Influence of calcium aluminate cement (CAC) on alkaline activation of red clay brick waste (RCBW)

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ABSTRACT

In this paper, the effect of calcium aluminate cement (CAC) additions on the alkali activation of red clay brick waste (RCBW) was studied at room temperature and at 65 °C. RCBW was partially replaced with CAC (0–50 wt.%) and blends were activated with NaOH and sodium silicate solutions. The compressive strength evolution was tested on mortars and the nature of the reaction products was analysed by infrared spectroscopy, X-ray diffraction, thermogravimetric analysis, microscopic studies and pH measurements. The results show that the use of CAC accelerates the activation process of RCBW so that 50 MPa were obtained in the blended mortars containing 40 wt.% CAC cured for 3 days at room temperature. CAC did not undergo normal hydration and only the C_3AH_6 phase was identified in the pastes blended with more than 30 wt.% CAC and cured at 65 °C, while the main reaction product was a cementitious gel containing Ca and Al from CAC.

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1. Introduction

Portland cement is the dominant binder used in concrete. However, the large amounts of energy and greenhouse gases emitted to the atmosphere during its production process have prompted the scientific community to propose different alternatives to reduce its environmental impact. As reviewed by Juenger et al. [1], alkali-activated binders are receiving more attention from among the different alternatives proposed, which is attributed to their excellent strength, durability and low environmental impact. Furthermore in this methodology, the solid material to be activated may be entirely (or almost entirely) composed of waste materials [1]. As described by Shi et al. [2], during the alkali-activation process, a solid silico-aluminous material is mixed with a highly concentrated alkali solution. The resulting paste is an aluminosilicate hydrate that has a three-dimensional structure, with both Al and Si tetrahedrally coordinated, and the alkali (Na or K) located in the voids of this framework, which compensate for electric charges.

A wide variety of industrial by-products and waste materials have been successfully activated by the scientific community [2–5], some of which are ceramics. Among them, Puertas et al. [6] achieved 13 MPa (compression) by the alkali activation of different types of ceramic tiles, cured at 85 °C for 24 h and at 20 °C for 7 days. Payá et al. [7] also developed mortars with compressive strength values above 10 MPa by the activation of hydrated-carbonated cement cured at 65 °C. Porcelain stoneware tiles were activated by Reig et al. [8], where the addition of $Ca(OH)_2$ proved essential to obtain mortar samples with up to 36 MPa under compression (7 days at 65 °C). Red clay brick waste has also been activated in a previous research work [9], where up to 50 MPa were reported under compression in mortars cured at 65 °C for 7 days. Although the development of binders by the alkali activation of ceramic materials has been extensively proved, what most of these studies have in common is that curing at high temperature was required for the activation process to take place.

In the works by Fernandez-Jimenez et al. [10] and Arbi et al. [11], calcium aluminate cement (CAC) was added to the system as a source of calcium and reactive alumina. Thus compressive strength values close to 13 MPa were obtained in the alkali-activated metakaolin pastes containing 20% CAC (cured at 85 °C for 20 h) [10]. Even higher compressive strength values (23.7 MPa) were achieved in Ref. [11] by the activation of blast furnace slag and CAC blends (80–20 wt.%) cured at room temperature for 2 days. Thus although

CAC production consumes natural resources (bauxite and limestone), emits CO_2 to the atmosphere and requires energy to reach clinkering temperatures, moderate amounts of this cement may improve the behaviour and properties of the blended system. As Pacewska et al. [12] described, CAC is a hydraulic binder with special properties, such as rapid strength gain, good durability in high sulphate environments, resistance to fire, chemical attack and abrasion. Monocalcium aluminate (CA) is the principal active phase in CAC cement, which reacts with water to give calcium aluminate hydrates. As described by Juenger et al. [1], hydration temperature is one of the most significant parameters to influence the phases that are formed and the transition rate from metaestable to stable hydrates (conversion process). Whereas CA hydrates at environmental temperatures (15–25 °C) to give hexagonal phases $CaAl_2O_4 \cdot 10H_2O$ (CAH_{10}) and $Ca_2Al_2O_5 \cdot 8H_2O$ (C_2AH_8), with an increased quantity of C_2AH_8 with rising temperature, curing within the 25–40 °C range yields C_2AH_8 as the main hydration product, together with alumina gel, which crystallizes with time to gibbsite $Al(OH)_3$ (AH_3). When temperature rises above 40 °C, and especially up to 60 °C, phase $Ca_3Al_2(OH)_{12}$ (C_3AH_6) is formed (cubic phase), together with hydrous alumina, which gradually changes to gibbsite. As extensively proved by the scientific community [1,13,14], CAH_{10} and C_2AH_8 are metastable products that inevitably convert into stable C_3AH_6 and AH_3 phases depending on time, temperature, humidity or pH. The conversion of these metastable hydrates into the stable cubic phase occurs in accordance with Equations (1) and (2) [13], and is accompanied by AH_3 gel formation and the release of water (H). As a result, the porosity of the paste increases, and the strength of the material subsequently diminishes [1,13–15].

$$3CAH_{10} \rightarrow C_3AH_6 + 2AH_3 + 18H \tag{1}$$

$$3C_2AH_8 \rightarrow 2C_3AH_6 + AH_3 + 9H \tag{2}$$

Carbonation of CAC hydrates may also occur if CO_2 from the atmosphere is absorbed, which results in the formation of $CaCO_3$ and AH_3. As explained in Ref. [14], the hexagonal phases carbonate faster than the cubic one as they are less stable and dissolve CO_2 more easily. The alkaline hydrolysis, a durability problem associated with CAC, has been described in Ref. [14] also as a carbonation process which occurs with high pH values and in the presence of alkalis, and which destroys the hexagonal and cubic hydrates that confer cementitious properties to the binder. In this process, the carbonated alkalis (Na_2CO_3) formed by the combination of NaOH and CO_2 react with the hydrated calcium aluminates (CAH_{10}, C_2AH_8, C_3AH_6) to form soluble alkali aluminates.

The scientific community has been seeking alternatives to mitigate the durability problems associated with CAC cements (conversion, carbonation and alkaline hydrolysis). Authors such as Pacewska et al. [16] and Hidalgo et al. [13] introduced into the cement system appropriate additions of spent catalyst FCC [16], and silica fume or fly ash [13] to stabilise CAC hydrates and to avoid, or to at least reduce, their conversion and negative effects on CAC composites. An alternative reaction for metastable hydrates was observed in both the above studies, with silicate ions reacting with calcium aluminate hydrates (CAH_{10}–C_2AH_8) to form Strätlingite (C_2ASH_8), a stable hydrate formed within the normal temperature range. In Ref. [10], metakaolin and CAC blends were alkali-activated with NaOH and sodium silicate solutions. None of the compounds normally observed in water-hydrated CAC (CAH_{10}, C_2AH_8, C_3AH_6, AH_3) was detected under the study conditions (curing at 85 °C for 2 or 20 h), and the Al and Ca from CAC were taken up in the aluminosilicate gel formed in the activation process. Through the hydration of CAC with NaOH solutions, Pastor et al. [17] also found that alkali activation accelerated the conversion process to yield the

cubic aluminate hydrate from very early ages (2 days in samples activated with 8 M and 12 M NaOH), instead of the hexagonal aluminates (CAH_{10} and C_2AH_8) that appeared during standard water hydration. These results have been corroborated in Ref. [18] by CAC hydration with highly alkaline NaOH (8 M) and sodium silicate solutions, where high pH values resulted in the formation of cubic hydrates from the outset, and no C_2ASH_8 was formed since silicon was taken up to form katoite-type phases ($C_3AS_nH_m$).

The work reported herein aims to understand the influence of calcium aluminate cement (CAC) additions and curing temperature on the mechanical strength and microstructure evolution of alkali-activated red clay brick waste (RCBW) cements. RCBW was partially replaced with CAC (0–50 wt.%), and blends were activated with NaOH/sodium silicate solutions and cured at room temperature and at 65 °C.

2. Experimental procedure

2.1. Materials

The studied samples were prepared with red clay brick waste (RCBW) and calcium aluminate cement (CAC), the latter produced by the company Cementos Molins S.A. (Barcelona, Spain). Red clay bricks were crushed in a jaw crusher (BB200, Retsch) to obtain a granular material with a particle size of less than 4 mm. This was then dry-milled in alumina media for 40 min, and powder with a mean particle size close to 21 μm and 90 vol.% less than 56.2 μm was obtained (determined by laser diffraction in a Mastersizer 2000, Malvern Instruments). The CAC particle size was similar, with a mean diameter of 27.7 μm and 90 vol.% under 64.3 μm. According to the SEM images in Fig. 1, both RCBW and CAC particles were irregularly shaped.

The chemical composition of RCBW and CAC, determined by X-ray fluorescence (XRF, Philips Magix Pro), is provided in Table 1. While CAC is composed mainly of Al_2O_3 and CaO, RCBW contains high levels of SiO_2 and Al_2O_3, which are essential for the alkali-activation process. The amorphous content of RCBW, determined following UNE EN 196-2, was around 35%.

2.2. Matrix preparation

Different percentages of calcium aluminate cement (0–50 wt.%) were used to substitute ceramic waste. The alkali-activating solutions were prepared by mixing sodium hydroxide pellets (98% purity, Panreac), water and sodium silicate (Merck, SiO_2 = 28%, Na_2O = 8%, H_2O = 64%). The activating solution dosage (SiO_2/Na_2O molar ratio of 1.60) was adopted from previous studies [9] and was kept constant for all the pastes and mortars mixed. A water to binder ratio (w/b) of 0.40 was used in the present research, which was lower than that previously reported in Ref. [9] due to the better workability of the RCBW-CAC blended mortars. A water-hydrated CAC paste (w/b 0.35) was prepared for comparison.

Pastes and mortars were produced according to the process previously described in Refs. [9,19]. They were cured in a thermostatically-controlled bath at 65 °C at a relative humidity (RH) of 96% for 3 and 7 days; and in a room temperature chamber (20 °C, RH 96%) for 3, 7, 14 and 28 days. A sand to binder (sum of CAC plus RCBW) ratio of 3:1 was used for all the prepared mortars. The process variables used in this study are summarised in Table 2.

2.3. Characterisation

The compressive strengths of the alkali-activated mortars were determined following UNE EN 196-1 using 160 × 40 × 40 mm samples. Pastes were used to assess the microstructure evolution of