Hydration of Blended Cement with Halloysite Calcined Clay

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Abstract. The effects of calcined kaolinitic clays as supplementary cementitious materials (SCMs) on the performance of pastes and mortars have been well studied. Less attention has been paid to the thermal transformation of halloysite than that of kaolinite and its possibility to be used as SCMs. Halloysite and kaolinite have identical chemical composition, except that halloysite may have two molecules of H_2O, as interlayer water. The content of additional water in the interlayers of halloysite has a decisive influence on the crystal morphology, which is generally curled rather than platy as in kaolinite. Common forms are elongated tubes and spheroids. The aim of this investigation is to study the hydration of blended cements with 25% of different calcined clays to evaluate the influence of the content and the morphology of halloysite in the development of the hydratation compounds, and compressive strength of mortars. Three clays with different halloysite/kaolinite content, and different morphology were analyzed. The hydrated phases present in pastes at 2, 7, and 28 days were identified by X-ray diffraction (XRD), and the content of CH by differential thermal analysis (DTA/TG). The compressive strength of mortars was tested at 2, 7, and 28 days. The pozzolanic reactivity of the calcined clays was influence by the kaolinite content and morphology of halloysite in natural clays. This results in different crystalline and amorphous aluminic phases obtained at different ages, and that the ensemble results differ, this affects the porosity and the compressive strength.

1 Introduction

One of the main objectives in the cement and concrete industry is promote reduce of CO2 emission and energy consumption, for this purpose the use of supplementary cementing materials (SCMs) in blended cements are a feasible option [1]. The effects of calcined kaolinitic clays as SCMs on the performance of pastes and mortars have been well studied [2–5]. Less attention has been paid to the thermal activation of halloysite than that of kaolinite and its possibility of use as SCMs [6]. Halloysite and kaolinite have identical chemical composition, except that halloysite may have two molecules of H2O, as interlayer water. Additional water in the interlayers of halloysite has a decisive

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The aim of this investigation is to study the hydration of blended cements with 25% of different calcined clays to evaluate the influence of the content and the morphology of halloysite in the development of the hydration compounds and the compressive strength of mortars. Three clays with different halloysite/kaolinite content, and different morphology were analyzed.

2 Materials and Methods

Three different halloysite/kaolinitic clays from Río Negro Province, Argentine, were select to study as SCMs in blended cements. For this purpose, the clays were calcined at 700 °C, to obtain metakaolinite (MK), an amorphous reactive phase, due to the complete dehydroxylation of clays minerals. Other crystalline phases, present as impurities, such as quartz, cristobalite, trydimite and anatase, remain stable after thermal treatment [8]. The calcined clays were ground and they were labeled as CC1, CC2 and CC3.

The clay minerals present in the natural clays have different morphologies. The halloysite present in natural clays corresponding to CC1 has a tubular morphology, while the halloysite present in natural clay corresponding to CC2 and CC3 has spheroidal morphology, and it coexists with hexagonal plates of kaolinite. The halloysite/kaolinite ratio is 100/0 for the natural clay corresponding to CC1, 75/25 for CC2 and 60/40 for CC3 [8].

To study the hydration of blended cements a normal Portland cement (PC) was used. For this PC, the mineralogical composition of clinker was $C_3S = 63.6\%$, $C_2S = 15.1\%$, $C_3A = 2.8\%$ and $C_4AF = 15\%$; 5.5% gypsum is used as set regulator and limestone is the minor component. Blended cements (bc) were formulated with 25% by mass of PC replacement by halloysite/kaolinitic calcined clays.

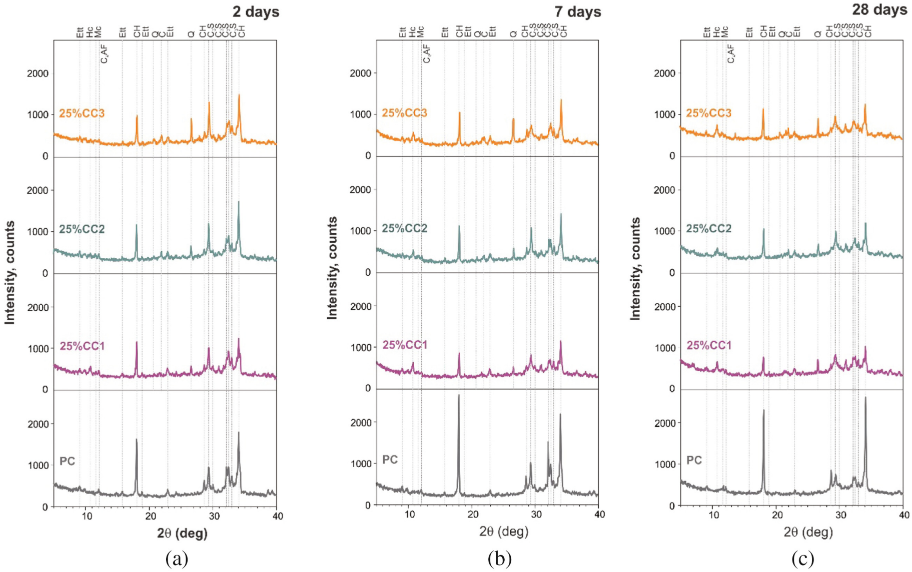
The hydration of blended cements (bc) was studied at 2, 7, and 28 days; the hydrated phases were identified on paste and the compressive strength was determined on mortar.

Blended cement pastes were prepared using water to bc ratio (w/bc) of 0.5. At the test-age fragments of paste sample was immersed in acetone during 24 h to stop the hydration, dry overnight in oven at 40 °C and then cooled in a desiccator. The crystalline phases were identified by X-ray diffraction (XRD) using a Bruker D2 PHASER diffractometer. Complementary, thermal analysis (DTA/TG) was performed to analyse the crystalline and amorphous hydrated phases, using a NETZCH STA 409 thermobalance. Pore size distribution was determined at 28 days in fragments of pastes using a mercury intrusion porosimeter (MIP-ThermoFisher Sc PA440), for pore size diameters from 7.3 to 14000 nm.

Compressive strength (CS) was assessed on mortars made with standard sand EN-196-1 (1:3) and w/bc of 0.50. The CS was determined as the average of five specimens using an universal testing machine Instron 4485 at 2, 7, and 28 days.

3 Results

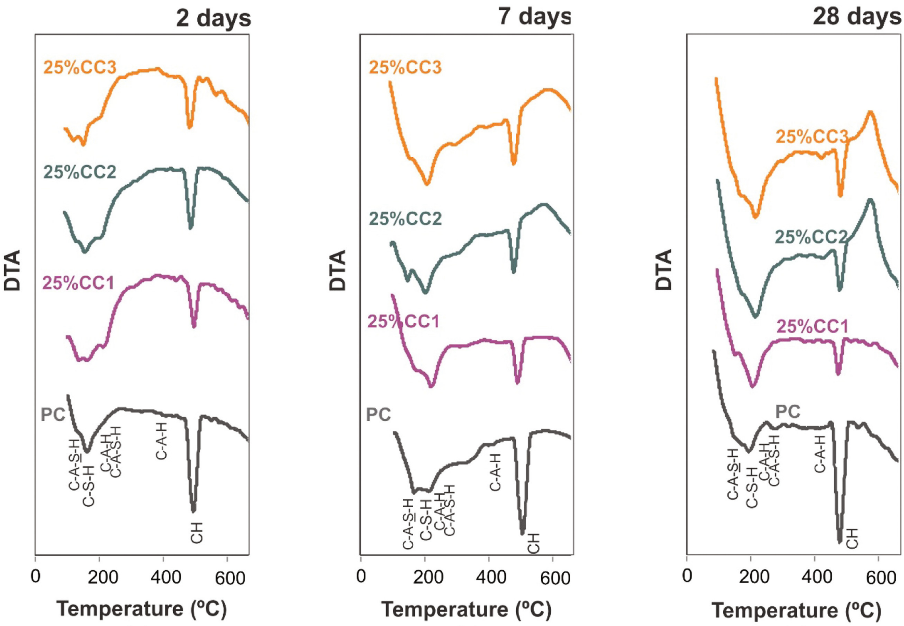
At 2 days, the hydrated crystalline phases detected from PC hydratation were ettringite (Ett) and calcium hydroxide (CH) for PC-pastes and blended cement pastes (Fig. 1a), and unhydrated phases C3S, C2S, and C4AF. For bc-pastes, the intensity of the CH-peaks is lower than that corresponding to PC-paste, showing dilution effect and some CH-consumption to form C-S-H and C-A-H/C-A-S-H phases by the pozzolanic reaction. The hemicarboaluminate (HC, C3A.CH0.5CC0.5.H12) and monocarboaluminate (MC, C3A.CC.H12) phases are formed by the pozzolanic reaction between the reactive alumina from the MK, the CH and calcium carbonate (C) from the limestone filler, a minor component in the PC used. At 2 days, the lowest intensity of the CH-peaks occurs for 25%CC3 paste, showing a high CH-consumption by pozzolanic reaction of this calcined clay obtained from the clay with the highest kaolinite content (halloysite/kaolinite ratio 60/40). The highest intensity of the HC-peaks is for 25%CC1 obtained from the clay with the highest halloysite content and tubular morphology. This allows concluding that the phases obtained as product of the pozzolanic reaction are different when the ratio halloysite/kaolinite is different and the halloysite has different morphology. At later ages (Figs. 1b, c) the intensity of the CH-peaks is low for the three blended cements, and the intensity of HC-peaks and MC-peaks is higher.



(a) (b) (c)

Fig. 1. XRD patterns for hydrated pastes: (a) 2 days, (b) 7 days and (c) 28days

The results obtained by DTA for hydrated pastes are presented in Fig. 2. The first endothermic peaks located at about 110–410 °C characterize the dehydration of C-S-H, C-A-H and C-A-S-H [9]. C-S-H gel is a product from PC hydratation and pozzolanic reaction. The C-A-S-H are cementing compound obtained from pozzolanic reaction where the C-S-H incorporate Al in its structure, like result of pozzolanic reaction too. C-A-H compounds include HC, MC and Ett. Ett (C-A-S-H) starts to loss water at very low temperature (~40 °C) and its complete decomposition into gypsum, hemihydrate (C-A-H) together with an amorphous material occurs at 120 °C [10]. Ett remains stable at 2, 7 and 28 days of hydration. The second endothermic peak located about 410–560 °C characterizes the CH dehydroxylation. Table 1 reports the percentage of CH in mass determined by DTA/TG. For PC-paste, the amount of CH increases with the age. On the other hand, bc-pastes show lower CH-content than the corresponding to PC-paste due to the consumption by the pozzolanic reaction, as determined by XRD (Fig. 1). At 2 days, 25%CC3-paste with calcined clay obtained from the clay with the highest kaolinite content consumes the highest amount of CH, while after 7 days, calcined clays obtained from the clays with high content of halloysite (25%CC2-paste and 25%CC3-paste) consume high amount of CH. At 28 days, 25%CC1-paste with calcined clay obtained from the clay with tubular halloysite consumes the highest amount of CH. The aluminic phases appears as a shoulder of the first endothermic peak in bc-pastes at 2 days (Fig. 2a), and it is more intense for all pastes after 7 days (Figs. 2b, c). At 28 days (Fig. 2c), the area of the first peak is greater for bc-pastes due to the dehydratation of compounds formed during the pozzolanic reaction: C-S-H, C-A-H and C-A-S-H.



(a) (b) (c)

Fig. 2. DTA curves of hydrated pastes: (a) 2 days, (b) 7 days and (c) 28 days.

Table 1. CH content and volume of pores in hydrated pastes. Compressive strength of mortars.

Sample	Amount of CH in hydrated pastes, mass%			Compressive strength of mortars, MPa			Volume of pore at 28 days mm^3/g	
	2 days	7 days	28 days	2 days	7 days	28 days	Diameter 100–14000 nm	Diameter 45–14000 nm
PC	12.75	16.43	16.93	17.5	30.5	37.9	40.7	92.0
25%CC1	6.80	7.09	5.68	12.9	34.8	58.5	13.8	21.2
25%CC2	7.76	7.71	5.96	15.2	35.7	49.1	16.2	19.3
25%CC3	2.33	8.15	6.38	15.9	32.2	48.8	39.4	48.3

For blended cements, the higher compressive strength was developed by the mortar 25%CC3 at 2 days and by the mortar 25%CC1 at 28 days (Table 1). The volume of pores with diameter up to 45 and 100 nm is lower at 28 days in pastes made with blended cements, and it is lowest for bc-pastes with calcined clays obtained from clays with high halloysite content (25%CC1 and 25%CC2), in this pastes the pore refinement is highest.

4 Discussions

The products obtained in pozzolanic reaction at different age were influenced by the disponibility of reactive aluminum: the reactive aluminum present in tubular calcined halloysite at early age produces mainly hemicarboaluminate, which remains stable (Fig. 1), while the calcined kaolinite has more amounts of aluminum available in surface, and then this is incorporated in the C-A-S-H gel (Fig. 2a). This causes that the consumption of CH in pozzolanic reaction to be different; it is higher at early age in blended cements elaborated with high kaolinite calcined clay (Table 1). At later age the CH reacts with the aluminum on the inner surface of the halloysite tubes, has more amount of available and incorporates in C-A-S-H gel (Fig. 2). For this, the volumen of pores that affect the compressive strenght is lowest, and the compressive strenght is highest for blended cements elaborated with tubular halloysite calcined at 28 days (Table 1).

5 Conclusions

Blended cements elaborated with 25% of replacement of calcined halloysite/kaolinitic clays as SCMs are pozzolanic. The hydrated phases obtained are characteristic of the system MK-cement. The CH content is lower than those determined in hydrated pastes elaborated with Portland cement and a higher content of aluminic phases were identified as products of pozzolanic reaction. The pozzolanic reactivity of the calcined clays was influence by the kaolinite content and the morphology of halloysite. This produced that different crystalline and amorphous phases were obtained at different ages, and the assemblage results different affecting the development of the porosity and the compressive strength.

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