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A study of the effect of light-burnt dolomite on the hydration of alkali-activated Portland blast-furnace slag cement

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HIGHLIGHTS

- In Na_2SO_4-activated Portland blast-furnace slag cement, the hydration heat increased with the addition of LBD.
- A delay of the initial setting time was observed with the addition of LBD.
- The compressive strength improved with the addition of LBD.
- The pore structure of the paste became dense after 28 days of aging.

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ABSTRACT

This study used the typical powder alkaline material anhydrous sodium sulfate (Na_2SO_4) as an activator in a system in which Portland cement (10–20%) and ground granulated blast-furnace slag (GGBS, 80–90%) are generally mixed and added to light-burnt dolomite (LBD), one of the economical lime materials. Their effect on the hydration and strength of the cement was then analyzed. According to the analysis, the 1st peak of the minute heat of hydration increased after mixing the LBD. On the other hand, for the 2nd peak, a slight delay was observed. As a result of the mixing, the cumulative heat of hydration increased. Although the rate of setting decreased, the strength of the material improved after the 3rd, 7th and 28th days. In other words, it was confirmed that the pore structure of the paste became dense after 28 days of aging.

1. Introduction

Portland cement is the most widely used construction material [1,2], but it accounts for approximately 5% of greenhouse gas emissions [2].

Therefore, there have been many studies on various materials to reduce the use of or substitute Portland cement with the goal of reducing environmental pollution [2]. In particular, alkali-activated slag cement (AASC) is economically advantageous because the industrial by-products can be effectively used. Furthermore, so far, great characteristics substituting Portland cement are reported through various studies in AASC, and some countries have partially used it [3]. However, AASC has lower resistance of carbonation than Portland cement [3–5], and it has greater drying shrinkage [3,6–10].

In addition, ground granulated blast-furnace slag (GGBS) which is commonly applied to the AASC, has been used to manufacture concrete along with Portland cement in concrete manufacturing in various countries with advanced steel industries [3,11,12].

On the other hand, there are some problems with AASC that prevent this material from being a practical replacement for Portland cement. For example, this material is not compatible with the existing facilities used to manufacture ready-mix concrete [13]. At present, there are two ways to manufacture AASC: the use of liquid alkaline materials and the use of powdered alkaline materials. In the former method, additional tank to store liquid activator is required to use these liquid materials in the conventional ready-mixed concrete factories. In the second method the powdered alkaline materials can be easily used in the conventional ready-mixed concrete manufacturing facilities thorough premixing when manufacturing either slag powder or slag cement.

Well-known representative powder-phase activators are sodium sulfate and sodium carbonate; sodium sulfate is slightly more

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economical (for the industrial product, the cost of sodium sulfate is about 50% of the cost of sodium carbonate), and sodium sulfate is known to improve the strength of cementitious materials by generating ettringite because of sulfate included in lime-based cementing materials [3].

The light-burnt dolomite (LBD) is one of economical powder-phased lime materials, and it generates $Ca(OH)_2$ from the reaction with water, leading to an applicability as an activator. In the conventional study [14,15], there was a practice of using (~10%) Magnesia (MgO) for the purpose of drying shrinkage reduce in AASC using liquid activator (mainly sodium silicate solution), and in this study, the effect mainly on strength development by using LBD (<2%) was to be analyzed.

Therefore, this study used the powder alkaline sodium sulfate anhydrous (Na_2SO_4) as an activator in alkali-activated Portland slag cement (AAPSC), in which Portland cement (10–20%) and GGBS (80–90%) were used and added to light-burnt dolomite (LBD). The effect of these materials on the hydration and strength of the cement was then analyzed.

2. Experimentation

2.1. Raw materials

Ground granulated blast-furnace slag (GGBS): GGBS was produced in Incheon, and its chemical composition and physical properties are shown in Table 1; ordinary Portland cement (OPC): OPC was produced in Danyang, and its chemical composition and physical properties are shown in Table 1; activator: sodium sulfate anhydrous with a purity of 99% used in the test; light-burnt dolomite (LBD): LBD was product calcinated under 900–1000 °C that was produced in Jeongseon, and its chemical composition and physical properties are shown in Table 1; the XRD pattern of the LBD is shown in Fig. 1.

2.2. Test method

The setting time was tested according to the Korea national standard KS ISO 9597 (ISO 9597) [16]. The strength of the cement mortar was tested according to the Korea national standard KS L 5105-2007 [17] (specimen size: 50 × 50 × 50 mm). The heat of hydration was measured using Tokyo-Riko's three-point, multipurpose conduction calorimeter with a water-to-solid ratio of 0.5. In addition, XRD was measured (Cu Kα1 radiation with 2θ ranging from 5° to 60°) using the apparatus (WDX 200; acceleration voltage: 40 KV; current: 35 mA; scanning speed: 3.00°/min; step width: 0.05°) manufactured by Skyray Instruments. Moreover, the pore structure was measured against the hardened cement paste specimens that were wet-cured for 28 days using Micromeritics' apparatus (AutoPore IV; applied pressure (measured pore size): 0.5–40,000psia (338 μm~4 nm)) with a water-to-solid ratio of 0.45.

3. Results and discussion

3.1. Heat of hydration

Fig. 2 shows that the heat of hydration after mixing sodium sulfate and LBD in the cementitious material that used GGBS (90%) and OPC (10%). Figs. (a and b) show the results after 2- and 48-h hydrations, respectively. In addition, Fig. (c) shows the cumulated heat of hydration measured every minute. Here, sodium sulfate with weight ratio of 0% and 2% and LBD with weight ratio of 0%, 1% and 2% were used. The samples are marked as follows: N0D0, N0D1, N0D2, N2D0, N2D1 and N2D2. Unless sodium sulfate was used (N0D0-N0D2), the 1st peak increased with addition of LBD. For the 2nd peak, a time delay was detected. The 1st peak is increased probably because the heat generated from hydration of LBD ($MgO{\cdot}CaO + 2H_2O$ – >$Ca(OH)_2 + Mg(OH)_2$) affected it.

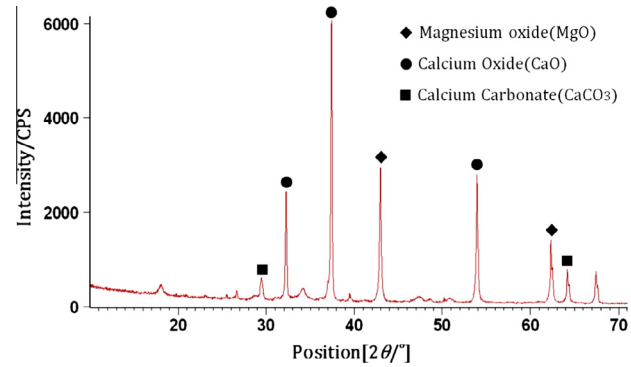

Fig. 1. XRD Patterns of the LBD.

With the same condition as in Fig. 2, the result of measuring characteristics of heat of hydration of LBD was shown in Fig. 3. As shown in Fig. 3, the heat of hydration of LBD is very high, but the heat of hydration generated from the use of small amount in the experiment is not high. However, in case where both GGBS and OPC exist as shown in this study, it is regarded that the hydration of LBD influences on activation of hydration of cementitious materials to increase the heat of hydration of GGBS or OPC. Such effect is considered to influence more on increase of heat of hydration of OPC or GGBS if LBD is used with sodium sulfate.

The reason the 2nd peak time was delayed due to mixing with LBD is not clear. Yet, LBD generates heat from the reaction with water (H_2O) initially, but it is assumed that insoluble $Mg(OH)_2$ is generated due to the reaction between dissolved Mg^{2+} and OH^- in solution, leading to decrease in hydroxyl ions in the solution to slightly reduce alkalinity of the paste [1]. The reaction of the cementitious materials was delayed accordingly.

When 2% of sodium sulfate was used (N2D0-N2D2), the hydration heat peak was mostly high in both the 1st and 2nd peaks. This result originated from the activated reaction of the cementitious materials by sodium sulfate similar to the results of conventional studies [3,18]. In addition, a delay of the 2nd peak time was observed after the addition of LBD in the N2 series. The cumulative heat of hydration (c) was high depending on the addition of LBD. In addition, it was higher when both sodium sulfate and LBD were used at the same time than when only LBD was added.

Fig. 4 shows the hydration heat of OPC and Portland slag cement (PSC, 55% of OPC + 45% of GGBS) under the same conditions. In terms of the 1st peak, the N2D2 was lower than the OPC but similar to the PSC. In addition, the 2nd peak was detected at approximately 12 h of aging in both the OPC and PSC but at approximately 30 h of aging in the N2D2. In terms of the cumulative heat of hydration, the N2D2 was similar to the PSC.

Table 1
Chemical composition and physical properties of the materials.

Material	Composition (%)										Density (g/cm^3)	Blaine specific area (cm^2/g)
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Alkali			Ig.loss		
							K_2O	Na_2O	Total alkali			
OPC	22.0	5.27	3.44	63.4	2.13	1.96	0.42	0.27	0.55	0.79	3.15	3419
GGBS	32.7	13.2	0.41	44.1	6.23	1.49	0.31	0.20	0.40	0.88	2.88	7042
LBD	0.89	0.32	-	52.8	32.2	–	–	–	–	1.85	3.12	3038