

HYDRATION CHARACTERISTICS AND MECHANICAL PERFORMANCES OF LC³ BINDERS WITH SPANISH KAOLINITIC CALCINED CLAYS

Isabel M. R. Bernal, Ana Cuesta, Angeles G. De la Torre, Isabel Santacruz, and Miguel A. G. Aranda
Departamento de Química Inorgánica, Universidad de Málaga, 29071-Málaga, Spain; imramirez@uma.es

Extended Abstract

Limestone Calcined Clay Cements (LC³) are binders with complex phase development and microstructures. Although the hydration chemistry of these cements are being widely researched [1], due to the clay mineralogy variability, more studies are needed to build full knowledge. The use of calcined kaolinitic clays as SCMs in Portland cement is one of the best approaches, as metakaolin shows exceptional pozzolanic properties. Here, we report a summary of our ongoing research dealing with LC³ binders based on Spanish calcined clays with different kaolinite content. The kaolinite contents [2], jointly with the particle size of the calcined clays [3] will determine the reactivity, and consequently, the mechanical performances. Initially, a selection of three commercially available Spanish kaolinitic clays was carried out. Mineralogical and elemental analyses were obtained by X-ray powder diffraction (XRPD) and X-ray fluorescence (XRF), respectively, are elsewhere [3]. The clay provenance and estimated average kaolinite contents are given in Table 1; the latter was obtained through the combination of three methodologies (LXRPD, thermal analysis and XRF) [3].

Table 1. Raw Spanish clays used in this study, including provenances and estimated average kaolinite contents (wt%).

Provider	Sample	Origin	Kaolinite content (wt%)
Caolines de Vimianzo, S.A.U.	FC35	A Coruña	~83
Comercial Sílices y Caolines de Aragón S.L.	SY1	Teruel	~74
Arcimusa, S.A.	CVPM3B	Zaragoza	~70

These clays were activated by calcining more than 20 kg of each sample at 860°C in a brick factory (Inducerama, Málaga, Spain). After that, they were milled to a median particle size by volume, $D_{v,50}$, between 6 and 11 μm (viz. 11.1, 10.5 and 5.8 μm for FC35, SY1 and CVPM3B, respectively). The resulting surface area values (BET) were 9.6(1), 9.1(1) and 23.7(1) m^2/g , respectively.

Firstly, the pozzolanic reactivity of the three calcined clays was checked. Here, we followed the calorimetric approach [4], where the heat flow curves were collected during the first 7 days at 20°C (starting after 45 minutes of mixing for temperature stabilization). For this, portlandite, calcined clays and limestone with the following mass ratios: CH/calcined clay = 3:1, Limestone/calcined clay = 1:2, and a water-to-binder (w/b) mass ratio = 1.2 were used [4]. It is expected a good pozzolanic activity in all cases, as the kaolinite content is higher than 50 wt%. At early ages, the surface area and the local disorder of metakaolin are key for the rate of the pozzolanic reaction. Figure 1 shows the calorimetry study, where CVPM3B released higher amounts of heat at every age. As an example, at 2 and 7 days, the heat released was 50.6 and 135.5 J/g for CVPM3B, 21.5 and 96.94 J/g for FC35, and 12.9 and 63.0 J/g for SY1, respectively. This behaviour is mainly justified by the higher surface area (and lower particle size) of CVPM3B (and its highly strained local structure [3]) despite having the lowest kaolinite content.

LC³ cements were prepared by mixing 52 wt% of a commercial PC (42.5 R, Financiera y Minera S.A, Malaga) with 30 wt% of calcined clay, 15 wt% of limestone and 3 wt% of additional gypsum. The latter was optimized through calorimetry to promote C₃S hydration by moving the so-called 'aluminate peak' well after the main hydration peak. The characterization of the employed PC as well as the LC³ binder prepared with FC35 calcined clay, including phase development by Rietveld analysis, microstructure characterization by X-ray synchrotron microtomography and their mechanical strength developments have been published elsewhere [5]. Here we present the full phase assemblage, obtained by Rietveld Quantitative Phase analysis (RQPA) and thermal analysis, for all LC³ binders with the three calcined clays (2, 7, 28 and 120 days of hydration).

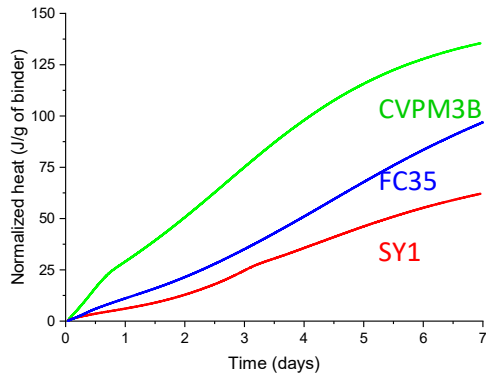


Figure 1. Heat released for calcined clay-portlandite-limestone blends at 20°C.

Pastes were prepared at water-to-binder mass ratio (w/b) of 0.40 with 0.40 wt% (active matter) of a polycarboxylate-based superplasticizer (Floodis1623, Adex Polymer S.L., Spain), which also contains defoamer in its formulation. As an example, Figure 2 shows the laboratory X-ray powder diffraction patterns (MoK α_1 , $\lambda = 0.71 \text{ \AA}$) of the three LC³ pastes (FC35-Cc-G, SY1-Cc-G and CVP3B-Cc-G) at 7 days of hydration. The main peaks are labelled following the cement notation, including those of the internal standard (in red): quartz (Q) for FC35, and alumina (A) for the other two.

All pastes showed a relatively large amount of ettringite (f.i. 7.5(6) and 4.0 wt% for FC35 at 2 and 7 days, respectively), and low crystalline portlandite contents (f.i. 3.4(2) and 3.7(2) wt% for FC35 at 2 and 7 days, respectively), similar lower for CVP3B, but slightly higher for SY1), which is indicative of the pozzolanic reaction. A low amount of crystalline Hemihydrate (Hc) was found in FC35-Cc-G paste from 7 days (viz. 1.3(4) and 3.5(4) wt% at 7 and 28d), and negligible for the other two pastes.

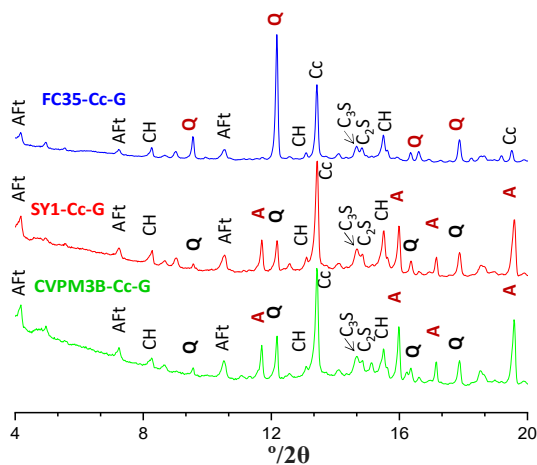


Figure 2. Laboratory X-ray powder diffraction patterns (Mo-K α_1 , $k = 0.71 \text{ \AA}$) of the three LC³ pastes (FC35-Cc-G, CVP3B-Cc-G and SY1-Cc-G) at 7 days.

Furthermore, crystalline Monocarbonate (Mc) was not detected. At 7d, the compressive strengths of the corresponding mortars (w/b=0.4, 0.4 wt% SP and binder/sand mass ratio: 1/3) were 42.6(2), 38.5(1) and 47.8(3) MPa for FC35-Cc-G, SY1-Cc-G and CVP3B-Cc-G, respectively, in very good agreement with the pozzolanic and diffraction studies, related with the higher surface area (lower particle size) and larger disorder of CVP3B calcined clay [3]. However, at later ages (28 and 120d), the tendency in compressive strength mainly depends on the kaolinite content (f.i. 66.5(7), 58.1(4) and 64(2) at 120d, for FC35-Cc-G, SY1-Cc-G and CVP3B-Cc-G, respectively). All results will be related and discussed.

Keywords: metakaolinite, pozzolanic reactivity, hydration, Rietveld analysis, microstructure

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