



Research article

Effects of compound chemical activators on the hydration of low-carbon ferrochrome slag-based composite cement



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ABSTRACT

Low-carbon ferrochrome slag (LCFS), a by-product of the ferrochrome alloy industry, has potential for use as a cementitious material due to its pozzolanic characteristic. The objective of the present study was to determine the optimum compound chemical activators for LCFS-based composite cement using an orthogonal test, in which 7 d and 28 d compressive strengths were used as the evaluating indices. The influences of compound chemical activators on the hydration of a composite cement mix were investigated using X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS) and thermogravimetry-differential scanning calorimetry (TG-DSC). The optimum activator to activate the composite cement was a compound of NaCl (NC) at a dosage of 0.6%, Na₂SO₄ (NS) at a dosage of 1.2%, NaF (NF) at a dosage of 0.6% and Al₂(SO₄)₃ (AS) at a dosage of 0.9% or 0.7%. The compressive strengths of the optimum composite cement mix at ages of 3, 28 and 180 d increased by 50.1%, 22.4% and 16.5%, respectively. More hydration products including ettringite and calcium silicate hydrate were formed at an early age of hydration. The compound chemical activators effectively activated the ferrochrome slag (FS), blast-furnace slag (BFS) and fly ash (FA) in the composite cement.

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1. Introduction

Composite Portland cement consists of more than two types of materials that are mainly derived from natural minerals (natural pozzolanic materials) or industrial wastes (fly ash (FA), blast-furnace slag (BFS), silica fumes, etc.) (Fu et al., 2000). The utilization of industrial by-products as a cement replacement provides many benefits including a considerable increase in the capacity of cement production and a significant reduction in greenhouse gas emissions. It was observed that a reduction of 47.5% in greenhouse gas emissions relative to that of a general-purpose-cement concrete-based blend occurred when a cement was partially replaced by ground-granulated blast-furnace slag (GGBS) (Crossin, 2015).

Therefore, it is highly advisable and beneficial to find suitable supplementary cementing materials to make use of all these benefits.

Various supplementary cementing materials such as FA, BFS, copper slag and phosphorous slag have been successfully utilized in cement production (Allahverdi and Mahinroosta, 2013; Hossack and Thomas, 2015; Mo et al., 2015; Nazer et al., 2016; Schöler et al., 2015). However, few studies have evaluated the utilization of ferrochrome slag (FS), a type of solid waste produced in the manufacturing of carbon-containing ferro-chrome alloys, which can be classified as high-carbon, medium-carbon and low-carbon ones according to their carbon content. High-carbon FeCr metal is produced from the oxide of chromium ore in electro-arc furnaces by a carbothermal process with coke as the reducing agent at approximately 1700 °C. Liquid of FeCr metal flows out into ladles together with slag liquid, and the mixed liquids stratify according to their specific gravities, with FeCr metal on top and the molten slag below (Zelić, 2005). The molten slag slowly cools in air to form a stable crystalline dense rock that has mechanical properties similar to basalt and is composed of SiO₂, Al₂O₃ and MgO. Therefore, high-

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carbon FS is often used as concrete aggregates due to its excellent mechanical properties and low calcium oxide content. Panda et al. (2013) evaluated the technical performance of concrete material containing high-carbon FS as aggregate material and assessed the environmental compatibility of the waste slag; this concrete aggregate material was suitably utilized with chromium immobilization in the cement concrete matrix without causing significant environmental pollution. Gencil et al. (2012), Lind et al. (2001), and Yilmaz and Karaşahin, (2010) researched the impact of high-carbon FS as a concrete aggregate in pavement or road construction and observed very low impacts on the underlying soil and groundwater.

Medium- and low-carbon ferrochrome can be obtained by reducing chromites and iron using silicon as a reducer in the form of silico-chrome in a shaft-type electric furnace lined with magnesia. During the metallurgical process, large amounts of high-purity calcium oxides are added to facilitate completion of the chromium reduction and to reduce the activity of SiO_2 in the slag. CaO and SiO_2 in the slag tend to form $2\text{CaO} \cdot \text{SiO}_2$, which is the major mineral composition of medium- and low-carbon FSs, and a small amount of chrome is also formed. When cooled in the air, the crystal $2\text{CaO} \cdot \text{SiO}_2$ in the slags changes from the β -form to γ -form, which promotes the constant pulverization of the slags. Unfortunately, only a small amount of medium- and low-carbon FSs have been used to date, and the remainder are usually disposed of without any pollution prevention or control or remedial measures. In recent years, increasing concerns about the environmental consequences of waste disposal have led researchers to investigate the utilization of these wastes as potential construction materials.

Our previous work (Hao et al., 2015a,b) showed that low-carbon ferrochrome slag (LCFS) could be utilized as supplementary material in blending with clinker, BFS, FA, gypsum and lime to prepare composite cement material. When the proportion of the cement was fixed at 40% LCFS, 20% BFS, 7% FA, 5% lime, 4% gypsum and 24% clinker, the compressive strengths of the cement at ages of 7 d and 28 d reached 32.57 MPa and 56.00 MPa, respectively. Moreover, the results of a standard leaching experiment showed that the leachable chromium was well immobilized in the cement matrix as nearly no chromium was detected in the leaching solution. Despite that the LCFS was suitable for use as a cement replacement without any significant environmental risks, an increase in the replacement by LCFS decreased the compressive strength of the composite cement. When the replacement level increased from 20% to 50%, the strength of the composite cement had decreased by 20%. As the replacement by LCFS increased further, there was an inverse relationship between the strength (especially the early strength) and the level of replacement. To solve this problem, a number of studies have investigated the activation of FA, phosphorous slag and BFS using chemical activators, including alkali and sulfate activation (Ben Haha et al., 2011; Fernández-Jiménez and Palomo, 2005; He and Liu, 2010). Rungroj and Suwimol (2011) investigated the performance of lime-BHA solidified plating sludge with Na_2SiO_3 and Na_2CO_3 as activators. The results showed that the addition of activators could improve the early strength and decrease the cumulative leaching of Fe, Cr and Zn from the lime-BHA solidified plating sludge. Alahrachea et al. (2016) researched the effects of chemical activators including 2 mass-% $(\text{K},\text{Na})_2\text{SiO}_3$, 3 mass-% Na_2CO_3 , 8 mass-% $\text{Na}_2\text{Oxalate}$ and 3 mass-% $\text{K}_3\text{Citrate}$ on the setting and hydration kinetics of a blend of 70 mass-% fly ash and 30 mass-% PC. The addition of the activators increased the pH and decreased the concentration of calcium ions in the pore solution, which led to a faster reaction for alite and thus to set fast increasing early strength. In this work, the effects of inorganic activators, such as NaCl (NC), Na_2SO_4 (NS), NaF (NF) and $\text{Al}_2(\text{SO}_4)_3$ (AS), on the mechanical properties and hydration of composite cement with a high content of LCFS were investigated by means of compressive strength, X-ray

diffraction (XRD), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS) and thermogravimetry-differential scanning calorimetry (TG-DSC). The results of this work will contribute to the utilization of high-volume LCFS in composite cement.

2. Experiments

2.1. Materials

The LCFS used in this investigation was collected from the Shuozhou Tiancheng Electric Smelting Co., Ltd., located in Shanxi Province, China. Merwinite ($\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$), gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) and dicalcium silicate (C_2S) were identified as the main crystalline phases of the LCFS (Fig. 1). BFS, clinker, gypsum, FA and lime were also obtained from Shanxi Province, China. The chemical compositions of the raw materials are given in Table 1. The LCFS, BFS, FA and clinker were dried in an oven at 105 °C for 24 h. The dried materials were ground for 2 h in a ball mill followed by sieving through a 0.08 mm mesh. The size distribution of the ground LCFS was shown in Fig. S1 in the support information, and the value of medium particle size was 14.8 μm .

The chemical activators used in this study consisted of NC (chemically pure), NS (chemically pure), NF (chemically pure) and AS (chemically pure).

2.2. Orthogonal test

An orthogonal test with a matrix model of $L_9(3^4)$ was employed to investigate the complex effects of the four types of chemical activators on the hydration behaviour and mechanical properties of the high-content LCFS-based composite cement. The four factors and the three levels of the matrix are listed in Table 2. The compressive strengths of the cement at ages of 7 d and 28 d were designated as the evaluation indices X and Y, respectively. The optimal level and combination of factors were determined according to the orthogonal experiment and subsequent data analysis. The test was repeated under the optimal conditions to verify the obtained data.

2.3. Specimen preparation

Paste specimens were manufactured as a mixture of LCFS/BFS/clinker/FA/gypsum/lime at a proportion of 50/15/20/6/4/5 and water/binder ratio of 0.32. The size of each specimen was 40 mm \times 40 mm \times 160 mm. After casting, the specimens were covered with burlap and polyethylene sheets and kept in the

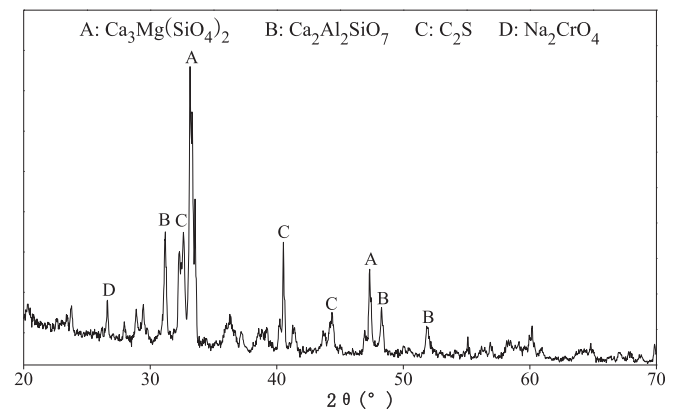


Fig. 1. XRD patterns of the LCFS.

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