

DEVELOPMENT OF GEOPOLYMER CONCRETE USING GROUND MOLTEN SLAG OF MUNICIPAL WASTE INCINERATION ASH

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ABSTRACT

In this study, the authors aim to develop a new type of geopolymer using ground molten slag of municipal waste incineration ash (GSWIA). Some influencing factors of strength and fire resistance of GSWIA-based geopolymeric concrete were investigated. During hardening, GSWIA-based geopolymeric concrete expanded because of the formation of H₂, thus the compressive and flexural strengths depended on demoulding time and size of specimen. The earlier the demoulding, the greater the strength. Larger size of specimen resulted in smaller strength. Compressive strength of GSWIA-based geopolymer concrete decreased if exposed to high temperature.

Keywords. Geopolymer, Municipal waste incineration ash, Strength, Fire resistance

INTRODUCTION

Utilization of concrete as a major construction material is a worldwide phenomenon and the concrete industry is the largest user of natural resources in the world. This use of concrete is driving the massive global production of cement, estimated at over 2.8 billion tonnes according to the recent industry data (Lloyd and Rangan, 2010). It is well known that a great amount of CO₂ is emitted during the production of portland cement (OPC). One ton of CO₂ is released into the atmosphere for every ton of OPC produced (Kong and Sanjayan, 2008). The carbon dioxide emissions from cement industry are estimated to be responsible for 5 to 7% of the total global production of carbon dioxide (Mehta, 2001).

Geopolymer concrete (GP-C) has been proposed as an alternative to portland cement concrete (PCC), which does not utilize any portland cement in its production so that leads to the significant reduce in the energy consumption and the CO₂ emission. It is reported by Davidovits that about less 3/5 energy was required and 80%-90% less CO₂ is generated for the production of geopolymer binder than that of portland cement (Davidovits, 1994).

Geopolymer binders behave similarly to portland cement. They can set and harden at room temperature, and can gain reasonable strength in a short period. Some proportions of geopolymer binders have been tested and proved to be successful in yielding synthetic mineral products with high early strength, high mechanical performance, lower creep and shrinkage, thermal stability, excellent durability, and high acid resistance.

Geopolymer is generally believed to possess good fire resistance, due to their ceramic-like properties (Davidovits, 1991). Therefore, geopolymer concrete may possess superior fire resistance compared to OPC concrete. OPC concrete degenerates at elevated temperatures due to chemical and physical changes since it contains a high level of chemically bound water essential to the gel structure. The decomposition and evaporation of the bound water is one of causes of OPC concrete's spalling occurring in a fire. However, the intrinsic chemistry of the geopolymer binder does not require the retention of water within gel phases to maintain structural integrity of the binder. This feature may reduce the spalling risk of GPC.

The molecular structure of geopolymer is similar to those of zeolites or feldspathoids, which are known for their excellent abilities to adsorb and solidify toxic chemical wastes such as heavy metal ions. Hazardous elements present in waste materials are tightly locked into the 3-D network of geopolymer.

Therefore, geopolymer has been gradually attracting world attention as potentially revolutionary materials. A wide range of natural Al-Si minerals, wastes, and slags would serve as potential source materials of geopolymers, such as kaolin, fly ash, blast furnace slag, red mud, sewage sludge slag, etc.

In Japan, the disposal of municipal waste incineration ash is one of serious social problems because of shortage of landfill sites, and pollution of dioxin and heavy metals. One of the solutions of this problem is to melt incineration ash and then make slag, or to directly make the molten slag from municipal waste now. This melting process can remove the dioxin in the incineration ash and lock the heavy metal ions in the slag. In 2008, the melting treatment facilities in Japan produced about 3.3 million tons of molten slag.

The molten slag is usually used in concrete products such as block, asphalt concrete, and roadbed, etc. (Hosokawa, et al., 2004), but it hasn't yet been used in structural concrete of building and civil engineering on a large scale because worries about the durability of concrete are remained. Especially, the expansion and pop-out phenomenon occur in the long run, which is resulted from the formation of gibbsite and hydrogen, because municipal waste always contains aluminium ($2\text{Al} + 6\text{H}_2\text{O} \rightarrow 2\text{Al}(\text{OH})_3 + 3\text{H}_2$).

However, because the molten slag consists of Al and Si oxides, ground molten slag may be used as an active filler of geopolymer. And the pulverization of the molten slag may speed up the reformation reaction of gibbsite and hydrogen, which may lead to that the expansion only occurs in the hardening stage. In this study, we aim to fabricate a new kind of geopolymer using the GSWIA, and investigate its fire resistance.

EXPERIMENTAL PROGRAM

Raw Materials. The molten slag of municipal waste residue, produced in Ube city, Yamaguchi prefecture by water-cooled system, was ground to use as an active aluminosilicate material of the geopolymeric materials in this study. The compositions of the molten slag may vary from the production period because kinds of municipal refuses may be different from the seasons. We took samples in the beginning of August 2012 (Sample 1), and November 2012 (Sample 2), respectively, to analyze their chemical compositions. The results of chemical analysis are shown in Table 1. The chemical compositions of the two samples were very close. The mean contents of SiO₂, Al₂O₃, and CaO were 44.5%, 15.4%, and 24.5%, respectively. The densities of the sample 1 and the sample 2 were almost the same, being 2.47 and 2.46g/cm³, respectively. We pulverized the molten slag by a planetary ball mill. A kind of powder (GSWIA 1) with a specific surface of 3810 cm²/g was gotten from the sample 1. Two kinds of powder (GSWIA 2-1 and GSWIA 2-2) were obtained from the sample 2, which had the specific surfaces of 3570cm²/g, and 3268cm²/g, respectively.

Alkaline activators in this investigation consisted of alkali silicate and hydroxide solution. The alkali silicate used was sodium silicate solution with a specific gravity of 1.54 g/cm³. The sodium silicate solution was diluted by adding purity water at a ratio 1:1 by volume. The hydroxide solution was 10 M sodium hydroxide solution. Then, we mixed the diluted sodium silicate solution and the sodium hydroxide solution at a ratio of 3:1 by volume to get an alkaline activator.

Sea sand, and crushed stone were used as fine aggregate and coarse aggregate, respectively. Their physical properties are shown in Table 2.

Mix Proportions. In this

study, we first performed flexural strength test using geopolymer mortar specimens in the experiment I for examining whether the GSWIA can be used as an active filler. In the experiment II, we mixed geopolymer paste (GP-P), mortar (GP-M), and concrete (GP-C) to investigate their compressive strength and fire resistance. The mix proportions of these geopolymeric materials and the experimental conditions are shown in Table 3.

Table 1. Chemical composition of GSWIA

Compound	Content (%)	
	Sample 1	Sample 2
SiO ₂	45.28	43.72
Al ₂ O ₃	15.18	15.61
CaO	24.18	24.76
Fe ₂ O ₃	4.07	3.88
MnO	0.14	0.14
TiO ₂	1.11	1.19
MgO	2.24	2.45
K ₂ O	2.1	1.79
Na ₂ O	2.29	2.11
P ₂ O ₅	2.48	2.53
SO ₃	0.05	0.03
BaO	0.093	0.1007
SrO	0.0436	0.0425
ZnO	0.2689	0.2216
PbO	0.0091	0.0106
CuO	0.3042	0.2836
NiO	0.0249	0.0216
ZrO ₂	0.0241	0.0373
Cl	0.0554	0.0437
Others	0.021	1.0393

Table 2. Physical properties of the used aggregates

Property	Sea sand	Crushed stone
Density in water-saturated state (g/cm ³)	2.57	2.73
Water absorption ratio (%)	1.36	0.47
Fineness modulus	2.90	6.68
Maximum size (mm)	5	25

Fabrication and Curing of Specimens. In the experiment I, mortar prismatic specimens with size of 2×2×8cm were produced and put into polyvinyl chloride bags to prevent the mixing water from evaporation in the hardening stage. One hour later after the production, the specimens with moulds and the bags were placed into an autoclave for curing 24 hours at 80°C. During the curing, when the curing time was 2 hours, the specimens were demoulded. After the 24 hours curing, the flexural strengths of the specimens were measured.

In the experiment II, geopolymer paste and mortars were mixed with a Hobart mixer for 3 minutes. But when producing the GP-C, We first mixed geopolymer mortar matrix, then put coarse aggregate into it and mixed the GP-C by hand. The sizes of the specimens are shown in Table 4. The specimens, packed into polyvinyl chloride bags, were cured for 24 hours at 80°C. The specimens of Series II-2* and II-2** were demoulded two hours later after they put into the autoclave. The demoulding of other specimens was done after the 80°C-curing. After the 80°C-curing, the specimens were further cured for 6 days at room temperature (20°C). Before the compressive test, the end faces of the specimens were polished with a grinder. During the curing, the specimens expanded due to the formation of Gibbsite.

Table 3. Mix Proportions of geopolymeric materials

Series			A/ GSWIA (%)	S/ GSWIA	Unit mass (kg/m ³)				
					GSWIS	A	W*	S	G
Exp. I	I-1	GP-M	65	2	GSWIA 1: 592	385	0	1184	-
	I-2				GSWIA 2-1: 591	384		1183	
Exp. II	II-1	GP-P	30	-	GSWIA 2-2: 1497	449	15.3	-	-
	II-2	GP-M	35	2.5	GSWIA 2-2: 938	328	28.6	821	-
	II-3		55		GSWIA 2-2: 699	384	0	961	-
	II-4		55		GP-C	GSWIA 2-2: 418	230	0	532

[Notes] A: alkaline solution, W*: additional water, S: sand, G: coarse aggregate

Table 4. Test conditions and results of geopolymeric materials

Series			Size of specimen (cm)	Elapsed time before demoulding (hour)	Age (day)	F_f (Mpa)		F_c (Mpa)		W_a (%)
						Unexposed	Temp. exposed	500°C	800°C	
Exp. I	I-1	GP-M	2×2×8	2	1	7.09	-	-	-	5.2
	I-2					8.57	-	-	-	-
Exp. II	II-1	GP-P	∅5×10	24	7	-	16.9	7.1	6.4	16.8
	II-1*			2		-	24.2	-	9.2	14.8
	II-2	GP-M		24		-	19.1	9.4	6.2	13.0
	II-2*			2		-	30.1	17.9	-	11.6
	II-2**			2		-	17.2	14.4		
	II-3	GP-C		24		-	13.9	10.5	4.3	-
	II-4			∅10×20		24	-	12.4	8.5	5.7

[Notes] lasting time of heating at 500 or 800°C for Series II-2** was 2 hours, other series were 24 hours, F_f is flexural strength, F_c is compressive strength, and W_a is water absorption ratio.

Elevated Temperature Exposure Regime. At the age of 7 days, the specimens were dried up at 105°C for 24 hours, then subjected to high temperatures of up to 800°C at an incremental rate of 100 °C /hour from room temperature. As soon as the target temperature (500, 800°C) was attained, it was maintained for an additional 24 hours or 2 hours before the furnace was shut down to allow the specimens in the furnace to cool down to room temperature, as shown in Fig.1. This cooling usually takes more than 12 hours. In the meantime, the concurrent counterparts were left undisturbed at room temperature after the 24 hours-drying for comparative study. The compressive test of the specimens unexposed to high temperature was performed after dried up.

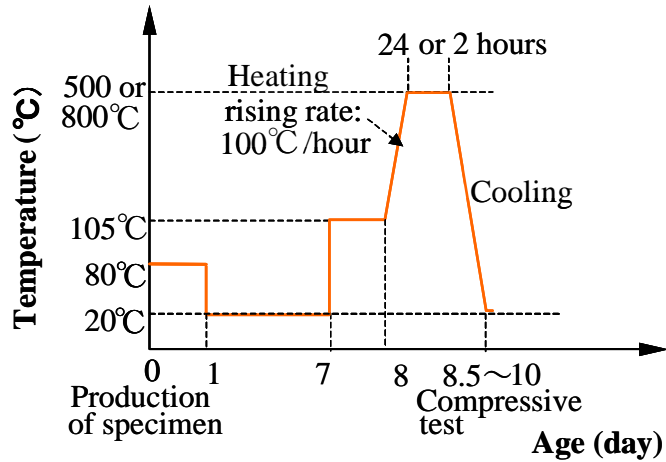


Figure 1. Heating regime of the specimens

TEST RESULTS AND DISCUSSION

Mechanical Property and Expansion Behavior. The flexural strengths of Series I-1 and I-2 that were cured at 80°C are shown in Table 4 and Figure 2. The flexural strengths of Series I-1 and I-2 were very close. With increasing the 80°C-curing time, the flexural strengths increased. But if the curing time exceeded 24 hours, the flexural strength almost didn't increase. Hence, in the experiment II, we cured the specimens at high temperature of 80 °C for 24 hours.

Figure 3 shows the flexural strengths of cement paste and mortar published in the reference (Ohgishi, at al., 1985). Compared to the cement paste and mortar with

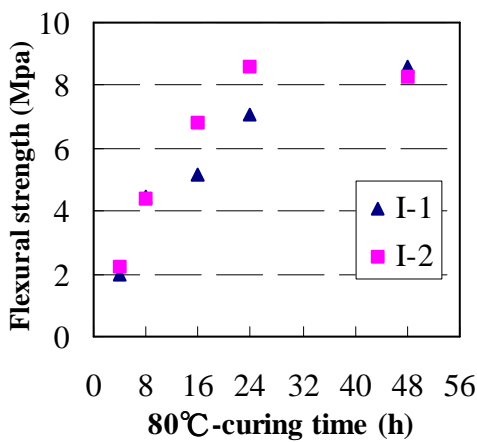


Figure 2. Evolution of flexural strength with curing

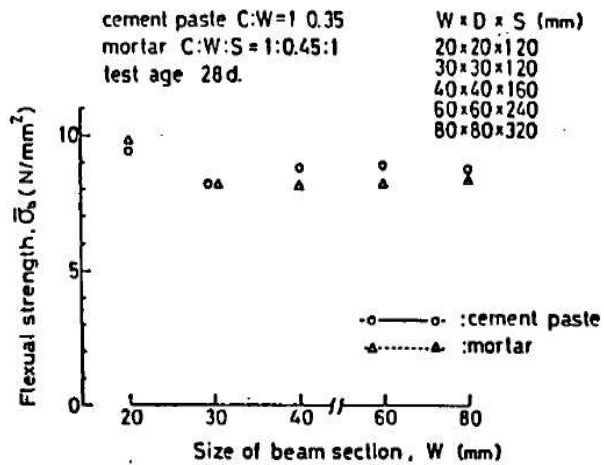


Figure 3. Flexural strength of cement paste and mortar (Ohgishi, at al., 1985)

water-cement ratio of 0.35, and 0.45, respectively, though the alkaline liquid-GSWIA ratio was 65%, the flexural strengths of the geopolymeric mortars I-1 and I-2 were greater. Thus, the GSWIA can be used as active filler of geopolymeric materials.

Figure 4 shows the increase of expansion of the specimens due to the formation of gibbsite with curing time. It can be seen from this figure that the expansion increased with the 80°C-curing time, but after 16 hours the expansion stopped.

Figure 5 indicates the variation of the water absorption ratio of Series I-1 with the 80°C-curing time. The longer the curing time, the smaller the water absorption ratio. Like the tendency of the flexural strength variation, once the curing time was more than 24 hours, the water absorption ratio approached to a certain value.

The compressive strengths of the specimens, unexposed to high temperature in the experiment II, are shown in Figure 6. All the compressive strengths were smaller. If

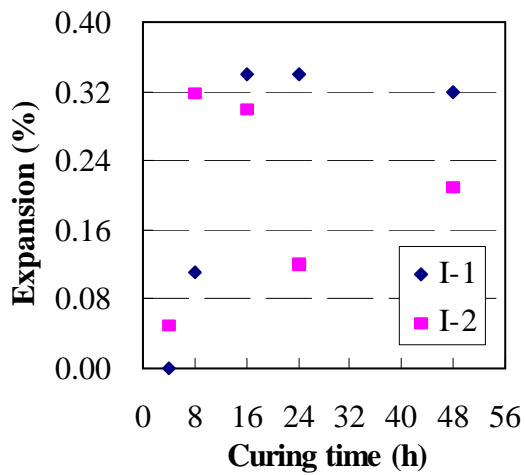


Figure 4. Variation of expansion ratio with curing time

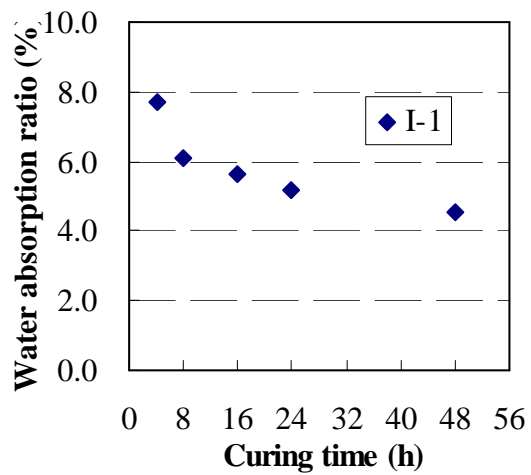


Figure 5. Variation of water absorption ratio with curing time

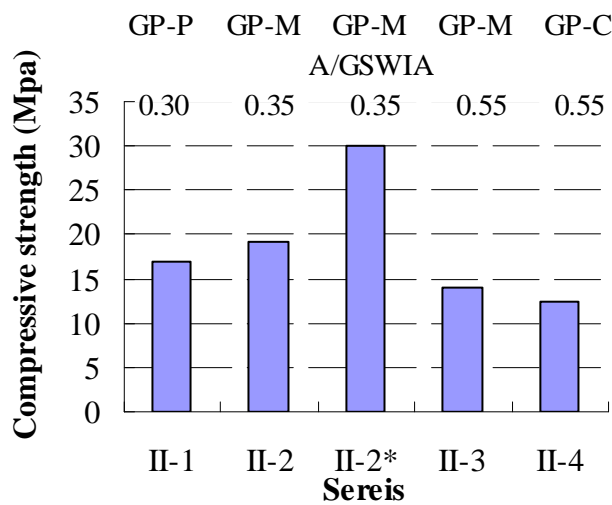


Figure 6 Compressive strength of the geopolymeric specimens unexposed to elevated temperature

compared the water absorption ratios shown in Table 4, we can find that the specimens produced in the experiment II had greater values. Greater pore amount maybe was one of the reasons of low strength. However, based on the compressive strengths of Series II-2 and II-2*, if the demoulding was delayed from 2 h to 24 h later after the specimens were put into the autoclave, the compressive strength decreased greatly. This probably is because the hydrogen generating during the formation of gibbsite was difficult to discharge from the specimen and formed many pores in it, if the demoulding was late. Due to the same reason, the specimens of the experiment I, which had smaller sizes and larger open surface before demoulding, had smaller water absorption ratio. Moreover, from the results of Series II-2 and II-3, it can be seen that the greater the alkaline solution-GSWIA ratio, the smaller the compressive strength like ordinary cementitious materials.

Fire Resistance. Figure 7 shows the residual ratio of compressive strength (F_c) of the geopolymeric specimens after exposure to elevated temperatures. No matter which kind of GSWIA-based geopolymeric material, if the specimens were heated at 500°C or 800°C, their compressive strengths decreased. The higher the elevated temperature, the smaller the compressive strength. When heated at 500°C, the compressive strength reduced to about 60%, but at 800°C, about 40% was remained. The phenomenon is very similar to cementitious materials.

When subjected to high temperature, due to different expansion ratio, cracks are generated in the interface between paste and aggregates. It is thus reasonable to consider that the strengths of mortar and concrete will decrease. The phenomenon of strength reduction of GSWIA-based geopolymeric paste exposed to high temperature is probably because of the existence of gibbsite and C-S-Al-H gel. According to the reference (Yamada,1981), the gibbsite will start to decompose greatly at about 200°C, as shown in Fig.8. The growth of cracks resulted from hydrogen gas's expansion in the pores maybe is another reason.

When the elevated temperature reached to 800°C, the effect of mix proportions on the residual ratio of F_c was smaller. However, at 500°C, the smaller the A-GSWIA

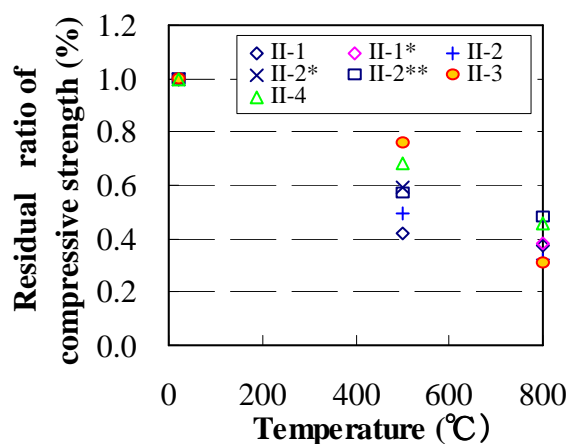


Figure 7. Residual ratio of F_c after exposed to elevated temperature

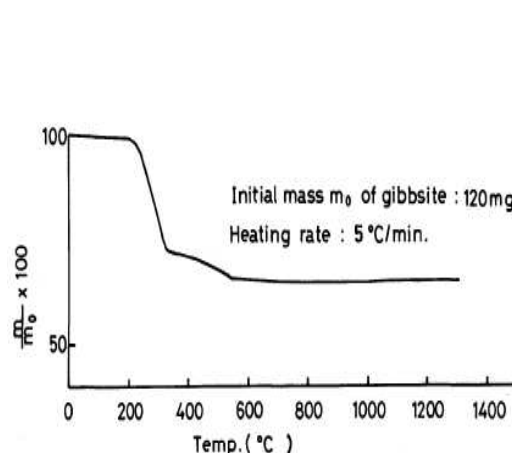


Figure 8. TGA curve of gibbsite exposed to high temperature (Yamada, 1981)

ratio, the smaller the residual ratio of F_c . This is because greater GSWIA content resulted in a large quantity of gibbsite. The results of Series II-1 and II-1* at 500°C show that the residual ratio of F_c was not related to strength level. Moreover, the reduction of the lasting time of heating at 500°C from 24h to 2h didn't greatly increase the residual ratio of F_c (see the results of Series II-2* and II-2**).

CONCLUSIONS

In this study, the authors tried to develop GSWIA-based geopolymeric concrete, and investigated its fire resistance. Obtained results are summarized as follows: 1) The ground molten slag of municipal waste incineration ash can be used as active filler of geopolymeric materials. 2) The strength of GSWIA-based geopolymeric materials was greatly dependent on discharge of hydrogen. Early demoulding and decreasing size of specimen was benefit to the improvement of strength. 3) Small alkaline solution-GSWIA ratio yielded high compressive strength. Better 80°C-curing period was 24 hours. 4) When subjected to high temperature of 500 or 800°C, the strengths of GSWIA-based geopolymeric materials decreased. The residual ratios of F_c were about 60% at 500°C, and 40% at 800°C, respectively.

Further works are to optimize the mix proportions and curing method, to develop the method of reducing the hydrogen content, to clarify the mechanism of property degradation when exposed to elevated temperature, and to investigate in detail the mechanical properties and durability of GSWIA-based geopolymeric concrete.

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