Construction and Building Materials 140 (2017) 293–300

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Effects of aluminate rich slag on compressive strength, drying shrinkage and microstructure of blast furnace slag cement

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HIGHLIGHTS

- Aluminate rich steel slag (ARS) is a byproduct generated form steelmaking process.
- ARS with high Al_2O_3 and CaO contents is mainly composed of $C_{12}A_7$ and C_3A.
- Slag cement with ARS and gypsum has high strength and low drying shrinkage.
- Thick ettringite are formed during the hydration of OPC-GGBFS-ARS-Gypsum binder.

ARTICLE INFO

Article history:
Received 23 September 2016
Received in revised form 18 January 2017
Accepted 19 February 2017

Keywords:
Aluminate rich slag
Blast furnace slag cement
Drying shrinkage
Steelmaking slag
Compressive strength
Ettringite

ABSTRACT

Aluminate rich steel slag (ARS) is a by-product of the steelmaking process. ARS contains high contents of Al_2O_3 and CaO and is mainly composed of $C_{12}A_7$ and C_3A. This work investigated the effects of ARS and gypsum on the mechanical and chemical properties of blast furnace slag cement. The compressive strength, drying shrinkage, hydration and microstructure characteristics of blast furnace slag cement were investigated based on the addition of different percentages of ARS and gypsum.

The results showed that a quaternary binder of OPC-GGBFS-ARS-Gypsum has a beneficial effect on the compressive strength and drying shrinkage. The ettringite formed in the OPC-GGBFS-Gypsum binder were like sharp needles while the ettringite formed in the OPC-GGBFS-ARS-Gypsum binder were like thick needles. Because of such ettringite formation differences, the compressive strength and drying shrinkage of the quaternary binder was better than that of the ternary binder.

1. Introduction

Blast furnace slag has a relatively constant chemical composition despite being an industrial by-product. The rheology (slump, etc.) of the ground granulated blast furnace slag (GGBFS) concrete is easier to control than that of the cement-based concrete and has a low viscosity, which makes for straightforward placement and finishing works at a construction site easier. Moreover, its latent hydraulic properties refine the microstructure of the cement paste, thereby obstructing the permeation of detrimental ions from the outside and thus improving the structural durability [1,2].

Generally, concretes with a high proportion of blast furnace slag shrink significantly, which increases the probability of the occurrence of cracks during the initial ageing process [3,4]. A number of research efforts have been performed on account for such shrinkage. The method most commonly used for shrinkage control is the use of expansive additives [5–8] such as calcium sulfoaluminate (CSA) [9–12]. This method controls shrinkage by volume expansion through crystal growth and ettringite formation during the early age [13]. However, such volume expansion control requires rigorous quality control and may lead to cracking due to excessive expansion [14,15]. Furthermore, most expansive additives present economic issues by being too expensive in comparison with the cement price.

Recently, research efforts have been conducted using secondary refining slag as a construction material [16,17]. Secondary refining slag is a by-product of the secondary refining process used to produce high quality steel. This process uses reducing agents with a very strong affinity for oxygen (such as aluminum, Fe-Si, and Fe-Mn) to remove very small amounts of oxygen from steel.

Secondary steel slag has hydraulic or latent hydraulic (pozzolanic) characteristics, which makes it a target of evaluation as a supplementary cementitious materials (SCMs) [13,18,20–22,28–30]. To improve the characteristics of secondary steel slag as a

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http://dx.doi.org/10.1016/j.conbuildmat.2017.02.111
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Table 1
Chemical compositions and physical properties of the raw materials.

	Chemical Compositions (%)								Physical Properties	
	CaO	SiO_2	Al_2O_3	MgO	Fe_2O_3	Na_2O	K_2O	SO_3	Density (g/cm^3)	Blaine (m^2/kg)
OPC	62.2	20.7	6.2	2.8	3.1	0.1	0.84	2.1	3.15	341
GGBFS	43.5	32.6	15.6	4.4	0.5	0.2	0.49	0.8	2.98	433
ARS	48.5	2.3	33.7	2.3	1.1	0.04	0.01	0.9	3.04	401
Gypsum	51.6	0.7	0.2	1.5	0.1	0.02	0.03	55.5	2.93	421

Table 2
Sieve analysis of the sand.

Square mesh size (mm)	Cumulative sieve residue (%)
2.0	0
1.6	7.6
1.0	32.1
0.5	67.6
0.16	88.3
0.08	99.7

supplementary cementitious material, pretreatment methods, such as artificial weathering, grinding, sieving and magnetic separation, as well as other methods including adding chemical admixtures (e.g. superplasticizers) have been created [12,13,18–20,23–27,29–31].

The physical and chemical properties of secondary refining steel slag differ depending on the steel process and the final steel product type. The secondary refining steel slag produced in Korea is finally transformed into a $CaO\text{-}Al_2O_3$ compound after the hot melt reaction of CaO (resulting from limestone, which is a supplementary material) included in the slag layer and aluminum inserted as main reducing agent. Such slag is called aluminate rich steel slag (ARS). The $CaO\text{-}Al_2O_3$ compound rapidly reacts with water forming $xCaO\text{-}yAl_2O_3\text{-}zH_2O$, and reacts with gypsum effectively forming ettringite in the early age. The chemical properties of this ARS can be used for shrinkage reduction and replacing existing expansive additives.

This research is aimed at the study of the properties of ARS as a supplementary cementitious material and the development of a shrinkage reduction method for blast furnace slag cement using ARS. To this end, the material properties of ARS were studied, and the compressive strength and shrinkage properties of ARS introduced into blast furnace slag cement were evaluated. Furthermore, in order to examine the hydration properties of cement with ARS, heat evolution, X-ray diffraction (XRD), thermogravimetric (TG), porosity, and scanning electron microscope (SEM) analyses were performed.

2. Experiment details

2.1. Materials

The chemical compositions and physical properties of the raw materials used are shown in Table 1. The GGBFS (Korea Cement Corp.), anhydrous gypsum (Hyundai Corp.), ordinary Portland cement (OPC) (Dongyang Cement Corp.) and the ARS had Blaine fineness values of 433 m^2/kg, 421 m^2/kg, 341 m^2/kg, and 401 m^2/kg, respectively.

The standard sand was used as fine aggregate. The absorption, specific gravity and fineness modulus of standard sand were 1.03%, 2.54 g/cm3 and 2.97, respectively. The size distribution of sand was listed in Table 2.

As shown in Fig. 1 the ARS powder is a non-magnetic slag collected through the processes of drying, crushing, and magnetic separation. The powdered ARS particles are similar to a rough plate type with a surface that appears to be hard as shown in Fig. 2.

Fig. 3 shows the XRD patterns of the ARS. The ARS forms as a $CaO\text{-}Al_2O_3$ compound due to the hot melt reaction between the calcium oxide included in the slag layer and the aluminum inserted as reducing agent during the steelmaking secondary refining process. The main crystalline phase of ARS is composed of $12CaO{\cdot}7Al_2O_3$ and $3CaO{\cdot}Al_2O_3$. Additionally, $12CaO{\cdot}7Al_2O_3$ and $3CaO{\cdot}Al_2O_3$ are characterized by forming calcium aluminate hydrates during the reaction with water.

The Al_2O_3 content of ARS is very high in comparison with that of OPC and GGBFS, thereby making ARS one of the steel processing by-products with the highest content of Al_2O_3. Furthermore, as the slag layer already has a large quantity of CaO, the resulting ARS also has a large CaO content. Generally, steel slag (normally less than 40 mm of diameter) has 20 ~ 25% Fe_2O_3 content. However, the Fe_2O_3 content of ARS is just 1% because only non-magnetic 2 mm-diameter slag was selected through the crushing, magnetic separation processes and then grinded. ARS does not include environmentally hazardous ingredients [36,37] and has large quantities of Al_2O_3 and CaO, thereby presenting a high potential as a supplementary cementitious material [38].

2.2. Mixture proportions

In this research, blast furnace slag cement with OPC and GGBFS weight proportion of 1:1 was used as Plain. A part of the GGBFS of this Plain was substituted with only ARS or ARS and gypsum on a weight basis. The quaternary binder system composed by OPC, GGBFS, ARS, and gypsum will be called O-B-AS-G binders. The O-B-AS-G binders were mixed in the ratios of 50:30:20:0, 50:30:15:5, 50:30:10:10, 50:30:5:15, and 50:30:0:20. Mixes with OPC 100% (O100) and OPC 50%+GGBFS 50% (O50B50, Plain) were also made as comparison samples. The mixture proportions of the mortars examined for compressive strength in this study are given in Table 3. The water/binder ratio was fixed at 0.5, and the binder, water, and sand were mixed in the ratio of 1:0.5:3.

For the evaluation of the drying shrinkage, the water/binder ratios of the pastes were fixed at 0.35. In addition, XRD, TG-DTA, and SEM analyses were performed using paste specimens with a water/binder ratio of 0.5.

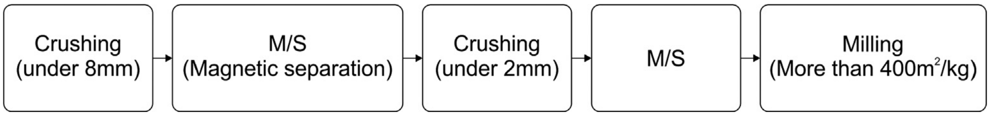

Fig. 1. Manufacturing process of ARS powder.