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Effects of manufacturing conditions on physical properties of integrated gasification combined cycle (IGCC) slag geopolymer

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In this study, we used integrated gasification combined cycle (IGCC) fused slag, a by-product of IGCC, to analyze its applicability as a high-strength geopolymer in terms of particle size, alkaline activator concentration, and solid-liquid ratio. We also examined its stability. A planetary ball mill was employed to pulverize the slag for 4, 6, and 8 h so as to adjust the particle size to a desired value. The results showed that the compressive strength of the geopolymer made of the 6 h pulverized material and 12 M alkaline activator was the highest (29.8 MPa). In the case of the 8h pulverized material, the compressive strength of the geopolymer got weaker. Therefore, it was found that an optimal particle size was necessary for strength development. When the IGCC fused slag was finely pulverized (average particle size = 128 μm, the strength increased with an increase in the molar concentration. At 18 M, the maximum strength was 59.908 MPa. A heavy metal dissolution test was performed. The specimen's heavy metal dissolution was detected to be lower than the reference value. Hence, the specimen was found to be safe. Therefore, if IGCC fused slag with an optimum particle size is used the resulting geopolymer can be applied as a construction material.

Key words: Integrated Gasification Combined Cycle (IGCC) slag, Particle size, Molar concentration (Mol), Compressive strength, Water/soild (W/S) ratio.

Introduction

Because of the global economic growth, the number of high-rise buildings constructed in construction areas has increased. For the construction of such buildings, more cement is consumed. In most of the construction sites, Portland cement is generally used as the binding material. The annual manufacturing volume of Portland cement has increased by 3%. 1.35 million tons of greenhouse gas emissions are produced every year from manufacturing processes. These greenhouse gases are the main causes of global warming and abnormal weather conditions, which cause natural disasters. Among the domestic industries, the steel, petrochemical, and cement industries generate about 45% of the total CO_2 emissions [1]. Since the 2000s, greenhouse gases have become the major environmental issue. Hence, low-carbon cement materials need to be developed to replace cement, which generates a massive amount of CO_2 during manufacturing processes. In Australia, the US, and Europe, alkali-activated concrete with fly-ash, blast-furnace slag, and metakaolin have been actively researched [2].

In 1978, French Davidovits activated alumino-silicate as an alkaline solution to develop a material with a structure similar to that of zeolite. This material uses the inorganic material 'alumino-silicate' for polymerization and has a three-dimensional structure similar to the structure of a polymer. For this reason, it is called a geopolymer. Alkali-activated materials react with alumino-silicates and alkaline solutions (generally, alkali hydroxide/alkali silicate solution), and hence are referred to as set and hardened materials. [3]

Generally, the strength of Portland cement concrete is improved by the C-S-H hydration products generated by the hydration reaction of cement and water. In the case of fly-ash-based geopolymers, the strength is improved by the reaction of fly-ash, which comprises of Si and Al, and alkaline activator at a high temperature. It has been known that a geopolymer forms a three-dimensional structure with Si-O-Al-O [4, 5].

Ryu et al. investigated the strength development mechanism and durability of geopolymer mortar using mixed fly-ash and blast-furnace slag fine particles. They reported that geopolymer mortar has high strength and freezing-thawing resistance than those of cement mortar [6]. Lee et al. investigated the effect of mechanical pulverization on the reactivity of cinder in the process of manufacturing geopolymer with the use of pond ash obtained from thermal power plants. The main composition of pond ash is bottom ash. They found that the cinder pulverized by a rod mill and planetary ball mill showed a rise in its compressive strength by up to 37% [7]. Ryu et al. never used cement as a binding material and tried to develop

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concrete with the use of 100% fly-ash. To achieve the purpose, they analyzed changes in compressive strength depending on alkaline activator concentration and the mixing ratio of NaOH and sodium silicate. The results showed that the higher the concentration of alkali activator, the higher the compressive strength, and the concentration of the activator greatly affects the initial strength.

When the mixing ratio of NaOH and Sodium silicate was 1 : 1 ($SiO_2/Na_2O = 8$), the concrete compressive strength was more than the reference value (40 MPa). Therefore, the material was found to be suitable to replace cement [8]. The results revealed that the physical properties of geopolymer including the compressive strength were influenced by the type of the raw material, average particle size, and type and concentration of the activator.

Integrated gasification combined cycle (IGCC) of the Taean Western Power Plant is based on a new concept that combines existing coal-fired power plants, chemical plants, and combined power plants. This combined power plant is more efficient than conventional coal-fired power plants and the amount of pollutant emission is small. Thus, IGCC is attracting attention as an eco-friendly clean power generation technology.

Integrated gasification technology is applied not only for the generation of IGCC power but also for the production facilities of Gwangyang SNG (Synthetic Natural Gas).

If the facilities are operated on a full scale, about 165,000 tons/year of fused slag would be generated. Therefore, it is necessary to develop an efficient recycling technology. Therefore, this study used IGCC fused slag to analyze the physical properties of the resulting geopolymer in terms of the particle size of the material and the molar concentration of the alkaline activator. We also conducted an experiment to evaluate the applicability of the resulting geopolymer as a construction material.

Experimental

IGCC fused slag

In this study, pulverized IGCC fused slag, a by-product of IGCC, was used. The slag was coarsely crushed into particles with an average size of 850 μm. It was also finely pulverized into particles with a size of 128 μm. The coarsely crushed IGCC fused slag was pulverized by a planetary ball mill (MTI Korea, SFM 1 Desk Top Planetary Ball

Miller) at 35 rpm. To analyze the basic physical properties of the slag, X-ray fluorescence (XRF), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and X-ray diffraction (XRD) analyses were conducted.

The Si/Al ratio was 2.066, as revealed by the XRF results. This suggests that the slag could be used as a material of geopolymer. The XRD pattern showed the presence of an amorphous peak, as shown in Fig. 1.

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

XRF		ICP-AES	
Materials	IGCC slag (wt%)	Elements	IGCC slag (ppm)
SiO_2	49.25	Al	96105.44
Al_2O_3	20.16	Ca	153288.73
Fe_2O_3	5.61	Mg	8714.20
CaO	21.67	Fe	41926.08
MgO	1.28	Cr	52.13
Na_2O	0.49	Mn	698.92
K_2O	0.48	Zn	Null
TiO_2	1.07	As	Null
C	0.06	Pb	Null
Loi	0	Cu	Null

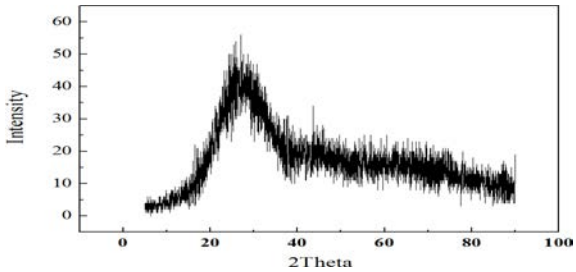

Fig. 1. XRD pattern of IGCC slag.

Alkaline activator

A material based on Si and Al undergoes geopolymerization as condensation polymerization in a strong alkali atmosphere. During geopolymerization, the dissolution level and degree of condensation polymerization of the starting material change depending on the type and molar concentration of alkali solutions such as NaOH, KOH, $Ca(OH)_2$, sodium silicate, or potassium silicate. As a result, the physical and chemical properties of the product change. Therefore, in this study, different types of NaOH alkaline activator with a concentration of 9, 12, 15, and 18 M were used.

Geopolymer manufacturing method

In this study, a geopolymer using IGCC fused slag was prepared. To analyze the optimal compressive strength and density, the experiment was conducted by taking into account the molar concentration, particle size, and water/solid ratio (W/S ratio) of the alkaline activator. The mixing ratios are given in Tables 2, 3, 4 and 5. The IGCC fused slag and alkaline activator were put and mixed in a bowl. The mixture was then transferred into a cube mold (50 mm × 50 mm × 50 mm) for determining the mortar compressive strength. Form oil was applied to the interior of the mold before

Table 2. Experimental parameters for making geopolymers with coarsely milled IGCC slag.

No.	W/S ratio	IGCC fused slag	Activator	Curing	Aging time
1	0.2	100 wt%	NaOH 9 M	70 °C 24 hrs	3 days
2			NaOH 12 M		
3			NaOH 15 M		
4			NaOH 18 M		

Table 3. Experimental parameters for making geopolymers with finely pulverized IGCC slag.

No.	W/S ratio	IGCC fused slag	Activator	Curing	Aging time
1	0.2	100 wt%	NaOH 9 M	70 °C 24 hrs	3, 7 days
2			NaOH 12 M		
3			NaOH 15 M		
4			NaOH 18 M		

Table 3. Experimental parameters and milling times for making geopolymers with coarsely milled IGCC slag.

No.	W/S ratio	Milling time	Activator	Curing	Aging time
1	0.2	4 hrs	NaOH 15 M	70 °C 24 hrs	3 days
2		6 hrs			
3		8 hrs			

Table 4. Experimental parameters and W/S ratios for making geopolymers with finely pulverized IGCC slag.

No.	W/S ratio	IGCC fused slag	Activator	Curing	Aging time
1	0.20	100 wt%	NaOH 15M	70 °C 24 hrs	3 days
2	0.22				
3	0.24				
4	0.26				

transferring the mixture for smooth removal of the form. Curing was performed in a dryer at 70 °C for 24 hrs. To prevent the generation of cracks by temperature induced rapid moisture evaporation, curing was conducted in a polyethylene zipper bag. After the removal of the form, the test specimen was left at room temperature and was aged for three days before the analysis.

Flow of paste

The flow table test or flow test, also known as the slump-flow test, is a method to determine the consistency of fresh concrete. Flow table test is also used to identify the transportable moisture limit of solid bulk cargoes. It is used primarily for assessing concrete that is too fluid (workable) to be measured using the slump test, because the concrete will not retain its shape when the cone is removed. In this study, the flow of geopolymer paste depending on the W/S ratio was analyzed in accordance with ASTM C1437-07 (Flow of Hydraulic Cement Mortar) [9].

Results and Discussion

The influence of Mol concentration of geopolymer using the coarsely crushed IGCC fused slag

Influence of molar concentration of the geopolymer with coarsely crushed IGCC fused slag By using the coarsely crushed IGCC fused slag (with an average particle size of 850 μm, a different type of geopolymer was formed with different at each concentration of 9, 12, 15, and 18 M of the activator.

As shown in Fig. 2, the overall compressive strength was very low. At 9 M, the compressive strength was 3.5 MPa (very weak). The compressive strength increased with an increase in the molar concentration. At 15 M, the compressive strength was the highest (7.55 MPa), and at 18 M the strength decreased. Given the result, it was judged that the particle size of the IGCC fused slag was very large and consequently its specific surface area was small. Therefore, geopolymerization did not occur properly and the overall compressive strength was very low. Accordingly, it was considered that it would be necessary to adjust the particle size to make the geopolymer.

Geopolymer by milling time

The coarsely crushed IGCC fused slag had an average particle size of 850 μm and the specific surface area was small. For this reason, we assumed that the geopolymerization did not occur properly and that the

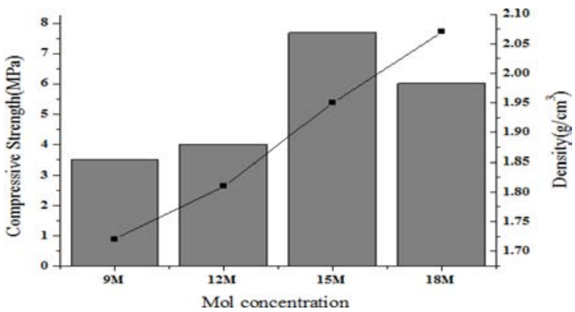

Fig. 2. Compressive strength and density as a function of the molar concentration of geopolymer.

Fig. 3. Compressive strength and density as a function of the milling time of the planetary ball mill.

overall compressive strength was weak. Therefore, in this study, a planetary ball mill was used to pulverize the slag at 35 rpm for 4, 6, and 8 hrs, respectively, and was then mixed with an alkaline activator of 12 M to make the geopolymer and was aged for 3 days at room temperature. In this state, its compressive strength and density were measured.

As shown in Fig. 3, when the slag was pulverized for 4 hrs by the planetary ball mill, its compressive strength was 18.5 MPa. Therefore, it was stronger than the non-pulverized slag. When the slag was pulverized for 6 hrs, the compressive strength reached the maximum value (29.8 MPa). This is likely to be because of the planetary ball mill-based pulverization, which helped to achieve a lower particle size and increased the specific surface area, which are the desired conditions for geopolymerization needed to improve the compressive strength. However, when the slag was pulverized for 8 hrs, the compressive strength decreased. This can be attributed to the too small particle size, which might have caused the electrostatic coagulation of particles, leading to a smaller specific surface area and no smooth reaction to decrease the compressive strength.

The physical properties of the geopolymer using finely pulverized IGCC fused slag by molar concentration

When the finely pulverized IGCC fused slag (with an average particle size of 128 μm was used, a geopolymer with a different molar concentration was obtained.

Fig. 4 shows the compressive strength and density of the geopolymer using the finely pulverized IGCC fused slag (with an average particle size of 128 μm with different molar concentrations. The 3-day aged geopolymer had the lowest compressive strength (12.18 MPa) at 9 M. With an increease in the molar concentration, its compressive strength tended to increase. At 18 M, the compressive strength was 38.425 MPa. Like the 3-day aged polymer, the 7-day aged geopolymer showed an increase in the compressive strength with an increase in the molar concentration. The compressive strength was the lowest (22.779 MPa) at 9 M, while it was the highest (59.908 MPa) at 18 M. The reason why the 7-day aged geopolymer had a higher compreesive strength than the 3-day one was that with an increase in the aging duration the alumino-silicate gel form generated by the continuous condensation polymerization and geopolymerization of reactive oxdies in a material gradually increased, and thereby a geopolymer with a fine structure was created. As the molar concentration increases, it becomes increasingly feasible to break a glass film and dissolve Si^{4+} and Al^{3+} ions involved in geopolymerization. Therefore, the higher the concentration of OH^-, the faster the decomposition of the SiO_2-Al_2O_3 vitreous bond, which generates a large amount of reactive ions. For this reason, an activator facilitates the dissolution of the reaction materials of IGCC fused slag and thereby leads to high compressive strength and durability [10].

Based on the results, it was found that the compressive strength of the IGCC slag geopolymer was affected by the particle size and molar concentration. Thus, it can be stated that the finely pulverized IGCC fused slag was the most appropriate material for creating the high-strength geopolymer.

The Influence of W/S ratio

In the above experiment, it was found that the finely pulverized IGCC fused slag with 128 μm average particle size was the most appropriate high-strength geopolymer. For the convenience of work, the fluidity of the paste was measured according to the amount of water and the compressive strength was measured.

Fig. 5 illustrates the compressive strength and density of the geopolymer depending on the W/S ratio. When the W/S ratio was 0.20, the compressive strength and density were highest, i.e., 65.9 MPa and 2.15 g/cm^3 respectively. Generally, with increasing W/S ratio, the compressive strength should decrease. This is because

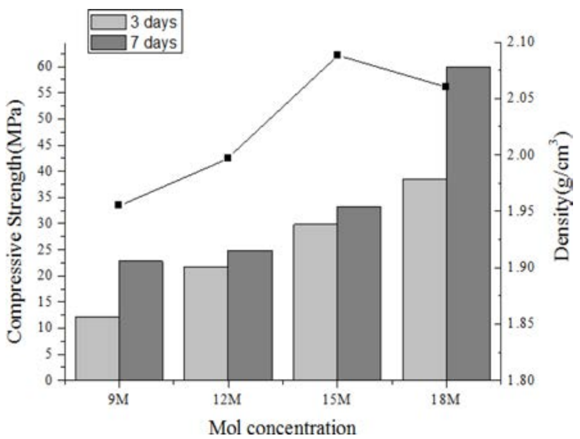

Fig. 4. Compressive strength and density of the geopolymer in terms of its molar concentration.

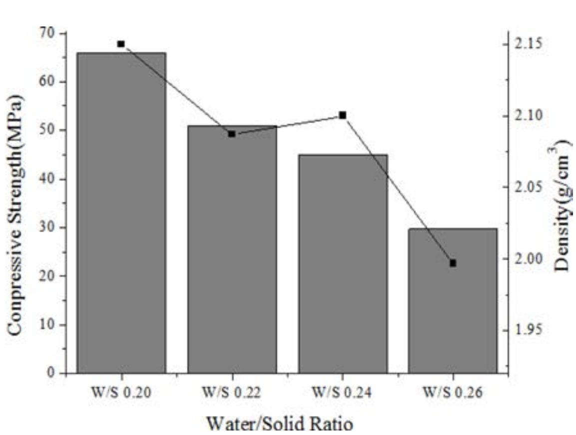

Fig. 5. Compressive strength and density of geopolymer by W/S ratio.

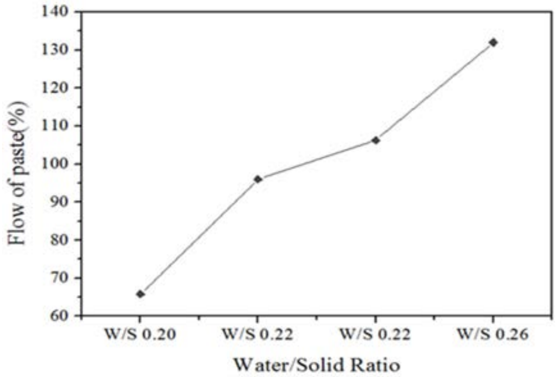

Fig. 6. Flow of paste as a function of the water/solid ratio of geopolymer.

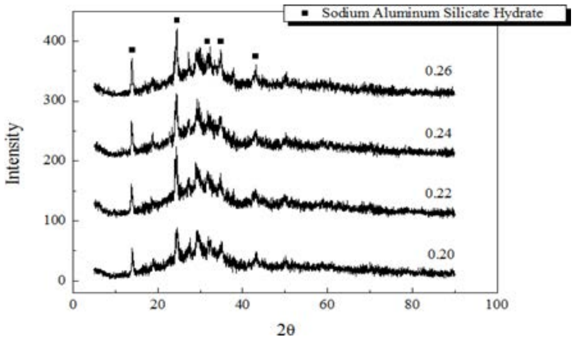

Fig. 7. XRD pattern of geopolymer for different water/solid ratios.

Table 6. Hazardous substances dissolution limit from designated waste.

No.	Item	Dissolution
1	Oil substance	5%
2	Pb and its compounds	3.0%
3	Cd and its compounds	0.3%
4	Cu and its compounds	3.0%
5	As and its compounds	1.5%
6	Cr(VI)	1.5%
7	Hg and its compounds	0.005%
8	CN	1.0%

Table 7. Dissolution test results for geopolymers with finely pulverized IGCC.

Test Item	Unit	Test method	Test Result	Remarks
Oil substance-ES 06302.1	%	(1)	Not detected (Limit of Quantitation 0.1)	–
Pb-ES 06402.2	mg/L	(1)		–
Cd-ES 06405.2	mg/L	(1)		–
Cu-ES 06401.2	mg/L	(1)		–
As-ES 06403.3	mg/L	(1)		–
Cr (VI)-ES06407.2	mg/L	(1)		–
Hg-ES 06404.1	mg/L	(1)	0.0013	–
CN-ES 06351.1	mg/L	(1)	0.02	–

a rise in the moisture content increases the amount of moisture that evaporates during curing at a high temperature and thereby leads to the formation of an increasing number of pores, which lower the compressive strength and density.

Fig. 6 showed the flow of paste depending on the W/S ratio. When the W/S ratio was 0.20, the flow and compressive strength were lowest and highest, respectively, at 65.875% and 65.9 MPa, respectively. When the W/S ratio was 0.26, the flow and compressive strength were highest and lowest, respectively, at 132% and 29.8 MPa, respectively.

To analyze the crystal phase of the geopolymer depending on the W/S ratio, XRD analysis was conducted. For XRD, 40 KV and Cu Kα were applied; data were collected in the following conditions: count time of 0.5 s, and a 2θ range from 5 to 90 °. Fig. 7 displays the XRD analysis patterns. All specimens were observed to have the sodium aluminum silicate hydrate phase, and had no change in the phase depending on the W/S ratio. The lower the W/S ratio was, the relatively smaller the main peak size was. This indicates a rise in the amorphous material content. This result was consistent with that of a previous report that the higher the fraction of an amorphous material, the more the compressive strength was.

Stability evaluation

After the experiments, the finely pulverized IGCC fused slag was judged to be an appropriate geopolymer material. However, given that the IGCC fused slag includes heavy metals, it is necessary to analyze its actual applicability. Therefore, this study requested Korea Testing Laboratory, an institution involved in analyzing wastes, to analyze the geopolymer that was cured for three days at 70 ºC, with 18 M and 0.20 W/S ratio, in accordance with Sub-paragraph 1 of Paragraph 2 of Article 17 of the Wastes Control Act. The hazardous substances in the designated waste (related to Paragraph 1 of Article 2) are presented in Table 6. The analysis results are shown in Table 7. According to the analysis, the dissolution levels of the heavy metals in the geopolymer were lower than the reference values for hazardous substances contained in the designated wastes specified by the Ministry of Environment, Government of the Republic of Korea. In conclusion, the geopolymer with the finely pulverized IGCC fused slag was found to exhibit high stability, and showed promise for commercialization. Thus, the finely pulverized IGCC fused slag is a potential alternative to concrete.

Conclusions

In this study, the applicability of IGCC fused slag, a by-product of IGCC, as a high-strength geopolymer was analyzed to provide a fundamental material for future research. In the case of the finely pulverized IGCC fused slag with particles with an average size of 128 μm the compressive strength of the 7-day-aged slag with 7 was 59.908 MPa at an W/S ratio of 0.20 and a concentration of 18 M. According to previous studies, as the number of aging days increases, the microstructure of geopolymers becomes increasingly denser due to the alumino-silicate phase and their strength increases. Therefore, although it is not measured, the compressive strength of the slag with 28-day aging is expected to be greater than 60 MPa [10]. The slag was found to be a suitable high-strength construction material under the experimental conditions. Nevertheless, in order to achieve this high strength, it is necessary to increase the W/S ratio and to reduce the molar concentration in terms of workability. It is necessary to develop geopolymers with a high strength at a high W/S ratio and a low molar concentration and to analyze the essential requirements of a construction material, such as stable long-term performance.

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