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Study on a Nano-Microstructure and Properties of Geopolymer by Recycling Integrated Gasification Combined Cycle Coal Ash Slag

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In this study, a geopolymer having a nano-scaled structure was fabricated using recycling fly ash slag discharged from IGCC (Integrated Gasification Combined Cycle), to assess the possibility of employing it to replace high strength concrete. Strength, density, crystal phase, and bonding structure, were measured and the nano-size crystal phase of the geopolymers was observed as a function of experimental parameters such as water-to-solid ratio (w/s ratio), flow of paste, and amount of sodium silicate in the alkali activator, NaOH. The geopolymer prepared with NaOH containing 50~70% sodium silicate and a w/s ratio of 0.26~0.28 showed a compressive strength of 75~80 MPa, which satisfied the design standard for high strength concrete in Korea, 40 MPa. The specimen made with NaOH containing 55% sodium silicate had plate-shaped crystals with a nano-scale size, 100 nm or less, and showed compressive strength of 77 MPa, 3.9 times higher than that made with only NaOH. From the viewpoint of microstructure, it was confirmed that nano-sized plate-like crystals and amorphous structure were both effective in improving the strength of the specimen. In conclusion, this study showed that high-strength geopolymer made from IGCC coal ash slag may replace cement used in building materials and concrete secondary products in the near future.

Keywords: Nano Crystal, Geopolymer, Recycling, IGCC, Coal Ash Slag.

1. INTRODUCTION

Most civil engineering and construction industries currently use Portland cement as a binder. However, in addition to excessive energy consumption in the cement manufacturing process, global warming is also accelerated by the large amount of CO_2 gas generated during heat treatment of limestone ($CaCO_3$), the main raw material of cement.

In recent years, geopolymer materials have been attracting attention as a new binder with little CO_2 generation during the manufacturing process.[1] The term geopolymer was coined by Davidovits[2] in France in 1978 and refers to a material that is cured and hardened by the addition of an alkali activator to kaolinite system minerals through condensation polymerization without a high temperature sintering process. Geopolymers have an amorphous structure composed of aluminosilicate and offer many advantages such as excellent chemical durability and mechanical properties, and the possibility of being manufactured from industrial wastes or low-grade materials.[3–6]

Recently, although the recycling rate of various waste resources is increasing with the rapid development of waste recycling technology, the amount of waste land-filled on the coast and in the ground is not decreasing.[2, 7–8]

Among various types of industrial wastes, fly ash, blast furnace slag, molten slag, and waste catalyst slag have appropriate components and structures for the manufacture of geopolymers. In this light, establishing technology for manufacturing geopolymers by recycling the waste resources would greatly expand the construction materials market. Recently, IGCC (Integrated Gasification Combined Cycle), which is a next generation coal power generation technology that can make not only electricity but also hydrogen and liquefied petroleum from coal raw materials, has received a great deal of attention.

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Most of the coal ash produced in IGCC thermal power generation is in the form of fused slag, and the annual emissions in Korea are about 81 thousand tons and this is expected to increase annually. Previously, most alkali activators that are mainly used in the production of geopolymers were based on a single material such as NaOH and KOH. However, research results have been published in which Na_2SiO_3, Na_2CO_3 or $NaAlO_2$ is added to NaOH or KOH to make a so-called 'complex activator.'[9–10] When a complex alkali activator containing NaOH and Na_2SiO_3 is used to make geopolymer paste, the concentration of OH^- group due to the hydrolysis reaction of Na_2SiO_3 and Si ions increases in the paste, as compared with the case of using a single activator such as NaOH. When the OH^- group is increased, the alkalinity of the paste increases and more Si and Al ions are eluted from the raw material.

As a result, long-chain silicate oligomers are well formed because the ions necessary for the geopolymerization process are abundant. Long-chain silicate oligomers then combine with $Al(OH)_4^-$ ions to form Al–O–Si bonds, i.e., geopolymer precursors.[5, 11]

In this study, we have investigated the process conditions for the production of high strength geopolymers by using IGCC slag as raw material. In particular, a complex activator composed of 0~75% sodium silicate and NaOH was used to enhance the mechanical strength of the geopolymer by promoting the geopolymerization reaction. Experiments were also conduct to-solid ratio (W/S ratio) to alleviate the deterio the fluidity of the paste due to the use of the complex activator.

2. EXPERIMENTAL DETAILS

The XRF results of IGCC slag (Table I) show that the raw material contains 49.25% of SiO_2 and 20.16% of Al_2O_3. The IGCC slag shows a typical amorphous pattern in the XRD measurement results. IGCC slag is suitable as a geopolymer raw material because materials of amorphous structure can easily elute Si and Al ions with the use of an alkali activator.

In this study, IGCC slag was finely pulverized by a rotary friction grinding method, to an average particle size of 128 μm. The experimental conditions for producing the geopolymer using IGCC slag are shown in Table II.

The raw material powder was mixed with an alkali activator to form a paste, and then the mixed paste was poured into a brass mold (5 × 5 × 5 cm) to form a green body. The green body was sealed in a plastic bag to prevent rapid water evaporation, and was cured at 70 °C for 24 hours. After curing, the specimens were demolded and aged at room temperature for 3 days.

Table II. Experimental parameters for fabrication of the geopolymer using IGCC coal ash slag.

Blended alkali activator				
NaOH	Sodium silicate	Water/solid ratio	Curing condition	Aging condition
15 M	0~75%	0.25~0.29	70 °C/24 h	Room temperature/ 3 days

A workability test was conducted according to ASTM C1437 to determine the flow of geopolymer paste containing the alkali activator and the raw material.

3. RESULTS AND DISCUSSION

Figure 1 shows the compressive strength and density of the IGCC slag-based geopolymer aged for 3 days. The parameters used were a W/S ratio of 0.26 and a complex alkali activator composed of 0~75% sodium silicate solution and NaOH. As the amount of sodium silicate added to NaOH was increased, the viscosity of the paste increased and the flowability decreased. If the flowability of the paste is lowered, the workability becomes poor and this may become a problem when applied to the actual field. However, if the e flowability is further improved, and the workability problem can be solved. These observations were quantitatively measured by a workability test and are shown in Figure 2.

As the amount of sodium silicate added was increased, the compressive strength of the specimen increased. The increase of the strength of the geopolymer made with a greater amount of sodium silicate is due to the increase of the pH caused by the hydrolysis reaction and also to the fast elution of Si and Al ions. Moreover, the increased viscosity of the paste by the increased amount of sodium silicate suppressed water evaporation, thereby sustaining the geopolymer reaction for a longer period.

Figure 3 shows the compressive strength and density of the IGCC slag geopolymer aged for 3 days. Two kinds of complex alkali activators, 50 and 75% sodium silicate in NaOH were used. The flowability of each paste was measured by a workability test and is shown in Figure 4. Overall, the compressive strength was higher when the amount of sodium silicate was 75% than at 50%, and the optimum W/S ratio showing the maximum compressive strength was 0.27.

Table I. Chemical composition of IGCC coal ash slag analyzed using by XRF (wt%).

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	C	LOI*	Total
IGCC slag	49.25	20.16	5.61	21.67	1.28	0.49	0.48	1.07	0.06	0	100

Note: *LOI: Loss on ignition.

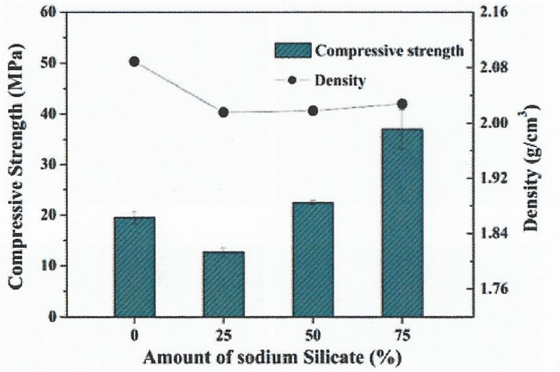


Figure 1. Compressive strength and density of geopolymers made with a 0.26 W/S ratio as a function of amount of sodium silicate added in the NaOH activator.

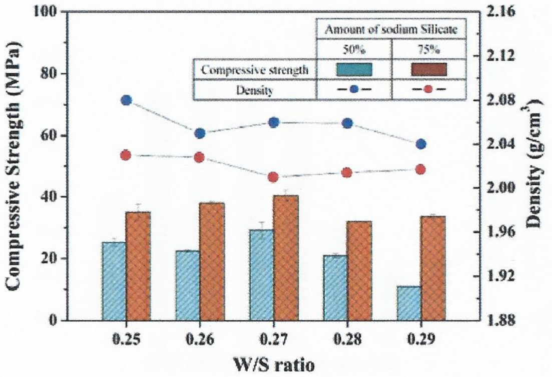


Figure 3. Compressive strength and density of geopolymers as a function of the amount of sodium silicate added and W/S ratio.

When the W/S ratio was 0.27 or more, the compressive strength of the geopolymer decreased again. However, the decline in strength was larger for the geopolymer made by using an alkali activator containing 50% sodium silicate. The flow value of both pastes, the 50 and 75% series pastes, increased as the W/S ratio increased, as shown in Figure 4. In particular, the paste made by using the alkali activator containing 50% sodium silicate and a W/S ratio of 0.29 was completely spread on table, and hence the flow could not be measured. The flow values for
50% sodium silicate and a W/S ratio
which is almost the same as that of paste made
75% sodium silicate and a W/S ratio of 0.28. Interestingly, the compressive strengths of the geopolymers cured from both pastes was similar, falling in a range of 26~30 MPa.

It was confirmed, therefore, that the geopolymer made by using a lower amount of NaOH could have a similar compressive strength as the specimen made by using a greater amount of NaOH through the control of the W/S ratio. The optimum value of the W/S ratio showing maximum compressive strength was 0.27 regardless of the amount of sodium silicate added to NaOH, as shown in Figure 3. The compressive strength and density of the geopolymer prepared with a W/S ratio of 0.27 are shown in Figure 5 as a function of the amount of sodium silicate added in a range of 50 to 75% to NaOH. As the amount of sodium silicate added in NaOH was increased, the compressive strength of the geopolymer also
a high level of compressive strength
0 MPa was shown in the specimens containing 55~70% sodium silicate, which is about four times higher than that of the sample containing 0% sodium silicate.

On the other hand, when the amount of sodium silicate was less than 50%, the strength enhancement was not significant. The compressive strength was also low when the amount of sodium silicate was greater than 75%. From these results, it was found that there is a proper

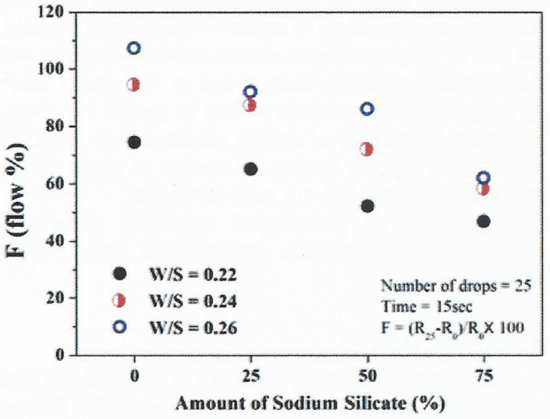


Figure 2. Flow (%) obtained from workability test of pastes for geopolymer fabrication as a function of the amount of sodium silicate added in the NaOH solution and W/S ratio.

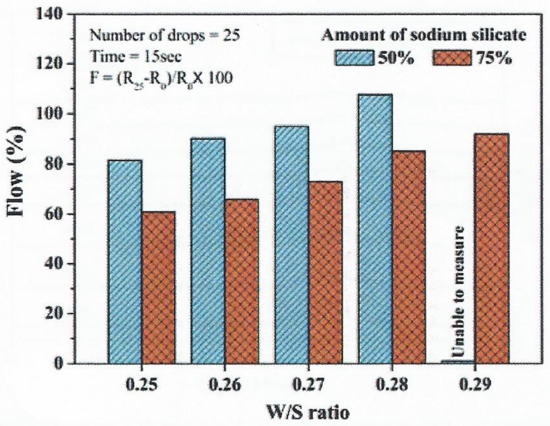


Figure 4. Workability test value of pastes as a function of the amount of sodium silicate added and W/S ratio.

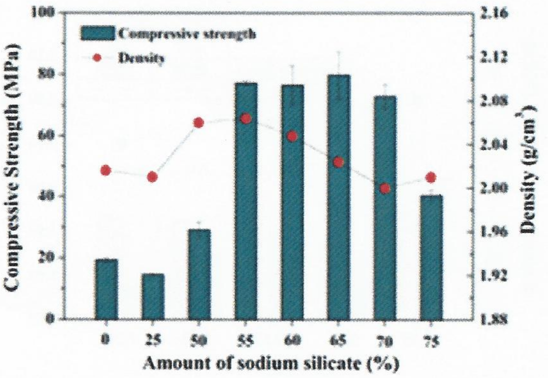


Figure 5. Compressive strength and density of geopolymers made with a 0.27 W/S ratio as a function of amount of sodium silicate.

ratio range for the amount of sodium silicate in a complex activator to induce an effective geopolymerization reaction. It is important that a large amount of Si and Al ions be quickly released from the raw material during the geopolymer curing process. However, the eluted ions should also form gels without rapid crystallization. A gel with high viscosity inhibits water evaporation and makes the geopolymer reaction last longer. Control of the w/s ratio is very effective in enhancing the flowability of the paste when the viscosity of the paste is too high.

By controlling the compositi
and w/s ratio in this study, it was po
geopolymer having compressive strength of 75~80 MPa, which is far higher than the design standard for high strength concrete in Korea, 40 MPa.

The results of a crystal phase analysis performed by XRD of the geopolymer prepared by using an alkali activator composed of 0~75% sodium silicate solution to NaOH are shown in Figure 6. Hydroxycancrinite [$Na_4(AlSiO_4)_3(OH)(H_2O)$], a zeolite mineral, was

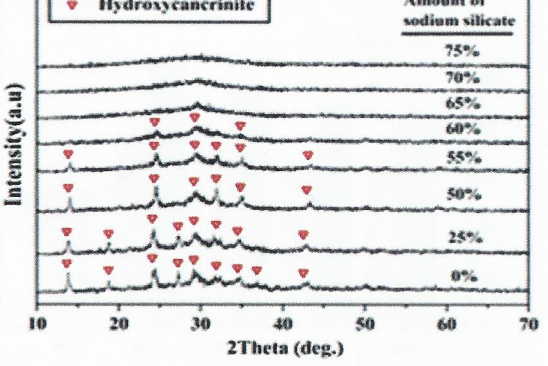
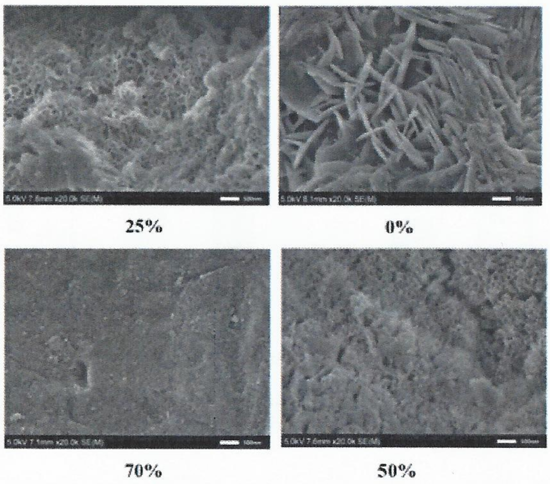


Figure 6. XRD patterns of IGCC slag-based geopolymers as a function of amount of sodium silicate added in the alkali activator of 15 M NaOH solution. [JCPDS #: Hydroxycancrinite (46-1457)].


25% 0%

70% 50%

Figure 7. Microstructures of IGCC slag-based geopolymers manufactured with blended alkaline activator composed of 0~75% sodium silicate and 15 M NaOH solution (×20,000).

produced in specimens made by using an alkali activator containing sodium silicate of 60% or less. The hydroxycancrinite crystal peak strength for the geopolymer made by using only NaOH was higher than that of the other specimens. As the amount of sodium silicate was increased, the intensity of the hydroxycancrinite crystal peak decreased
ddition more than 65% of sodium sil-
of crystalline phase disappeared and only the an amorphous pattern appeared. An amorphous halo pattern was observed at around 30° in the XRD graph.

The nano-scale structure observed by SEM of the fracture surface of the geopolymer made by using 0~75% sodium silicate in NaOH is shown in Figure 7. There is a large amount of plate-shaped crystals having a thickness of 50 to 90 nm and a diameter of 1.0 to 1.3 μm in the specimen made by using only NaOH as an activator. However, as the amount of sodium silicate was increased, the size of the plate-shaped crystals decreased rapidly, and the crystals completely disappeared in the sample made by using above 65% sodium silicate in NaOH. For example, when the amount of sodium silicate added was 25%, plate-shaped crystals having a thickness of about 30 nm and a size of about 200 nm were produced.

In addition, no plate-shaped crystalline phase was observed in the specimens with 65% or more sodium silicate.

4. CONCLUSION

A geopolymer prepared by recycling IGCC coal ash slag and using a complex alkali activator containing 50% or more of sodium silicate and NaOH showed compressive strength up to 80 MPa, which is significantly higher than the design standard for high strength concrete in Korea, 40 MPa. Hydroxycancrinite, a zeolite mineral, was produced in most of the geopolymer specimens prepared in this study. There is a large amount of plate-shaped crystals having a thickness of 50 to 90 nm and a diameter of 1.0 to 1.3 μm in the specimen made by using only NaOH as an activator. However, as the amount of sodium silicate was increased, the size of the crystals decreased rapidly to nanometer level, and the crystals completely disappeared in the sample made with 65% sodium silicate in NaOH. If the W/S ratio is adjusted even when a large amount of sodium silicate is mixed with NaOH, a flow value of more than 80% can be obtained for the geopolymer paste, which would lend sufficient workability. It is thus anticipated that commercialization of the geopolymer developed in this study as a substitute for concrete products will be possible in the future.

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