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Quality control and assessment of geopolymer cements based on reacted and free alkalis

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HIGHLIGHTS

- Reacted and free alkalis were proposed as geopolymer quality control parameters.
- Reacted alkali is correlated to compressive strength.
- Free-alkali is correlated to efflorescence formation intensity.

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ABSTRACT

In this paper, new parameters based on reacted and free alkalis are introduced to assess and control the qualitative properties of geopolymer cements. For this, Fly ash-based geopolymer paste were prepared to study the correlation between compressive strength and reacted alkali at different curing time and temperatures. Since the properties of geopolymers strongly depend on the reactive oxides content $(Al_2O_3 + SiO_2)_{reactive}$ and composition $[Al_2O_3/(Al_2O_3 + SiO_2)]_{reactive}$ of the precursors, variation of this ratio on the relationship between compressive strength and reacted alkali and between efflorescence intensity and free alkali were also investigated using by blended natural pozzolan/calcium aluminate cement and fly ash/calcium aluminate cement geopolymer pastes. The results confirm the existence of strong correlations between compressive strength and reacted alkali and between efflorescence intensity and free alkali. The findings, therefore, prove the suitability of the reacted and free alkali contents as proper quality control parameters in geopolymer cements.

1. Introduction

Quality control is one of the most important activities of a production unit, because it plays a critical role in the continuity, permanence and stability of the products. Cement as a commodity is produced during a complex process accompanied by persistent variations of the raw materials quality. Since cement is used in almost all construction applications, the issue of quality and special attention to it is important. Various factors including physical and chemical properties of cement (cement fineness, expansion, initial and final setting times, compressive strength and heat of hydration, chemical and mineral composition and free lime content) have direct influence on the performance and soundness of Portland cements. Measurement and control of these parameters will result in the quality control and assessment of Portland cement [1,2]. As an example, the relatively high free lime content in Portland cement clinker which indicates the insufficient progress of alite formation reaction in rotary kiln can cause unsoundness of Portland cement (destructive expansion). Therefore, the amount of free lime in the kiln output clinker is constantly measured to obtain the information about progress of alite formation reaction, providing the control of the production process and ensuring the product quality and soundness [3].

Concerns related to energy consumption and environmental issues in Portland cement manufacturing have resulted in significant interest in finding binders alternative to Portland cement [4]. Geopolymer cements are a group of clinker-free binders that are synthesized by combining aluminosilicate materials such as metakaolin and fly ash with strong alkali solutions such as sodium hydroxide and/or sodium silicate (in most cases). Based on Davidovits (1994), the molecular structure of geopolymer include a three-dimensional aluminosilicate network of AlO_4 and SiO_4 tetrahedral groups linked by oxygen bridges and the negative charge of

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aluminum atoms in polymer network is charge-balanced by alkali cations (typically Na^+ and K^+). However, this nomenclature system was modified later by other researchers [5]. The properties of geopolymers were found to be influenced by the nature, chemical composition, fineness and reactivity of the source materials as well as the type and composition of alkali activator and curing regimes [6,7]. Various researchers have come to an agreement that variations of any of these parameters pose a significant effect on the compressive strength [8–11], setting time [8,12,13], shrinkage [8,14], durability [15–17] and tendency toward efflorescence [18,19] of the resultant geopolymer cements.

The quality control and assessment of geopolymer cements are essential to produce a sustainable product, indicating the need to find a general test method, which besides being valid, is quick and acceptable for accuracy. The suggested methods are mainly based on the Portland cement quality control standards (such as fineness, compressive strength, bending strength, etc.) and no study on the quality control and assessment of geopolymer cements has been found in the literature, which is causing problem in terms of commercializing geopolymer technology [20]. Due to the total contrast in hydration reactions of geopolymer and Portland cement, establishment of standard testing methods, especially designed for geopolymer cements, is necessary to monitor the soundness and quality of these cementitious materials. The measurement of reacted and free alkalis might be one of the ways to assess the reaction progress of geopolymerization, supported by the fact that the negative charge on AlO^{-4} group in geopolymer gels is charge-balanced by alkali cations [21]. Hence, valuable information including the relative amounts of cementitious compounds formed and efflorescence potential are gained by determination of reacted and free alkalis, which can then be used as a basis for soundness and quality control in the fabrication of geopolymer cements.

Generally, three types of alkali can be found in the geopolymer cements: alkali existed in the source materials (initial alkali), alkali consumed in the geopolymerization reactions (reacted alkali) and alkali remained un-reacted in the structure (free alkali), among which the reacted and free alkali has a direct relationship with the mechanical properties and potential for efflorescence formation in geopolymers, respectively. Methods of measurement of reacted and free alkalis, similar to measurement of free lime in Portland cement clinker, are relatively simple, inexpensive and fast and can provide a cost-effective and quick tool for product quality control and assessment. In other words, by measuring these amounts as well as providing information related to the changes of compressive strength with reacted alkali and also variations of efflorescence formation intensity in terms of free alkali, quality and soundness of the products can be assessed and required actions can be planned if necessary. For instance, a relatively low amount of reacted alkali along with a relatively high free alkali content represent a lack of sufficient progress of geopolymerization reactions. As a result, the reactivity of source materials and the ability to produce geopolymer, the optimal dose of activator and consequently the compressive strength and the potential for efflorescence formation in geopolymer cements can be investigated by measurement of the reacted and free alkalis.

Although the soundness and quality control and assessment of geopolymer cements based on direct measurement of mechanical properties and efflorescence formation intensity are accurate and in some cases necessary, but due to being time-consuming, they cannot provide the required qualitative information quickly and timely in the production line. In this paper, attempts are made to introduce a simple, rapid and innovative method in order to assess the quality and soundness of geopolymer cements. This method is based on the determination of free and reacted alkali contents in the produced geopolymer cement and finding the correlation factors of these values with compressive strength and efflorescence formation intensity, respectively. Desirable features of this method include; simplicity, cost-effectiveness, and rapidness of analysis as well as small cementing material requirement, approximately a few grams, to assess the soundness and quality of the geopolymer cement.

2. Materials and methods

2.1. Materials

Materials used in this study consisted of fly ash (FA), natural pozzolan (NP), calcium aluminate cement (CAC) (Fundo from Kerneos, France), sodium silicate solution, and sodium hydroxide. NP was prepared from Taftan Mountains located in the south east of Iran and FA was supplied from a French power plant. Physical and chemical properties of Taftan NP, FA and CAC are presented in Table 1.

In order to prepare activator solution, sodium hydroxide pellets and sodium silicate solution, purchased from Merck were used. Characteristics of sodium silicate solution are as follows: solid content of 37% with SiO_2=25.5–28.5%, Na_2O=7.5–8.5% and a silica modulus (M_S; mass ratio of SiO_2/Na_2O) of 3.35.

2.2. Preparation of geopolymer cements

The geopolymer pastes were all activated using the same activator solutions containing Na_2O = 8 wt% (by weight of dry source materials) with silica modulus (M_S) of 1.5. To prepare geopolymer cement paste, source materials, activator solution, and given amount of water for a water-to-cement ratio (W/C) of 0.300 were mixed for three minutes in a planetary mixer.

The pastes were then cast into $20 \times 20 \times 20$ mm^3 cubic molds and subjected to humid curing regime in an environment of more than 95% relative humidity at 25 ± 2 °C for 24 h. After demolding, the specimens were further cured to testing time either in the same condition as applied in the first 24 h or hydrothermally at different temperatures. The experimental work of this study was designed in such a way that the effects of curing conditions and the amount and composition of the reactive oxides (SiO_2 and Al_2O_3) present in source materials on the reacted and free alkali contents, compressive strength and efflorescence formation intensity of the examined geopolymer cements can be studied.

2.3. Testing and characterization

The compressive strength test was performed using a 300 kN capacity hydraulic testing machine at a loading rate of 0.5 MPa/s until failure. The compressive strength value was determined as the arithmetic average of six specimens. The standard deviation of the compressive strength was less than 4% (±3 MPa). Molecular structure of the synthesized geopolymer cements were studied by Fourier transform infrared (FTIR) spectroscopy. FTIR spectra of the specimens were obtained by PerkinElmer spectrometer using KBr tablets in the range of 400–4000 cm^{-1} with a resolution of 1 cm^{-1}. The amounts of reactive oxides (Al_2O_3 and SiO_2) of the precursors were measured using a modified procedure described by Fernandez-Jimenez et al. [22]. The source materials were first leached by 1% sulfuric acid in order to dissolve and extract the reactive oxides in acid. The reactive silica and alumina contents were then determined conventionally as the difference between total amounts of silica and alumina present in the source materials and the insoluble residue remained after acid leaching process. The total content of alumina and silica were measured by using an alkali fusion/coagulation gravimetric method according to the ASTM C114 [23].

Table 1
Chemical composition and physical properties of the materials.

	Pozzolan	Fly ash	Calcium aluminate cement
Chemical composition (%)			
SiO_2	61.57	47.00	3.75
Al_2O_3	18.00	29.00	39.50
Fe_2O_3	4.93	8.50	16.00
CaO	6.69	3.00	38.00
MgO	2.63	3.00	<1.50
SO_3	0.10	0.60	–
$K_2O + Na_2O$	2.60	5.20	<0.40
Physical properties			
Specific gravity (g/cm^3)	2.22	2.26	3.25
Blaine specific surface area (m^2/kg)	380	412	315
Mean particle size (μm)	14	12	18