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Synthesis of mesoporous geopolymers containing zeolite phases by a hydrothermal treatment

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ABSTRACT

The present study investigates the synthesis of mesoporous geopolymers containing different nanocrystalline zeolite phases. A hydrothermal treatment procedure was utilized to synthesize the mesoporous geopolymers using fly ash, slag and alkaline solution. The effects of slag addition and molar ratio of alkaline solution on the microstructure and mechanical strength of the geopolymers were investigated and evidenced by XRD analysis, compressive strength and nitrogen adsorption tests. The test results showed that the geopolymers incorporating fly ash and slag consisted of Na-P1 and Sodalite zeolite phases, and had the characteristic of mesoporous materials ($2 \text{ nm} < \text{pore size} < 50 \text{ nm}$) in which capillary condensation may occur. The highest compressive strength of the geopolymers was 16.57 MPa, and the desired mesoporous characteristics were met by adding 20% slag content to fly ash and adopting the hydrothermal process at a relatively low temperature. The highest BET surface area and single point adsorption pore volume of the mesoporous geopolymers were 114.16 m^2/g and 0.2677 cm^3/g, respectively.

1. Introduction

Geopolymers, first introduced by Davidovits in 1978 [1], are inorganic aluminosilicate binders synthesized by the alkali-activation of materials containing Al_2O_3 and SiO_2, i.e., kaolinite clays or industrial byproducts (e.g., fly ash or slag) [2]. These binders provide a better alternative to OPC due to their lower environmental footprints and reduced CO_2 emissions into the atmosphere, compared to the cement industry [3–6]. A number of studies have reported the effects of different parameters, i.e., the raw materials, composition of the alkali-activator, or the alkali-activator/binder ratio, on the properties of geopolymers [7–11].

The mechanism of geopolymerization includes the following steps: (1) the dissolution of Si and Al in an alkali medium (through hydrolysis), (2) the condensation of the dissolved species into monomers, and (3) polycondensation into polymeric structures, which is similar with the mechanism of zeolite formation apart from several differences in the synthesis conditions [12–14]. However, geopolymers are amorphous to semi-crystalline aluminosilicate gels, while zeolites have well-developed nano-crystalline structures [12,15]. Due to similar mechanisms, zeolitic structures are often detected in geopolymeric gels [16,17]. Given the similarity of the raw materials and the chemical compositions of geopolymers to those of zeolites, geopolymers are often regarded as zeolite precursors from which zeolites can be synthesized by a hydrothermal treatment [18–20]. As geopolymers and zeolites are suitable for different applications owing to their structural differences, hybrid geopolymer-zeolite materials can have synergic effects while complementing one another; geopolymers has high mechanical strength and zeolites has a high absorption capacity.

Hybrid geopolymer-zeolite materials have interesting potential applications, such as for humidity control in buildings [21], as self-supporting zeolite membranes [22,23] or as zeolite molecular sieves for the adsorption of heavy metals [24]. Despite the high potential for different applications, zeolite-geopolymer hybrid materials have not received much attention from the research community [25]. To date, a limited number of studies have reported the transformation of an amorphous geopolymer gel into crystalline zeolites [12,13,20,21,24–27]. Provis et al. [25] conducted a detailed analysis of existing results to confirm the presence of

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zeolitic nanocrystals in an amorphous geopolymer gel phase. The authors concluded that the crystals on the lengths scale of 2–5 nm were only detectable by electron diffraction experiments and not by XRD.

Given that the formation of zeolitic phases can significantly alter the potential of geopolymers for different applications [12], investigations of conditions, suitable for the formation of zeolites in geopolymers are important. Criado et al. [20] used four types of alkaline solutions having different silica contents where lower SiO_2/Na_2O ratio (0 and 0.19) led to the increase in crystallinity. The compressive strength of fly ash-based geopolymers decreased as the crystalline content increased [12]. There was a correlation between compressive strength and Si/Al ratio of raw material (kaolinitic clays) and zeolite crystalline size [21]. Recently, Qiu et al. [24] used fly ash to synthesize zeolite P in geopolymer blocks, which can be used as molecular sieves or for the adsorption of heavy metals. The optimum conditions were found to be 24 h of hydrothermal treatment at 100 °C with 2 mol/L of a NaOH solution.

The literature on the formation of crystalline zeolite in amorphous geopolymers remains very limited, especially studies considering hydrothermal treatment. To determine the potential benefits of these highly promising materials, more detailed and representative studies should be conducted (e.g., the effects of different parameters on the crystalline content and structure). Therefore, in the present study, geopolymers with crystalline zeolites were synthesized, as this material has the potential to be used as a zeolite sieves for the adsorption of heavy metals, or for the purification of water. This study explored the effects of addition of slag and the molarity of the NaOH solution on the microstructure and compressive strength of the geopolymers. A simple method for the synthesis of hybrid geopolymer-zeolite materials that may save time and energy is also proposed.

2. Experimental program

2.1. Materials and mix proportion

In this study, Class F fly ash and blast furnace slag (BFS) were used as binder materials. The Class F fly ash (classified according to ASTM C 618 [28]) and the blast furnace slag were obtained from a coal power plant and a steel plant, respectively, both of which were located in South Korea. Their chemical compositions are listed in Table 1.

The alkaline solution used was a mixture of a chemical-grade sodium hydroxide solution and commercial water glass (Korean industrial standards (KS) Grade-3; SiO_2 (29%), Na_2O (10%), H_2O (61%), with a specific gravity of 1.38 g/mL) with a ratio of the water glass to NaOH solution of 0.5 in accordance with the procedure developed by Lee and Lee (2013) [5]. NaOH solutions with different concentrations (8 or 12 mol/L) were prepared by adding solid NaOH pellets with a purity level of 98% to distilled water. The ratio of the alkaline solution to the binder was close to 1.0 for all of the specimens.

Table 1
Chemical composition of the raw materials.

Oxide (wt.%)	Fly ash (FA)	Blast furnace slag (BFS)
CaO	4.79	47.7
SiO_2	57.0	32.4
Al_2O_3	21.0	11.5
Fe_2O_3	9.97	0.561
SO_3	1.03	2.66
MgO	1.29	2.98
TiO2	1.45	0.518
K_2O	1.35	0.501
P2O5	1.45	0.642

Sample names (C, S0, S40, CM, CSS and T) are denoted with specific codes. Sample 'C' represents the control sample, with 20% of fly ash replaced with slag. S0 and S40 represent the samples with slag contents of 0 and 40%, respectively, to investigate the effects of the slag addition. CM and CSS were activated with different types of alkaline solutions, i.e., in CM, the molarity of the NaOH solution was 8 mol/L, while CSS was synthesized with only 12 mol/L of the NaOH solution without any water glass. T was identical to control sample C except for the different curing conditions.

The method of manufacturing the mesoporous geopolymers was as follows; after mixing fly ash and slag with the alkaline solution, the geopolymer pastes were casted into 25 mm cubic molds. Immediately after the casting process, the molds were sealed and two curing methods were utilized to synthesize the mesoporous geopolymers. The first of these was a two-step method in which the geopolymer pastes (C, CM, CSS and S0) were initially cured at 80 °C and at a relative humidity of 95 ± 5% for 24 h. The samples were then treated by a hydrothermal method at 90 °C for an additional 24 h in an autoclave. The second method was a one-step method in which the geopolymer paste (Sample T) was directly put into an autoclave for a hydrothermal treatment after mixing the fly ash and slag with an alkaline solution for about 10 min.

2.2. Experimental details

X-ray diffraction (XRD), scanning electron microscopy (SEM), and nitrogen gas (N_2) adsorption-desorption tests were utilized to investigate the evolution of the crystalline phases in the mesoporous geopolymers and to examine their microstructure. Compressive strength tests were also performed at the ages of 3 and 28 days to check for any improvement in the mechanical strength of the samples.

Powdered samples for the XRD test were prepared by mechanical grinding. The XRD data were recorded on a Rigaku SmartLab machine using Cu Kα radiation at a scanning rate of 1°/min from 5° to 70° in the 2θ mode. Powder diffraction analysis software (Rigaku, PDXL2) was used for phase identification and for the quantitative phase analysis. N_2 adsorption tests and SEM investigations were conducted at a curing age of 28 days. After the 28-day compression tests, fractured samples were used for the N_2 adsorption test and for a SEM analysis. For the N_2 adsorption test, nearly spherical specimens were prepared with diameters of less than 1 cm, while relatively flat samples were prepared for the SEM analysis. These were coated with gold as well.

The textural properties of the samples were investigated using an ASAP 2020 device by Micromeritics. The parameters of the specific surface area, pore volume, and pore size distribution were measured at -195.85 °C by analyzing the N_2 adsorption/desorption isotherms. The specific surface area was determined based on the Brunauer–Emmett–Teller (BET) method at a p/p0 value between 0.06 and 0.3 (p and p0 are the equilibrium and saturation pressures of nitrogen, respectively). The pore volume (V_p) was determined from the volume of adsorbed nitrogen at a p/p0 pressure ratio of 0.9891. The pore diameters (D_p) were calculated in accordance with the following formula: $D_p = 4V_p/S_{BET}$, where S_{BET} is the BET surface area. A nitrogen sorption analysis was also conducted to calculate the pore volumes and pore size distributions via the Barrett–Joyner–Halenda (BJH) method.

2.3. Compressive strength of mesoporous geopolymers

Fig. 1 shows the compressive strength results of the geopolymer samples measured at 3 and 28 days. The highest strength was