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Carbon dioxide activated ladle slag binder

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HIGHLIGHTS

- Ladle slag with higher SiO_2 content and lower free lime showed stronger carbonation reactivity.
- Heat treatment at 1100 °C with silica addition is effective to produce more dicalcium silicate phases.
- The total CaO content of slag should not be considered as the only factor for its CO_2 reactivity.
- The products based on carbonation activated slag have shown reduced natural material consumption.

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ABSTRACT

The viability of converting steelmaking ladle slag into cementing binder through carbon dioxide activation was studied. Two typical ladle slag materials were examined: one with higher silica content and one with higher alumina content. It was found that ladle slag with higher silica content contained more calcium silicate compounds and less free lime, leading to higher carbonation reactivity in its as-received form. Ladle slag with higher alumina could not be activated directly by carbon dioxide to gain strength. Heat treatment with silica addition was thus developed to produce more calcium silicates and reduce free lime content. Findings reveal that carbonation reactivity is not solely based on chemical compositions of the material, rather, the constituting mineralogical phases. Calcium silicates of any polymorph played a critical role in the formation of the strength-contributing binder matrix activated by carbonation. Strength gain was the result of simultaneous formation of calcium silicate hydrates and calcium carbonates. To produce value-added ladle slag as cementing binder to replace Portland cement, silicon is recommended as deoxidation agent in steel refinery process. The building products based on carbonation activated ladle slag have shown much reduced embodied energy and much reduced natural material consumption.

1. Introduction

Ladle furnace slag is a by-product of steel refining process. Approximately 30 kg of ladle slag will be created from every tonne of steel produced [1]. During the steel refining process known as secondary metallurgy process, the liquid steel from basic oxygen furnace (BOF) or electrical arc furnace (EAF) is poured into a ladle furnace where it is deoxidized, desulphured and suitably alloyed under the protection of the basic slag. Ladle slag contains more than 50% of calcium oxides. The other major components are silicon and aluminum oxides [2]. In comparison to BOF and EAF steel slag, ladle slag is basic with higher calcium, higher free lime and lower iron content. Because of the slow cooling, disintegration occurs, making ladle slag more powdery [3]. The make-up of ladle slag depends heavily on the composition of the initial raw material, as well as the amount/type of additives and fluxing agents used to justify the required composition for different applications. Of those parameters, silicon and aluminum as the deoxidization agents play critical role in determining the process cost and the property of the final slag [4].

Regardless of this variability, ladle slag has a composition resembling Portland cement and therefore may have the potential to be used as cementitious material. Studies have shown that ladle slag in general has shown weak hydraulic properties because it is mainly composed of γ-C_2S [5]. Ladle slag with high silica content (23%) can be used as pozzolanic material [6]. Ladle slag can be alkali activated to develop strength. Because of high free lime content, ladle slag has to be blended with blast furnace slag to make alkali-activated materials as cementing binder [3,7]. The high calcium ladle slag is also used to replace lime in making autoclaving lime–silica products [5]. Ladle slag has been successfully used in Europe in masonry mortar application [8].

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The low hydraulic behavior of steel slag can be improved by heat treatment at high temperature. It is also useful tool to reduce free lime content and control the particle size. Heat treatment can be divided into two approaches: molten-stage process and secondary melt process. It has been found that adding fluxing agents that are rich in CaO and SiO_2 during steel refining process can improve the steel slag's hydraulic properties [9]. Zong et al. [10] added 5% fly ash as an additive to the molten steel slag to change the structure of slag to improve its grindability. In another study by Li et al. [11], BOF and EAF slags were mixed and re-heated at high temperatures varying from 1250 to 1350 °C followed by fast-cooling quenching. The resulting slag showed higher C_3S and lower C_2S content compared to its as-received form. Adolfsson et al. [12] suggested that fast cooling of ladle slag can produce more β-C_2S. They re-heated the mixture of few steel slags including ladle slag with additives at 1200 °C followed by water cooling. The compressive strength of the fast-cooled slag reached to 12 MPa after 28 days hydration.

Because of high calcium content, steel slag and ladle slag are CO_2-reactive. This property has been successfully utilized in mineral carbonation to sequester carbon dioxide in steel slag [13]. Ladle slag fines are investigated for its capacity to capture and store carbon dioxide. The carbonated ladle slag is capable of taking 5–10% carbon dioxide by mass in 2-h carbonation and is used as fine aggregates in concrete [14]. Although there is no report on carbonated ladle slag as a cementing binder, there are a few demonstrated applications of CO_2 activated steel slag for strength gain. Isoo et al. [15] reported that EAF steel slag block of one m^3 size reached a compressive strength of 18.4 MPa after 12 days of carbonation for seaweed bed application. Stainless steel slag compacts exposed to carbon dioxide for 1 h achieved a compressive strength of 9 MPa and a carbon dioxide uptake of 18% [16]. The underlying principal for strength gain by carbonation activation is described by Eqs. (1) and (2) [17]. The carbonation reactions of dicalcium silicate (C_2S) and tricalcium silicate (C_3S) produce cementing binder as a hybrid of calcium silicate hydrates (C–S–H) and calcium carbonates ($CaCO_3$).

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

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

There is no previous study on carbon dioxide activation of ladle slag for binder application. Because of the difficulty of using ladle slag directly as cementitious material, it is interesting to know if ladle slag can be activated to gain strength by carbonation. The purpose of this paper is to explore the feasibility of converting ladle slag into a ladle slag binder through carbonation activation for building material application. Two ladle slags are collected from the same production line in the same steel mill but at different time. They are typical for each: one ladle slag compact can be activated in its as-received form to develop sufficient strength as cementing binder and the other one is totally cracked due to the heat generation by carbonation of free lime. The conditions for carbonation activation are therefore examined. Compositional variation plays a critical role in the slag carbonation. Heat treatment is developed to alter the composition of the slag which is unsuited to direct carbonation in as-received form and tailor it to carbonation reaction. Silica rich industry waste such as waste glass is employed as silica additive to create more calcium silicate compounds in the treated slag for carbonation. Both as-received and treated ladle slag products after carbonation activation are characterized by carbon dioxide uptake, strength development and microstructure changes. The study is aimed at developing a recommendation for steel refining process to produce structurally useful ladle slag for cementing binder application.

2. Experimental program

2.1. Materials and carbonation setup

Two ladle slags (L2 and L3) were received from a steel mill in Montreal, Canada. They were collected from the same production line of the steel mill at different time. They were received about two years apart from each other. Because of the slow cooling, ladle slag was produced as powder which was then packed into porous "cakes" for shipping and handling. The as-received dry ladle slag "cakes" were first crushed and then further pulverized into powder with Blaine number of 318 and 247 m^2/kg for L2 and L3, respectively. L2 slag was received two years early than L3.

The chemical compositions of as-received ladle slag (L2 and L3) were determined by the X-ray Fluorescence (XRF) analysis and are presented in Table 1. The variability between the two raw forms of slag is apparent. The difference in composition of ladle slag is possibly caused by the changes in process and the different steel products. As shown in Table 1, ladle slag L2 demonstrates a higher calcium and silica content, while ladle slag L3 had higher alumina, iron and magnesium content. The carbon dioxide content was determined by infrared based carbon analyzer. They were relatively low. The free lime content of ladle slag was also measured using the Franke method, in accordance with ASTM C114 [18] and are shown in Table 1. Ladle slag L3 contains high free lime than ladle slag L2. To evaluate hydration and carbonation behavior of ladle slag, it is crucial to determine the mineralogical phases, mainly the dicalcium silicate (C_2S) and tricalcium silicate (C_3S). It was accomplished by using semi-quantitative X-ray diffraction (QXRD) analysis with 10% TiO_2 as internal reference [19]. By comparing the XRD peaks of pure C_2S, pure C_3S, pure TiO_2 and ladle slag, the percent of C_2S and C_3S in ladle slag can be estimated. The results are also presented in Table 1. Ladle slag L2 has shown much higher C_3S than ladle slag L3. Ladle slag is possible to contain C_3S [20] since the process temperature could go over 1500 °C [21]. Table 1 also shows chemical composition of ground waste glass as silica additive for heat treatment in case the as-received ladle slag cannot be activated directly by carbonation possibly due to the lack of calcium silicates. The waste glass is the by-product of recycling process of efflorescence lamps and is ground to a powder having a Blaine number of 600 m^2/kg.

For each ladle slag, total of nine slab specimens of 76 × 127 × 12 mm were compact formed at pressure of 12.5 MPa with a water to slag ratio of 0.1. Six specimens were subjected to carbonation activation right after specimen formation. Of the six carbonated slabs, three were tested immediately after carbonation for compressive strength and the other three were tested after subsequent hydration of 35 days in sealed plastic bags. Three hydration reference specimens were cured in sealed plastic bag and tested after 35 days of hydration. The carbonation set up is shown in Fig. 1. A CO_2 gas with a purity of 99.5% was used in carbonation. The gas was first warmed up by a heater and then injected into the chamber to a pressure of 0.15 MPa for a duration of 24 h. The pressure was maintained as a constant by the regulator so that the consumed carbon dioxide by slag products can be replenished.

2.2. Heat treatment for ladle slag L3

Both ladle slags L2 and L3 were tested first in as-received form. Ladle slag L2 compacts were CO_2-reactive and could develop strength in 24 h by carbon activation. However ladle slag L3 compacts were totally cracked due to the extreme heat generated from carbonation. Therefore heat treatment was adopted to modify the chemical composition of ladle slag L3. The poor reactivity of L3 was expected from its calcium silicate phases. Therefore waste glass was used as silica additive to ladle slag L3 through heat treatment in an attempt to increase the reactance for carbonation. Based on preliminary tests, waste glass powder was added to slag at a glass to slag ratio of 20% by mass. The glass powder was mixed with slag powder in a pulverising machine for 30 s. The mixed powder was then compacted in a steel mold under 50 MPa pressure to form prism pellets of 20 × 20 × 14 mm. The prism pellet compacts were then placed on refractory trays and carefully positioned inside the furnace. The heat treatment temperature was set at 1100 °C to minimize the energy consumption and maximize the formation of dicalcium silicates. It took about 3.5 h for the furnace to reach 1100 °C at a rate of 5 °C/min. The pellets were held at 1100 °C for 30 min and then removed from the furnace immediately for cooling in an open air at ambient condition at the cooling rate of 600 °C per hour with the help of a cooling fan. It took about 2 h to cool down to the ambient temperature. The pellet compacts were then ground to a powder by using a pulveriser to a Blaine number of 286 kg/m^3. The resulting treated ladle slag is referred to herein as L3T (T denoting "treated"). The treated slag powder was then used to make nine slab samples similar to the ones used in L2 and L3 tests. Six were carbonated by 24 h. Of the six, three were tested immediately after carbonation for compressive strength and three were tested after subsequent hydration of 35 days. Additional three were tested as hydration reference after sealed in plastic bag for 35 days.

2.3. Characteristics of reaction products

Three different methods were used to quantify the carbon dioxide uptake by steel slag slabs subject to carbonation. The results are complementary and comparable. They are mass gain method, mass curve method and CO_2 analyzer method.