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Effects of mineral admixtures and lime on disintegration of alkali-activated slag exposed to 50 °C

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HIGHLIGHTS

- Alkali activated pastes (AAS) lose strength after exposure to 50 °C.
- The strength loss can be prevented by addition of silica fume (SF).
- SF performed better than fly ash (FA) in reducing strength loss.
- FA can effectively reduce strength loss when AAS were cured at 60 °C.
- Addition of lime leads to high strength loss of AAS after exposure to 50 °C.

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ABSTRACT

Alkali-activated slag can totally disintegrate when exposed to 50 °C. This paper presents a study of possible solutions to avoid this disintegration by using silica fume (SF) and fly ash (FA) to partially replace slag. It was found that partial replacement of slag with SF significantly reduces strength loss. A mixture of 50% slag 50% SF (cured at 25 and 60 °C) showed no strength loss after the exposure. In comparison, a 55% drop of strength was observed in a mixture of 50% slag 50% FA (cured at 25 °C) after the same exposure. However, the strength loss of this mixture was reduced by 50% when cured at 60 °C. The presence of lime in AAS pastes increases the degree of strength loss after the exposure. The mechanisms for the above strength results are discussed in terms of hydration products and microcracking.

1. Introduction

Alkali-activated slag (AAS) is a clinker-free binder made of ground granulated blast-furnace slag (GGBS), and is activated by alkaline activators. Commonly used alkaline activators are sodium hydroxide and sodium silicate solutions. As slag is waste material from other manufacturing processes, the use of AAS in construction has many environmental advantages, such as reduction of costs for industrial waste disposal, low energy cost and low greenhouse gas emission [1]. Furthermore, AAS has been reported to exhibit mechanical and durability characteristics similar or superior to those of ordinary Portland cement (OPC) binder [2–6]. Consequently, AAS has been established as a method for producing sustainable binders for construction.

However, safety concerns about the structural use of AAS concrete have been raised recently because AAS pastes can totally disintegrate when exposed to oven drying at 40–50 °C [7]. This disintegration has been found to be correlated with the alumina content in slags [8]. The authors attributed the disintegration of AAS pastes at 50 °C to crystalline conversion from the hexagonal hydrates CAH_{10} and C_4AH_{13} to the cubic hydrate C_3AH_6 with a lower specific weight. In essence, this conversion causes a remarkable increase in porosity which is responsible for the decrease in strength, because of the transformation of the voluminous hexagonal phases into the denser cubic phase.

Although the occurrence of conversion in the AAS system has been identified only recently, the detrimental effects of conversion on the strength of high alumina cement (HAC) have been known

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since the 1970s. Since then, prevention of conversion has been of great concern to civil engineers and has resulted in extensive study of HAC systems. Collepardi et al. [9] investigated the effects of mineral admixtures including fly ash (FA) and silica fume (SF) on preventing the conversion of HAC pastes. They found that SF performed better than FA in reducing the conversion of hexagonal aluminate hydrates (CAH_{10} and C_4AH_{13}) into the cubic hydrate (C_3AH_6) which is responsible for the strength loss of HAC pastes at higher temperature (>20 °C). Majumdar and Singh [10] also agreed that the conversion could be avoided by the addition of SF in HAC pastes. They reported that the compressive strength of HAC/SF pastes (HAC/SF mass ratio = 60/40) remained almost unchanged up to one year when the pastes were water-cured at 40 °C. However, the strength of the HAC/SF pastes was significantly lower than that of plain HAC pastes. The low strength is attributed to the presence of large amounts of unhydrated SF on the hydrates' surface, which can serve as defect sites in HAC systems. To promote the dissolution of silica, sodium sulphate has been added into HAC/SF systems. It was found by Ding et al. [11] that the presence of sodium ions could significantly reduce the amounts of unhydrated SF. The increase in dissolved silica had beneficial effects not only in enhancing strength, but also in reducing the risk of conversion, as dissolved silica can react with CAH_{10} or C_4AH_{13} to form stratlingite (C_2ASH_8). The authors reported that a 28 days' strength of 40 MPa was developed in HAC/SF/Na_2SO_4 pastes and the strength of the samples was improved to 50 MPa when water-cured at 38 °C up to 90 days. Under the same curing condition, plain HAC pastes experienced significant strength loss.

It is noted that the use of both FA and SF in AAS concrete is recommended for different purposes. Fly ashes and slags are by-products that are commonly used to produce blended cements and concretes. However, rates of slag utilization are much higher than those of FA [12]. Attempts have been made, therefore, to replace partial blast furnace slag with FA in AAS pastes to increase the utilization of fly ashes [13,14]. Initial studies [15,16] of slag/FA blends have indicated an optimum slag/FA mass ratio of 50/50. These slag/FA blends exhibit engineering properties comparable to their plain AAS counterparts [15] but superior to those of OPC counterparts [16]. Unlike FA, which is used to replace blast furnace slag, SF is often used as an additive (the replacement rate generally being less than 15%) to improve the properties of AAS concrete. The replacement of slag with SF has been found to improve the strength [17] and workability [18] of AAS pastes and to increase their resistance to exposure to high temperatures [19].

Besides SF and FA, lime is also added to AAS concrete to improve its properties. Lime has been found to be a suitable retarder to control the setting time of AAS concrete [20]. Collins and Sanjayan [21] studied the effects of lime on the strength development and found that the presence of lime could significantly increase the strength of AAS pastes. In a recent study, Yang et al. [22] even attempted to develop an AAS system using lime as the main activator. At a water to binder ratio of 0.3, 7.5% $Ca(OH)_2$ and 1% Na_2SiO_3 activated mortars developed a compressive strength of 32 MPa at the age of 28 days. When $Ca(OH)_2$ is served as an activator for slags, C_4AH_{13} has been identified as one of the main hydration products in AAS pastes. It is noted that C_4AH_{13} is metastable phase that converts with time to the more stable and denser hydrogarnet C_3AH_6. This conversion reaction produces an increase in porosity and results in lower strength. This phenomenon has been observed in HAC systems [23].

From the existing research concerning the use of additives to augment the properties of cementitious materials, it can be concluded that (1) FA, SF and lime have been proposed for use in making AAS concretes; (2) these additives have significant influences on the strength of HAC systems due to conversion reactions. Although conversion reactions also take place in AAS pastes, the effects of the three additives on the strength of AAS pastes under conditions favouring conversion have never been investigated. Thus the aim of this paper is to investigate the effects of FA, SF and lime on the strength of AAS pastes when exposed to 50 °C.

2. Experimental program

2.1. Materials

The primary raw materials used in this study were provided by local suppliers. The chemical compositions and properties given by the manufacturers are summarized in Table 1. The alkaline activators used were liquid sodium silicate (grade D) comprising 29.4% SiO_2, 14.7% Na_2O, and 55.9% H_2O; wt. ratio: $SiO_2/Na_2O = 2$ and sodium hydroxide solution (8 M). The 8 M NaOH solution was prepared by dissolving 98% purity NaOH flakes in distilled water and then cooling the solution for 24 h. The activators were mixed in proportions, providing the constant modulus in solution (mass ratio of SiO_2 to Na_2O), Ms, equal to 1.0 and 8% Na (mass of the total binder) was used as the concentration of the activators. Hydrated lime was also used for some AAS paste samples to facilitate alkali activation.

2.2. Mix proportions and sample preparation

The mix proportions of samples are given in Table 2. The alkaline activator consisted of 0.2136 kg liquid sodium silicate, 0.1644 kg sodium hydroxide solution and 0.0498 kg free water. The water to binder (w/b) ratio of AAS was fixed to 0.5 and the total water content consisted of free water content and activator water content. Sodium hydroxide solution (8 M) was prepared 24 h prior to mixing and stored in an air-tight container. Then the sodium hydroxide solution was mixed with liquid sodium silicate and free water to form the activator mixture. The blast furnace slag was blended with admixtures (FA or SF) and lime, after which the activator mixture was added. Mixing was performed using a Hobart mixer for 5 min. The samples were cast in plastic molds 50 mm high and 25 mm in diameter. A thin layer of oil was sprayed into the plastic molds prior to filling to aid in the removal of hardened paste upon curing. The plastic molds were vibrated on a vibration table for 2 min to remove any air bubbles and sealed immediately afterwards. A total of nine mixtures were prepared and 20 samples were cast from each mixture.

2.3. Curing conditions

Two curing methods were selected, steam curing and 60 °C oven curing. The AAS paste samples with admixtures (FA or SF) at 50 wt% dosage underwent both curing methods. The remaining samples underwent only steam curing. Before curing, all the samples kept in the molds were set at room temperature for 24 h to allow the AAS paste to harden. Then the moulds were removed and the samples were exposed to steam for 28 days. For oven curing, within 1 h after the samples were prepared, they were placed in an oven preheated to 60 °C with circulating air for one day, then set in the air (kept at a temperature of 23 °C and relative humidity of 50%).

2.4. Compressive strength testing

In general, the conversion occurs very slowly at 20 °C and below, and its effects may not be appreciable after many years. At higher temperatures, however, conversion can occur extremely rapidly, within a few weeks or even days. Therefore, some of the AAS paste samples were oven dried at an operating temperature of 50 °C for one day, with the measured relative humidity and air circulation rate of 14% and 2.3 m/s, respectively. Compressive strength testing was conducted on specimens using a Baldwin universal testing machine. The displacement rate used was 0.5 mm/min. The 28 days compressive strength of specimens was measured before and after exposure to 50 °C. To obtain the average compressive strength, three samples from each mixture were tested.

2.5. X-ray diffraction (XRD) testing

The XRD tests were conducted on a small portion of specimens after the completion of the compressive strength test. The material was ground with mortar and pestle and then sieved through a No. 200 sieve. The material that passed through the No. 200 sieve was placed on a specimen holder prior to testing. The XRD tests were performed using a Rigaku D/Max X-ray diffractometer with Bragg–Brentano parafocusing geometry, a diffracted beam monochromator, and a conventional copper target X-ray tube set to 40 KV and 30 mA.

2.6. Ultrasonic pulse velocity (UPV) testing

Ultrasonic pulse velocity (UPV) testing was performed using a portable ultrasonic nondestructive digital-indicating device. Ultrasonic pulse transmission time was determined parallel to the specimen axis before and after exposure to 50 °C,