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Influence of calcium aluminate cement on geopolymerization of natural pozzolan

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HIGHLIGHTS

- Pozzolan geopolymer mixtures were designed adding CAC up to 24% of total binder.
- CAC enhances compressive strength development under hydrothermal curing condition.
- Workability and setting time reduced with increase of CAC.

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ABSTRACT

This paper presents a study on the influence of calcium aluminate cement (CAC) on the geopolymerization of natural pozzolan. CAC was incorporated at 0, 8, 16 and 24% replacement by weight of pozzolan and aqueous solutions of NaOH and sodium silicate with different SiO_2/Na_2O ratios (M_S) and Na_2O contents were used as alkali activators. The setting time, workability, compressive strength, $(SiO_2 + Al_2O_3)_{reactive}$ content and free alkali content of cured cement samples were determined. Complementary studies using semi-adiabatic calorimetry, FTIR spectroscopy and XRD were also performed. According to the results, incorporation of CAC increases the reactive Al of the binder, accelerates the dissolution of reactive contents and facilitates the progress of the polycondensation reactions. These improvements in the geopolymerization reactions result in the formation of a more cross-linked aluminosilicate network that exhibits higher compressive strength.

1. Introduction

Natural pozzolans are alumina-silicate materials, which when react with calcium hydroxide, form compounds with cementitious properties. Natural pozzolans including raw and calcined natural materials—such as volcanic ash, opaline chert, tuff, some shale, and some diatomaceous earth-are often used as an addition to Portland cement to create blended cements [1]. The production of geopolymer cements may be another utilization of these materials [2].

Geopolymer cement is a type of inorganic polymer that is made from chemical reaction between alumina-silicate materials and alkaline activator typically sodium hydroxide and sodium silicate to form a solid binder with properties comparable to ordinary Portland cement (OPC). The role of alkali activator is to dissolve the reactive silica and alumina present in source materials and provide a high alkaline liquid medium during polycondensation reaction. The main reaction product formed in this case is a three-dimensional polymeric chain and ring structure consisting of Si—O—Al bonds [2]. Geopolymer cements have economical and environmental benefits since their production requires less energy and resource consumption than Portland cement and generates less CO_2 emission [3]. Besides these benefits, in some cases geopolymer cements present some advantages over ordinary Portland cements such as earlier and higher mechanical strengths, lower heat of hydration and superior durability [4].

Depending on the type, chemical composition and reactivity of the raw materials, geopolymer cements exhibit different properties [5]. Prior studies have shown that alkali activation of materials with optimum proportions of reactive silica and alumina contents, generate good cementitious binders. Hence, to obtain satisfactory strength development in the geopolymer cements, a minimum amount of reactive silica and alumina in starting materials is needed [5,6]. The most common materials that are used in

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geopolymer cement production are fly ash and metakaolin. Attempting to develop low cost and abundant raw materials, natural pozzolans can be used to substitute fly ash or metakaolin [7].

Natural pozzolan is a good source of reactive silica, but often it has not enough reactive alumina to guarantee the geopolymer formation. The proposed solution is to modify the $(Si/Al)_{reactive}$ ratios of initial mix formulation by addition of certain amount of reactive alumina containing materials [8–10]. Calcium aluminate cement (CAC) is an Al-rich material which might be suitable as a secondary source of reactive alumina when added to natural pozzolans to synthesize geopolymer cements. It should be noted that the local availability of CAC is the most important reason that caused using it to modify Si/Al ratio in this study and any other materials (such as aluminum hydroxide waste), which provides required reactive alumina can be used.

Calcium aluminate cements (or high-alumina cements) are a group of hydraulic binder of the cement family, containing different amounts of alumina ranging from 38% up to about 95%, which are manufactured by either fusing or sintering a proportioned mixture of limestone and bauxite. CACs are known for their advanced properties such as rapid strength development [11] and resistance to aggressive chemicals and high temperatures [12]. The main reactive constituent of CAC is monocalcium aluminate (CA) that's high in reactive alumina content [11]. Due to their reactive alumina content, CACs are potentially capable of being added to precursors of low reactive alumina content in geopolymerization process to enhance the reactivity of the mix [13].

Limited studies have been conducted on the effect of calcium aluminate cement on the properties of geopolymer system. Reig et al. [14] investigated the effect of CAC addition on the geopolymerization of red clay brick waste (RCBW) at room temperature and at 65 °C. They indicated that CAC enhances the compressive strength, so that 50 MPa were achieved in the blended mortar with CAC content of 40% cured for 3 day at room temperature. Fernandez et al. [8] also developed geopolymer pastes with highest compressive strength of 13 MPa by the alkali-activation of metakaolin and CAC blend (20 wt%) cured at 85 °C for 20 h.

The aim of this study is to investigate the effect of addition of CAC on the alkali activation of natural pozzolan in respect to the compressive strength, workability and setting time characteristics. Based on preliminary experimental results and literatures, mortar specimens were prepared using four different CAC–natural pozzolan blends and compressive strengths were determined at three levels of both sodium oxide (Na_2O) concentration and activator modulus. The chemical analysis and calorimetric measurements were used to study the geopolymerization process. Moreover the molecular structures of the geopolymer matrices were analysed with XRD and FTIR techniques.

Table 1
Properties of the binder materials.

	CAC	Pozzolan
Chemical composition (%)		
SiO_2	3.75	61.57
Al_2O_3	39.5	18.00
Fe_2O_3	16	4.93
CaO	38	6.69
MgO	<1.5	2.63
SO_3	–	0.10
$K_2O + Na_2O$	<0.4	2.6
Physical properties		
Specific gravity (g/cm^3)	3.25	2.22
Blaine specific surface area (m^2/kg)	315	380
Mean diameter size (μm)	18	14

2. Experimental program

2.1. Materials

The materials used in this study were natural pozzolan, calcium aluminate cement, sodium silicate and sodium hydroxide. The natural pozzolan was obtained from Taftan Mountain in Iran, which is used to produce Portland pozzolan cement by the regional cement factories. Calcium aluminate cement was provided by Iran Refractory Cements Company. The blend of natural pozzolan and CAC was used as aluminosilicate precursors. The physical properties and chemical compositions of Taftan pozzolan and CAC are shown in Table 1. DIN 1164 Standard sand was used as a fine aggregate in the manufacture of mortars. Sodium hydroxide (NaOH) pellets and sodium silicate solution, supplied by MERK International Ltd, were used to produce the alkali activators. The sodium silicate has a solid content of 37% with SiO_2 = 25.5–28.5%, Na_2O = 7.5–8.5% and a modulus (mass ratio of SiO_2/Na_2O) of 3.35.

2.2. Mix design and specimen preparation

Geopolymer mortars were prepared by mixing natural pozzolan-CAC blends with activator solution and standard sand. Mix variables included the Na_2O concentration of activator solution, the activator modulus, and the amount of CAC as a replacement of pozzolan. The nomenclature used in the variables and levels definition is shown in Table 2. The mortars were made according to ASTM C109 with fine aggregate-to-binder of 2.75. The workability of mortars was maintained to have a flow of 110 ± 5% with water-to-cement ratios adjusted in the range of 0.480–0.560. All mortar mix proportions used are summarized in Table 3.

All specimens were produced with the following procedure: Initially, pozzzolan-CAC blend and sand were mixed in a dry state and then the activator solution was added. The mixture was mixed together manually for 3 min and the resulting mortar was cast into 50-mm test cubes. The cubes were kept in the molds in the humidity cabinet for 24 h at about 23.0 ± 2.0 °C and a relative humidity more than 95%. Then the specimens were de-molded and cured under hydrothermal conditions at 95 °C for 20 h. After curing, the physical and chemical properties of the geopolymer mortars were characterized.

2.3. Methods

2.3.1. Workability and setting time

To investigate the effect of CAC on properties of fresh geopolymer mortar at constant water content, the spread diameter of fresh geopolymer mortars were determined immediately after mixing by the standard flow table test according to the ASTM C1437 and C230 [15,16]. The setting time of the geopolymer mortars were also measured by means of the modified Vicat needle according to ASTM C807 [17]. For these tests, the water-to-binder ratio was kept constant at 0.500.

2.3.2. $(SiO_2 + Al_2O_3)_{reactive}$ content

The percentage of vitreous phase and reactive silica and alumina contents of starting materials were determined by the gravimetric method. The vitreous (soluble) and crystalline (insoluble residue) phases of pozzolan-CAC blends were quantified by the acid treatment using 1% HF solution using the following procedure: 1.00 g of blend was added to100 ml of 1% HF, stirred for 6 h at room temperature and then filtered. After that, the filter paper was washed to a neutral pH, oven-dried for 1–2 h at 100 °C and calcined at 1000 °C. The vitreous phase was determined by subtracting the insoluble residue from the initial mass [18]. The reactive silica and alumina contents of blends examined, were estimated conventionally as the difference between the total amounts of silica and alumina present in the start-

Table 2
Factors and their levels considered in Full-factorial design.

Factors	Unit	Level 1	Level 2	Level 3	Level 4
A = Na_2O content	wt%	8	10	12	–
B = modulus ratio	wt ratio (Molar ratio)	1(1.01)	1.5(1.52)	2(2.03)	–
C = CAC content	wt%	0	8	16	24