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Characterization of natural pozzolan-based geopolymeric binders

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ABSTRACT

Properties and characteristics of fly ash- or slag-based geopolymers have been extensively explored but comparatively less information is available for natural pozzolan-based geopolymers. The present work focuses on microstructural characteristics of natural pozzolan-based geopolymers activated by sodium hydroxide and a mixture of sodium hydroxide and sodium silicate. Synchrotron XRD and SEM-EDS studies combined with compressive strength tests successfully demonstrate the feasibility of the use of natural pozzolan for sustainable construction material. It is concluded that the geopolymers have sufficient strength as structural materials and matrices contain C–S–H like crystal as well as zeolites of hydroxysodalite and zeolite Y. Two zeolites of hydroxysodalite and zeolite Y are found as the main activation products in sodium hydroxide activation. Substitution with sodium silicate solution yields higher compressive strength and a denser microstructure with dominant activation products of C–S–H like crystal, zeolite Y, and phillipsite. It has been proposed that the crystal size of the activation products ranges from 10 nm to 1 μm. Different microstructural characteristics found herein provide a valuable information to develop natural pozzolan-based sustainable structural materials with improved properties.

1. Introduction

Natural pozzolans (also known as volcanic pozzolan) have been widely used as substitutes for Portland cement, because of the advantages of cost reduction and increased durability [1–3]. Natural pozzolan in cement enhances the ultimate compressive strengths by producing additional calcium–silicate–hydrates (C–S–H) and reduces the heat of hydration which is particularly useful in massive-scale construction. Furthermore, the environmental impact of the production of conventional cement offers a new merit to natural pozzolan as a supplementary cementitious material. For instance, natural basaltic pozzolan from Saudi Arabia has been reported as a possible replacement of 25 mass% Portland cement [4]. Portland cement-based ternary and quaternary blends containing fly ash, silica fume, blast-furnace slag, and natural pozzolans can also be utilized by optimizing their mixing proportions [5].

On the other hand, geopolymers have emerged as a new promising alternative for ordinary Portland cement. Not only it has lower environmental impact but it also has advantages of high compressive strength, low shrinkage, fast setting, and low thermal conductivity [6–8]. Considerable research have been done to investigate the possibility of utilizing various industrial by-products and natural raw materials for the production of geopolymer cements. Aluminosilicate materials including granulated blast-furnace slag and fly ash and calcined natural mineral of kaolinite have been reported as possible candidates for the geopolymer production. The fundamental properties and structural characteristics of geopolymers derived from fly ash, slag, and metakaolin have been investigated regarding raw material selection, solution types, curing conditions, and resulting microstructures [7–9]. When the aluminosilicate raw materials are activated by alkalis, complex chemical and physical reactions result in the formation of geopolymer. The structure of main binding matrix in geopolymer is known to be similar to synthetic or natural crystalline zeolites but it is mostly amorphous [7,10–12].

Although natural pozzolans are also aluminosilicate materials, the use of natural pozzolans as a geopolymer was recently reported. Alkali-activated Taftan pozzolan in Iran was found to be suitable for construction applications [13,14]. A mixture of sodium hydroxide and waterglass produced the formation of a geopolymer binder with appropriate workability. As subsequent research on geopolymerization of the Taftan pozzolan, the effect

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Table 1
Chemical composition of natural pozzolan.

Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	LOI
wt.%	3.39	8.73	14.74	46.48	0.629	1.27	8.78	2.31	0.19	12.16	1.324

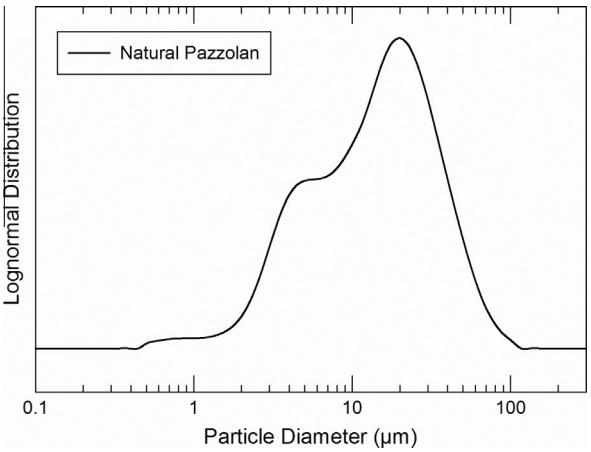

Fig. 1. Particle size distribution of natural pozzolan.

of various curing conditions and engineering properties of geopolymer concrete were investigated for practical applications [15,16]. In addition, the effect of mineral additives including kaolinite, lime, and slag [17,18] and heat treatment on Taftan pozzolan [19] were lately studied. However, the reactive components of the pozzolan and associated hydration products have not been described in detail.

As a supplementary material for Portland cement, the mechanism of natural pozzolan in concrete is well understood, which can be explained as so-called pozzolanic reaction [1–3,20,21]. However, the use of natural pozzolan as a full cement replacement is still being explored. Especially, previous study on geopolymerization of natural pozzolan is only limited to one case of Taftan addesite from Iran [14,17,22]. The present work describes the potential use of natural volcanic pozzolan from Saudi Arabia as a construction material for the production of geopolymer cements. Since this new type of alkali-activated geopolymer cement will have different chemistry from fly ash- or slag-based geopolymer, microstructural characterization is vital to understand mechanical behavior, durability, and binding characteristics of the gel with aggregates. This work, therefore, examines the properties of alkali-activated natural pozzolan-based geopolymers by focusing on the microstructure using high-resolution synchrotron X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS), and compressive strength tests.

2. Experimental methods

2.1. Materials

Natural pozzolanic material from basalt fields in the Kingdom of Saudi Arabia was used in this study. During strombolian-type volcanic explosions, numerous pyroclastic cones with basaltic lava fields were formed in Harrats, Saudi Arabia. Although the basaltic ash deposits are widespread in the Harrats, a few industrial applications of it have been reported. One of the applications is used as a lightweight coarse aggregate [23]. The pozzolan also satisfies the requirements of ASTM C618 for Class N natural pozzolan for

Table 2
Mixture proportions of activated samples (s/b = 0.45).

Label	Natural pozzolan (g)	NaOH solution (10 M, g)	Sodium silicates (Ms = 3.22, g)	Curing temperature (°C)
NP + SH	300	135	0	80
NP + SH/WG	300	108	27	80

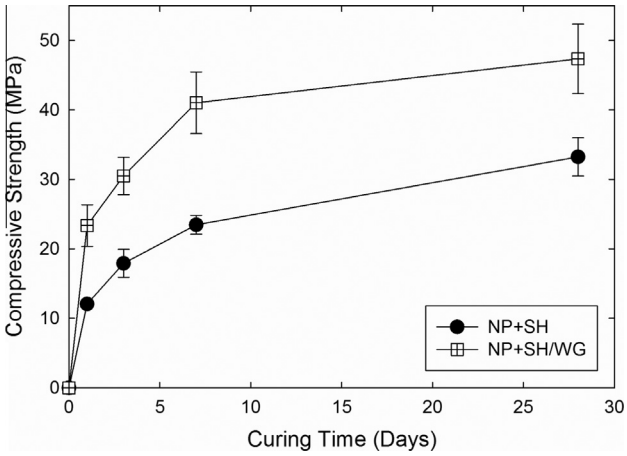

Fig. 2. Strength development of alkali-activated natural pozzolan.

supplementary cementitious materials [24–26]. Bulk density, specific gravity, and absorption properties of it were previously investigated [26,27]. Petrographic and XRD studies found a gel-palagonite as the most abundant component and other crystals of forsterite, anorthite, and diopside as minor phases [27]. The bulk chemical composition of the natural pozzolan was determined using a Phillips X-ray fluorescence (XRF) spectrometer and is given in Table 1. The natural pozzolan has more Ca content (i.e., CaO 8.78 mass%) than typical Class F fly ash but it is less than Class C fly ash. Particle size distribution of ground natural pozzolan is shown in Fig. 1 [27].

2.2. Sample preparation

The ground raw materials were activated with 10 M analytical grade sodium hydroxide solution (SH) (Fisher Scientific, S318-1) and a mixture of 80 mass% of sodium hydroxide solution and 20 mass% of sodium silicate solution (SH/WG) (PQ Corporation, N®38, also known as waterglass). The provided mass ratios are SiO_2/Na_2O = 3.22, mass% of Na_2O = 8.2, mass% of SiO_2 = 26.4, and mass% of H_2O = 65.4. The solution to binder (s/b) ratio was kept as 0.45. Curing condition of 80 °C and 100% RH was selected. In cases of fly ash- and slag-based geopolymer, the geopolymer binder is known to be synthesized in a temperature range of 20–90 °C. More amorphous phases are expected at low temperature and more crystalline at higher temperature [6]. As a feasibility study, 80 °C and 100% RH were chosen for enhanced characterization of activation products. All samples were cast in cylindrical