Properties of an aged geopolymer synthesized from calcined ore-dressing tailing of bauxite and slag

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ABSTRACT

The strength evolution of a geopolymer synthesized from calcined ore-dressing tailing of bauxite and slag and cured at ambient temperature for 6 years was investigated. Changes in products and microstructure were studied as well. The results indicated that the strength steadily increased from 50.0 MPa at 28 days to 75.0 MPa at 6 years. The hardened samples became more compact with advancing age due to progressive geopolymerization to form the coexisted C–A–S–H and N–A–S–H gels, which explains the lower porosity of the aged geopolymer. An X-ray amorphous phase corresponding to geopolymerization gel was detected in both the early-age and long-term geopolymers, but calcite and natron were present in the aged specimens, indicating that carbonation occurred and the studied geopolymer is vulnerable to carbonation in an atmospheric environment. Despite carbonation, the high stability of the N–A–S–H gels in this relatively low-calcium system and the compact matrix combined to increase the strength.

1. Introduction

The term geopolymer applies to a class of solid materials that are synthesized from the reaction of an aluminosilicate powder with an alkaline solution [1]. Research involving the preparation, geopolymerization, microstructure, performance and applications of geopolymers has been conducted by numerous investigators over the past several decades as a result of the low energy requirements and low CO_2 emissions of the material compared to traditional OPC [2]. Many previous reports demonstrated several desirable performance properties for geopolymers, such as high early-age strength [3], resistance to chemical attack [4] and thermal insulation [5], but the commercial application of the technology to date are limited [1]. One of the two barriers that are responsible for this slow progress is difficulty in determining the durability of concrete that contains geopolymer; structural concretes are required to last for at least several decades, but data on such time scales are not available for the newly developed material [6].

Published laboratory studies on several middle- and long-term laboratory samples are helpful for understanding the service life of geopolymers. Metakaolin-based geopolymer pastes that were continuously cured at 40 °C and 95% RH for 7 months showed a reduction in strength due to crystallization of the originally amorphous material [7], suggesting that long curing periods under elevated temperature should be avoided in the preparation of geopolymers with improved strength.

An increase in strength was observed for a geopolymer that was synthesized from fly ash and metakaolin and cured at 20–25 °C with a relative humidity of 45%–55% for 9 months. However, the strength deteriorated due to gradual precipitation and crystallization of aluminosilicate gels in geopolymers that were contaminated with salts such as KCl and $CaCl_2$ [8]. The incorporation of 20% limestone powder in alkali-activated slag was found to improve the compressive strength following a 560-day curing period that included 1 day at 40 °C and 559 days at 25 °C [9]. In addition to the results described above for air curing, solution-based experiments have also provided useful information for understanding the long-term performance of geopolymers. Although geopolymers are known to be resistant to chemical attack, long-term acceleration results indicated that degradation occurred when samples were subjected to an aggressive solution, such as sulfate for 12 months or acid for 18 months [10,11]. After 2 years of immersion in water, 15% Na_2SO_4 solution, and Dead Sea water, the strength of a pressed specimen that was made of ground porcellanite and quartz sand decreased by 17.5%–20% [12]. As illustrated by these previous studies, the long-term performance, especially the strength, of geopolymers is susceptible to the formulation and curing environment.

Prolonged curing also causes a change in the microstructure and phases of geopolymers. The silicate gel formed by gelation of waterglass was partially consumed to form long, linear Al-substituted C–S–H chains in alkali-activated slag at an early age, but extra Al is likely substituted into the C–S–H to facilitate additional cross-linking at 1 year

[13]. A longer curing age of 3 years not only led to the formation of crystalline phases, such as nacrite, but also resulted in the removal of water that was incorporated during the early geopolymerization process and increased the degree of amorphicity [14]. These changes clearly affect the long-term performance of geopolymers because the evolution of physical characteristics such as strength always depends on composition and structure.

The above-mentioned experimental results make an important contribution to understanding the service properties of geopolymers, but the drastic difference between laboratory and service conditions creates difficulty in directly using laboratory data to assess the service life of geopolymers in real applications. Several attempts have therefore been made to confirm their long-term performance under natural conditions. A negligible carbonation depth value (2 mm), precipitation of $Ca(OH)_2$ in the microcracks that favors the self-healing process, and a highly dense interfacial transition zone were observed in 7-year alkali-activated slag concrete that was cured in open air at 19–38 °C and 70%–76% RH, indicating that well-designed geopolymers have the potential to remain durable and maintain stable microstructures with advancing age [15,16]. An increase in the strength of alkali-activated slag concrete that was manufactured in Kiev, Ukraine between 1964 and 1982 was reported by Hua Xu, et al. [17]. The durability was attributed to the combination of a highly polymerized, relatively low-Ca, amorphous C–S–H outer product, with an inner product that underwent continuous hydration via a cyclic process involving carbonate anions. The longer service data of this geopolymer emphasized its good stability in a natural environment. Concrete made with Purdocement, a commercial product invented by Arthur Oscar Purdon using slag, is vulnerable to carbonation, but the residual mechanical strength was still high after 60 years [18]. These previous studies are suitable only for explaining the long-term performance of alkali-activated slag. Changes to the starting materials require additional studies. In this work, the starting materials, including slag and calcined ore-dressing tailing of bauxite, are different from those of the existing studies. Therefore, it is necessary to investigate the evolution of strength and microstructure and the changes in the products of an aged tailing-slag specimen that was cured in air.

2. Experimental

2.1. Raw materials

The ore-dressing tailing of bauxite (herein referred to as the tailing) was supplied by the Zibo factory of the Aluminum Corporation of China Limited in Shandong province, China. Its chemical composition is listed in Table 1 and the mineral composition is shown in Fig. 1. Note that mullite in the original and calcined tailing results from the addition of fly ash into the mud of the tailing for easier filtering. Further information related to this tailing is available in Jiayuan Ye's [19] work.

Slag powder with a specific surface area of 405 m^2/kg was supplied by the Shougang Group in Beijing, China and used to aid setting at ambient temperature. The chemical composition of the slag is also listed in Table 1.

To obtain a highly active powder, the tailing was heated in a muffle furnace at 800 °C for 1 h. After heating, the kaolinite content changed into an X-ray amorphous phase as a result of dehydration and disordering, which will facilitate the reactivity of the calcined tailing with an alkaline solution. The calcined tailing shows a platelet-like morphology that is a finger-print characteristic of metakaolin, as shown in Fig. 2. Corundum derived from diaspore was detected in the calcined tailing, while other minerals such as anatase and muscovite in the tailing underwent no change. The calcined tailing was ground in a ball mill to a fineness of 10% residue on a 45 μm sieve by weight.

The chemical composition was determined by chemical titration. LOSS is loss on ignition of tailing and slag and was measured at 900 °C to constant weight. $Na_2O_{eq.}$ is the equivalent content of Na_2O and is calculated using the equation $Na_2O + 0.658K_2O$.

A sodium silicate solution was modified using solid sodium hydroxide to modulus (molar ratio of SiO_2 to Na_2O) of 1.80. A well-mixed solution containing 45.77% of solid species was sealed using glass plates and heated to boiling on an electric resistance heater, then the cooled solution was stored at 20 °C in a room for a minimum of 24 h to allow equilibration to be reached prior to use.

ISO quartz sand was provided by China Building Materials Academy (CBMA) and used as the fine aggregate in the mortars. The chemical and physical parameters of the sand such as the particle size are consistent with ISO 679.

2.2. Experimental procedures

The blended powder, which was composed of 70% calcined tailing and 30% slag, was activated using a 20% sodium silicate solution (by weight, but excluding water). After 4 min of mechanical mixing, the mortar with powder/sand ratio of 1/3 and water/powder ratio of 1/2 (including water in sodium silicate solution) was poured into a 40 × 40 × 160 mm mold and then vibrated for 2 min. After 24 h of curing at 95% ± 5% RH and 20 °C ± 1 °C in a chamber, the mortar was removed from the mold and cured under the above conditions for 1 year. Following the ambient and wet curing period, the mortar was moved from the humidity chamber to a base room and stored for an additional 5 years. The relative humidity in the base room varied between 40% and 80% and the temperature ranged from 18 °C to 22 °C from the use of a heater in the winter and an air conditioner in the summer. In order to estimate the strength development during 6 years, a reference of mortars cured in the humidity chamber for 3 days and 28 days is used. It is noted that there is nearly no difference in humidity between base room and the local climate of Beijing, which provides the comparability between laboratory and service condition to some extent.

Pastes with a thickness of 1 cm were prepared using the same mixture and curing procedure as the mortars and used for the XRD, TG-DSC and SEM-EDS analyses.

Three mortars were used for flexural strength testing and the resulting six halves were used to test the compressive strength. The strength tests were performed on a TYE-300D flexural and compressive strength-testing machine (Wuxi Jianyi Instrument, China). The pore parameters of the mortars were measured using a Micromeritics Autopore III 9420. XRD patterns were collected on a Bruker AXS D8-Advance automated diffractometer with Cu-Kα radiation generated at 40 kV and 250 mA, from 5° to 80° at 4° (2θ) per minute and in steps of 0.02° (2θ). TG-DSC was examined using a Netzsch STA 449F3 from room temperature to 1000 °C at 20 °C/min in nitrogen. The cross-section morphology of a freshly fractured paste surface was taken without a carbon or gold film using an FEI QUANTA 250G in the low vacuum mode of 70 Pa. Energy dispersive spectroscopy (EDS) was performed using an OXFORD X-MAX.

Table 1
Chemical composition of the tailing and slag (%, in weight).

	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	MnO	TiO_2	$Na_2O_{eq.}$	SO_3	LOSS	Σ
Tailing	32.24	8.67	37.39	3.15	0.85	–	2.31	0.85	–	13.74	99.20
Slag	33.54	1.17	12.52	37.93	9.29	0.57	0.95	–	2.51	1.25	99.73