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Quantitative evaluation of free CaO in electric furnace slag using the ethylene glycol method

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HIGHLIGHTS

- Free CaO contents in electric furnace oxidizing and reducing slags were evaluated.
- Ethylene glycol method has been used for the evaluation.
- Free CaO decreases with the increase in the aging period.
- Free CaO content is <0.5% in all the oxidizing slag samples.
- EOS is suitable for use in construction applications due to low free CaO content.

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ABSTRACT

Worldwide increase in the amount of slag production, a by-product of steel manufacturing, has led to efforts to recycle the slag into value-added products. However, the presence of unstable constituents like free CaO limits the applications of electric furnace slag, which is stabilized by the aging process. Herein, by measuring the free CaO content as a function of aging period, source region, company, and storage position, using the ethylene glycol method, the feasibility of using electric furnace slag as a construction material is confirmed. The free CaO contents of electric furnace oxidizing slag (EOS) samples were found to be below 0.5%. This satisfies the criteria specified in KS F 4571, which states that the CaO content should be below 40% and CaO/SiO_2 ratio should be below 2.0. In addition, it was confirmed that free CaO content difference appears to be dependent on the aging period and storage position.

1. Introduction

Electric furnace slag is a type of industrial waste obtained as a byproduct during the production of steel. Typically, 130–200 kg of slag is obtained per ton of manufactured steel [1]. In 2014, Korea produced 71.54 million tons of steel, and this making it the fifth among the world's leading steel manufacturing nations. That fact also resulted in the production of a substantial amount of slag as by-products.

Numerous studies related to environmental conservation are being conducted worldwide, including studies on the recycling of industrial by-products, with the ultimate goal of conserving energy and resources [2–5]. Specifically, studies are being conducted on the recycling of slag into a high value industrial material, which can lead to economic profits. While blast furnace slag can typically be recycled as a value-added material [6,7], it is difficult to recycle electric furnace slag owing to its instability due to the free CaO content [8–10]. Free CaO combines with H_2O to produce a hydrate, the volume of which is approximately double the initial volume of the slag. This volume expansion limits the usage of the recycled slag as a construction material.

While free CaO is generated in all types of steel slag during the plasticizing process (i.e., granulated ground blast furnace slag (GBFS), electric furnace oxidizing slag (EOS), electric furnace reducing slag (ERS), and converter slag (CS)), the free CaO content may vary depending on the plasticizing temperature and cooling conditions in each steel mill [11].

Blast furnace slag has low free CaO content and can be recycled as either a cement raw material or as an aggregate. In the case of electric furnace slag, however, the free CaO content is variable and depends greatly on the oxidation and reduction of the electric

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furnace slag. In particular, electric furnace oxidizing slag (EOS) has a low free CaO content and is therefore a stable aggregate. However, the electric furnace slag can be used only for a limited number of applications such as road base layer, hot asphalt mixture, and ground reclamation [12–14].

Slag from revolving and electric furnaces, which are prone to expansion and collapse during use as a construction material for road or as concrete, must be sufficiently stabilized before use. The methods for stabilizing the slag can be largely divided into two types, namely reforming and aging.

Since the slag after reforming does not contain free CaO, volume expansion due to the hydration of free CaO does not occur. Therefore, CaO can react and form other compounds. Thus, the free CaO can be made sufficiently stable by adding additives such as sand, waste foundry sand and aluminate-based waste refractory as well as oxygen to the molten slag, resulting in the formation of a stabilized mineral.

However, since the additives react with the free CaO, additional heating sources are required to maintain the molten state. As a result, this method is expensive. While the slag can be stabilized very reliably by this method, it is generally suitable only for the treatment of low quantities of slag as the unit treatment cost is high. Additionally, since the reforming process does not impact the production and quality of steel, research on this front has not received priority. Therefore, the reforming process is still in the research stage and yet to be commercialized. Therefore, to implement this method, problems related to the need for additional heating sources should be resolved and cheap additives need to be developed.

On the other hand, in slags treated with the aging method, hydration can occur without expansion or collapse. In this method, the hot slag is cooled slowly, pulverized into an appropriate particle size, and allowed to stay in the atmosphere, to artificially transform the CaO into $Ca(OH)_2$. Further, the slag is generally stacked in the open at an approximate height of 3 m. However, when the hydration reaction between the free CaO and water, or between the free CaO and CO_2 is promoted, the aging period can be reduced. However, at least three months of aging is required to stabilize the electric furnace slag. If the free CaO content is higher, a longer period is required for stabilization.

To stabilize the free CaO, most of the steel mills use an aging process. However, the long storage duration and large storage area requirements introduce additional costs. Recently, studies have been conducted on the development of concrete from electric furnace slag. In particular, the compressive strength of concrete and its durability are being investigated [15–17].

The free CaO content is an important factor in the preparation of concrete from electric furnace slag. However, while factors such as compressive strength and durability of concrete have been investigated, the free CaO content has not been quantitatively evaluated so far. Additionally, quantitative evaluation of free CaO could help optimize the aging duration, thereby minimizing the costs associated with the aging process.

The chemical composition and physical properties of electric furnace oxidizing slag in Korea, as suggested in KS F 4571 (Electric Arc Furnace Oxidizing Slag Aggregate for Concrete) [18], are shown in Table 1. The levels of four constituents, namely calcium oxide, magnesium oxide, total iron, and basicity, are specified in KS F 4571. In particular, the CaO content should be maintained below the maximum allowed value of 40%.

Table 1
Quality standard for electric furnace oxidizing slag (KS F 4571).

Chemical constituent	Composition
CaO	Not more than 40.0%
MgO	Not more than 10.0%
FeO	Not more than 50.0%
CaO/SiO_2	Not more than 2.0%

In Korea, there are guidelines for the recycling of steel slag. According to these guidelines, the maturation periods for various sizes of slag are determined. For example, when the slag size is over 100 mm, it should be stored in the open for longer than 3 months, whereas the steel slag should be stored for at least over a month when the slag size is below 100 mm. Additionally, in order to achieve sufficient permeability, the stacking height during open storage should be 3–8 m. Therefore, the slag should be stacked for as long as possible for sufficient aging treatment, owing to the expansion of free CaO inside the steel slag. However, this can be a limitation in some steel slag by-product treatments.

In this study, the ethylene glycol method was used for the quantitative evaluation of free CaO in electric furnace slag produced by number of steel mills in Korea as a function of the aging period and aging position. The ethylene glycol method can be used for swiftly and quantitatively analyzing small doses of free CaO. The ethylene glycol method is currently used as an experimental method in cement companies for the quantitative evaluation of free CaO, by wet rendering the free CaO in the cement [19–21]. According to the ethylene glycol method, the wet rendering should be controlled based on the composition of each material. Ethylene glycol will form a compound with any free CaO present, but will also combine with some, but not necessarily all, of the $Ca(OH)_2$ present [22].

2. Experimental program

2.1. Ethylene glycol method

A 1 g sample is placed along with 50 mL of ethylene glycol in a 100 mL conical flask, which is placed in a water bath maintained at 60 °C for 30 min. Each treated sample is filtered using two layers of No. 5B filter bed through a Buchner funnel, and is washed thrice with 30 mL of ethylene glycol. The filtrate is then collected in an induction conical flask and titrated with N/10-HCl standard solution with 2–3 drops of Brome-cresol green solution added as the indicator. The terminal point is set when an N/10-HCl standard solution turns from blue to green. Using the amount of N/10-HCl standard solution consumed, the amount of free CaO can be calculated, as shown in Eq. (1). Fig. 1 illustrates the various steps in the ethylene glycol method, while Fig. 2 shows the materials used for the experiments.

$$\text{Free CaO } (\%) = \frac{\text{ml HCl} \times \textit{normality of } \text{HCl}}{10 \times \textit{sample weight}} \times 28 \quad (1)$$

2.2. Materials

For the quantitative evaluation of free CaO in electric furnace slag, EOS and electric arc furnace reducing slag (ERS) samples were acquired from several companies for the experiments. For comparison, cement, blast furnace slag, and converter slag were used. For the experiments using the ethylene glycol method, the samples were directly obtained from the open storage fields and pulverized into predetermined particle sizes. The pulverized materials were placed in a drying machine and dried completely for an hour at a temperature of over 80 °C. The materials were then pulverized again to a particle size below 100 μm using a disk mill and stored. Table 2 shows the chemical composition of each material determined by XRF analysis.