



Micro Structures of Rapidly Cooled Ladle Furnace Slag Matrix Mixed with Gypsum†

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In this study, we investigated the hydration characteristics of the binder which mixed gypsum to rapidly cooled Ladle furnace slag, a by-product generated from steel industry. The results of XRD and SEM analysis showed that the binder mixed with gypsum created large amounts of Ettringite after 1 day. Compared to the binder using only the rapidly cooled Ladle furnace slag, the binder mixed with gypsum had a decreasing “total porosity” and an increasing micro-pore distribution due to continuous hydration reaction over the age, although it had large pore initially.

Keywords: Ladle furnace slag, Hydration reaction, Pore distribution, XRD, SEM.

INTRODUCTION

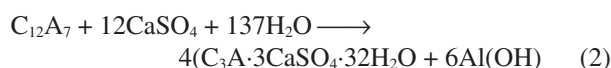
Ladle furnace slag, which is one of the by-products of steel industry, contains large amounts of CaO and Al₂O₃ because a massive amount of solvent such as Al or Si and ash are fed into the Ladle furnace to achieve high quality steel. Although the Ladle furnace slag contains the CA-based minerals such as C₁₂A₇, C₁₁A₇·CaF₂, etc., which have rapid-setting properties, the Ladle furnace slag also contains high content of f-CaO posing the risk of “expansion collapse” which made the recycling difficult. However, the safety can be assured for the lime glass when the Ladle furnace slag is rapidly cooled by high-pressure air injection. In addition, Ladle furnace slag has very fast hydration reaction rate.

This research team has proceeded with the research into the recycling of Ladle furnace slag. The rapidly cooled Ladle furnace slag generates high initial-hydration heat during the hydration reaction as shown in the eqn. 1 and forms impermeable film on the surface of anhydrated particles due to the bond of hydration product and CAH gel. Such film was found to block the water supply to the rapidly cooled Ladle furnace slag, hinder continuous hydration reaction, resulting in low strength development and complicating the volume stability. To resolve these problems, we conducted research using the gypsum as shown in eqn. 2¹⁻³.

1) When the Ladle furnace slag was used alone



2) When the gypsum was added to the Ladle furnace slag



This study was part of the research that aimed to use the rapidly cooled Ladle furnace slag as rapid-hardening inorganic binder. In this study, an experiment was performed to examine hydration reaction characteristics of the binder that mixed the gypsum to the rapidly cooled Ladle furnace slag. In other words, we mixed the gypsum to rapidly cooled Ladle furnace slag in our research with an aim to determine optimum gypsum mixing ratio to ensure the creation of Ettringite at early phase of hydration for initial strength development and induce continuous hydration reaction through the destruction of impermeable film of CAH gel.

EXPERIMENTAL

In this study, we carried out an experiment to use the rapidly cooled Ladle furnace slag as rapid-hardening inorganic binder and observed hydration characteristics of rapidly cooled Ladle furnace slag binder. The mixing ratio of gypsum was set to 0, 10, 20, 30, 40 % and analysis of micro-pore structure and hydrate products was conducted.

Regarding the rapidly cooled Ladle furnace slag used in this experiment, the molten Ladle furnace slag was rapidly cooled by high speed air injection and pulverized with the

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TABLE-1
CHEMICAL COMPONENT OF RAPIDLY COOLED LADLE FURNACE SLAG AND GYPSUM

Binders	Physical properties		Oxide content (wt. %)					
	Density (g/cm ³)	Fineness (cm ² /g)	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃
RCLFS	2.97	5,500	10.9	44.5	26.6	4.3	6.6	–
Gypsum	2.72	1,100	2.6	40.0	0.9	0.4	0.3	55.8

RCLFS: Rapidly cooled ladle furnace slag

ball mill. The α -hemihydrated gypsum of domestic “A” company was used in this experiment, which had higher solubility than other types of gypsum. Table-1 presents the physical and chemical properties of rapidly cooled Ladle furnace slag and gypsum used. The rapidly cooled Ladle furnace slag was used by diluting the retarder 0.5 % of the binder quantity with the mixing water in order to ensure workability arising from acceleration.

X-ray diffraction (XRD) measurement was performed at an angle of 10-60° of analysis range to analyze hydration products. For the observation of hydration products, the scanning electronic microscopy (SEM) was carried out at 5,000 magnification. To observe the micro-pore structure, mercury intrusion porosimetry (MIP) was used to measure distribution by size based on pore size ranging from 3.2 nm to 350 μ m at a pressure of 10 to 60,000 psi. The cement paste test specimen for XRD, SEM and MIP measurement was cut into cubes measuring 10 mm \times 10 mm \times 10 mm in dimension to be used in time for the age after the hydration discontinued.

RESULTS AND DISCUSSION

Pore structures: Fig. 1 illustrates the pore distribution of rapidly cooled Ladle furnace slag binder based on pore size. The binder that used only the rapidly cooled Ladle furnace slag did not exhibit significant change in pores. By contrast, the binder mixed with gypsum and substituted at a ratio of 10, 20, 30 and 40 % showed a reduction of relatively large-sized pores over the age and an increase in micro-pore distribution, suggesting that the hydration reaction was progressed conti-

nuously. However, expansion occurred in binder substituted at a ratio of 40 % due to the creation of large amounts of Ettringite, leading to the distribution of many micro-pores with a size of 350-1 μ m. Therefore, the adverse effect on durability may result from the failure to control the expansion reaction properly in case that the gypsum is mixed with rapidly cooled Ladle furnace slag at a ratio of over 40 %.

Hydration product: Fig. 2 illustrates the comparison through XRD between initial hydration product of binder substituted with gypsum at a ratio of 30 % and binder that used only rapidly cooled Ladle furnace slag fine aggregate. The binder that used only rapidly cooled Ladle furnace slag had CAH hydration product even peaking at 10 min due to initial hydration reaction and had even clearer peak over time. In addition, the unhydrated C₁₂A₇ was measured even after the age of 1 day. The binder substituted with gypsum at a ratio of 30 % was found to have the peak of gypsum that did not react in the initial 10 min. After 1 h, Ettringite peak was measured, along with some dehydrate gypsum which was generated from the reaction between hemihydrated gypsum and water. After 1 day, many Ettringite peaks were observed.

Scanning electron microscopy (SEM) shows binder substituted with gypsum at a ratio of 30 % and binder that used only rapidly cooled Ladle furnace slag fine aggregate based on age (Fig. 3). The rapidly cooled Ladle furnace slag fine aggregate contains a large amount of C₁₂A₇ that has high reactivity and therefore forms CAH hydrate through rapid reaction at initial phase of hydration and also forms steady state C₃AH₆ (hydrogarnet) within a few hours. The CAH film layer is formed

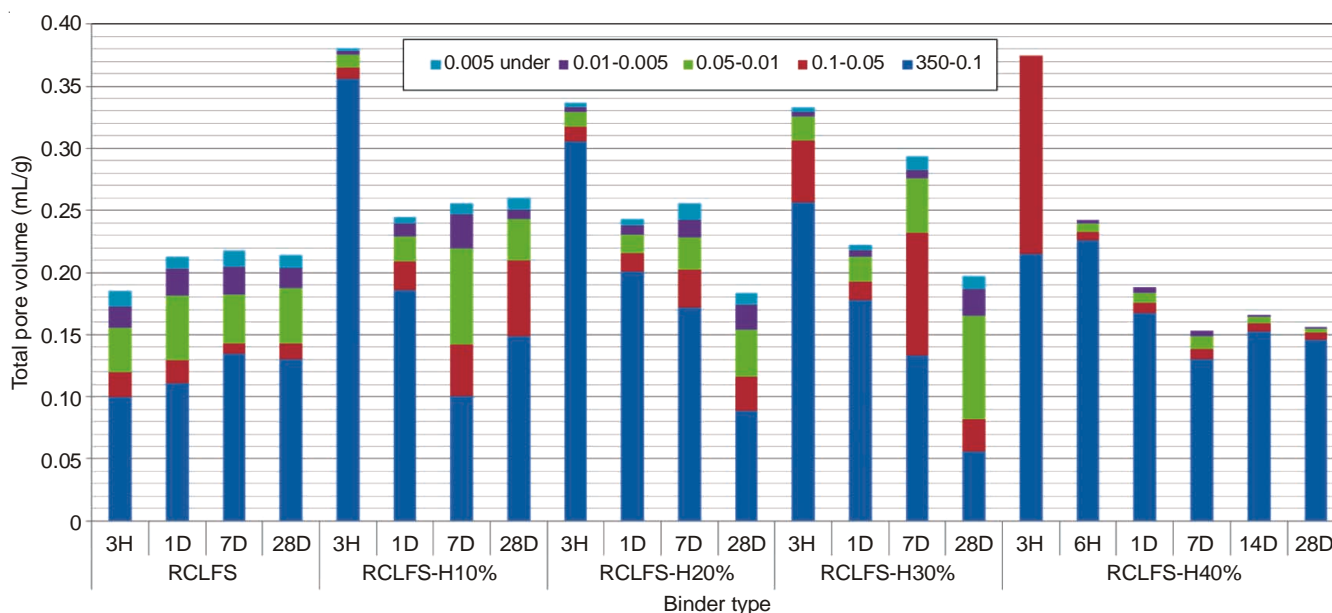


Fig. 1. Pore distribution of rapidly cooled Ladle furnace slag binder based on pore size

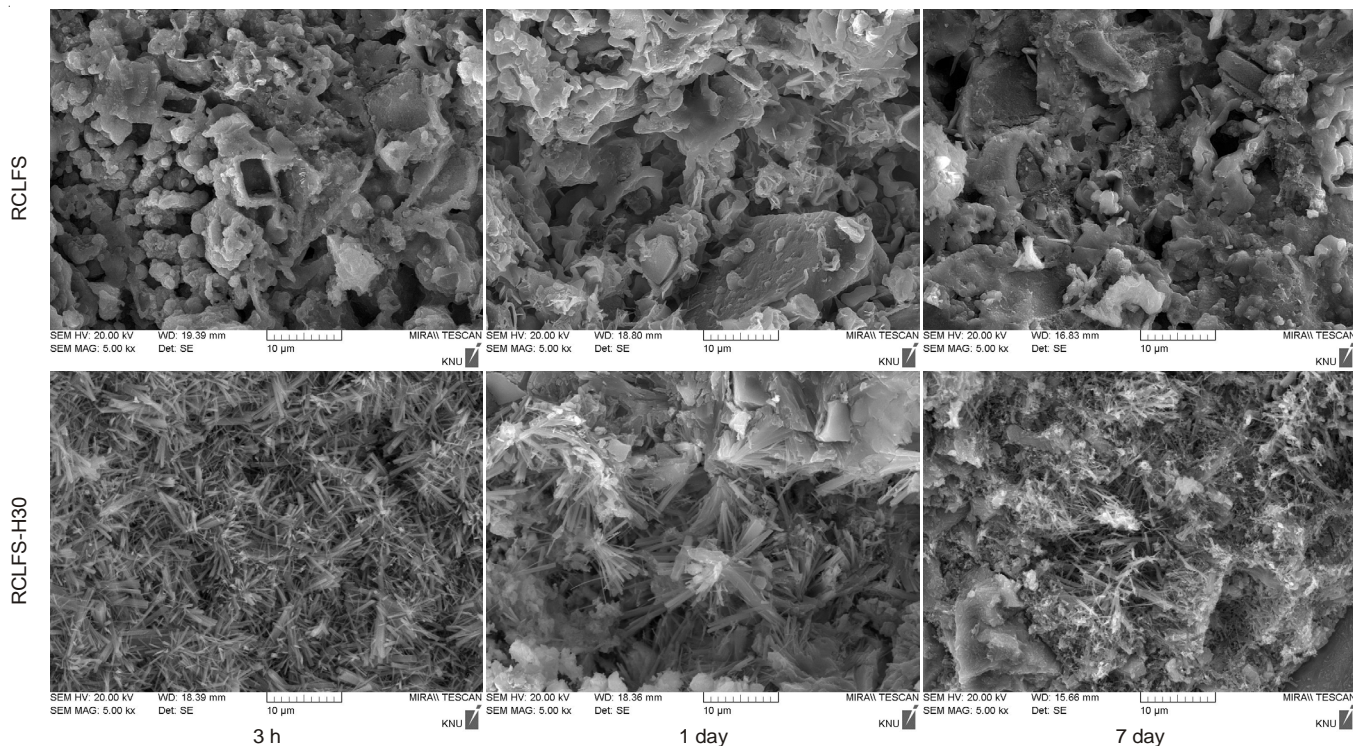


Fig. 3. SEM result of binder substituted with gypsum at a ratio of 0 and 30 %

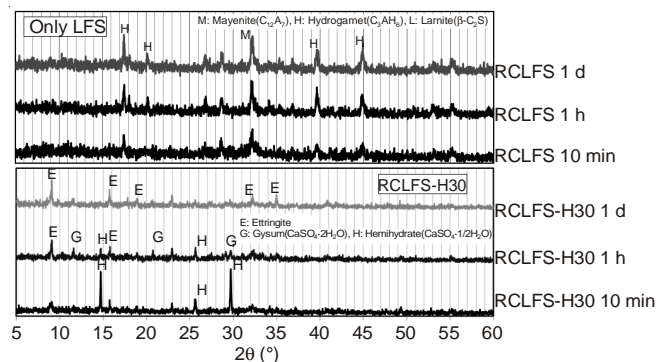


Fig. 2. XRD results of binder substituted with gypsum at a ratio of 0 and 30 %

around anhydrous particles with strong binding force even in the 3 h at the early phase of hydration. At the age of 7 days, the large-sized pores are maintained causing the long-term strength increase and degradation of durability. The binder substituted with gypsum at a ratio of 3 % was found to have created the Ettringite with large elongated aspect ratio due to the Ettringite crystal growth without disruption to mass transfer since the liquid phase reaction occurs mainly at initial phase of hydration, thus contributing to early strength development.

Conclusion

In this study, we have investigated the hydration characteristics of binder that mixed gypsum to rapidly cooled Ladle

furnace slag. Based on the results of this study, we draw the following conclusions within the scope of this study.

- The binder that mixed gypsum to rapidly cooled Ladle furnace slag showed the reduction of relatively large-sized pores and an increase of micro-pore distribution over the age, suggesting that the hydration reaction was progressed continuously. However, in case of substitution at a ratio of 40 %, there was extensive distribution of pores with a size of 350 to 1 µm due to the expansion cracking which resulted from the creation of large amounts of Ettringite.
- The results of XRD analysis and scanning electron microscopy showed that large amounts of Ettringite were created at after 1 day in the binder mixed with gypsum.

ACKNOWLEDGEMENTS

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