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≫ 硏究論文 ≪

EAF-Slag의 콘크리트用 骨材로의 活用을 위한 炭酸化 處理 硏究†

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Carbonation Treatment of EAF Slag for Using Aggregate of Concrete†

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요 약

본 연구에서는 철강 산업 부산물인 전기 아크로에서 발생되는 슬래그(이하 EAF-slag 표기)를 탄산화 반응에 따른 슬래그이 물성 변화 및 몰탈 시험을 통해 콘크리트용 대체 골재로써의 가능성을 검토하였으며, 특히 본 연구에서는 탄산화 처리에 따른 EAF-slag의 물성 변화에 대하여 논하였다. 연구 결과 EAF-slag의 탄산화 처리에 따라 EAF-slag 입자 표면에 칼사이트가 생성되면서 골재로써의 표면 기공율을 감소하였으며, pH도 7까지 안정화되는 것을 확인할 수 있었다. EAF-slag를 모래 대체에 따른 몰탈 압축 강도 실험 결과 EAF-slag의 모래 대체 50%의 경우 7일 강도 뿐만 아니라 28일 강도 증가도 함께 관찰되었다.

주제어 : 전기 아크로 슬래그, 탄산화, 압축강도, 안정화

Abstract

The objectives of this study are focusing on the issue with efficiently recycling for EAF slag as construction material such as an aggregate of concrete. This study can be classified mainly into two categories: the first section is the carbonation treatment of Electric Arc Furnace(EAF)-slag for obtaining soundness as using aggregate of concrete. And the second section is the application of carbonated EAF-slag on the mortar test to evaluate the stability and mechanical property, which is compressive strength, according to the replacement of EAF-slag on the mortar. It was known that pH of EAF-Slagle according to carbonation time decreases drastically to 7 within several sec of carbonation, and a calcite is formed on the surface of EAF slag. The formation of calcite during the carbonation process of EAF slag lead to fill at pore in the texture of EAF-Slag surface, and than the porosity of EAF-slag decreases with carbonation process. In the mortar test, compressive strength, according to the replacement of EAF-Slag to sand on the mortar, the compressive strength of mortar increased as the 50% replacement ratio of EAF slag for sand was above 10% higher than that of reference mortar according to 50% replacement of EAF slag.

Key words : EAF-Slag, Carbonation, Compressive strength, Stabilization

1. INTRODUCTION

On the stature of fine aggregates in Korea, many disadvantages appeared in infrastructure of sea sand due to the huge amount of collection of fine aggregate from sea. Environment of collection of fine aggregate is going hard and severe more and more from the point of view of scenery, protection of environment. Thus, the collection of aggregate from sea regulated more and more severely due to the environmental problem, and enough construction waste concrete are also investigated eagerly, and the construction wastes is obliged to be re-use, it needs further investigation from the point of quality. Therefore, many kinds of slag had been investigated and fine aggregate of blast furnace slag and ferro-nickel slag and coarse aggregate of copper slag are regulated for concrete aggregate.

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The steel-making slag is difficult to use for industrial raw materials or aggregate for concrete, form the reason that the chemical components and structure of steel-making slag vary so much with its process and/or the kind of steel producing and that the content of free lime is also high.

On the other hand, the emission of carbon dioxide is one of worldwide matter of concern for the green house effect. In this study, Electric Arc Furnace(from here EAF slag) is prepared as fine aggregate by using CO_2 gas. The characteristic properties of this process are in the raw materials and also energy consumption in this process is very small except that for grinding and transportation.

Because the composition of the slag contain much $2CaO{\cdot}SiO_2(C_2S)$ and $3CaO{\cdot}SiO_2(C_3S)$ and also free lime in some case. Therefore, the slag has the potential to make useful materials by solidifying CO_2 gas.

A small amount of water layer is important for the carbonation reaction, as it is the case for the carbonation of concrete. Under the condition of too little water, carbonation does not proceed because of the lack or very small space to reaction Ca^{2+} and CO_3^{2-}, and also in the case of too much water, the reaction does not proceed, because the reaction proceeds only at the surface of the liquid. It is desirable that the water exists to make a meniscus between particles. Both Ca^{2+} and CO_2 gas must dissolve into the water layer. Then they meet to react and to produce calcium carbonate. When there is too much water, the precipitates will produce a film at the surface of water, far from the particle. These films do not work to bond thee particles and binds them to develop the strength. When the products fill up the space between the particles, there is no water space, so the reaction stop and no expansion occurs. In contrast, in the carbonation of concrete, sometimes shrinkage occurs. This should be due to the effect of silica gel.

Some treatment to stabilize expansion component is necessary to obtain the sound aggregate of EAF slag. It is reported that Free-CaO or Free-MgO contained in slag causes to occur the crack of construction. Fig. 1 shows the progress of crack in the particle of slag.

In this study, we suggest carbonation process to stabilize EAF slag, so that EAF slag can be used as the sound aggregate for concrete. In particular, CO_2 gas has been focused in all the world because CO_2 gas emission causes to global warming. These chemical formulas show the carbonation reaction of expansion component of slag and the change of the free Gibbs energy of them. Free-CaO and β-C_2S form calcium carbonate via carbonation process, which is very stable phase. And the reaction of free-MgO with CO_2 gas forms magnesium carbonate. It has also very low activity. So we expect that EAF slag carbonated can be used as the sound aggregate for concrete.

$$\text{Free–CaO}+H_2O \rightarrow Ca(OH)_2+CO_2 \rightarrow CaCO_3+H_2O$$

ΔG_o^{298} :-603.75kcal·mol-1 $\quad$ ΔG_o^{298} :-894.96kcal·mol-1 $\quad$ ΔG_o^{298} :-1,133.03kcal·mol-1

$$\text{Free–MgO} \rightarrow MgO+H_2O \rightarrow Mg(OH)_2+CO_2 \rightarrow MgCO_3+H_2O$$

ΔG_o^{298} :-601.83kcal·mol-1 $\quad$ ΔG_o^{298} :-833.75kcal·mol-1 $\quad$ ΔG_o^{298} :-1,029.35kcal·mol-1

2. EXPERIMENTAL PROCEDURES

Table 1 shows the chemical composition of EAF slag. SiO_2 and CaO content were 32.78 wt% and 28.18 wt%, respectively. Fe_2O_3 content was 2.30 wt% and this low value seems to be due to recovery of ferrous minerals by magnetic separation. Table 2 shows contents of heavy metals and free-CaO in the EAF-slag, target materials in this study. Cr content is 19,000-22,000

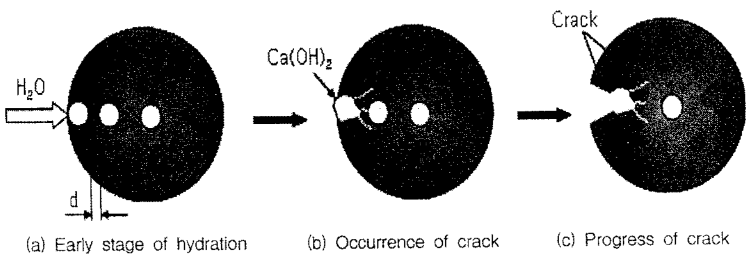

Fig. 1. Schematic diagram of progress of creak in the particle of slag.

Table 1. Chemical Composition of EAF-Slag

Element	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO
Content(wt.%)	32.78	1.27	5.26	2.30	2.78	5.97	28.18

Table 2. Contents of Heavy Metals and Free-CaO

Particle size(mm)	Heavy metals(mg/kg)			F-CaO(wt%)
	Cu	Cr	Ni	
2.36/1.18	85	22,000	455	0.2
1.18/0.6	79	16,200	402	0.2
0.6/0.3	114	20,800	455	0.2
-0.3	69	18,500	601	0.2
Total	86	19,191	469	0.2

Table 3. Leaching Amount of Heavy Metals in EAF-Slag (mg/l)

Particle size (mm)	Cu	Ni	Cr	Pb
Amount	<0.1	<0.1	0.27	<0.1

mg/kg, which is very high compared with other considered heavy metals. But leaching of each heavy metal is not detected except for Cr which its leaching concentration was 0.3 mg/l, as shown in Table 3. Therefore, EAF slag is classified as general waste. The amount of free-CaO, which causes to occur the crack in the slag, is about 0.2 wt%.

Particle size of EAF slag shows in the range from 2.36 mm to 0.15 mm, and this presents that it was selected by screening for the use of fine aggregate. The soundness result of EAF slag by use of sodium sulfate was 0.7%. Main mineral phases are silicates such as akermanite, wollastonite, bredigite, gehlenite and magnetite as shown in Fig. 2.

Carbonation experiments using a dry method (with a water content of 20wt%) with EAF slag were performed in a reactor that was maintained at 25°C. A sample of 50g EAF slag in 10 ml of distilled water was allowed to equilibrate with a CO_2 flow rate of 1.0 l/min. Fig. 3 shows the experimental equipment of carbonation reaction. When carbonation treatment were carried out with dry process, the ratio of liquid to solid is 0.2. In the case of flow rate of CO_2, controlled at 1.0 l/min.

The volume expansion rate of mortar containing EAF slag was measured to estimation of stabilization for aggregate by KS L 5017 "Test for volume expansion

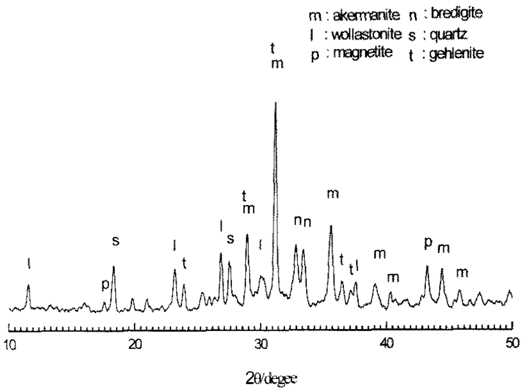

Fig. 2. X-ray diffraction patterns of EAF-slag.

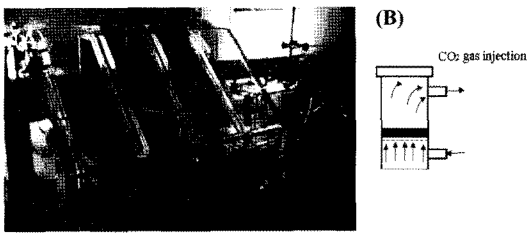

Fig. 3. Experimental equipment of carbonation reaction, (A) carbonation equipment, (B) dry-carbonation reactor.

fine aggregate with Autoclave. The samples were prepared in the autoclave under 21 kg per kg/cm^2 for 3hr as shown at Fig. 4.

The mortar test followed by Korean Industrial Standard (KS 5105) was carried out for investigating the effect of EAF slag replaced instead of sand. EAF slag was replaced to 20%, 50% of sand by the mass and all the mortar mixtures were manufactured at the same

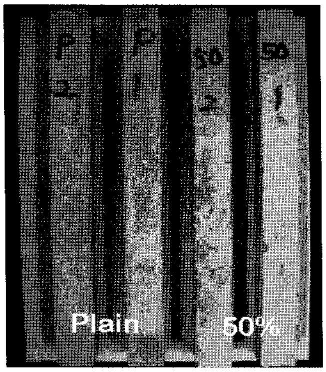

Fig. 4. Estimation of stabilization for aggregate.

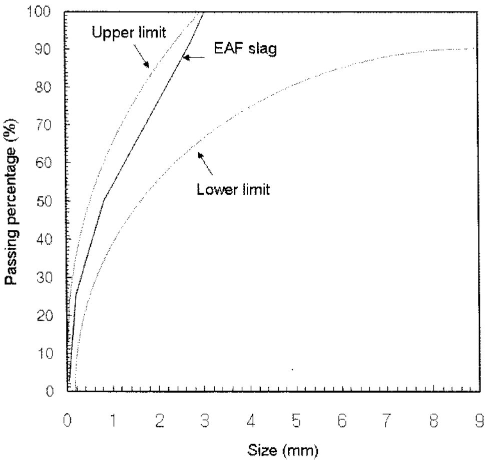

Fig. 5. Distribution of particle size of EAF-slag.

water/binder ratio(w/b=0.485). Compressive strength was measured on 50 mm cube, which were cured in water at the various times.

3. RESULTS AND DISCUSSION

The particle size distribution of EAF slag was measured to determine the adaptability for concrete. And the test was performed as presented in KS F 2526 "Test for adaptability of fine aggregate for concrete". In Fig. 5 upper dot lime indicates upper limit of large size, and lower dot line is lower limit. Black line represents the size distribution of EAF slag. Fig. 5 shows that EAF slag is adapted to use fine aggregate for concrete.

Fig. 6 shows the pH change of EAF slag particle according to carbonation time. As you can see in the graph, the pH of EAF slag particle decreases drastically

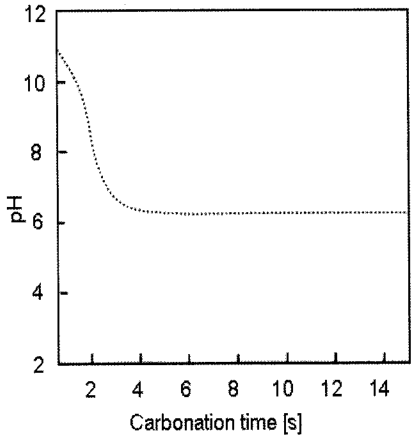

Fig. 6. pH change of EAF-Slag with carbonation time.

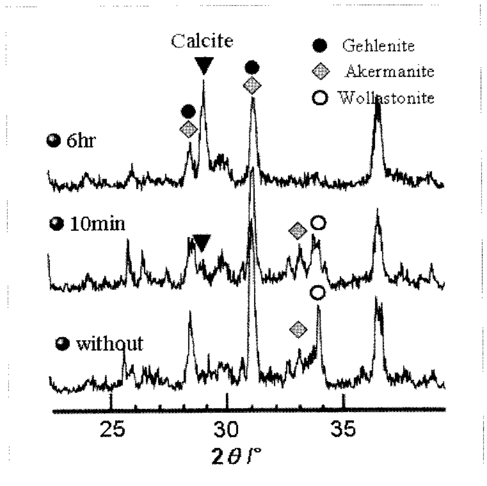

Fig. 7. Change of mineral phases of EAF-slag with carbonation.

to 7 within several sec of carbonation. Therefore it is believed that carbonation treatment is very effective for neutralizing alkaline slag.

Fig. 7 illustrates the results of X-ray diffraction pattern of carbonated slag changing with the reaction time. The formation of calcite increases in the process of carbonation. Fig. 8 shows illustrate the surface morphology of EAF slag before and after carbonation for 6hr. The new products formed on the surface of carbonated EAF slag. From the X-ray diffraction measurement, this carbonates was determined as calcite. Table 4 shows BET surface area, volume and pore size from fresh and carbonated EAF slag. The surface area and volume for EAF slag after the dry carbonation

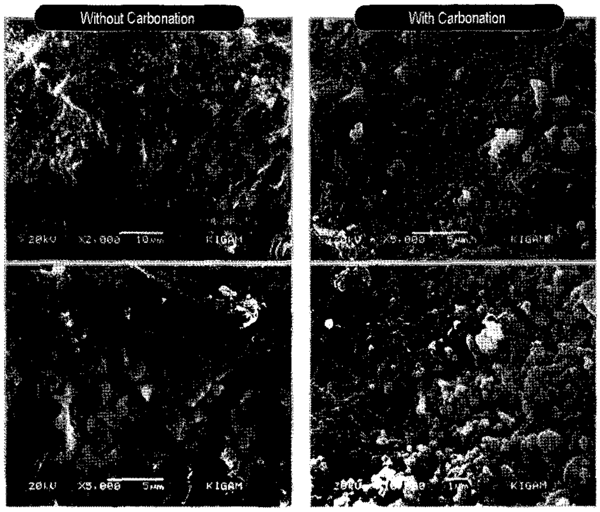

Fig. 8. Surface morphology of EAF-slag with carbonation reaction.

Table 4. The BET Surface Area, Volume and Pore Size from Fresh and Carbonated EAF-Slag

	Fresh EAF-Slag	EAF-Slag after dry carbonation
BET surface area(m^2/g)	1.2233	2.3892
Volume area(m^2/g)	0.1047	0.3317
Pore size area(cm^3/g)	0.000154	0.000046

were higher compared to fresh slag, as the particles of carbonated slag were surrounded with compounds with an carbonated salts. The other hand, The formation of calcite during the carbonation process of EAF slag lead to fill at pore in the texture, and than the porosity of EAF slag decreases with carbonation process.

Fig. 9 shows the rate of volume expansion of the mortar according to the content of EAF slag. The result indicates that the rates of volume expansion of the mortar with EAF slag satisfy the standard limit. Therefore, it is believed that EAF slag carbonated can be used as aggregate for concrete.

Fig. 10 shows the compressive strength results of mortar with 20% and 50% replacements of sand. As you

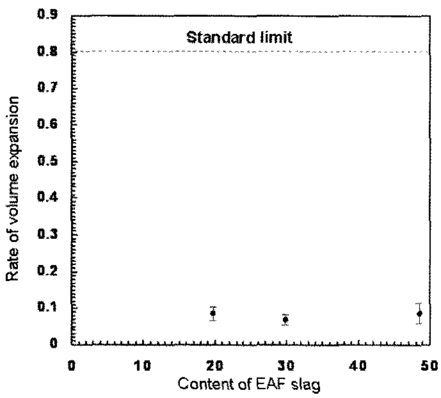

Fig. 9. Estimation of stabilization for aggregate.

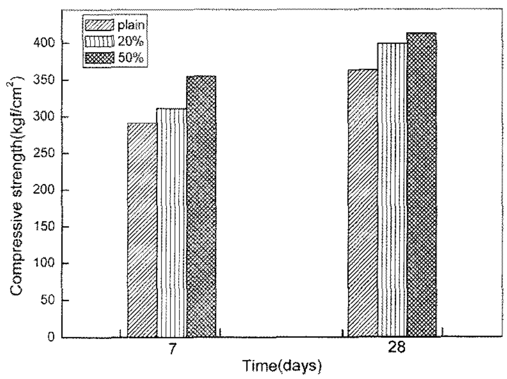

Fig. 10. Compressive strength as a function of time of reference mortar and mortar with 20% and 50% replacement of EAF slag for sand at the curing time of 7days and 28days.

can see, the compressive strength of mortar increased as the replacement ratio of EAF slag for sand increased; the compressive strength of mortar with 50% replacement of EAF slag was above 10% higher than that of reference mortar at the curing time of 7 days and 28 days.

4. CONCLUSIONS

The objectives of this study are focusing on the issue with efficiently recycling for EAF slag with carbonation treatment, and the results of this study are summarized as follows.

1. Main component of EAF slag were CaO, SiO_2, Fe_2O_3, Al_2O_3 and MgO, and these elements existed in form of akermanite, wollastonite, bredigite, gehlenite and magnetite.
2. The particle size distribution of EAF slag is determined the adaptability for concrete aggregate.
3. pH of EAF slag particle according to carbonation time decreases drastically to 7 within several sec of carbonation.
4. A calcite is formed on the surface of EAF slag carbonated for 6 hours.
5. The formation of calcite during the carbonation process of EAF slag lead to fill at pore in the texture, and than the porosity of EAF slag decreases with carbonation process.
6. The rates of volume expansion of the mortar with carbonated EAF slag satisfy the standard limit.
7. Compressive strength of mortar increased as the 50% replacement ratio of EAF slag for sand was above 10% higher than that of reference mortar according to 50% replacement of EAF slag.

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