

The influence of process conditions on ground coal slag and blast furnace slag based geopolymer properties

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Preliminary communication



Quyen V. Trinh^{1,2}; Gábor Mucsi³; Thai V. Dang^{1,2}; Ly. LePhuong⁴; Van H. Bui⁵; Sándor Nagy³

¹Institute of Theoretical and Applied Research, Duy Tan University, Hanoi, 100000, Vietnam

²Faculty of Environmental and Chemical Engineering, Duy Tan University, Da Nang, 550000, Vietnam

³Institute of Raw Material Preparation and Environmental Processing, University of Miskolc, H-3515 Miskolc Egyetemváros, Miskolc, Hungary

⁴Institute of Concrete Technology, Nghia Tan, Cau Giay, Hanoi, 100000, Vietnam

⁵Faculty of Physics, VNU Hanoi University of Science, 334 Nguyen Trai, Hanoi, 100000, Vietnam

Abstract

In this study, the material characterization of Vietnamese ground coal slag and ground granulated blast furnace slag (GGBFS), such as particle size distribution, chemical composition, bulk density and particle density are shown. The geopolymer specimens were prepared by mixing an 80 m/m% mass of solid materials (ground coal slag and GGBFS in a different ratio) with 20 m/m % of a 10M NaOH alkaline activator. A systematic experimental series was carried out in order to optimize the preparation process. In that series, the heat curing temperature was 60°C for 6 hours, and then selected specimens were heat treated at a high temperature (1000 °C) for 1 hour. After 7 days of ageing, the physical properties of the geopolymer (compressive strength, specimen density) were measured. Also, after 180 days of ageing, the pH values of water in the geopolymer leaching preparation were determined. The results show that the geopolymer can be used for refractory applications due to its good heat resistance properties. However, geopolymers that were heated at 1000 °C had lower compressive strength, specimen density and pH values of water containing the geopolymer than those that were cured at 60 °C.

Keywords:

Coal slag, blast furnace slag, compressive strength, geopolymer.

1. Introduction

Davidovits (1988, 1994) proposed that certain alkaline liquids could be used to react with the silicon (Si) and aluminum (Al) bearing phases of various raw materials of geological origin or with by-product materials to produce binders. Since the chemical reaction that takes place in this case is a polymerization process, he coined the term ‘geopolymer’ to represent these binders.

The fire-resistant character of geopolymers has led them to be suggested for use in applications where fire damage can be critical for the structure or its occupants. Special geopolymer formulations are suitable for refractory applications. Low water content and highly pure geopolymers suit industrial refractory applications where the material may be subjected to temperatures in excess of 1200 °C (Riessen et al., 2009).

Blast furnace slag (abbreviated GGBFS, for ‘ground granulated blast furnace slag’) is broadly described as a mixture of poorly crystalline phases with compositions resembling gehlenite ($2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$) and akerman-

ite ($2\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2$), as well as depolymerized calcium silicate glasses (Tsuyuki and Koizumi, 1999). The degree of depolymerization largely controls reactivity. As slag is generated at a high temperature as a liquid in the blast furnace during iron production and subsequently quenched, its composition is essentially that of an overcharge-balanced calcium aluminosilicate framework - i.e., there is more than sufficient calcium available to charge-balance aluminum, with the remainder contributing to depolymerizing the glass network (Duxson, 2009).

Villarreal et al. (2011) studied that the existence of an optimum curing temperature, 60 °C to obtain the best geopolymerization process for their circumstances. According to our previous research Trinh et al. (2019) in the case of ground coal slag (maximum particle size 262 μm) based geopolymer, the optimal conditions were as follows: 80 m/m% ground coal slag and 20 m/m% of 10M NaOH, which resulted in the highest compressive strength (7.45 N/mm²).

Do et al. (2019) studied fly ash-based geopolymer concrete using a sodium silicate solution and seawater. They had very good performance with a value of 180 day-compressive strength of 58 MPa, water absorption

Corresponding author: Quyen V. Trinh
trinhvanquyen@duytan.edu.vn

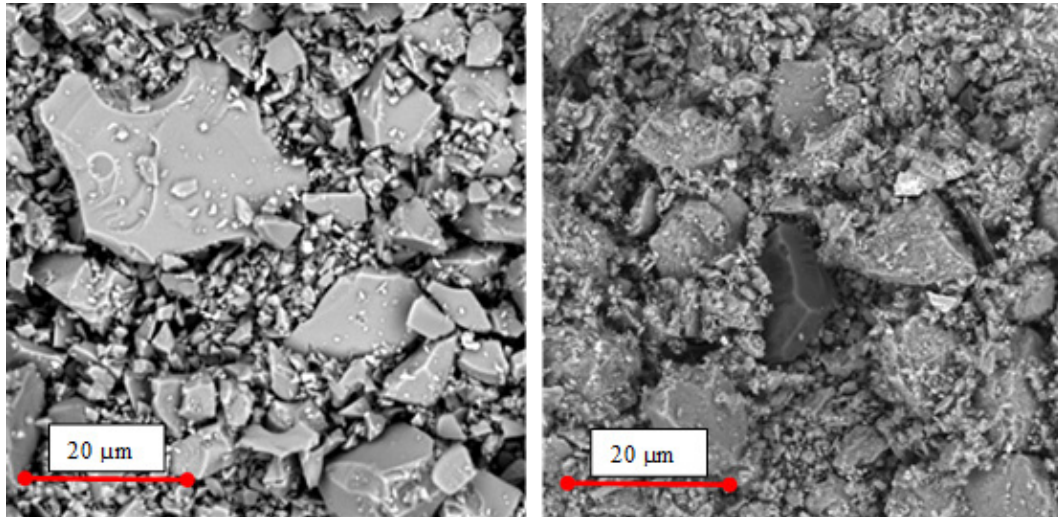


Figure 1: Scanning electron micrographs of GGBFS (left) and ground coal slag (right)

and volumetric weight were 180 kg/m^3 and 2200 kg/m^3 , respectively. The effect of steel slag substitution as a coarse aggregate on compressive strength in fly ash based-geopolymer concrete was studied by **Ashadi et al. (2015)**. The corrosion rate of geopolymer concrete with a steel slag substitution was found to be lower compared to normal geopolymer concrete. The corrosion rate was found to be very high at an early stage and decreased with time.

Based on the Decision No 428/QĐ-TTg, the **Prime Minister** of Vietnam approved the adjustment of the National Power Development Plan VII, on March 18th, 2016, total fly ash, coal slag generated from thermal power plants by 2020 is estimated at 22.6 million tons per year. In Vietnam, the iron and steel industry has developed rapidly and therefore the generation of blast furnace slag increases considerably. The annual production is predicted to exceed 7 million tons in 2020 (**Le, 2016**). According to **Kumar et al. (2015)**, the different size fractions of fly ash collected from different hoppers have significant variations in chemistry, mineralogy, particle size distribution and glass content. **Bedekević et al. (2019)** reported that a non-structural polystyrene concrete can be produced by using waste granulated expanded polystyrene. The strength and bulk density of polystyrene concrete increases with an increase in the proportion of sand and cement.

Petlovanyi et al. (2019) investigated the use of man-made formations and the recycling of the valuable extracted components (including microspheres), such as an active mineral admixture and small aggregate in light, heavy concrete and artificial cement, an analog for clay parts in the production of a cement clinker, and the production of ceramic bricks, a component for the preparation of hardening backfill. **Krupnik et al. (2020)** studied whether or not polymer concrete is able to replace metal as the transfer case component in production. Actually, it has a number of advantages: less product weight, high

strength, and resistance to corrosion. **Kumar et al. (2005)** proved that the addition of mechanically activated slag to a clinker and replacing the clinker with ground slag can produce better compressive strength and a better hydration reaction.

Mucsi et al. (2014, 2015, 2019) reported that the optimum NaOH concentration of the alkaline activator was 8 M for 60 °C heat treatment (the maximum compressive strength was 14.3 MPa) and 10 M for 90°C in cases of ground fly ash base geopolymers. Geopolymerization of mechanically activated fly ash has been carried out with various proportions of red mud ranging between 0 - 30% by weight, and the compressive strength of fly ash based geopolymers increased with the addition of up to 15% of red mud. A strong relationship was shown between the geopolymer physical property (compressive strength) and fly ash fineness (median particle size, specific surface area) and relative span. **Nguyen and Chu,**

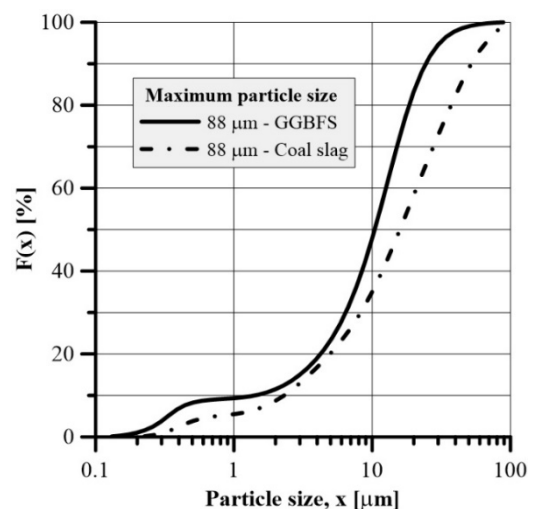


Figure 2: Particle size distribution of ground coal slag and GGBFS samples

(2020) revealed that 30% GBFS in the replacement of cement is suitable content in this sand concrete.

Therefore, in order to ensure the stable operation of coal-fired power plants and different steel plants, it is necessary to urgently seek solutions to consume coal slag, fly ash and blast furnace slag which continue to arise and exist in the storage areas. Based on the above problems, the goal of our research was to optimize the production process of coal- and metallurgical slag based geopolymers.

2. Materials and methods

2.1. Materials

Ground coal slag and ground granulated blast furnace slag (GGBFS) were selected for the production of building materials and reducing environmental pollution. Coal slag which originated from the Quang Ninh province and Vietnam (Mao Khe Thermal Power Plant), and GGBFS which originated from the Hai Duong province and Vietnam (Hoa Phat Hai Duong steel joint stock company) were used for our experiments.

Each type of raw material was analyzed through scanning with an electron microscope (see **Figure 1**). It can be observed that the ground coal slag and GGBFS are regularly shaped with a spherical form and compact structure.

The particle size distribution of ground coal slag and GGBFS samples were determined using a Horiba LA950 V2 type laser particle size analyzer, as shown in **Figure 2**. Specific surface areas were calculated by laser sizer software. In the case of ground coal slag, the characteristic particle size values were as follows: $x_{10} = 2.3$ mm, $x_{50} = 15.8$ mm, $x_{90} = 52$ mm, and the specific area was 14533 cm²/g. In the case of GGBFS, these values were $x_{10} = 1.4$ mm, $x_{50} = 10.4$ mm, $x_{90} = 24$ mm, and the specific area was 25655 cm²/g.

Based on XRF (type: Supermini200) analysis, the measured chemical composition of GGBFS and ground coal slag are given in **Table 1**. Analysis of the SiO₂/AlO₃ ratio determined it was 2.2 and the sum of the SiO₂, Al₂O₃ and Fe₂O₃ content of the ground coal slag was 82.51 m/m%. In the case of GGBFS, the SiO₂/AlO₃ ratio was 3.8 and the sum of the SiO₂, Al₂O₃ and Fe₂O₃ content of the ground coal slag was 49 m/m%. The GGBFS is a nonmetallic product, consisting essentially of silicates and aluminosilicates of calcium and other bases. The major oxide phases consist of SiO₂, CaO, Al₂O₃, and MgO. Others minor oxides are: Fe₂O₃, Na₂O, TiO₂, and P₂O₅.

In the determination of the loss on ignition (L.O.I.), 1.0 g of a burned powder sample was used, every sample was analyzed 3 times, and these values were averaged. The values were 2.5 m/m% in the case of GGBFS and 3.52 m/m% in the case of ground coal slag.

Table 1: Chemical composition, moisture content and density of the GGBFS and coal slag

Components	Mass concentration [m/m%]	
	GGBFS	Coal slag
SiO ₂	38.7	54.4
Al ₂ O ₃	10.2	24.2
MgO	7.35	1.40
CaO	28.7	1.30
Na ₂ O	0.36	0.43
K ₂ O	1.08	3.59
Fe ₂ O ₃	0.15	3.91
MnO	1.31	0.029
TiO ₂	0.36	0.781
P ₂ O ₅	0.029	0.077
S	1.49	1.17
F	< 0.3	< 0.3
Moisture content	4 m/m%	3.3 m/m%
Bulk density	1068	1537 kg/m ³

2.2. Experimental procedure

2.2.1. Geopolymer production

The geopolymer samples were produced by mixing an 80 m/m% mass of materials (including ground coal slag and GGBFS in different ratios) with 20 m/m% of 10M NaOH. The compacted mixture was kept in molds for 24 hours insulated at ambient temperature. One part of the geopolymer was heat cured at 60°C for 6 hours by oven and the other part of the geopolymer was heat treated at a high temperature (1000 °C) for 1 hour in a furnace. After that, the specimens were cooled down to ambient temperature. The compressive strength tests were carried out using a Compression Testing Machine after a period of 7 days. The pH values of geopolymer leaching were measured in the case of heat treated at 60 °C, 1000 °C and 180 days old.

2.2.2. Measurement of density and compressive strength

The geometric parameters of the cubic samples were measured by a Vernier caliper, mass was measured, and density was calculated. For compressive strength, 20 x 20 x 20 mm cubic samples were prepared by vibro-casting of geopolymer paste. Compressive strength was tested on an Automatic Compression Testing Machine SZF-1 type hydraulic 7 days after casting the samples at 27°C followed by curing at 60 °C for 6 hours and heating at a high temperature (1000 °C). The average from three samples was determined for each result.

2.2.3. The pH measurement

For the ground coal slag and GGBFS, each geopolymer sample at 60 °C, 1000 °C and 180 days old was soaked with 50ml of distilled water for 10 days. Then the

pH values of water in the geopolymer leaching preparation were measured by a pH meter (type HI 3220).

3. Results and discussion

3.1. Ground coal slag and GGBFS based geopolymer

In this part, the geopolymer samples are shown in **Figure 3**. The research results are presented focusing on the relationship between geopolymer heating at a high temperature with those mechanical properties. In the case of geopolymer cubic specimens which were cured at room temperature for 7 days, the geopolymer made at 60 °C had a better interface than those made at 1000 °C. However, it was observed that a white powder (efflorescence) appeared on the geopolymer surface, when the geopolymer made of 100% GGBFS was heat treated at 60 °C and after 180 days of ageing, while efflorescence has not appeared on the geopolymer surface when the geopolymer made of 100% GGBFS was heat treated at 1000 °C and after 180 days of ageing.

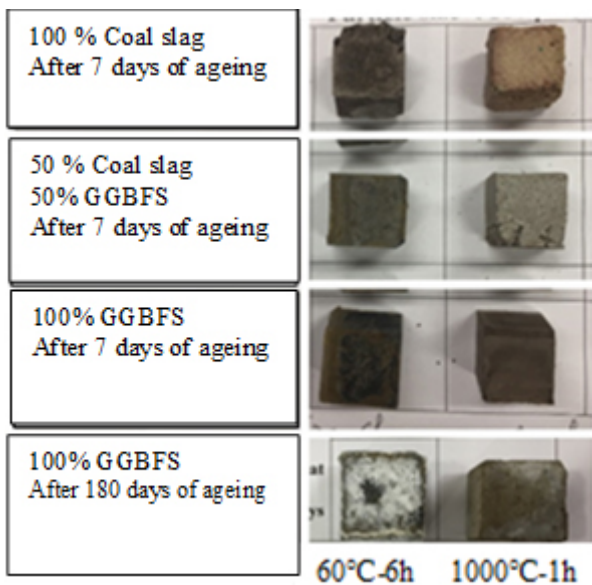


Figure 3: Geopolymer cubic specimens produced from ground coal slag and GGBFS

The reason for this may be the high amount of Na in the geopolymer, which has been released from the geopolymer sample in the case of 60 °C heat treated after 180 days of ageing. Otherwise, the excess Na exists in the geopolymer and is built into the structure due to the high temperature treatment (1000 °C).

It was observed that an increase in the GGBFS mass ratio resulted in higher compressive strength and density of geopolymer cubic specimens. In the case of specimens heat cured at 60 °C, the highest compressive strength (CS) was 49 N/mm², and the highest specimen density (SD) was found to be 2.15 g/cm³, which was for

a 100% GGBFS mass ratio. The lowest compressive strength (30 N/mm²) and the lowest specimen density (1.69 g/cm³) was for a 100% ground coal slag. In the case of specimens heat-treated at 1000 °C, the highest compressive strength was 45 N/mm², and the highest specimen density was 2.14 g/cm³, which was for a 100% GGBFS mass ratio. The lowest compressive strength was 25 N/mm² and the lowest specimen density was 1.64 g/cm³, which was for a 100% ground coal slag (see **Figure 4**).

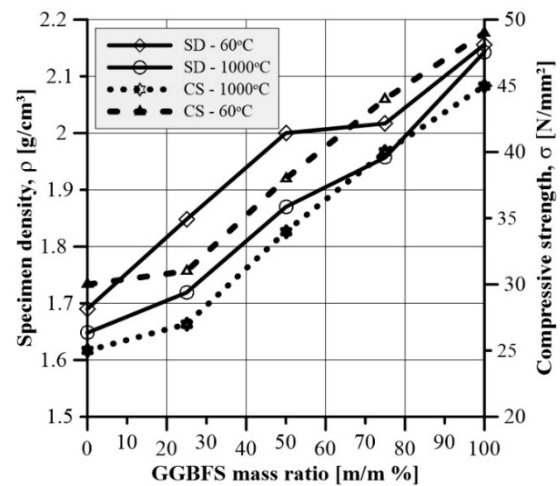


Figure 4: Effect of GGBFS mass ratio on the geopolymer mechanical properties

The reason for that is that generally, GGBFS was effectively used as a mineral admixture in modifying the microstructure of geopolymers and also in the polymerization process. It also developed very good binding properties with alkaline liquids to yield a better strength and alkali activation process (**Rajarajeswari and Dhinakaran, 2016**).

3.2. The influence of pH on the leaching behavior of geopolymers

In the case of the geopolymer cubic samples kept at 1000 °C for 1 hour, geopolymers made from a higher GGBFS mass ratio had higher pH values of water in the geopolymer preparation. In the case of the difference in heating temperatures, geopolymers which were heated

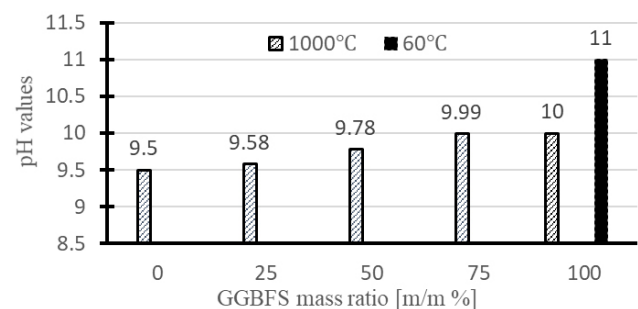


Figure 5: The pH values of water in the geopolymer leaching

at 1000 °C had lower pH values than those that were cured at 60 °C (see **Figure 5**).

The reason for that is the fact that the thermal treatment temperature influences the pH values of the aluminosilicates. The higher the temperature, the lower the pH values of the geopolymer (**Davidovits, 2008**).

4. Conclusions

The present study investigated the compressive strength of ground coal slag and GGBFS based geopolymer (mixing 80 m/m % mass of solid materials with 20 m/m % of 10M NaOH alkaline activator) cured at 60 °C and heat treated at 1000 °C, after 7 days of ageing. Additionally, the pH values of water in geopolymer leaching were determined after 180 days of ageing.

If the same production condition (after 7 days of ageing, 20 % m/m of 10M NaOH), the increase in the GG-BFS mass ratio resulted in a higher compressive strength (25 - 45 MPa range at 1000 °C; 30 - 49 MPa range at 60 °C), pH values of water in the geopolymer leaching (9.5 - 10 range at 1000 °C) and specimen density of geopolymer cubic specimens (1.64 - 2.14 kg/m³ range at 1000 °C; 1.69 - 2.15 kg/m³ range at 60 °C). The geopolymer cubic specimens kept at 1000 °C had lower values of water pH in geopolymer leaching, compressive strength, and specimen density than those kept at 60 °C.

In the case of geopolymer cubic specimens, which were cured at room temperature for 180 days, the relationship between the geopolymer interface and the heating temperature were determined. Geopolymer quality can be improved by thermal treatment at 1000 °C (the efflorescence did not appear on the geopolymer surface). Therefore, the optimal production process was 100% GGBFS content geopolymer consisting of 80 m/m % of GGBFS with 20 m/m % of 10 M NaOH and heat treated at 1000 °C.

The addition of sea-water and water-glass to the activator solution in the case of a GGBFS and a ground coal slag based geopolymer should be studied in future work.

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SAŽETAK

Utjecaj uvjeta postupka dobivanja mljevene troske taljenjem ugljena u visokoj peći uz uporabu geopolimera

U ovome istraživanju donose se obilježja vijetnamskih granulata ugljene troske i troske željezne rude na osnovi njihove veličine, kemijskoga sastava i gustoće. Uzorci geopolimera pripremljeni su miješanjem 80 % m/m (mase otopljenoga / masa otopine) ugljene i željezne troske (u različitim omjerima) s 20 % m/m 10M NaOH kao alkalnoga aktivatora. Sustavnim serijama eksperimenata optimiziran je postupak pripreme, pri čemu je temperatura iznosila 60 °C tijekom 6 sati, nakon čega su odabrani uzorci zagrijavani 1 sat na 1000 °C. Nakon sljedećih 7 dana izmjerena su fizička svojstva geopolimera (tlačna čvrstoća, gustoća). Zatim je poslije 180 dana određena pH-vrijednost vode korištene u postupku ispiranja geopolimera. Rezultati su pokazali kako geopolimeri mogu biti korišteni za namjene u vatrostalnim uvjetima zahvaljujući toplinskim svojstvima. Također, geopolimeri koji su zagrijavani na 1000 °C imaju niže vrijednosti tlačne čvrstoće, gustoće i pH-vrijednosti vode u njima od onih koji su grijani na 60 °C.

Ključne riječi:

ugljena troska, troska visokih peći, tlačna čvrstoća, geopolimer

Author's contribution

Quyen V. Trinh (Ph.D) initialized the idea, completed literature review and participated in all work stages, such as data analysis and tested its accuracy. **Thai V. Dang** (Ph.D); **Ly P. Le** (Ph.D); **Van H. Bui** (Ph.D) participated in compressive strength and pH measurement. **Gábor Mucsi** (Associate Professor) and **Sándor Nagy** (Associate Professor) managed the whole process and supervised it from the beginning to the end.