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Improving the mechanical properties of rapid air cooled ladle furnace slag powder by gypsum

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HIGHLIGHTS

- Ladle furnace slag, the waste from steelmaking industry can be recycled.
- Rapidly air cooled ladle furnace slag is a rapid hardening binder.
- Rapid air cooling method prevent expansion of the steel slag.
- Rapidly air cooled ladle furnace slag produce hydrogarnet during the hydration.

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ABSTRACT

The aim of this research is supporting the recycling of ladle furnace slag from steel making industry. Ladle furnace slag is generally treated as a waste because of its volume instability with free-CaO and free-MgO crystalized during the slow cooling process. Regarding this by-product, from the previous research, rapid cooling technique with high pressured air was introduced, and rapid hardening properties of rapidly cooled ladle furnace slag (RCLFS) was introduced. In spite of outstanding rapid hardening performance, because of hydrogarnet, the main hydration product of main component for rapid reaction, RCLFS has low compressive strength and severe shrinkage as the drawbacks. In this research, to resolve these drawbacks, gypsum was incorporated and induced formation of ettringite. By using modified Bogue equation, the required appropriate amount of gypsum was determined as 37% of RCLFS weight, and a series of experiments were conducted to prove it. From the results of the experiment, when the RCLFS contained gypsum, ettringite was generated and due to the ettringite, compressive strength was continuously increased with decreased porosity. This result is expected to contribute to recycle the RCLFS as a rapid hardening material with more stable performances.

1. Introduction

Slag, a by-product occurred from iron manufacturing process, has been increased its generation amount with the development of steel making industry [1]. Currently reported applications of slag materials for construction materials are mainly blast furnace slag from blast furnace of producing pig iron [2]. The blast furnace slag consists high content of CaO as well as cement, thus it is known as a hydraulic material with glassy amorphous phase [3]. Therefore, as a supplementary materials for cement powder, blast furnace slag has been used as a good supplementary material which can decrease the consumption of cement powder [4], and heat of hydration [5–7]; and improve the durability of cementitious materials [8]. Steel slags from steel making process can be categorized into the slag from the converted furnace which making steel from pig iron, and the slag from the electric arc furnace which making steel from scrap metal [9]. These slags other than blast furnace slag has been generally wasted or used as a filler for pavement because of no hydraulic property. There is the reason of this poor recycling rate of slags on its treating processes including cooling and dumping of steel slags. Currently, the steel slags have been dumped in the outdoor field and cooled slowly by the ambient conditions right after the slag generation. This slow cooling process provides the conditions for crystalizing of the oxides in the slags and the crystalized free-CaO, free-MgO, and iron oxides consists a large portion of the steel slags. These crystalized free-CaO, free-MgO, and iron oxides can react with the mixing water of the cementitious mixtures and produce $Ca(OH)_2$, $Mg(OH)_2$, and iron hydroxides of expanding substances in the cementitious

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matrix. Eventually, the steel slags with these expandable oxides can expand severely, and destroy the hardened cementitious materials when they are used as a cementitious materials' component such as aggregate, or powder [10–12].

According to the previous research [13,14], regarding these drawbacks of the steel slags, especially, the pulverized ladle furnace slag from electric arc furnace, the rapid setting properties without severe expansion was provided when the ladle furnace slag was rapidly cooled down by high pressured air. The rapid setting properties of rapidly cooled ladle furnace slag (RCLFS) is caused by the high content of $C_{12}A_7$ as a main component of it. $C_{12}A_7$ experiences the process of "conversion" of making hydration products with very high reactivity [2,15]. Eventually, the final hydration product of C_3AH_6 has a feature of low strength comparing with the metastable products of CAH_{10} or C_2AH_8. Additionally, as shown the SEM images of Fig. 1, the hydration product of $C_{12}A_7$ cover the unhydrated particles and hinder the additional hydration.

Eventually, RCLFS showed very low compressive strength because of rapid reactivity and hydration products of $C_{12}A_7$ while it contained β-C_2S of a good source of the stable strength development. Furthermore, the microstructure of this rapidly formed hydrogarnet contributed on a high shrinkage of the hardened structure. Therefore, to obtain a mechanically stable and high durable cementitious materials, these drawback should be solved.

Aluminum oxide is the chemical component with very high reactivity [16–18]. As a cement component, C_3A shows very fast reaction with the mixing water, and causes the "flash set" unless it is not controlled properly [3]. Regarding this problem, the most well-known solution is the intention of hydration product by incorporating gypsum. Namely, using the hydration between gypsum and aluminum oxide, ettringite or monosulfoaluminate can be produced and especially, the ettringite can prevent the occurrence of hydrogarnet by consuming alumina with sulfate, and provide the conditions of continuous hydration of other chemical component by surrounding the C_3A. Therefore, in this research, by incorporating gypsum, the solution of the RCLFS' drawbacks of low compressive strength and volume instability is suggested. According to the former research, the increasing strength was reported by inducing ettringite at early age in spite of the collapse of matrix and losing strength by ettringite formation during the hardened cementitious materials [19–22].

In aspect of sustainability of construction materials, recycling slag as a construction material is very important idea. In this view point, from previous research [13,14], the possibility of RCLFS as a rapid setting cementitious materials, and in this research, the drawbacks of low compressive strength and high shrinkage are solved. Hence, the results of this research are expected to contribute on the providing the application method of steel slag as a materials of rapid hardening cement with high value, and to provide the solution of stable performance of rapid hardening cement produced from steel slag.

2. Experiment

2.1. Determining gypsum content

The reason of no strength development of RCLFS is caused by the reaction between $C_{12}A_7$, the main component of RCLFS, and water to produce hydrogarnet as follow:

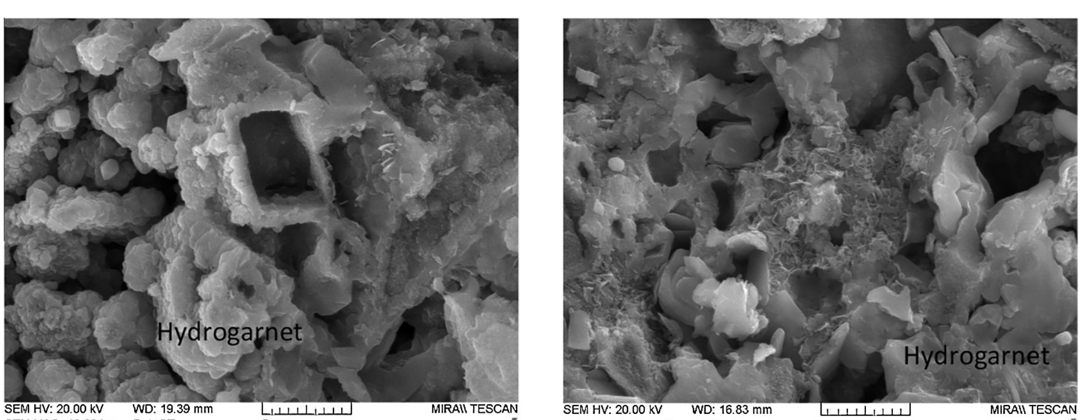
$$C_{12}A_7 + 51H_2O \rightarrow 6C_2AH_8 + AH \rightarrow 4C_3AH_6 + 6AH + 18H_2O \qquad (1)$$

The Eq. (1) is not an entire reaction process of $C_{12}A_7$; as Juenger et al.'s report [2], $C_{12}A_7$ is turned through various phases, eventually, it produces C_3AH_6, and this hydration product prevent the continuous hydrations of $C_{12}A_7$.

By adding gypsum on this chemical reaction process, it is considered that the formation of hydrogarnet can be prevented while ettringite can be produced, and thus both early and continuous strength developments can be achieved as follow:

$$C_{12}A_7 + 12CaSO_4 + 137H_2O \rightarrow 4(C_3A \cdot 3CaSO_4 \cdot 32H_2O) + 6AH \qquad (2)$$

Hence, the amount of gypsum to react with $C_{12}A_7$ should be determined. In this research, first, the amount of $C_{12}A_7$ was calculated based on the modified Bogue equation [23]. Originally, the Bogue equation is used to calculate the amount of C_4AF, C_3A, C_2S, and C_3S from cement powder, it starts based on the assumption of the orders of oxides consumption and chemical components formation in rotary kiln during the cement manufacturing process. Therefore, in this research, the amount of $C_{12}A_7$ was calculated with modified Bogue equation based on the assumption of the situation for produced the chemical components inside of RCLFS, and the amount of gypsum for reaction with $C_{12}A_7$ was calculated. In the case of ladle furnace slag, similar to cement, the chemical components are produced under the high temperature conditions in furnace by molten oxides. Namely, the order of formation of chemical components are determined by the melting points of oxides. As shown the bottom line in Fig. 2, by the XRD analysis, the main components of ladle furnace slag were found as $C_{12}A_7$ of high reactivity, β-C_2S of stable long-term strength development,



(a) Three hours after water contact (b) Seven days after water contact

Fig. 1. Formation of hydrogarnet covering unhydrated ladle furnace slag particles.