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Stabilization of basic oxygen furnace slag by hot-stage carbonation treatment

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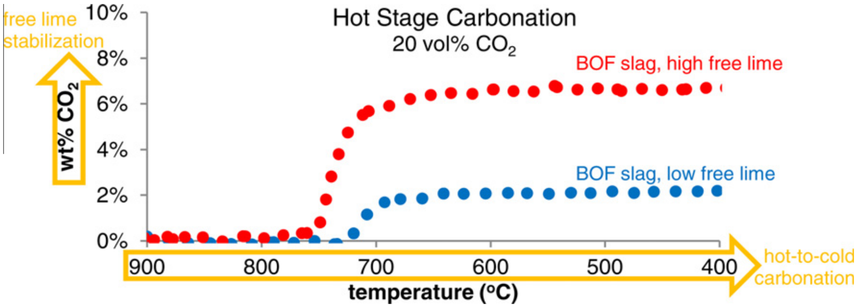
HIGHLIGHTS

- Novel hot-stage carbonation approach to Basic Oxygen Furnace (BOF) slag presented.
- Optimum carbonation rate at boundary of equilibrium (830–850 °C at 1 atm CO_2).
- Limited effect of pressure (0.2–20 bar CO_2) and steam (8 bar H_2O) on CO_2 uptake.
- Slag CO_2 uptake proportional to particle size, surface area and free lime content.
- Carbonation stabilizes free lime, reducing basicity and leaching of Ba, Co and Ni.

GRAPHICAL ABSTRACT



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ABSTRACT

Treatment and disposal of Basic Oxygen Furnace (BOF) slag, a residue of the steel production process characterized by high basicity and propensity for heavy metal leaching, is a costly burden on metallurgical plants; a sustainable valorization route is desired. The stabilization of BOF slag utilizing hot-stage carbonation treatment was investigated; this approach envisions carbonation during the hot-to-cold pathway followed by the material after the molten slag is poured and solidified. Three experimental methodologies were employed: (i) in situ thermogravimetric analyzer (TGA) carbonation was used to assess carbonation reaction kinetics and thermodynamic equilibrium at high temperatures; (ii) pressurized basket reactor carbonation was used to assess the effects of pressurization, steam addition and slag particle size; and (iii) atmospheric furnace carbonation was used to assess the effect of carbonation on the mineralogy, basicity and heavy metal leaching properties of the slag. Free lime was found to be the primary mineral participating in direct carbonation of BOF slag. Initial carbonation kinetics were comparable at temperatures ranging from 500 to 800 °C, but higher temperatures aided in solid state diffusion of CO_2 into the unreacted particle core, thus increasing overall CO_2 uptake. The optimum carbonation temperature of both BOF slag and pure lime lies just below the transition temperature between carbonation stability and carbonate decomposition: 830–850 °C and 750–770 °C at 1 atm and 0.2 atm CO_2 partial pressures, respectively. Pressurization and steam addition contribute marginally to CO_2 uptake. CO_2 uptake progressively decreases with increasing particle size, but basicity reduction is similar

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independent of particle size. The solubility of some heavy metals reduced after carbonation (barium, cobalt and nickel), but vanadium and chromium leaching increased.

1. Introduction

Integrated carbon steel production consists of ironmaking in the Blast Furnace (BF), steelmaking in the Basic Oxygen Furnace (BOF), and continuous casting of steel billets, slabs and blooms. For over a century, with iron and steel industry booming worldwide, a vast amount of slag has been produced as an inevitable by-product of the steelmaking process. While valuable applications have been found for BF slag, mostly in the construction sector such as in cement manufacturing and as a cement replacement in concrete, much of BOF slag production, estimated at 60–120 kg/t steel presently, still ends up in landfill sites [1–3]. The traditional use of BOF slag in road construction, as an aggregate, base or sub-base coarse, has been restricted due to the slag's undesirable expansive nature, resulting in rapid deterioration of the roads [4]. The volume expansion (up to 10% [5]) is attributed to the short term hydration and the long term carbonation of free lime (CaO) and magnesium oxide (MgO) content [6].

To date, four forms of treatment have been commercially used to stabilize BOF slag: (i) weathering in slag pits to convert free lime into hydrated lime, which has been found slow and inefficient [7]; (ii) steam hydration of the slag, utilized by Nippon Steel [8]; (iii) additions of SiO_2 and O_2 (to keep the slag molten) to the slag pot, which act to dissolve the free lime and chemically bond it as silicate, utilized by Thyssen Krupp [7]; and (iv) control of the slag cooling path to stabilize the C_3S (tri-calcium silicate) phase (which otherwise is transformed into C_2S, di-calcium silicate, plus free lime), utilized by Baosteel [9,10].

An alternative and possibly more attractive and low-cost route is the reaction of the alkaline oxides with CO_2, leading to the formation of geochemically stable carbonates (e.g. $CaCO_3$) [11]. Besides capture of CO_2, desirable for emissions reduction, mineral carbonation has also been reported to yield positive effects in terms of the leaching behavior of alkaline earth metals, heavy metals and metalloids from steel slag [12], which can lead to further valorization of the waste material. Numerous studies in recent years have assessed the potential of steel slag carbonation for storage of CO_2 utilizing a variety of aqueous carbonation routes, including slurry carbonation [13,14], wet carbonation [15], block carbonation [16], and two-step carbonation (i.e. leaching of Ca and Mg followed by carbonation of the extracted solution) [17]. However, the major drawbacks of these approaches include the required energy intensive steps (e.g. crushing/milling of the iron-rich monolith slag, prolonged mixing, pressurization, separation, and regeneration of extractants) and the generation of products having low market demand (e.g. carbonated powdery materials) or that are still troublesome (e.g. destabilized heavy-metal containing residual solids, and salt and heavy metal laden wastewater).

To overcome the aforementioned disadvantages of conventional mineral carbonation a novel approach is herein explored, hot-stage carbonation. This approach utilizes two domains of process intensification, namely functional (thus maximizing synergistic effects from partial processes) and temporal (thus optimizing the driving forces and maximizing the specific area to which these apply) [18]. The principal concept is to take advantage of the high temperature source of the slag, and perform mineral carbonation during slag cooling at still high (optimized) temperatures, where the kinetics are more favorable and the (thermal) energy is freely available. In particular, it is envisaged that in order to carbonate the slag while (a) it is still hot, (b) it is solidified, and (c) the material surface area is compatible with requirement for carbonation (i.e. not a monolith), a practical approach to hot-stage carbonation would be to apply it concurrently with hot-stage granulation (see Fig. SC-1 in the Supplementary Content for a conceptual scheme).

High temperature carbonation is already applied in CO_2 capture and separation systems that utilize lime-based sorbents subject to looping carbonation/calcination cycles, which typically conduct carbonation in the flue gas temperature range of 600–700 °C at atmospheric pressure [19–21]. Prigiobbe et al. [22] tested high temperature carbonation of air pollution control residues in the temperature range of 350–500 °C, obtaining fast carbonation kinetics (50% conversion in less than 1 min) and high conversions (nearly 80%). Mikhail and Turcotte [6] were the first investigators to report carbonation of BOF slag at high temperature; while limited, their findings provided proof-of-concept for this approach. BOF slag was carbonated at 550 °C in moist CO_2 in a thermogravimetric analyzer (TGA), and 8% mass gain was attributed to $CaCO_3$ formation. More recently, Kao [23] studied the high temperature carbonation of BOF slag for the purpose of using the slag as a CO_2 sorbent. Breakthrough curves of the CO_2 content of the outlet gas from a tubular reactor, analyzed by infra-red (IR) detection, were reported, with optimum conditions identified as being 500 °C, 40% CO_2 inlet concentration and 10% inlet gas relative humidity. Characteristics of the carbonated solids were not extensively assessed. Yu and Wang [24] found BOF slag to carbonate well (up to 20% calcium utilization after 20 min reaction time) at temperatures between 500 and 550 °C, using CO_2 concentrations between 10% and 100%; however data and analyses were insufficient to provide clear insight on mineralogical effects or carbonation mechanisms and kinetics.

The present work presents a detailed and systematic study of high temperature BOF slag carbonation, with particular emphasis on carbonation kinetics and conversion. The effect of several process parameters (particle size, temperature, pressure, time and steam addition) on CO_2 uptake and free lime conversion are tested. In addition, the chemical behavior of the treated materials, namely basicity and heavy metal leaching, is assessed. The investigation is centered on the concept of hot-stage carbonation of the slag, that is, experimental methods are designed to simulate the hot-to-cold stage path of the just-produced slag and to elucidate the susceptibility of the slag to carbonation along this route. To achieve these objectives, three hot-carbonation methodologies are applied, which provide varying levels of insight into the technology.

2. Materials and methods

2.1. BOF slag

2.1.1. Slag feedstock

Two freshly produced BOF slag batches were used, containing differing amounts of free lime; they will be referred to as BOF_I (lower free lime) and BOF_{II} (higher free lime). The slags, having been solidified under production conditions, were crushed (jaw crusher) and sieved to four particle size fractions for carbonation studies: <0.08 mm, 0.08–0.5 mm, 0.5–1.0 mm and 1.0–1.6 mm. These particle sizes were chosen as they are analogous to values reportedly produced during BOF slag dry granulation ([10,25]). The three coarser fractions were wet-sieved to remove fines; calcium saturated water was used to limit dissolution. Finely milled samples were also produced using a McCrone Micronizing Mill.