

## Effect of addition of As-received IGCC slag in making geopolymer

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It is a known fact that the cement production is responsible for almost 5% of total worldwide CO<sub>2</sub> emission, the primary factor affecting global warming. Geopolymers are valuable as ordinary Portland cement (OPC) substitutes because geopolymers release 80% less CO<sub>2</sub> than OPC and have mechanical properties sufficiently similar to those of OPC. Therefore, geopolymers have proven attractive to eco-friendly construction industries. Geopolymers can be fabricated from aluminum silicate materials with alkali activators such as fly ash, blast furnace slag, and so on. Integrated gasification combined cycle (IGCC) slag has been used for fabricating geopolymers. In general, IGCC slag geopolymers are fabricated with finely ground and sieved (<128 mesh) IGCC slag. The grinding process of as-received IGCC slag is one of the main costs in geopolymer production. Therefore, the idea of using as-received IGCC slag (before grinding the IGCC slag) as aggregates in the geopolymer matrix was introduced to reduce production cost as well as to enhance compressive strength. As-received IGCC slag (0, 10, 20, 30, 40 wt%) was added in the geopolymer mixing process and the mixtures were compared. The compressive strength of geopolymers with an addition of 10 wt% as-received IGCC slag increased by 19.84% compared to that with no additional as-received IGCC slag and reached up to 41.20 MPa. The enhancement of compressive strength is caused by as-received IGCC slag acting as aggregates in the geopolymer matrix like aggregates in concrete. The density of geopolymers slightly increased to 2.1–2.2 g/cm<sup>3</sup> with increasing slag addition. Therefore, it is concluded that a small addition of as-received IGCC slag into the geopolymer can increase compressive strength and decrease the total cost of the product. Moreover, the direct use of as-received IGCC slag may contribute to environment protection by reducing process time and CO<sub>2</sub> emission.

**Key words:** Geopolymer, IGCC slag, Aggregates, As-received IGCC slag.

### Introduction

As worldwide environmental regulations grow stricter, cement production is of concern for aggravating global warming as it accounts for as much as 5%–8% of global CO<sub>2</sub> emission [1]. However, the demand for cement, the most frequently utilized construction material, is soaring on the daily basis owing to rapid social growth. In this situation, studies have been active to develop an alternative to cement [2]. In 1978, Davidovits developed “geopolymer.” This new material has received attention for use in coating and adhesives and as an alternative to cement [3]. Geopolymer is synthesized by mixing alkaline activator materials such as fly ash having aluminosilicate as the main ingredient with blast furnace slag, silica fume, and metakaolin [4]. Geopolymer consists of an aluminosilicate gel network including SiO<sub>4</sub> connected to tetrahedral AlO<sub>4</sub>, and it has cations such as Na<sup>+</sup> in framework cavities to strike a balance. Therefore, the quantities of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> as well as alkali activator concentration come to affect geopolymer properties deeply [5–7].

The IGCC (integrated gasification combined cycle) slag used in this study as a raw material is a slag

generated during IGCC generation. It is an industrial byproduct rich in SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> [8]. IGCC generation is environmentally friendlier and delivers a higher efficiency than existing coal thermal power generation. However, in the process of synthetic gas production for power generation, it creates a large quantities of slag [9]. The IGCC system in Spain (Puertollano, Ciudad Real) generates a huge amount of slag, including 80,000 tons of IGCC slag each year. In this situation, studies on IGCC slag recycling technology development are even more necessary for both environmental and economic gains [10].

According to an investigation on the reserves of aggregate utilized in concrete, aggregate demand exceeds its supply. Thus, future aggregate supply and demand would be problematic to a serious extent [11]. Against this backdrop, in this study we conducted an experiment by mixing as-received IGCC slag in its natural state before IGCC slag pulverization. To use the IGCC slag from IGCC as a raw material, pulverization is required. In geopolymer production, pulverization is an expensive process, accounting for a large part of the total cost.

Therefore, for economic and environmental gains, in this study we mixed finely milled IGCC slag processed with coarse and fine grinding as a raw material with as-received IGCC slag as an aggregate. The study experiment was performed based on various mixtures

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to explore how to reduce geopolymer production cost while improving its physical properties.

## Experimental Method

### Raw materials

This study utilized finely milled IGCC slag as a raw material and as-received IGCC slag as an aggregate. Finely milled IGCC slag and as-received IGCC slag are byproducts of the IGCC generation process. As-received IGCC slag is produced by water granulating and pulverizing bulk slag immediately after IGCC slag creation. Finely milled IGCC slag can be produced by coarse grinding as-received IGCC slag then fine grinding it to an average particle size of 128  $\mu\text{m}$ . Fig. 1. shows the X-ray diffraction (XRD, Rigaku MiniFlex2, 40 kV, 40 mA, and  $\text{CuK}\alpha$  radiation) pattern of the raw material. Table. 1. lists its chemical composition based on X-ray fluorescence (XRF) and inductively coupled plasma atomic emission spectroscopy (ICP-AES, OPTIMA 4300DV, Perkin Elmer, USA). The XRD pattern was found to have an amorphous peak. Given that geopolymer actually reacts with amorphous Si and Al, this is expected to be a very useful property. As a result of XFR analysis, the raw material was found to have enough  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  to form the aluminosilicate gel

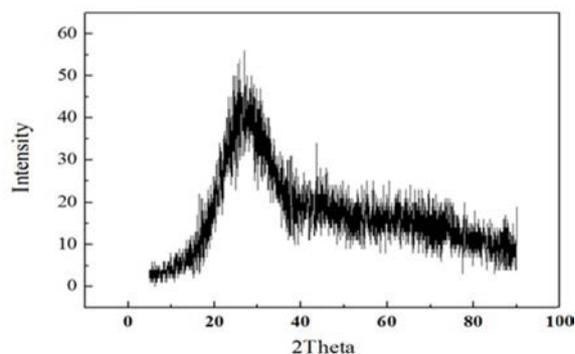


Fig. 1. XRD pattern of IGCC slag.

Table. 1. Chemical composition of IGCC slag obtained by using XRF and ICP-AES.

Material	XRF		ICP-AES	
	IGCC slag (wt%)	Element	IGCC slag (ppm)	
$\text{SiO}_2$	49.25	Al	96105.44	
$\text{Al}_2\text{O}_3$	20.16	Ca	153288.73	
$\text{Fe}_2\text{O}_3$	5.61	Mg	8714.20	
CaO	21.67	Fe	41926.08	
MgO	1.28	Cr	52.13	
$\text{Na}_2\text{O}$	0.49	Mn	698.92	
$\text{K}_2\text{O}$	0.48	Zn	Null	
$\text{TiO}_2$	1.07	As	Null	
C	0.06	Pb	Null	
Ig. Loss	0	Cu	Null	



Fig. 2. As-received IGCC slag.

Table 2. Conditions for fabricating geopolymer.

Series	As-received IGCC slag	Amount of as-received IGCC slag (wt%)	Water/solid ratio	Size of as-received IGCC slag
Series 1	addition			before sieve
	substitution	10	0.2	before sieve
Series 2	substitution	20		>5 mm
		30		0.8-5 mm
		40	<5 mm	

network of geopolymer, indicating its appropriateness for use as a geopolymer material.

Fig. 2. shows a photograph of the as-received IGCC slag. As-received IGCC slag in its raw state without granular separation exists in diverse forms such as needle shaped and rounded, ranging from 5 to 0.8 mm in size. The needle shape forms as IGCC slag is stretched while being released; it is a melted slag generated at high temperature. The rounded shape results from large particles becoming smaller and rounded in the water granulating and pulverizing procedures. As-received IGCC slag in such shapes is expected to affect properties within the geopolymer matrix in a complex manner.

### Synthesis method

To produce geopolymer, finely milled IGCC slag was mixed as a raw material with as-received IGCC slag as an aggregate. Then, a 15 M sodium hydroxide (NaOH) alkali activator was put under the forming process under the condition of a water/solid (W/S) ratio of 0.2. The alkali solution was made 3 h before the formation process by using NaOH pellets (<97.0% purity, DAEJUNG, Korea) and distilled water together in the appropriate concentration. A saturated status was maintained using a stirrer. The paste mixed in line with the requirements was poured into a brass cubic mold ( $50 \times 50 \times 50 \text{ mm}^3$ ) for forming. To prevent cracking by rapid moisture evaporation, the mold was placed in a

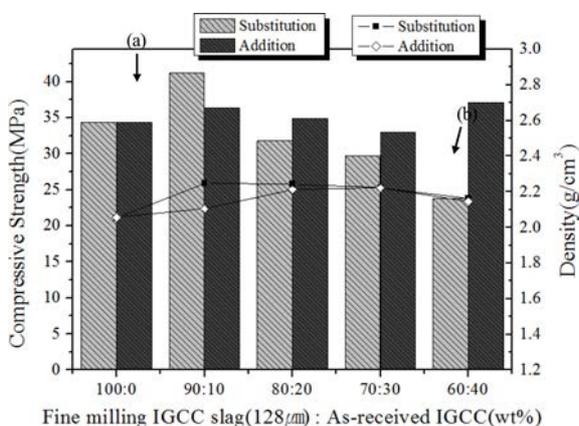
polyethylene film to implement curing at high temperature. The high-temperature curing is implemented at 70 °C and 100% relative humidity for 24 h. Table. 2. lists the conditions of the experiment conducted to identify the effect of as-received IGCC slag. The W/S ratio was 0.2, and the as-received IGCC slag substitution or addition amount was set at 10, 20, 30, and 40 wt%. As indicated in Table. 2, as-received IGCC slag without sieve separation was used in Series 1 and as-received IGCC slag sized >5 mm, between 0.8 and 5 mm, and <5 mm was used in Series 2; these slags underwent granular separation but not sieve separation.

## Results and Analysis

### Physical characteristics of as-received IGCC-slag-added geopolymer

Fig. 3. shows the physical characteristics of geopolymer produced by substituting and adding as-received IGCC slag. As a result, in the case of substitution, compression strength fell rapidly with 10 wt% to 41.20 MPa and the fall was slowed as substitution increased. This seems to occur because the amount of finely milled IGCC slag, working as a binder, decreased as the substitution increased to slow the geopolymer reaction and reduce the strength. Also, because the as-received IGCC slag had a relatively smaller specific surface area, the activator that had been supposed to react failed to do so and remained unreacted, increasing paste viscosity and reducing the compression strength.

However, with 10 wt% substitution, the W/S ratio was 0.2 and as-received IGCC slag fulfilled its role as an aggregate in increasing compression strength. In contrast, the as-received IGCC-slag-added geopolymer showed higher compression strength continuously than that without added as-received IGCC slag. This occurs because the specific surface area that can react increased when as-received IGCC slag was added, so the paste

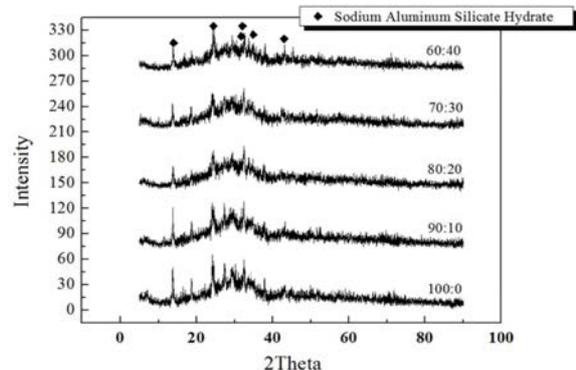


**Fig. 3.** Mechanical properties of geopolymer with various as-received IGCC slag additions (10, 20, 30, and 40 wt%): (a) compressive strength; (b) density.

viscosity decreased and increased the strength, in contrast to the case of as-received IGCC-slag-substituted geopolymer. Generally, concrete strength is more affected by its paste rather than its aggregate strength. Thus, if as-received IGCC slag is substituted, the relative ratio of liquid increased, thereby lowering viscosity and creating more pores, thus lowering paste strength and, ultimately, affecting the overall geopolymer strength, compared with the case of addition [12]. The as-received IGCC-slag-substitution-based geopolymer showed a rapid increase in density value at 10 wt% but then decreased with substitution increase.

The addition-based geopolymer density rose until 30 wt% then started to fall at 40 wt%. This general tendency seems to result from the density increasing with increasing substitution and addition since the density of the as-received IGCC slag was as high as 2.6 g/cm<sup>3</sup>. This is higher than the specific gravity standard for light-weight aggregate, contradicting the existing study findings that density dropped as the aggregate addition amount rose. Consequentially, in this study it was found that, to improve the physical characteristics, as-received IGCC slag needed to be substituted to deliver better properties.

Fig. 4. shows the comparison of the XRD patterns used to identify the geopolymer reaction under the optimal as-received IGCC slag substitution to improve its physical characteristics. The XRD patterns were found to show a sodium aluminum silicate hydrate (SASH) phase reduction with substitution amount increase. As in Fig. 1, IGCC slag in its amorphous phase reacted with the alkali activator and produced SASH. SASH is reported to appear mainly as a geopolymer reaction byproduct. This indicated that, just as for the compression strength results, finely milled IGCC slag decreased slowly as as-received IGCC slag substitution increased, reducing the specific surface area for the geopolymer reaction and discouraging geopolymer reaction and reducing the compression strength and the amount of SASH phase. However, in the case of 10 wt% substitution, a level of crystal phase was observed that was similar to that in



**Fig. 4.** XRD patterns of substituted geopolymer with various as-received IGCC slag additions (10, 20, 30, and 40 wt%).

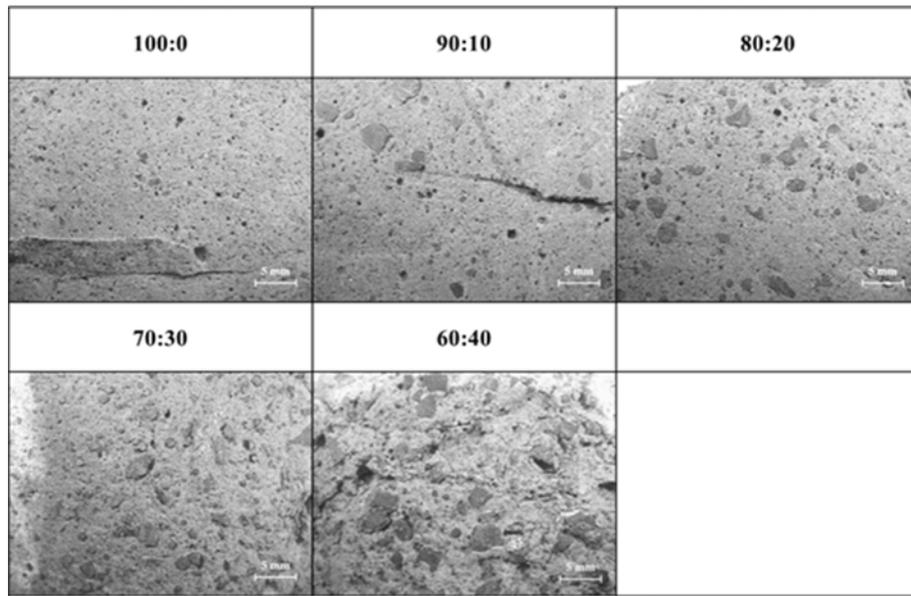


Fig. 5. Cross section of substituted geopolymer with various as-received IGCC slag additions (10, 20, 30, and 40 wt%).

the nonsubstitution case, indicating that the optimal substitution amount for geopolymer reaction is 10 wt%. Therefore, for 10 wt% substitution, an optimum geopolymer reaction takes place regardless of the amount of liquid to maintain the SASH phase and function as an aggregate to help improve the compression strength.

Fig. 5. shows the cross section of pulverized geopolymer specimens with substituted and added as-received IGCC slag. The greater the amount of as-received IGCC slag substituted, the less there is of the geopolymer matrix. When the substitution amount rose from 30 to 40 wt%, the cross section became less homogenous. This occurs because, just like in the XRD results in Fig. 3, the geopolymer reaction gradually became less active. Such a tendency is similar to the findings in other studies that the larger the aggregate substitution amount, the lower the compression strength and density [13-15]. The cross section at 40 wt% showed very low homogeneity in the matrix. Heterogeneous parts between as-received IGCC slag and geopolymer matrix function as crack paths, causing early failure. Under any load, cracks could be easily connected to fine pores. For this reason, the compression strength was found to be very low as in Fig. 2. [16] Given the failure characteristics of concrete, when an aggregate fails and cracks continue, adhesion between the matrix and the aggregate should effectively increase the strength. If failure and cracks occur along the matrix and aggregate interface, adhesion between the matrix and the aggregate is low, thereby lowering strength. In the cross section in Fig. 5, the as-received IGCC slag is maintained as an aggregate, indicating low adhesion. If a method to improve this adhesion is found, better physical characteristics would be achieved.

**Physical characteristics of granular separated as-received IGCC-slag-added geopolymer**

The as-received IGCC slag was divided into thick aggregate and thin aggregate according to the standard of 5 mm. Fig. 6. shows the physical characteristics of aggregates thicker than 5 mm or thinner than 5 mm in the case of substitution. Aggregates thicker than 5 mm showed very low strength compared with aggregates of other sizes. This is because the 5 mm or thicker as-received IGCC slag has lower strength and a smaller specific surface area to react, resulting in low compressive strength. As-received IGCC slag sized between 0.8 and 5 mm showed the highest strength among the as-received IGCC slag with granular separation. This finding is similar to that of other studies that the smaller the aggregate size the higher the strength. [18-20] For a fixed liquid to solid ratio, aggregates with a smaller size between 0.8 and 5 mm have a larger specific surface area, thus retaining more

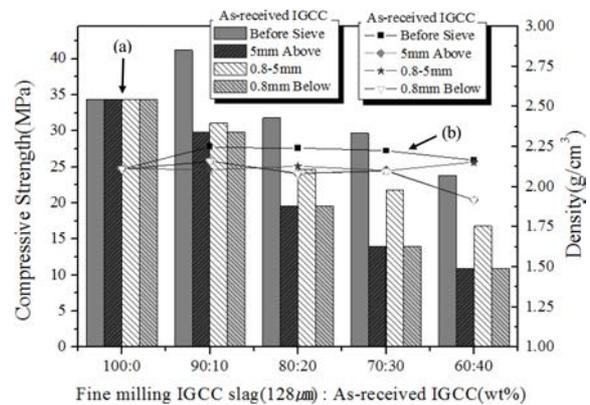


Fig. 6. Mechanical properties of geopolymer for as-received IGCC slag of various sizes: (a) compressive strength; (b) density.

moisture and improving their strength. Nevertheless, however, the as-received IGCC slag before sieving delivered the highest strength among all the materials tested. This is because the post-sieved as-received IGCC slag has more efficient packing owing to its more diverse sized as-received IGCC slag than the 0.8- to 5-mm as-received IGCC slag. The post-sieved slag, thus, had a higher density, which resulted in a higher strength. The smallest aggregate utilized in this study is 0.8 mm in size; though it has the largest specific surface area, its size is too small compared with other normal aggregate size. Therefore, it seems to have worked not as a usual aggregate but as more as a source of impurities to deliver low strength.

### Conclusions

For economic and environmental gains, this present study used as-received IGCC slag produced by water granulating and pulverizing IGCC slag from IGCC generation along with finely milled IGCC slag with an average particle size of 128  $\mu\text{m}$  after coarse and fine granulation. The two materials were mixed to produce geopolymer and the effects of as-received IGCC slag on its physical characteristics were examined. First, Series 1 compared the physical characteristics according to the methods of mixing as-received IGCC slag. Substitution-based and addition-based mixing methods were compared. The maximum strength (41.20 MPa) was found at the 10 wt% substitution level. In Series 2, as-received IGCC slags were divided into thick and thin ones based on the standard of 5 mm in size and their physical properties were identified after granular separation. As a result, granular separation was found to show the highest strength. This results from the material before sieving having diversified sizes and thus being packed more efficiently than post-sieved material, resulting in a higher compressive strength and density. Consequentially, a compressive strength as high as 41.20 MPa was found in this study when the as-received IGCC slag was substituted and added in 10 wt% amount. By doing so, the cost of pulverization can be reduced to create economic and environmental gains.

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