Effect of MgO content of synthetic slag on the formation of Mg-Al LDHs and sulfate resistance of slag-fly ash-clinker binder

Yuxuan Chen [a,b], Zhonghe Shui [a,b], Wei Chen [a,b,*], Qiu Li [a], Guowei Chen [b]

[a] State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, China
[b] School of Material Science and Engineering, Wuhan University of Technology, Wuhan 430070, China

HIGHLIGHTS

- Amount of LDHs increased with MgO content in synthetic slag during slag hydration.
- Sulfate resistance increased with MgO content in slag due to favored formation of LDHs.
- No correlation between MgO content of slag and mass change or porosity.

ARTICLE INFO

ABSTRACT

The effect of MgO content of synthetic slag on the formation of layered double hydroxides (LDHs) and sulfate resistance of slag-fly ash blended cement was studied. Hydration products of alkali-activated synthetic slag were LDHs and C-S-H. The content of LDHs increased with MgO content of slag due to the introducing of Mg, and C-S-H content did not change much with addition of different slags. Sulfate resistance of slag-fly ash-clinker mortar and paste under wetting-drying cycles increased with MgO content of synthetic slag, due to the favored formation of LDHs by high MgO content, denser microstructure and less porosity. There is no correlation between MgO content of slag and mass change and porosity of specimens during wetting-drying cycles in sulfate solution.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Ground granulated blastfurnace slag (GGBS) is widely used in modern concrete as a mineral admixture with beneficial effects on improving the resistance to sulfate attack, which is well proved in literatures through experimental investigations [1,2]. The activation of GGBS by calcium hydroxide formed from the hydration of ordinary Portland cement (OPC) is reported to improve the microstructure of the concrete, refine the pore structure and consequently impede the migration of sulfates into concrete [3–5].

Mg-Al layered double hydroxides (LDHs), namely the hydrotalcite-like phase, were formed during the hydration of slag, due to the magnesia (MgO) in slag [6–8], which has been extensively proven in various literatures, either through being activated by alkalis [9,10] or clinker [11]. LDHs represent family of minerals with a general formula $[M_{1-x}^{2+}M_x^{3+}(OH)_2]A_{x/n}^{n-}\cdot yH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, A^{n-} is the interlayer anions and x is $M^{3+}/(M^{2+}+M^{3+})$ molar ratio [12,13]. The amount of LDHs formed from the slag hydration depends primarily on the magnesia contents in slag [6]. LDHs are known with an anion exchange and adsorption capability that may have the potential to improve the durability of concrete related to ingression of anions into concrete. It has been proven that the carbonation resistance and chloride immobilization of concrete were improved with the presence of synthetic LDHs [14,15]. Bernal et al. reported that the high MgO content in slag can enhance the carbonation resistance of alkali-activated slags due to the formation of hydrotalcite-like phase [16].

The layered structure of LDHs is built by periodically stacking positively charged $(M^{2+}, M^{3+})(OH)_6$ octahedral layers related to brucite (in case of calcium and other large M^{2+} ions) or $M^{3+}(OH)_6$ octahedrons and $M^{2+}O_7$ polyhedrons (in case of smaller ions such as magnesium), and negatively charged interlayers consisting of anions and water molecules [17]. The interlayer anions can be substituted by other types of anions with larger charge density

and smaller ionic radius [18]. The affinity order of anions in the interlayers of LDHs is as follows [19].

$$CO_3^{2-} > SO_4^{2-} > OH^- > F^- > Cl^- > Br^- > NO_3^- \qquad (1)$$
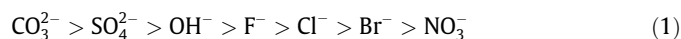
The amount of LDHs formed from the slag hydration depends highly on the amount of MgO in slag, as being theoretically proved [6–8] and experimentally observed [16]. It is hence hypothesized that more MgO in slag will result in the formation of more LDHs in the hydration products in concrete and will in turn promote the resistance to sulfate attack due to the anion exchange capacity of LDHs by immobilizing sulfate ions in the matrix.

In this study, slag with different MgO content was synthesized, and the hydration products and microstructure of alkali-activated slag and slag-fly ash-clinker pastes were characterized by a range of analytical techniques to evaluate the effect of MgO content on the formation of LDHs. The sulfate resistance of synthesized slag-fly ash-clinker paste and mortar under wetting-drying cycles was analyzed to assess the effect of MgO content of synthesized slag.

2. Materials and experimental

2.1. Materials

Analytically pure grade chemicals (CaO, SiO₂, Al₂O₃, MgO) were used for synthesizing slag. Sodium hydroxide (NaOH) and sodium sulfate (Na₂SO₄) were used for slag activation and sulfate resistance test, respectively. Deionized water was adopted to prepare paste mixes. Portland cement clinker from Huaxin Cement Co. Ltd., China and coal fly ash from Wuhan Iron and Steel (Group) Corp., China were used as binder and supplementary materials in this study and the chemical compositions are shown in Table 1. The particle size distribution of the clinker and fly ash is plotted in Fig. 1. Local river sand was used as fine aggregate.

2.2. Preparation of synthetic slag

The oxides recipe for synthetic slag was designed according to the oxides ratio of industrial slag, which is shown in Table 2. Three types of synthetic slag, namely S1, S2 and S3, were prepared with

different magnesium oxide content. The degree of depolymerization of the slag, quantified by the number of non-bridging oxygen atoms over tetrahedrally coordinated atoms (NBO/T), calculated from Formula (2).

$$NBO/T = (2O^{2-} - 4T)/T \qquad (2)$$

where NBO is molar amount of non-bridging oxygen atoms, O^{2-} is molar amount of oxygen, T is total molar amount of Ca^{2+}, Si^{4+}, Mg^{2+} and Al^{3+}. S1, S2 and S3 have the same NBO/T value by optimizing Al₂O₃, SiO₂ and CaO content, in order to obtain the same activity.

The procedure of synthesizing slag was as follows. The oxides were mixed in high speed mixer for 2 min, then transferred to a silicon-molybdenum-bar electric furnace for calcination in the corundum crucible. The oxides were heated up to 1450 °C with a heating rate of 5 °C·min⁻¹, and kept for 2 h for the mixture to reach complete melting. Then the melted mixture was cooled to the room temperature by quenching in water. The vitreous material was collected and dried at 60 °C in an oven until reaching a constant weight. The dried material was then ball-milled in a grinder for 1 h to obtain the synthesized slag.

2.3. Paste and mortar specimen preparation

2.3.1. Alkali-activated slag paste

Mix design of alkali-activated slag paste is shown in Table 3. The water/binder ratio was 0.3 and the concentration of NaOH solution was 5 mol·L⁻¹. The specimens were in size of 40 mm × 40 mm × 160 mm and cured under 20 °C and relative humidity of 100% in stainless steel molds. After 24 h, the specimens were demolded and cured until 28 and 112 days for tests. For compressive strength test, three specimens were used for each batch.

2.3.2. Cement paste and cement mortar with addition of synthetic slag

Paste mixes were designed at water/binder ratio of 0.4. The synthetic slag substituted binder by 30 wt%. Mix design of mortars and pastes are shown in Table 4. The specimens were in size of 25 mm × 25 mm × 280 mm with stainless steel molds according to Chinese standard GB/T 749-2008. After 24 h curing at 20 °C

Table 1
Chemical composition of clinker and fly ash (wt%).

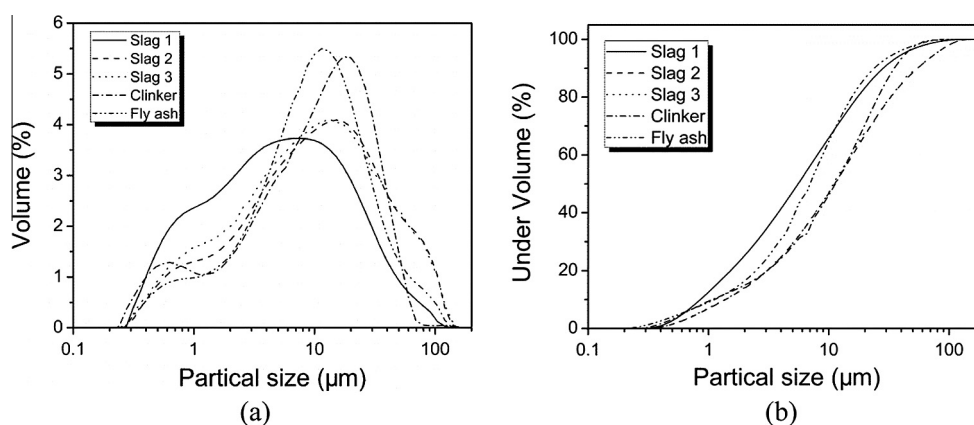|	Al₂O₃	SiO₂	Fe₂O₃	CaO	K₂O	SO₃	Na₂O	MgO	LOI[#]
Clinker	4.93	20.96	3.22	64.98	0.90	0.59	0.12	1.95	1.48
Fly ash	36.55	45.44	1.50	3.12	0.23	0.95	0.74	3.26	6.94

[#] Loss on ignition at 800 °C.

Fig. 1. Particle size distributions of clinker, fly ash and ground synthetic slag. (a) Particle size distribution and (b) cumulative particle size distribution.