzolanic reaction.

3.3 Porosity

Table 1 presents the cumulative pore volume of pastes.

From 2 to 28 days, there is a great reduction of the total porosity with great increases of volume of finer pores (10 to 50 nm) indicating the pore size refinement process of pozzolanic reaction (Table 1). For all hydrated blended cements, the volume of pores with diameter larger than 50 nm decreased from 2 to 7 days and the largest decrease was for 10F30CC cement. The volume of pores with diameter 10 to 50 nm decreases for the PC paste from 2 to 28 days (55 to 41 mm^3/g). However, it increases for some blended cements pastes, especially for 10F30CC where the filler fraction (quartz + limestone) is high.

4 Conclusions

- The blended cements containing 0–10 % of limestone filler (F) and 0–30 % of calcined clay (CC) develop compressive strength similar than that PC at 28 days, due to the interaction between these two components and the contribution of quartz filler. Compressive strength of blended cement 5F15CC is comparable with that PC since 2 days.
- Hydrated phases obtained correspond to the pozzolanic reaction (contribution kaolinitic calcined clay) and phase stabilization (contribution limestone filler) modifying the pore structure.

– The addition of kaolinitic calcined clay and limestone filler modify the pore system increasing the volume of pores with minor diameter.
– All factors contribute to develop acceptable mechanical properties with a large reduction of energy consumption and CO_2 emission: blended cement 10F30CC with 40 % replacement of PC has compressive strength greater than 40 MPa at 28 days.

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