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Activation of ground granulated blast furnace slag by using calcined dolomite

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HIGHLIGHTS

- We use calcined dolomite to activate GGBS.
- Two prepared calcined dolomites can effectively activate GGBS.
- The properties of activated slag rely on calcination temperature of dolomite.
- Calcined dolomites induce slower activation than CaO.
- Calcined dolomites induce faster activation than reactive MgO in the early age.

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ABSTRACT

Both reactive MgO and CaO are alternative activators for ground granulated blast furnace slag (GGBS). In this study natural dolomite, as a source of MgO and CaO, was calcined at 800 °C (D800) and 1000 °C (D1000) in air. The activation of GGBS with the calcined dolomites was investigated using compressive tests, pH measurement of pore solutions, powder X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The results indicated that both calcined dolomites can effectively activate GGBS. D800 showed a relatively slower acceleration to GGBS than D1000 and both were slower than CaO. The use of D800 produced similar compressive strengths as did D1000 after 7 days curing but lower strengths at later ages. By increasing the dosage of activators, significantly higher strengths were obtained using D800 while only small increases were observed using D1000. The detected hydration products by XRD and TGA were mainly C–S–H and hydrotalcite-like phases, similar to those from other alkali-activated slags. The comparison to other activators indicated that using calcined dolomite can induce faster hydration of slag than using reactive MgO in the early age while slower than Portland cement in this study.

1. Introduction

The pursuit of more sustainable and environmental friendly construction materials to reduce the use of ordinary Portland cement (OPC), which is associated with high energy consumption and global greenhouse gas emission [1,2], has lasted for decades. By re-using industrial by-product blast furnace slag, alkali-activated slag (AAS) is one of the most promising precursors in large scale production and shows a huge potential to replace OPC [3], although still faces hurdles. Extensive studies have suggested that the advantages of AAS include the development of earlier and higher mechanical strengths [4–6], better resistance of chemical attack [7–9], stronger aggregate-matrix interface formation [10,11], and lower heat of hydration [12,13].

The most commonly used alkali activators for AAS are sodium hydroxide, sodium silicate, sodium carbonate and potassium hydroxide [14]. It is generally agreed that the mixture of sodium hydroxide with sodium silicate is the most effective activator and provides the best formulation for high strength and other advantageous properties. However, most of these activators do not exist naturally and require energy intensive manufacturing processes [12,14], making them less economical efficiency. In addition, some issues such as the fast setting time, the high drying shrinkage, the highly corrosive nature of alkali solution, the viscosity of alkali solution and the heat released by the dissolution of the alkali compounds, especially alkali hydroxide, during preparation of the solutions should be carefully considered when using these activators [3,4,15–17]. These problems have led researchers to pursue

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alternative effective activators or additives. Among others, calcium hydroxide [$Ca(OH)_2$] and calcium oxide (CaO) are potential alternatives to alkali activators, either as additives or main activators, due to their lower cost and durability enhancement [12,14,18]. It has been reported that $Ca(OH)_2$, as an additive, can increase the early strength (<7 days) of AAS whilst later strength might be slightly reduced [19]. Collins and Sanjayan [5] found that AAS concrete activated by a combination of sodium silicate and $Ca(OH)_2$ demonstrated considerably better workability and higher strength than concrete activated by a NaOH and Na_2CO_3 mixture. When $Ca(OH)_2$ is used as a main activator, with different auxiliary activators (Na_2SO_4 and Na_2CO_3), the activated slag concrete displays enhanced workability, delayed setting time and a similar increasing rate of compressive strength to PC concrete [20]. The comparison between the effect of CaO and $Ca(OH)_2$ in activating slag revealed that the use of CaO demonstrated a superior potential for the activation of GGBS and produced a higher mechanical strength than $Ca(OH)_2$ [18].

More recently, some investigations have indicated that reactive magnesium oxide (MgO) could also serve as an effective activator for GGBS, showing its advantages in the generation of more voluminous hydration products than C–S–H gel therefore providing a more compacted microstructure [21–24]. The results by Yi et al. [24] showed that the reactive MgO activated GGBS achieved higher 28-day compressive strength than that of the equivalent $Ca(OH)_2$–GGBS system due to the larger content of the voluminous hydrotalcite-like phases formed. The reason may be the better pore filling effect of hydrotalcite-like phases. Considering the slow hydration in the early age of reactive MgO activated slag and the limited global MgO production, the properties of slag pastes activated with MgO–CaO mixtures with various MgO–CaO ratios by weight were investigated by Gu [25]. That study found that the use of a small amount of CaO (MgO/CaO = 19/1 by weight) could significantly accelerate the early hydration of MgO-slag without sacrificing the long-term strength. In addition, when the MgO/CaO ratio was $\leqslant$1 by weight, only a small difference in compressive strengths of pastes was observed.

Dolomite is a naturally occurring mineral with abundant reserves around the world (i.e., North America, Northwestern and Southern Europe, North and West Africa, the Middle East, and the Far East [26]). In China, dolomite reservoirs in Liaoning, Neimenggu, Shanxi, Jiangsu, Fujian, Hunan, Hubei and Guangxi were found, with reserves over 4 billion tons [27]. The thermal decomposition of dolomite includes two stages [28–30]:

$$CaMg(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2 \quad \text{Stage1}$$

$$CaCO_3 \rightarrow CaO + CO_2 \qquad \text{Stage2}$$

where the second stage usually takes place at higher temperature. Calcined dolomite may therefore consist of MgO, CaO, $CaCO_3$ and possibly $MgCO_3$ and their proportions would vary depending on the calcination temperature. Nevertheless, calcined dolomite can be considered as a potential source of MgO–CaO blends as activators for slags.

The objective of this paper is to explore the use of calcined dolomite in the activation of GGBS. Two calcined dolomite samples produced under different temperatures were investigated. The performance of the different calcined dolomite activated slag pastes were then compared using compressive tests, pH measurement of pore solutions, powder X-ray diffraction (XRD) and thermogravimetric analysis (TGA). In addition, CaO activated slag paste was prepared as a reference.

Table 1
Chemical compositions and physical properties of materials (from suppliers' datasheet AND * using ICP-OES).

	GGBS	CaO	Dolomite (SD)*
Chemical composition			
SiO_2	37.0	0.9	0.037 (0.00)
Al_2O_3	13.0	0.13	0.001 (0.00)
CaO	40.0	94.0	33.7 (0.17)
MgO	8.0	0.5	18.9 (0.14)
K_2O	0.6	–	0.011 (0.00)
Na_2O	0.3	–	0.016 (0.00)
SO_3	1.0	0.06	NM
Fe_2O_3	–	0.08	0.006 (0.00)
$CaCO_3$	–	3.7	–
CO_2	–	–	47.3 (0.28)
LOI	–	2.2	–
Physical properties			
Specific surface area (m^2/g)	0.49	–	1.70
Bulk density (kg/m^3)	1050	1020	900

NM-not measured.

* The data was obtained by using ICP-OES technique.

2. Materials and methods

2.1. Materials

The chemical compositions and physical properties of the GGBS (from Hanson, UK) and CaO (from Tarmac and Buxton Lime and Cement, UK) are summarised in Table 1. The dolomite [$CaMg(CO_3)_2$] (DRB20) was supplied by IMERYS, UK and its elemental compositions determined after acid dissolution with 1 mol/L HNO_3 by inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmar 7000) in triplicate, are also shown in Table 1. The Ca–Mg molar ratio of the dolomite is 1.07. For calcination, approximately 50 g of raw dolomite was placed in individual ceramic crucibles and heated in air to 800 °C or 1000 °C in an electric furnace. The highest temperature was maintained for 1 h and then left to cool to room temperature. Two calcined products were obtained, namely D800 and D1000, referring to the products calcined at 800 °C and 1000 °C respectively, which were then stored in air tight plastic bags.

The calcined dolomite (D800 and D1000), as well as the raw dolomite, were characterised by XRD and TGA. The XRD patterns were collected using a Siemens D5000 X-ray diffractometer with a scanning range between 5° and 55° 2θ. The scanning speed of 1 s/step and resolution of 0.05°/step were applied. The TG measurements were carried out using a Perkin Elmer STA 6000 machine by heating the samples from 40 °C to 1000 °C at the rate of 10 °C/min. The XRD and TGA results are shown in Figs. 1 and 2, respectively.

The XRD pattern of the raw dolomite reveals that it also contained $CaCO_3$ (Fig. 1) and is consistent with the Ca–Mg molar ratio being >1 as indicated by ICP-OES analysis (Table 1). The TG curve of the raw dolomite indicates that its

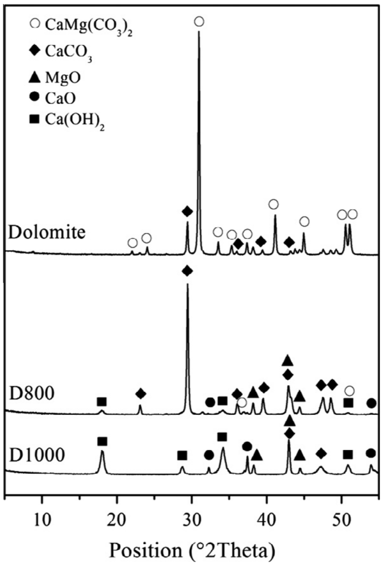

Fig. 1. XRD patterns of raw dolomite, D800 and D1000.