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Mechanical, Swelling, and Thermal Properties of Geopolymer Mixture Containing Basic Oxygen Furnace Slag Aggregates

Aizhan Tukaziban[1,a], Chang-Seon Shon* [1,b], Islam Orynbassarov[1,c], Saken Sandybay[1,d], Daniyar Syzdykov[1,e] , Dichuan Zhang[1,f], and Jong Ryeol Kim[1,g]

[1]Department of Civil and Environmental Engineering, School of Engineering and Digital Sciences, Nazarbayev University, 53 Kabanbay Batyr Ave., Nur-Sultan, Kazakhstan, 010000

[a]aizhan.tukaziban@nu.edu.kz, [b]chang.shon@nu.edu.kz, [c]islam.orynbassarov@nu.edu.kz, [d]saken.sandybay@nu.edu.kz, [e]daniyar.syzdykov@nu.edu.kz, [f]dichuan.zhang@nu.edu.kz, [g]jong.kim@nu.edu.kz

Abstract. Basic oxygen furnace slag (BOFS) is a waste product generated during steel production. The utilization of BOFS in construction applications is considerably limited because of its inherent characteristics leading to volumetric expansion behavior caused by the chemical reaction between free lime (f-CaO) and water. The main objective of this paper is to investigate the material properties of normal mortar and geopolymer mixtures that contain BOFS aggregates. Three different aggregates were used to compare their performance, including siliceous river sand, fresh BOFS aggregate (within 1-month age), and stockpiled (more than 5-year age) BOFS aggregate. Test methods included a compressive strength test, accelerated mortar bar expansion test, and thermal conductivity test. Test results revealed that (1) geopolymer mixtures containing BOFS aggregate had comparable compressive strength with mortar mixture with river sand, (2) geopolymer mixtures have very low volume expansion, (3) thermal conductivity of geopolymer mixtures having both river sand and BOFS was lower than normal cement mortar mixture containing river sand. Therefore, geopolymer technology seems a key solution for converting BOFS slag into valuable construction materials. Therefore, a geopolymer mixture containing BOFS aggregate can be used as an energy-saving material.

1. Introduction

Steel slags are industrial wastes produced in the steelmaking process. Depending on the type of furnace employed, different types of steel slags are generated [1]. These include blast furnace slag (BFS), basic oxygen furnace slag (BOFS), electric arc furnace slag (EAFS), and ladle slag (LS). Since landfilling these wastes can lead to environmental pollution, many efforts have been made over the past two decades to use these steel slags in construction applications, reducing environmental impact due to their resource-conservation and energy-saving properties. For example, the utilization rate of these slags reaches 98,4% in Japan, and 87,0% and 84,4% in Europe and USA, respectively [2]. Although Kazakhstan produced 355 thousand tons of steel in 2021, the utilization rate of steel slags is too low [3].

It is typically known that 100-200 kg of BOF slag might be generated per ton of steel produced depending on the used raw material [4]. However, the utilization of BOFS as aggregate components in construction applications is considerably limited since its inherent characteristics contain free lime (f-CaO) and free magnesia (f-MgO). In the presence of water, f-CaO and f-MgO from BOFS form calcium hydroxide (Ca(OH)2) and magnesium hydroxide (Mg(OH)2), causing volume expansion up to 127% [5]. One of the ways to minimize this volumetric expansion of BOFS may be to implement implementing geopolymer technology. The geopolymerization (sometimes called alkali-activation) is a complex reaction containing solid alumino-silicate minerals, where sodium hydroxide (NaOH) or potassium hydroxide (KOH) along with sodium silicate solution act as an alkali activator [6-7]. During this reaction, rapid dissolution of silico-aluminate reactive materials occurs. As a result of the complex reaction chain, a 3-dimensional (3D) geopolymeric network is formed [8]. Thus, geopolymerization that uses free silicon (geopolymer matrix system) to react f-CaO or f-MgO (BOFS) into a stable calcium silicate or magnesium silicate compound would prevent the volume expansion.

This study examined the mechanical, swelling, and thermal properties of geopolymer mixture containing BOFS aggregates. The obtained properties of geopolymer mixture are compared with normal cement mortar mixture to confirm the efficiency of geopoymerization to use BOFS aggregate as construction material.

2. Experimental Program

2.1 Materials

This study prepared two types of mortar mixtures: normal cement mortar and geopolymer mixtures. As a binder, ASTM type I cement was used to make cement mortar mixture, while ground granulated blast furnace slag (GGBFS) and low calcium fly ash (FA) were used to make geopolymer mixture. Natural siliceous river sand and two BOFS aggregates of different ages. The first BOFS was obtained after air cooling with the assistance of water cooling. Because this BOFS was excavated and processed through a metal recovery facility where entrapped steel is removed for a short period (within one month), it is classified as Fresh BOFS in this study. The second BOFS was excavated from stockpiled BOFS yards and subjected to natural weathering for approximately more than five years. Hereinafter, the second BOFS is mentioned as stockpiled BOFS. Both BOFS aggregate and river sand were sieved with different fractions to make specimens for each test (2.36 mm of 10%, 1.18 mm of 25%, 600 µm of 25%, 300 of µm of 25%, and 150 µm of 10%). Materials properties for mix design are given in table 1.

Table 1. Specific gravity and absorption capacity values of materials.

Material name	Specific gravity, %	Absorption capacity, %
Siliceous river sand	1.143	0.286
Fresh BOFS	1.143	0.067
Stockpiled BOFS	2.571	1.667
GGBFS	3.05	-
FA	1.87	-

2.2 Mixture Proportions

For the geopolymer mixture, GGBFS and FA were used in equal proportion, and their amount of constitutes was 70% of total solid content. 30% of river sand, fresh BOFS, or stockpiled BOFS aggregate occupied the remaining portion. For all cases, the water to binder ratio was kept constant at 0.32. During calculation, the specific gravity and water absorption capacity of each material was taken into consideration. The activator was made at 12 M concentration through adding mixing water to a sufficient amount of NaOH flakes and then flipping for 5 min. Since NaOH generates heat during melting, the solution should be cooled down for a sufficient period until it reaches room temperature. The prepared NaOH solution was slowly added to commercial sodium silicate (Na2SiO3) with a ratio of 0.4 and mixed thoroughly before casting geopolymer samples. The geopolymer mixture was activated with an alkali-activated solution (AAS) of Na2SiO3 and NaOH at the ratio of 2.5.

2.3 Test Method and Procedure.

In this study, compressive strength test, accelerated mortar bar test, and thermal conductivity test were conducted to measure mechanical, thermal, and expansion properties of geopolymer mixture concrete and normal cement mortar mixture. Curing conditions of samples were different depending on the test method. Cubical compressive strength specimens with dimensions of 50×50×50 mm were subjected to 1-day air curing under the plastic film and then were submerged in water at room temperature until a specific test period. The compressive strength test was carried out according to ASTM C109/C109M Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 50 mm Cube Specimens).

According to ASTM C 1260 procedure (Potential Alkali Reactivity of Aggregates), 8 bar samples with dimensions 25x25x285 mm were prepared. They were also cured in the air for 24 hours first. After that, half of them were submerged into the water at 80°C, while the rest of them were submerged into 1 M NaOH solution at 80°C to investigate their expansion behavior in water and ASR resistance. The bar length was measured daily using a length comparator device until 10-day. After that, length change measurement was taken with 3- or 4- day intervals until 28 days. The expansion of bars is calculated by equation (1):

$$L = \frac{\left(L_0 - L_i\right)}{G} \times 100 \tag{1}$$

In the equation (1), L = change in length at x age, %; L_x = comparator reading of specimen at x age minus comparator reading of reference bar at x age (mm); L_i = initial comparator reading of specimen minus comparator reading of reference bar at that same time (mm); G = nominal gauge length (250 mm).

Samples with the shape of rectangular parallelepiped and with dimensions of 150×150×30mm were cast and air-cured for a thermal conductivity test. The thermal conductivity of each specimen was measured with the equipment called ‘ИТС-1 «150»’ using stationary heat flow (ASTM D 5470 Standard Test Method for Thermal Transmission Properties of Thermally Conductive Electrical Insulation Materials).

3. Results and Discussion

3.1 Compressive Test

Figure 1 represents compressive strength test results of normal cement mortar and geopolymer mixtures. Except for geopolymer made of river sand, the compressive strength of all mixtures increases over time. The exception might be caused by micro-cracking inside samples or consolidation error during sample preparation. All compressive strength values are the average of three test results. At 7-day age, the compressive strength of geopolymer mixture is slightly higher than that of normal mortar mixture, while geopolymer mixture has higher 28-day compressive strength than normal mortar mixture. The strength of the geopolymer mixture can be enhanced by adjusting the amount of GGBFS and FA [9]. The sufficient ratio of GGBFS to FA positively affected strength development and made the geopolymer mixture comparable with the conventional mortar mixture. Interestingly, the compressive strength of the mixture containing fresh BOFS aggregate is higher than that of the mixture with stockpiled BOFS aggregate regardless of normal mortar and geopolymer mixtures. This result may be attributed to micro-cracks inside stockpiled BOFS. It should be noted that the stockpiled BOFS was naturally weathered, and an expansion reaction due to the formation of Ca(OH)2 occurred, which made BOFS micro-cracked.

3.2 Accelerated Mortar Bar Expansion Test

Figure 2 shows the results of accelerated mortar bar expansion tests of normal mortar and geopolymer mixtures submerged in the water. Regardless of normal mortar and geopolymer mixtures, the expansion of river sand and stockpiled BOFS mixtures is insignificantly low. If ASTM C 1260 criterion is applied to judge the expansion, these mixtures remain non-reactive. However, as expected, the mixture containing fresh BOFS aggregate showed a gradual increase up to 5-day. After that, the expansion was sharply increased, and all specimens were broken at 9-day. The presence of f-CaO and f-MgO in the chemical composition of fresh BOFS can explain this result. In the presence of water, Ca(OH)2 and Mg(OH)2 can be formulated in the presence of water, consequently leading to volumetric expansion with about 127% and 118%, respectively [10,11]. Moreover, silica that comes from AAS reacts with f-CaO and f-MgO and converts them into a stable calcium silicate compound, consequently preventing the expansion. In the stockpiled BOF mixture, since BOFS aggregate was naturally weathered for a long time, f-CaO and f-MgO were already consumed, reacting with ambient carbon dioxide (CO2) and producing stable calcium carbonate (CaCO3) and magnesium carbonate (MgCO3). Thus, the expansion behavior of stockpiled BOFS is more stable than fresh BOFS.

Figure 3 illustrates the expansion behaviors of specimens submerged in 1M NaOH solution. all cement mortar and geopolymer mixtures exceeded 0.1% at 14-day, classifying the aggregates as potentially reactive. It should be noted that both river sand and BOFS aggregate contain reactive silica that causes an alkali-silica reaction (ASR). All geopolymer mixtures showed no expansion, although the mixture containing fresh BOFS aggregate had relatively higher expansion than the other mixture. Volumetric instability was eliminated due to silicons from the geopolymer matrix that reacted with oxides of f-CaO and f-MgO in the BOFS and formed stable products. It can be described by the following reaction equations [5]:

$$\text{f-CaO} + \text{Si} \rightarrow \text{CaSiO}_3 \tag{2}$$

$$\text{f-MgO} + \text{Si} \rightarrow \text{MgSiO}_3 \tag{3}$$

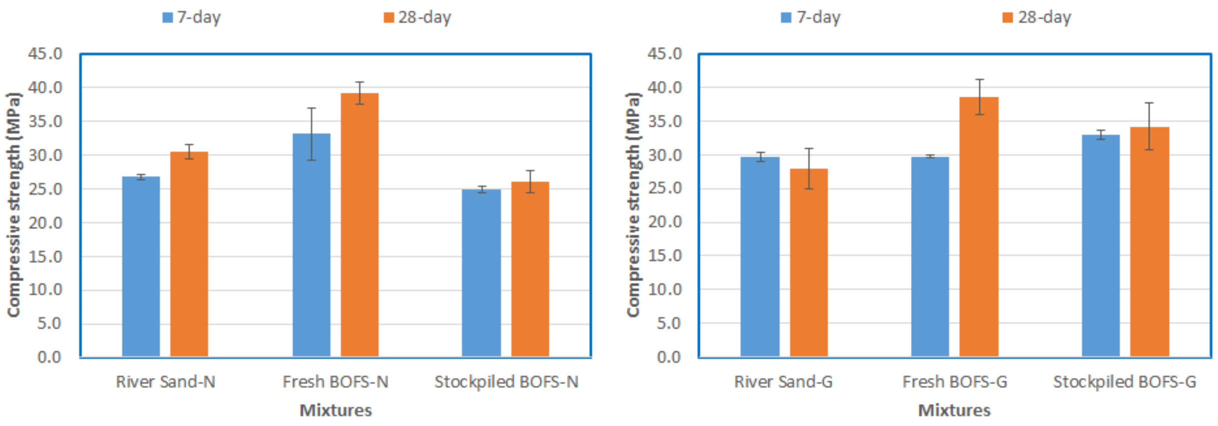

Figure 1. Compressive strength development of normal cement mortar and geopolymer mixtures.

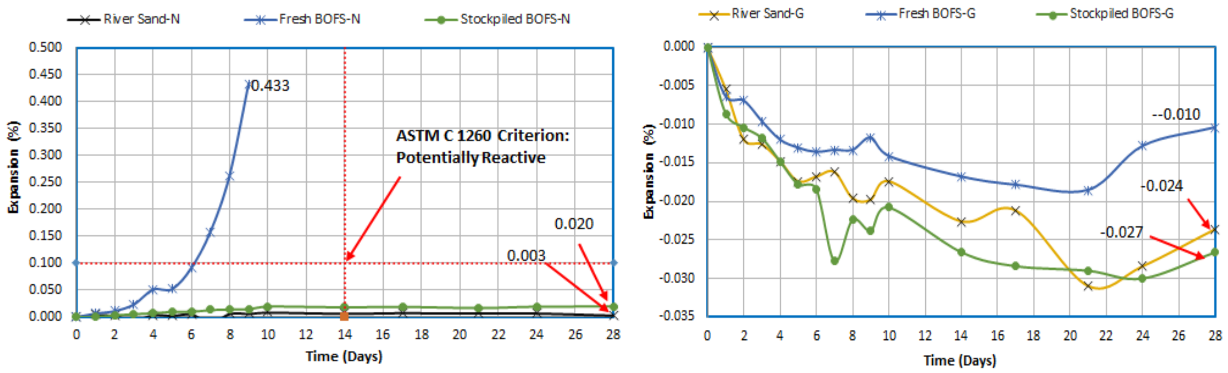

Figure 2. Expansion characteristics of normal mortar and geopolymer mixtures in the water.

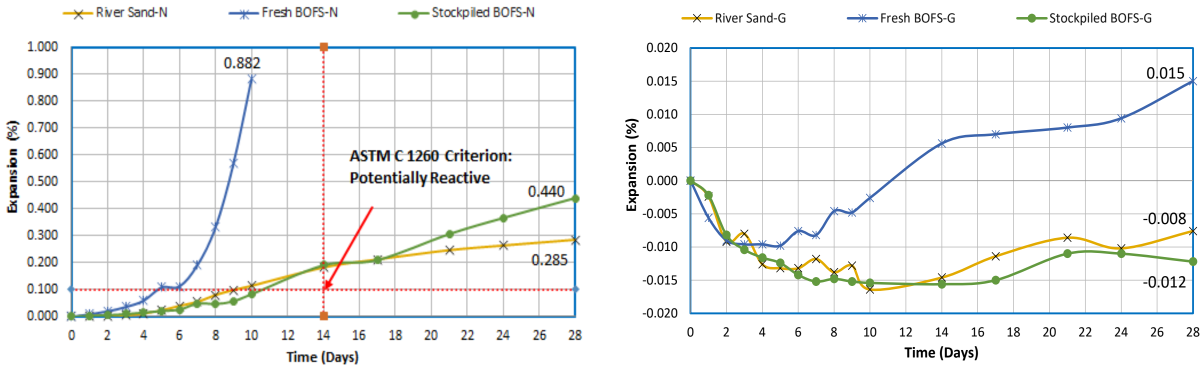

Figure 3. Expansion characteristics of normal mortar and geopolymer mixtures in the 1 M NaOH solution.

3.3 *Thermal Conductivity*

Only geopolymer mixtures were tested for thermal conductivity test since only their expansion behaviors were satisfactory. The results of the thermal conductivity test are represented in figure 4. The measurements were taken at the age of 7 and 14 days. The thermal conductivity of geopolymer concrete containing BOFS is lower than conventional cement mortar mixture. In addition, containing BOFS aggregate performed lower or comparable thermal conductivity than the mixture containing river sand. Perhaps it is due to the calcium silicate mineral phase, the main component of BOFS having a thermal conductivity of 0.042–0.055 W/(m·K) [12].

Over time, the thermal conductivity value decreases for all mixtures. This result may be attributed to the hydration process and geopolymerization. An increase in bulk density increases or decreases pore sizes inside the mixture matrix, which affects “heat transfer average distance”. As a result, the thermal conductivity of the material decreases [13]. Therefore, a geopolymer mixture containing BOFS aggregate can be used as an energy-saving material.

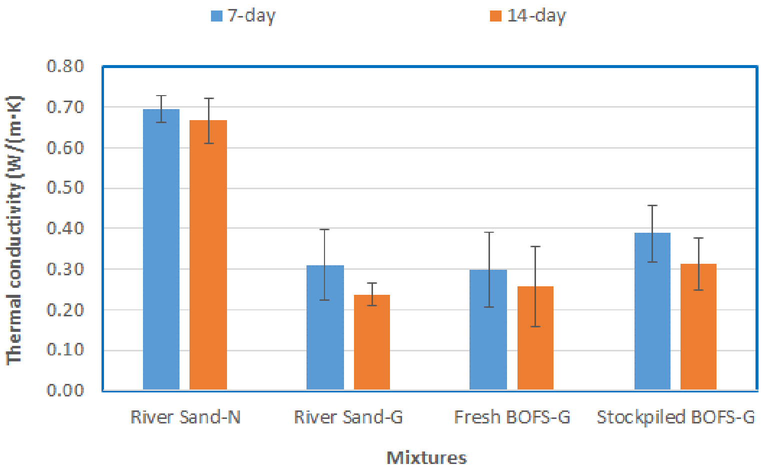

Figure 4. Thermal conductivity of cement mortar mixture with river sand geopolymer mixtures.

4. Conclusion

This paper investigates the mechanical, swelling, and thermal properties of geopolymer mixture containing BOFS aggregates compared to a control group of normal cement mortar mixtures containing river sand and BOFS aggregates. Based on the results, the following conclusions can be made:

1. Geopolymer mixture demonstrated higher strength development than normal cement mortar mixture in identical water to binder ratio.
2. All geopolymer mixtures showed no expansion in water and 1M NaOH solution regardless of aggregate type.

3. The thermal conductivity of geopolymer concrete containing BOFS is lower than conventional cement mortar mixture.

BOFS can be considered as suitable construction materials demonstrating better thermal and strength characteristics. However, to utilize it as a construction material, the key criteria are to eliminate volume expansion. Application of geopolymer technology to BOFS converts it to a stable material. However, further research is needed to analyze and verify other durability properties such as sulfate attack and corrosion resistance for a deeper investigation of material characteristics of geopolymer concrete containing BOFS aggregate.

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