Construction and Building Materials 99 (2015) 175–183

Contents lists available at ScienceDirect

Construction and Building Materials

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

High-strength KOBM steel slag binder activated by carbonation

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HIGHLIGHTS

- Carbonation-activated steel slag can create a 2 h strength of 80 MPa and 28-day strength of 109 MPa.
- The early strength is attributed to the carbonation of γ-C_2S.
- The late strength is due to the hydration of β-C_2S.
- Carbon-activated steel slag can be used as a green cementing binder to replace OPC.

ARTICLE INFO

Article history:
Received 6 January 2015
Received in revised form 8 July 2015
Accepted 19 September 2015
Available online 25 September 2015

Keywords:
KOBM steel slag
Carbonation activation
Strength
Carbon uptake
Slag binder

ABSTRACT

The feasibility of developing a high strength KOBM (Klockner Oxygen Blown Maxhutte) steel slag binder activated by carbonation as an alternative cementing material was investigated. After two-hour carbonation reaction, steel slag compacts displayed a 2 h compressive strength of 80 MPa with a CO_2 uptake of 13%. Early strength gain was attributed to the carbonation of the slag's γ-C_2S component. Subsequent hydration enhanced the ultimate strength to 109 MPa, owing to the latent hydraulic reactivity of the β-C_2S component. The carbon-activated slag presented a more sustainable alternative to Portland cement as a primary binder for building products. In addition to conserving the natural resources and recycling the wastes, a potential carbon sink for the steel industry can be realized through its use.

1. Introduction

Steel slag is a by-product from the steel refining process. The production of one ton of steel generates 90–100 kg of slag, making global slag production reach approximately 130 million tons annually [1]. Currently, more than 43% of this residue is used in road construction as the aggregate component [2]. Internal metallurgical use within the refining process accounts for 11%, cement production 5%, interim storage 19% and landfill disposal 13% [2]. Rich in calcium and silica, and a derivative of a high temperature process, steel slag can serve as a value-added source of calcium–silicates.

Efforts were made to use steel slag as a cementitious supplementary material in blended cements. Unlike ground granulated blast furnace (GGBF) slag, steel slag is neither hydraulic nor pozzolanic due to its lack of tri-calcium silicates and amorphous SiO_2 content [3]. However, steel slag can be modified to become hydraulic through high temperature thermodynamic manipulation [4,5]. Heat treatments can change slag's compositional constitution to generate cementitious phases suited for cement blends. It was reported that blending Portland cement with 20% thermally-treated steel slag yielded equivalent concrete strength [6].

On the other hand, steel slag has shown high reactivity to CO_2, making it a suitable candidate for mineral sequestration – one of the techniques proposed for carbon emission reduction. It was reported that carbonating 1 kg of powder steel slag via hydrothermal processing could sequester up to 0.25 kg of CO_2 [7]. Calcium ions were extracted from slag and reacted with carbon dioxide in an autoclave reactor to form calcium carbonates. This process had been recently commercialized to produce precipitated calcium carbonates (PCC) as a value-added product [8].

In addition to sequestration, carbonation reactivity of steel slag presents the possibility of developing a no-clinker binder to replace Portland cement in building products. This is a challenging and rewarding application. Unlike PCC production, which associates the heavy use of consumables and generation of wastes, employing carbonation-activated steel slag as a binder demonstrates a closed-loop application, whereby no solid or liquid waste by-products are generated. Efficacy is strongly dependent on a

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http://dx.doi.org/10.1016/j.conbuildmat.2015.09.028
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sufficiently high content of calcium silicate compounds within the slag. The basic mechanism for strength development is described by Eq. (1). Di-calcium silicates in the slag react with carbon dioxide to form calcium–silicate–hydrates and calcium carbonates [9]. Research had shown that non-hydraulic γ-C_2S compact could develop a compressive strength of 50 MPa after undergoing 15 min carbonation at 10 bar gas pressure [10].

$$2(2CaO \cdot SiO_2) + CO_2 + 3H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + CaCO_3 \quad (1)$$

Research on CO_2-activated steel slag as a primary binder for building products is relatively new. In Japan, steel-slag-bond blocks had been produced from a continuous carbonation process. One cubic meter of blocks were produced at a CO_2 gas pressure of 1 bar and an exposure duration of 12 days. The resulting slag blocks had a strength of 18 MPa and a density of 2.2 g/cc [11]. Johnson et al. had demonstrated that stainless steel slag undergoing a one-hour carbonation at 3 bar and 28-day subsequent hydration generated a compressive strength of 9 MPa [12]. Similarly, electric arc furnace (EAF) slag activated by carbon dioxide achieved a strength of 17 MPa and a carbon uptake of 11% after 2 h of carbonation [13]. Ladle slag had also been shown to respond favorably to carbonation, yielding a strength of 35 MPa after a CO_2 exposure of 24 h and a gas pressure of 1.5 bar [14]. To improve the strength gain of stainless steel slag, high temperature and high pressure carbonation was reported. At a gas pressure of 20 bar and a temperature of 80 °C, the compressive strength was found to reach 50 MPa after 2 h of autoclave carbonation [15]. In addition to strength activation, carbonation of steel slag compacts reportedly reduced leachability of chromium and molybdenum and ensured compliance with regulatory limits dictating the safe reuse of waste [15].

Steel slag's resourceful compositional makeup and high specific reactivity to CO_2 gives more ground to exploring this material's beneficial use as a binder, whereby further improvements to compressive strength and carbon uptake can be achieved dually from combined carbonation and hydration. The key parameter is the chemical composition of the as-received steel slag. This paper presents a study on this effort. Steel slag originating from the KOBM (Klockner Oxygen Blown Maxhutte) process of a local mill was investigated. The slag fines collected were sieved to remove metallic iron solids. The de-ironized slag was then ground, molded into cylindrical compacts, and assessed for its carbonation and hydration behavior. Reaction products within the carbon-activated slag binder were analyzed using quantitative X-ray diffraction (QXRD), thermogravimetry (TG), and micro-hardness testing. The ultimate goal of the devised processing route aims to valorize slag in a manner that can maximize the binding strength and CO_2 sequestration capacity.

2. Experimental program

2.1. Materials and composition

The steel slag used in this study was obtained from RioTinto, Fer et Titane (RTFT) operation located in Sorel-Tracy, Quebec, Canada. The slag was originated from the plant's KOBM (Klockner Oxygen Blown Maxhutte) process, a variant of the more conventional Basic Oxygen Furnace (BOF) process. To promote the recyclability, steel slag was processed at slag yard by crushing and sieving for road aggregate applications. Magnetic separation of the crushed slag also ensued for enhanced iron recovery. Residual slag fines passing a sieve size of 0.5 mm typically have no value for aggregate use. Sparing amounts of these are sometimes recycled back into the steel-making process for use as fluxing agents to benefit from their high calcium content. In this study, the as-received slag fines will be examined for their hydration and carbonation behavior in order to assess their value-added use as a primary binder material. Sieve analysis revealed that about 90% of this material was finer than 212 μm. Fig. 1 shows the slag portions, both, passing and retained on the 212 μm sieve. Energy dispersive X-ray spectra (EDS) of the coarser portion found that it was mainly comprised of iron and magnesium-oxide particles. Only the finer portion was employed to develop the proposed clinker-free binder use.

2.2. Sample preparation

Steel Slag fines passing 212 μm sieve were further ground to a finer powder using a vibratory pulverizer for a duration of 1 min. This ensured size homogeneity. The energy of grinding, estimated from power consumption and grinding duration, was 0.017 kW h/kg slag. The Blaine fineness of the slag powder was measured using an air-permeability apparatus, in accordance with ASTM C-204. The measured Blaine fineness was 316 ± 41 m^2/kg for the ground slag. General-use ordinary Portland cement (OPC) was used as control, and measured 384 ± 35 m^2/kg for fineness. The chemical compositions of the ground slag and OPC were obtained from X-ray Fluorescence (XRF) and carbon/sulfur analyses. Results are presented in Table 1. They are the average of two XRF tests.

Cylindrical compact specimens were selected to facilitate consistent evaluation of strength and CO_2 uptake. These were formed using a specially designed stainless steel mold. The powder slag was first mixed with water at a water-to-slag ratio of 0.15 and then compact formed by applying a 16 MPa compaction pressure. Each freshly molded compact had a 15 mm diameter and 30 mm height, and weighed around 8 g.

2.3. Curing procedure

Hydration curing was achieved by sealing cylindrical compacts in air-tight plastic bags for durations of 2 h, 1, 7, and 28 days. After completing the specified hydration ages, respective compacts were tested for compressive strength, which served herein as the physical indicator of hydration.

Carbonation was carried out immediately after the de-molding of compacts to evaluate its early strength contribution. It was carried out in a pressure chamber using high purity (99.5%) CO_2 gas. The apparatus is presented in Fig. 2. The chamber pressure was fixed at 1.5 bar and carbonation was varied for durations of 2 h, 4 h,

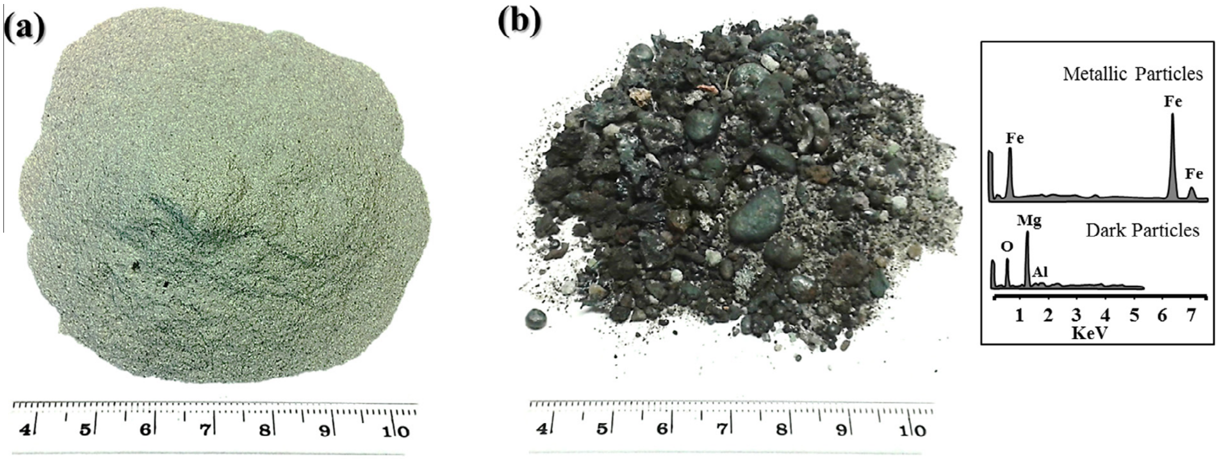

Fig. 1. As-received KOBM slag (a) passing 212 μm sieve; (b) retained on 212 μm sieve (scale bars in cm).