Assessment of Cuban Kaolinitic Clays as Source of Supplementary Cementitious Materials to Production of Cement Based on Clinker – Calcined Clay – Limestone

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Abstract. Four new calcined kaolinitic clays as source of supplementary cementitious materials to production of cement with high level of clinker replacement were assessed in this research. Anhydrous cements were characterized by particle size distribution (PSD), specific surface (BET) and thermogravimetric analysis (TGA). The pastes were assessed by X ray diffraction (XRD), TGA and mercury intrusion porosimetry (MIP). The behavior of blends was too assessed by compressive strength in standard mortars. The specific surface of LC^3 cement depends mainly on the specific surface of calcination product of clay, which depend as well on the mineralogical composition of the raw material and the calcination temperature. Results indicated an agreement with the kaolinite content in the original clay, pozzolanic reactivity and the performances of blended cements. The research showed the potentialities of cuban clay deposits from different geologic origin to be used in the production of ternary blended cements with similar performances to the Portland cement.

1 Introduction

Previous research have demonstrated the potential of thermal activation of clays with kaolinite contents of only 40% to obtain a high reactivity pozzolanic material [1, 2]. However, the simple substitution of clinker for this pozzolanic material is only practical up to 30%, which in many cases as in Cuba, where energy costs have a strong influence on the costs of calcination, this option is not economically viable [3]. Development of a new family of cements named LC^3 (Limestone Calcined Clays Cement), allows to increase the clinker replacement levels and maintains or improve the performance of Portland cement (PC) with high clinker content [4, 5], which compensates for

calcination costs while decreasing environmental impact and costs production with respect to the PC [5, 6].

In Cuba took place the first industrial trial for the calcined clay production to be used as pozzolan in LC^3 cement manufacture [5]. The main limitations for the generalized production of LC^3 in the country is the lack of knowledge about the characteristics and availability of kaolinitic clays with potential to be used as raw material in the production of Supplementary Cementitious Materials (SCMs). Currently, clays resources available are limited to satisfy the characteristics demanded by the ceramic industries, refractories and the white cement production, which require deposits of high kaolinite and low iron content, considerations that are not limiting for the production of SCMs [7]. Reason why the study of clays with high levels of impurities, but its kaolinite content justifies their use as source of SCMs, is a need for the new cementitious system manufacture. The aim of this paper is to assess four new cuban kaolinitic clays as source of SCMs to production of cement based on clinker- calcined clay and limestone.

2 Methods

Four kaolinitic clays (LL, LS, YG, CG) from different deposit of different geological origin were selected. Tables 1 and 2 presents the chemical and mineralogical composition of the composite samples performed by X-ray Fluorescence (XRF) and X-ray Diffraction (XRD), respectively. Clay minerals content in the raw material was determined by Thermogravimetric Analysis (TGA) from the mass loss during clays dehydroxylation, between 350 °C and 850 °C, and reported as equivalent kaolinite (K^E). Clays were calcined at 750 °C and 850 °C. After calcination were grounded in a ball mill. Pozzolanic reactivity of the calcined clays was assessed by R^3 test [8].

Seven LC^3 blended system (LC^3-LL 750, LC^3-LL 850, LC^3-LS 750, LC^3-LS 850, LC^3-YG 750, LC^3-YG 850, LC^3-CG 850) were prepared by mixing of the calcined clays, clinker, pulverized limestone and gypsum, processed previously by separate grinding. The LC^3 systems refers to cements with 45% of substitution of clinker by 30% of calcined clay and 15% of limestone, with a clinker content of 49% and 6% of gypsum. Differences of each blend set in the clay composition and calcination temperature. The chemical composition of the components is presented in Table 1.

Table 1. Chemical composition of the original clays, clinker, gypsum, limestone and PC

	SiO₂	Al₂O₃	Fe₂O₃	CaO	MgO	SO₃	Na₂O	K₂O	TiO₂	P₂O₅	Others	LOI
LL	61,40	18,86	9,61	0,07	0,15	0,02	0,26	0,90	0,62	0,13	0,24	7,80
LS	50,88	25,23	12,58	0,28	0,95	0,02	0,08	0,32	0,98	0,05	0,33	8,39
YG	46,58	20,06	14,41	2,94	0,74	0,04	0,11	0,06	1,12	0,13	0,87	12,74
CG	39,55	31,58	12,68	0,05	0,53	0,13	0,14	0,17	0,52	0,04	0,38	14,37
Clinker	20,81	5,01	4,37	65,70	0,90	0,34	-	-	-	-	-	0,50
Gypsum	8,10	2,03	1,97	30,27	2,81	31,39	-	-	-	-	-	20,91
Limestone	3,02	0,94	0,49	51,49	0,71	-	-	-	-	-	-	41,74
P-35	20,37	4,55	3,08	62,91	1,15	2,49	-	-	-	-	-	3,49

Table 2. Mineralogical composition of the clay samples

	Origin	Clay minerals 1:1	Clay minerals 2:1	Associated minerals	Kaolinite content, %
LL	Hydrothermal	Kaolinite	Muscovite	Quartz, hematite, goethite	42,16
LS	Hydrothermal	Kaolinite, nacrite	Vermiculite, montmorillonite		57,78
YG	Redeposited	Kaolinite, nacrite, halloysite	Vermiculite	Calcite, quartz, goethite, anatase	46,13
CG	Weathering	Kaolinite, halloysite	Kaolinite – montmorillonite	Gibbsite, quartz, hematite, goethite	81,06

Anhydrous cements were characterized by particle size distribution (PSD) and specific surface (BET). A qualitative assessment of the hydration of pastes was carried out by XRD. Bound water, portlandite and calcite content was determined by TGA. Mercury Intrusion Porosimetry (MIP) was used to assess pore structure of LC^3 pastes with calcined clays at 850 °C. Standard mortars were cast in order to determine the strength development of the LC^3 blends according to NC-506 [9]. A Portland cement named P-35 as reference was used.

3 Results

3.1 Reactivity of Calcined Clays

Higher pozzolanic reactivity and lower values of specific surface were obtained for calcined clays at 850 °C (Table 3). Anomalous behavior for YG at 850 °C seems to be related with the rough decrease of the specific surface. In general, the pozzolanic reactivity is in agreement with K^E content.

Table 3. Cumulated heat and specific surface for calcined clays at 750 °C and 850 °C

	LS		LL		YG		CG
Calcination temperature, °C	750	850	750	850	750	850	850
Cumulated heat released at 132 h (J/g)	125,88	137,85	97,00	101,31	118,82	62,43	167,42
Specific surface (m²/g)	57,08	46,11	19,06	11,61	50,18	5,41	28,86

3.2   Particle Size Distribution and Specific Surface of Anhydrous LC³ Blends

LC³ blended system shows similar particles size distribution (Fig. 1). As observed the curve practically are superposed, which it is caused, by the similar preparation conditions of the raw materials. However, more difference, in the specific surface of LC³ system is observed (Fig. 2a). The specific surface of the LC³ blends is directly proportional to the specific surface of the calcined clays (Fig. 2b). Decrease of specific surface for samples could not be explained by assuming particle coarsening. Lower specific surface for similar particle size distribution is obtained when grinding clays after calcination. Grinding after calcination have little effect on overall specific surface, as compared with calcination temperature. Therefore, the specific surface of the LC³ blended system can be controlled by the activation temperature of clays. In addition, decrease of the specific surface from 750 °C to 850 °C seems to be too related with the presence of clay minerals type 2:1 and associate phases. The presence of calcite and vermiculite in YG and vermiculite and montmorillonita in LS sample cause break down at high calcination temperature decreasing specific surface, whereas LL contains more stable minerals (moscovite, quartz) to the analyzed temperatures.
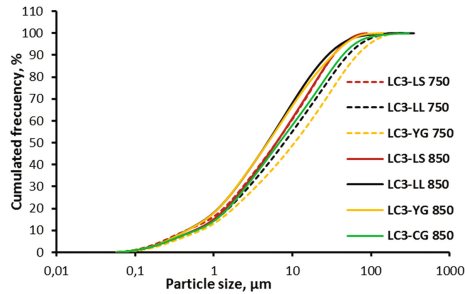

Fig. 1. Particle size distribution of LC³ blended systems

3.3   Characterization of the LC³ Pastes

The XRD patterns (Fig. 3) for the LC³ system show at 2 days the formation of ettringite, hemicarboaluminate (Hc) and a formation growing of portlandite (CH). The presence of Hc is associated at early reaction of the aluminates and calcium carbonate. The peaks assigned to this phase are more intense for LC³ with calcined clays with higher availability of reactive alumina (higher K^E content). At 28 days decrease the peaks of Hc and monocarboaluminate (Mc) are observed, indicating the advance of the reaction between the aluminates and limestone. Ettringite formation is stabilized at 28 days due to the formation of Hc and Mc allowing a higher sulphate availability. Reduction of the peaks assigned to the CH of 2 to 28 days is a qualitative evidence of the advance of the pozzolanic reaction. Practically imperceptible CH peaks is observed in the paste that contains more reactive calcined clay CG (LC³–CG 850).
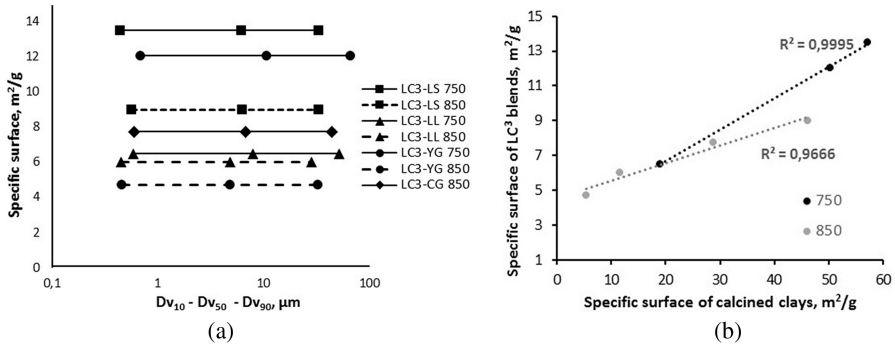
Fig. 2. (a) Specific surface and particles size distribution of the LC³ blends. (b) Relation between specific surface of the LC³ blends and the specific surface of the calcined clays
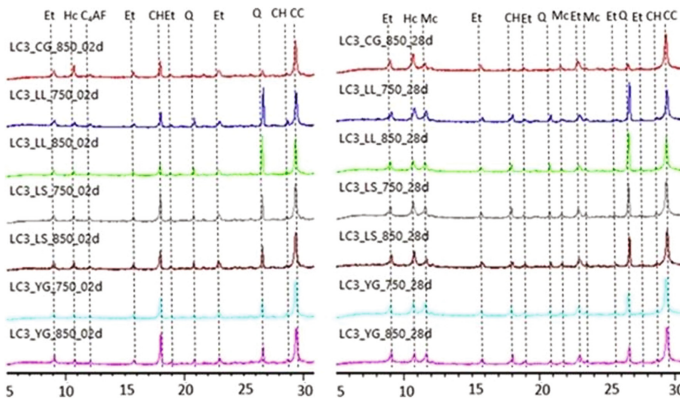

Fig. 3. XRD patterns of the LC³ paste at 2 days (left) and 28 days (right) of hydration. Et (Ettringite); Hc (Hemicarboaluminate); C₄AF (Ferrite); Mc (Monocarboaluminate); CH (Portlandite); CC (Calcite); Q (Quartz)

For all blended cements, the amount of bound water increases and portlandite content decrease from 2 to 28 days (Fig. 4a). Both are a clear evidence of the pozzolanic reaction in the LC³ pastes. Decrease of the calcite content (Fig. 4b) from 2 and 28 days show the participation of the calcite as active component in the pozzolanic reaction to form Hc and Mc. Results are in correspondence with the pozzolanic reactivity of the calcined clays determined by the R^3 test (Table 3). In general, the portlandite consumption and bound water at 2 and 28 days are higher in LC³ pastes containing calcined clays with higher K^E content.

Figure 5 presents the results of pore size distribution of the LC³ at 2 and 28 days of hydration. In all LC³ pastes is reduced the total porosity due to the hydration progress.
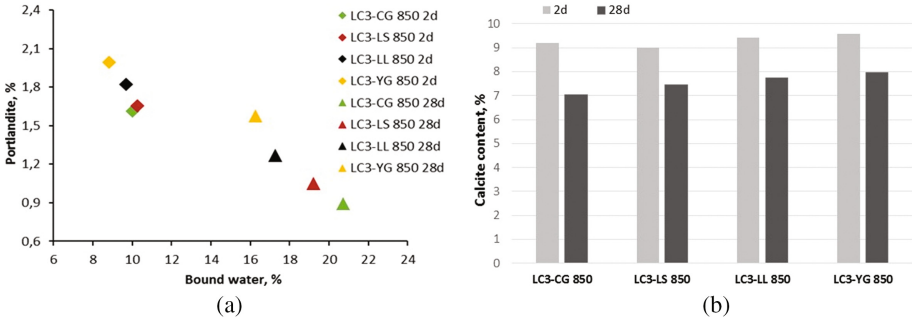
(a)   (b)

Fig. 4. (a) Relation between Portlandite content and bound water to 2 (2d) y 28 (28d) days of hydration for LC^3 series with calcined clay to 850 °C. (b) Calcite content at 2 (2d) y 28 (28d) days of hydration

The accumulated porosity seems to be related to the pozzolanic reactivity of the different calcined clays. The reduction of the accumulated porosity and the pore structure refinement are associated to the increase in the volume of hydration products due to the formation of AFm and AFt phases as observed by XRD. Later phases present low density, which contributes very efficiently to the pore structure refinement.
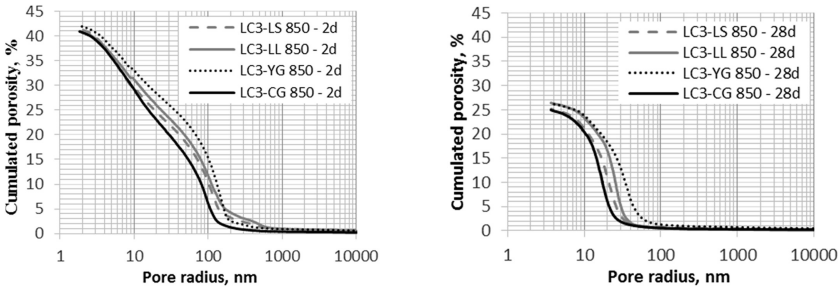
Fig. 5. Cumulated porosity as a function of pore entry radius at 2 and 28 days obtained by MIP

3.4   Performance of the LC^3 Mortars

Compressive strength in standard mortars of the LC^3 blends with calcined clays at 850 °C is presented in Fig. 6. At 3 days, LC^3 blends exhibit lower compressive strength than the reference. However, from 7 days the behavior among the different series begins to be differentiated. The best results are observed for LC^3-LS 850 and LC^3-CG 850, which at 28 days reach and improve, respectively, the reference. Difference between the blended systems is accentuated in relation directly proportional to the calcined clays reactivity.
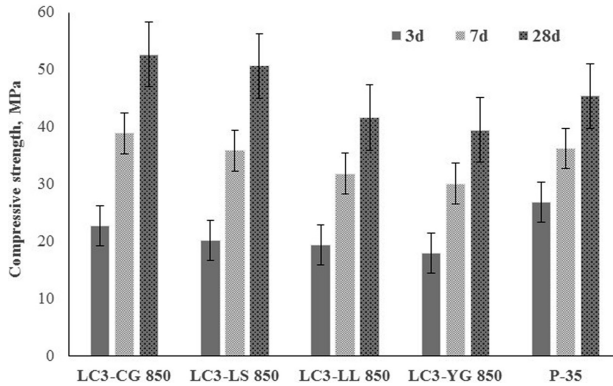
Fig. 6. Compressive strength of the LC³ mortars at 3, 7 and 28 days

4 Conclusion

Pozzolanic reactivity is consistent with the clay minerals content reported as equivalent kaolinite. For a similar particle size distribution, the specific surface of the LC³ blended is determined by the specific surface of the calcined clay, which depends on calcination temperature and the mineralogical composition of the original clay. The formation of AFm and AFt phases enhance the reduction of the pore structure. Bound water and portlandite consumption are in agreement with the pozzolanic reactivity of the calcined clays. LC³ blended systems mortars exhibit compressive strength similar to Portland cement. Results shows the good potential of the clay deposits studied, to be used as a source of MCS in the LC³ in Cuba.

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