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Statistical Analysis of the Physical Properties in a Slag-OPC-Gypsum System as a Compound Mixing Ratio

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ABSTRACT

The effect of the mixing ratio of compounds in a slag-OPC-Gypsum system on the physical properties of Slag cement is investigated in this study. Na_2SO_4 was used as an alkali activator. Blast furnace slag cement was prepared from a mixture of blast furnace slag, ordinary Portland cement and anhydride gypsum. The fluidity and the compressive strength according to the ratio of each mixture were analyzed in statistical analyses in order to discover the parameters influencing the fluidity and compressive strength. The results showed that the hydration of blast furnace slag took place with the addition of Na_2SO_4 and that column-crystalline ettringite was created as the main hydration product of the blast furnace slag. In addition, it was found that the compressive strength of blast furnace slag cement tends to increase when the ordinary Portland cement content is higher up to three days. However, it is known that the compressive strength tends to increase as the blast furnace slag content becomes higher with increases in the level of OPC after 28 days. As a result of this analysis, it is believed that the ordinary Portland cement content influences the initial compressive strength of blast furnace slag cement, and that in later days this is highly influenced by the slag content.

Key words*: *Blast furnace slag, Activator, Hydration Activity, Ettringite, Ordinary Portland cement

1. Introduction

The primary goal of all new developments of cement and concrete materials is to improve the strength and durability of these materials. However, the potential to improve ordinary Portland cement using existing methods has been exhausted. Additionally, with the increase in environmental and energy-related problems, there has been a great deal of interest in utilizing industrial waste by-products. Research is currently underway that has the use of waste materials as a substitute for cement as its goal. Slag, a by-product in the production of steel, is often used in construction and civil engineering fields as an additive to cement, as an aggregate, or as roadbed material. A type of slag known as blast furnace slag, a by-product of the pig iron production process, has been used as a new type of binder in concrete in what is known as blast furnace slag cement. The advantages of blast furnace slag cement include a low level of heat generation during hydration reactions, the long-term strength improvement of concrete, chemical endurance, and the fact that it is an energy-saving utilization of industrial by-products.[1,2] However, blast furnace slag cement has a low early strength compared to ordinary Portland cement owing to the slower early hydraulic reactivity of this type of cement. Such a disadvantage can be offset by promoting an early hydration reaction with the addition of an alkali activator and by adjusting the fineness of blast furnace slag as well as the mixture ratio using OPC.[4,5] Typically, when blast furnace slag is put into water, an impermeable layer of alumino-silicate is formed on the surface of the slag particles. Due to this impermeable layer, no hydration reaction can take place. However, in an alkaline solution, OH radicals in the solution destroy the alumino-silicate bonds of the impermeable layer, leading to the dissolution of slag particles and the subsequent hydration of the slag. Dissolved silicate and aluminum ions react with calcium ions, water molecules and OH radicals in the solution to form the hydrates of C-S-H and C-A-H.[6,7] The present study was carried out with the purpose of providing hydraulic reactivity to blast furnace slag with the addition of a Na_2SO_4 activator and to increase the fineness of blast furnace slag. In addition, to design low-energy blast furnace slag cement, the mixture ratio in a three-component system of blast furnace slag, ordinary Portland cement and anhydride gypsum was adjusted. The fluidity and the compressive strength according to the mixture ratio of each were analyzed using statistical analyses in order to discover the parameters influencing the fluidity and compressive strength. Through this statistical method, the most suitable mixing ratio of blast furnace slag cement with the three-component system of blast fur-

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Table 1. Chemical Analysis of Starting Materials

Raw materials	Chemical Composition (wt %)								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	Ig.loss
Blast Furnace Slag	32.7	15.0	0.6	43.6	4.8	0.19	0.46	2.8	0.1
OPC	21.4	6.3	2.9	61.4	2.7	0.13	0.90	2.2	1.7
Anhydrite Gypsum	3.7	0.7	0.1	38.3	0.2	0.01	0.03	54.4	2.9

Table 2. Experimental Conditions and Mixing Ratios

No.	Experimental point			Mixing ratio (wt %)			Remarks
	Slag(X1)	OPC(X2)	AG(X3)	Slag	OPC	AG	
1	1	0	0	90	5	5	Extreme vertices
2	0	1	0	70	25	5	
3	0	0	1	70	5	25	
4	2/3	1/3	0	83.33	11.67	5	Side
5	1/3	2/3	0	76.67	18.33	5	
6	0	2/3	1/3	70	18.33	11.67	
7	0	1/3	2/3	70	11.67	18.33	
8	1/3	0	2/3	76.67	5	18.33	
9	2/3	0	1/3	83.33	5	11.67	
10	1/3	1/3	1/3	76.66	11.67	11.67	Center

-The addition of alkali activator (Na_2SO_4) 1.0% and superplasicizer (naphthalene series) 0.5%

nace slag, ordinary Portland cement and anhydride gypsum was determined.

2. Experimental Procedure

The blast furnace slag (referred to henceforth as "Slag") and anhydrite gypsum (henceforth "AG") used as raw materials in this study are the byproducts generated from the manufacture of steel and phosphoric acid by companies P and A, respectively. Ordinary Portland cement (henceforth "OPC") is a product of company S in Korea. The Blaine index of the raw materials used were 4,200 (Slag), 3,200 (OPC) and 5,000 (AG) cm^2/g; the chemical compositions are shown in Table 1. Reagent-grade Na_2SO_4 was used as an alkali activator. In this study, the effect of Na_2SO_4 on the hydration of slag was investigated via measurements of the hydration rate with a conduction calorimeter as well as observations of the microstructure in the paste produced after hydration. The measurement of the hydration rate was carried out at 20°C using an isothermal conduction calorimeter. The solid-to-liquid weight ratio was 1 and the fineness of the slag used for this test was 4,200 cm^2/kg.

The physical properties of slag cement including the fluidity and compressive strength of blast furnace slag cement containing the three components of slag, OPC and AG were measured. In this study, the factors that influence the fluidity and initial compressive strength of blast furnace slag cement were evaluated through statistical analyses.

The raw materials were mixed according to the simplex screening design in a restricted area. The simplex design is

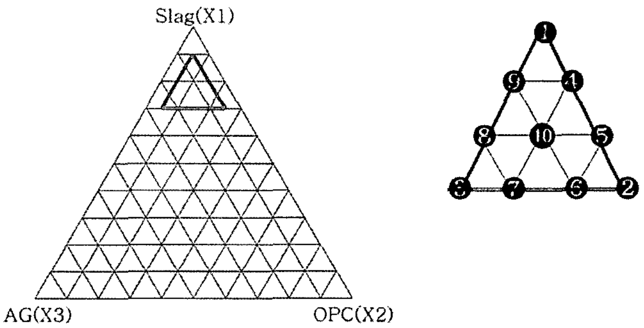

Fig. 1. Three-component diagram model by mixture design of experiment.

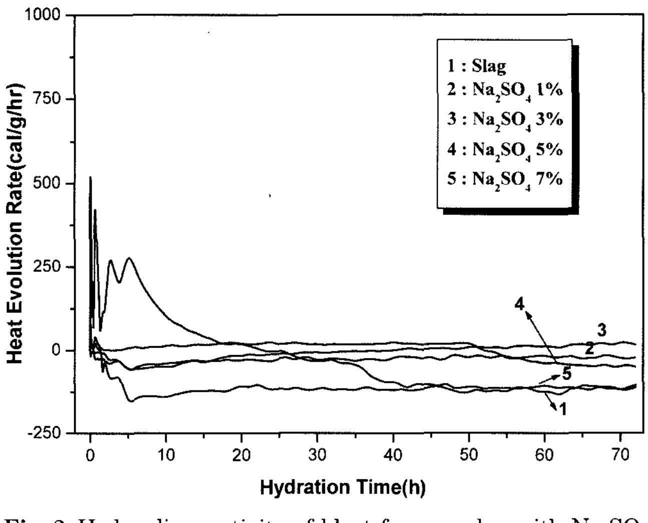

Fig. 2. Hydraulic reactivity of blast furnace slag with Na_2SO_4 according to a conduction calorimeter.

an experimental mixture design for the three-component diagram of Slag-OPC-AG,. For a restricted area three-component diagram, a limited zone to conduct a simplex statistical analysis using triangular coordinates was selected in the range of 0.70~0.90 for Slag (X1), 0.05~0.25 for OPC (X2) and 0.05~0.25 for AG (X3), as shown in Fig. 1. Table 2 shows the mixture ratios by experiment design with an alkali stimulant (Na_2SO_4) set at 0.5% of the mixture. The mortar was prepared by the mixture designed from the three-component diagram of Slag-OPC-AG, standard sand, and water at a ratio of 1:2.45:0.485. It was molded into a 5×5×5 cm cube mold. To test the compressive strength, it was cured in water for several days at room temperature before the molds were removed, and the compressive strengths of the specimens were then measured. The fluidity of the mortars was measured according to the Korea Standard method for the testing method of slump: KS F 2402, and the measurement of the compressive strength of the mortars was carried out according to the Korea Standard method for the testing of the compressive strength of hydraulic cement mortar; this involved the use of a compression testing machine (Heung Jin, Model HCT-DS200).

3. Results and Discussion

Fig. 2 shows the hydraulic reactivity of blast furnace slag with Na_2SO_4 according to the conduction calorimeter. Na_2SO_4 greatly promoted hydraulic reactivity and brought about a low level of heat generation during the initial stage which in this case was within three hours since the start of the reaction. It is believed that because Na_2SO_4 is also widely used as an endothermic agent, it absorbed the latent heat generated from the hydration reaction of the slag. Fig. 3 shows a SEM photo of the paste microstructures of the slag mixed with 5 wt % of Na_2SO_4 after 10 hours of hydration. In the slag paste containing Na_2SO_4, it was observed that a substantial amount of hydration product, identified as column-crystalline hydrate, had formed. Such a result coincides with earlier results that supported early hydraulic reactivity in slag as measured with a calorimeter. From the results of the XRD analysis, it was determined that the column-crystalline hydration product is ettringite.

Table 3 shows the fluidity and compressive strength of the mortar created from the three-component diagram mixture of Slag-OPC-AG in Table 2. In terms of the physical prop-

Table 3. Experimental Conditions

No.	Mixing ratio (wt %)			Flow (mm)	Compressive strength (kgf/cm^2)		
	Slag (X1)	OPC (X2)	AG (X3)		3 days	7 days	28 days
1	90	5	5	225	105	150	214
2	70	25	5	221	286	426	511
3	70	5	25	228	89	128	165
4	83.33	11.67	5	216	183	252	325
5	76.67	18.33	5	215	233	344	436
6	70	18.33	11.67	210	182	293	408
7	70	11.67	18.33	214	153	215	282
8	76.67	5	18.33	211	97	144	189
9	83.33	5	11.67	213	101	152	205
10	76.66	11.67	11.67	210	176	236	315

Table 4. Statistical Analysis by Mixture Design of Experiment

Characteristic values			Analysis of variance table				Coefficient of determination (R^2)
			S	Φ	V	Fo	
Flow (%)		Regression	349.81	5	69.96	27.2**	0.971
		Residual	10.29	4	2.57		
		Sum	360.09	9			
Compressive strength (kgf/cm^2)	3 days	Regression	371522.30	5	7430.46	33.6**	0.977
		Residual	884.22	4	221.06		
		Sum	38036.5	9			
	7 days	Regression	86031.80	5	17206.4	315.4**	0.998
		Residual	218.20	4	54.55		
		Sum	86250.0	9			
	28 days	Regression	122462	5	24492.5	8942**	0.999
		Residual	109.57	4	27.39		
		Sum	122572	9			

**: Degree of significance of 99%

Fig. 3. SEM of photo of paste microstructures of blast furnace slag mixed with 5 wt % of Na_2SO_4.

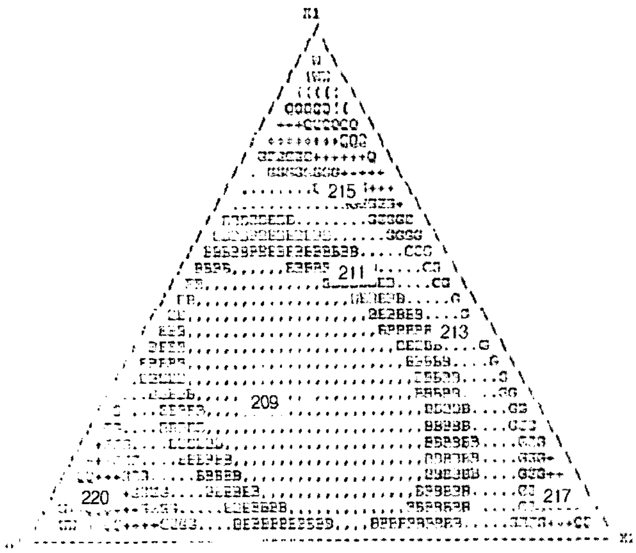

Fig. 4. Distribution of the flow values for each factor (unit: mm).

erty values, an analysis of variance and the coefficient of determination according to statistical methodology were obtained. These results are shown in Table 4. In the F test in the variance analysis table, all the characteristic values show a high degree of significance at 99% or greater. The value of the coefficient of determination (R^2) was 0.970 or greater, which shows that the relationships between the secondary regression model factors (X1, X2, and X3) and the characteristic values (Y) of the mixture are adequate.

Fig. 4 shows the distribution of the fluidity values by level. The fluidity showed a tendency to increase as the test progressed from test sample 10, which was at the center of the three-component diagram, to test samples 1, 2 and 3, which were at the extreme vertices. The flow tends to increase as each vertex point of samples 1, 2 and 3 moves, indicating that a higher ratio of the content of slag, OPC, or AG in the mixture is correlated with a higher the flow value. In addition, the distribution of the flow is higher as the AG content increases, as observed in sample 3. In contrast, when the OPC content increases, the distribution of the flow tends to have a lower value compared to the results of the other con-

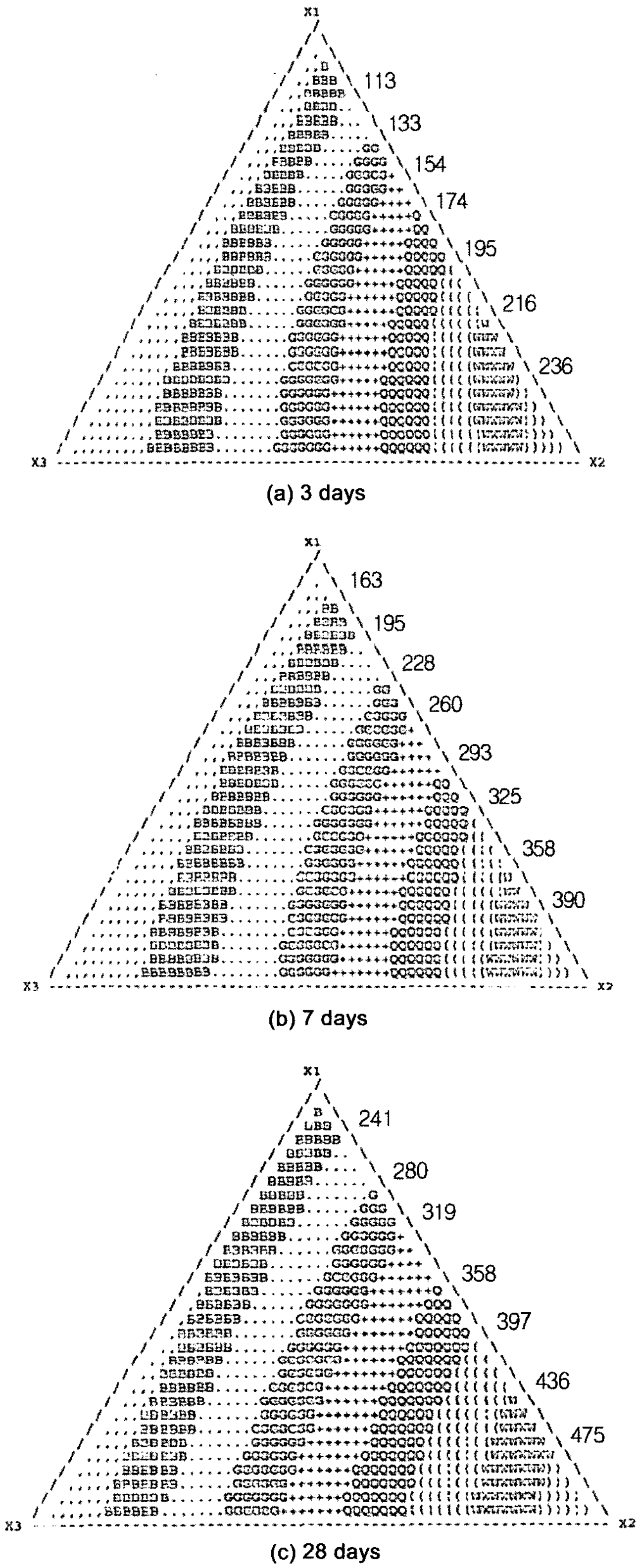

Fig. 5. Distribution of the compressive strength values for each factor (unit: kgf/cm^2).

tents. The mixture that achieved the maximum flow value was 70 wt% of slag, 5 wt% of OPC and 25 wt% of AG. The mixture that achieved the minimum flow value was the cen-

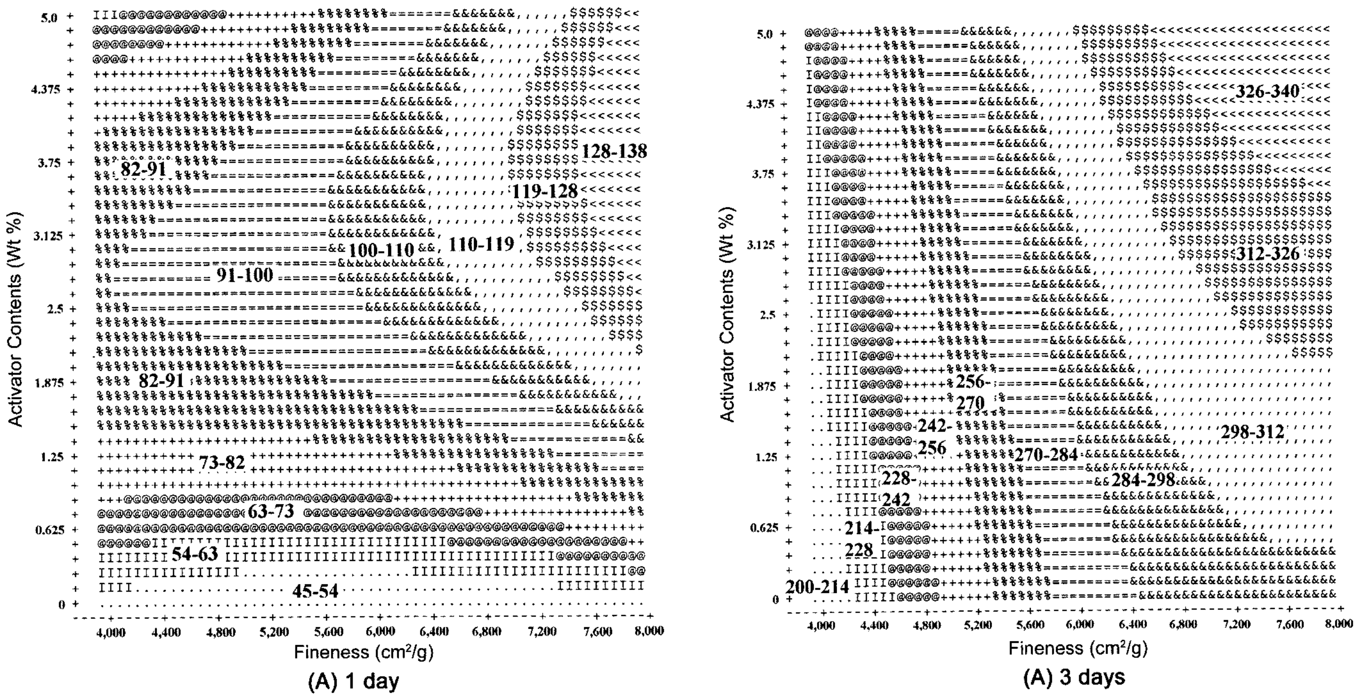

Fig. 6. Effect of the activator content and the fineness of the blast furnace slag on the strength of mortar (unit :kgf/cm^2).

tral point of the three-component diagram.

Fig. 5 shows the distribution of the compressive strength that resulted from curing periods of 3, 7 and 28 days. The distribution of the compressive strength in a three-day curing period showed a tendency to increase as the content of OPC increases. The compressive strength expression characteristics showed a range of 92~272 kgf/cm^2 for 3 days, 131~423 kgf/cm^2 for 7 days and 163~514 kgf/cm^2 for 28 days. Thus, the difference in the compressive strength increases according to the component ratio of the mixture of the three-component diagram of Slag-OPC-AG. At 7 days and 28 days, the value of the compressive strength showed a tendency to increase as the content of OPC increases. In addition, as the curing period becomes longer, the compressive strength distribution value tended to increase as the content of slag increases. In Fig. 5, the component ratio with a strength equal to or greater when compared to OPC alone is 70~77% of slag, 15~25% of OPC and 5~8% of AG. As the result of this analysis, it is clear that the OPC in the mixture affects the early strength. Additionally, as the curing period increases, the late strength is affected greatly by the amount of slag.

Fig. 6 shows the effect of the activator content as well as the effect of changes of the fineness of the slag on the initial strength of the mortar. Up to day 1, the initial strength is influenced by the fineness of the slag rather than by the activator content. However, after three days, the activator content and the fineness of the slag are important elements in the increase of the compressive strength of slag mortar. Therefore, it was determined that the fineness of the slag rather than the activator content is a more important factor in the improvement of the initial strength of slag cement.

4. Conclusion

As a result of the analysis of the physical properties of mortar by a statistical method according to the mixture design of an experiment that utilized a three-component diagram of Slag-OPC-AG with slag as the main constituent, the following conclusions were obtained:

1. Na_2SO_4 as used as an activator in this research was very effective in promoting hydraulic reactivity of blast furnace slag.

2. Ettringite was formed as the main hydration product of blast furnace slag containing Na_2SO_4.

3. The fluidity of blast furnace slag cement is higher when the blast furnace slag content increases. On the other hand, when the content of ordinary Portland cement increases, the distribution of the fluidity tends to have a lower value compared to the results of the use of other contents.

4. Considering the initial improvement of the compressive strength of blast furnace slag cement, however, the fineness of blast furnace slag and the content of OPC are factors that are more important than the alkali activator content.

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