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

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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 reaction 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 ^{o}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 ^{o}C and 750-770 ^{o}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 independent of particle size. The solubility of some heavy metals reduced after carbonation (barium, cobalt and nickel), but vanadium and chromium leaching increased.

Keywords: Mineral carbonation; Steel slag; Basic Oxygen Furnace; Hot-stage; In-situ; Heavy metal leaching

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 to 700 ^oC 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 ^oC, obtaining fast carbonation kinetics (50% conversion in less than one minute) 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 ^oC 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 ^oC, 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 minutes reaction time) at temperatures between 500 and 550 ^oC, using CO_2 concentrations between 10-100%; 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. Pure oxide minerals (CaO, 99% purity; Fe_2O_3, >99% purity; MgO, 98% purity; Sigma Aldrich) were also utilized for carbonation for comparison purposes.

2.1.2 Slag Characterization Methodology

Particle size analysis was performed by laser diffraction (LD, Malvern Mastersizer). Specific surface area (S_{BET}) was measured by nitrogen adsorption (Micromeritics TRISTAR 3000) using the BET (Brunauer–Emmett–Teller) model. Material specific density was measured using a pycnometer (Micromeritics AccuPyc 1330). The chemical composition of each BOF slag batch was determined by X-ray Fluorescence (XRF, Panalytical PW2400), and the mineral composition was determined by X-ray Diffraction (XRD, Philips PW1830) with Rietveld refinement technique (Topas Academic v4.1). The distribution of the mineral phases in BOF slag was observed by analysis of the polished cross-sections of millimetre-sized particles of BOF_I slag by Scanning Electron Microscopy (SEM) coupled with Backscattered Electrons (BSE) and Energy Dispersive X-ray Spectroscopy (EDX) (Philips XL30 FEG).

2.2. High Temperature Carbonation Methodology

To study the carbonation reaction of BOF slag at high temperature, three experimental approaches were used to provide different insights into the effects of material properties and process conditions on the CO_2 uptake, carbonation conversion of the mineral phases, basicity and heavy metal leaching stabilization. The thermodynamics of the relevant carbonation reactions were assessed by FactSage 6.2 modeling.

2.2.1 In-situ TGA Carbonation

The first experimental methodology made use of a thermogravimetric analyzer (Perkin Elmer Lab System Diamond TGA-DTA) to conduct in-situ studies of BOF slag carbonation; this method and the equipment used were adapted from the methodology applied in Larachi et al. [26] for the carbonation of chrysotile mining residues. Three variations of this experimental method were used (depicted in Fig. SC-2). All experiments used approximately 50 mg of sample (finely-milled BOF slags, or reference pure materials CaO, MgO and Fe_2O_3), which was placed in a tared alumina crucible. All experimental variations commenced with a calcination step to produce 'fresh slag' as is produced industrially from the hot-stage process. This step consisted in heating the sample to 900 ^oC in nitrogen atmosphere (100 ml/min gas flow rate) at 20 ^oC/min heating rate to decompose pre-existing hydrates/hydroxides/carbonates from the material. It should be noted that as all samples underwent this initial calcination step, they experienced equal thermal histories (an important distinction as reported by Bhatia and Perlmutter [27]). Following calcination, experiments denominated as "hot-to-cold TGA carbonation" consisted in cooling the samples from 900 ^oC to 200 ^oC in 20% or 100% carbon dioxide atmosphere (100 ml/min gas flow rate) at 5 ^oC/min cooling rate to carbonate the material. Several flue gas streams in steel plants contain roughly 20% CO_2 [28-29], therefore this value was used for comparison with pure CO_2, which could also be produced from flue gas using one of several established CO_2 separation processes. Experiments denominated as "cold-to-hot TGA carbonation" consisted in cooling the samples from 900 °C to 80 °C in inert nitrogen atmosphere at 20 °C/min cooling rate, followed by heating from 80 °C to 1000 °C in carbon dioxide atmosphere at 5 °C/min heating rate to carbonate the material. Finally, experiments denominated as "fixed temperature TGA carbonation" consisted in cooling the samples from 900 °C to a desired temperature (between 500 °C and 800 °C) in inert nitrogen atmosphere at 20 °C/min cooling rate, followed by holding at the desired temperature in carbon dioxide atmosphere for 60 minutes to carbonate the material. For all experiments the sample weight (loss during calcination step and gain during carbonation step) was continuously monitored to determine CO_2 uptake. A mass spectrometer with quadrupole analyzer (Thermostar Prisma QMS200, Pfeiffer Vacuum) was used to monitor the outlet gas composition and to confirm that the gas composition transition (from N_2 to CO_2) occurred quickly enough; for all practical purposes it was found that the gas composition reached nearly complete transition (> 90% CO_2) in less than one minute.

2.2.2 Pressurized Basket Reactor Carbonation

The second experimental methodology (depicted in Fig. SC-3) made use of a pressurized basket reactor to study carbonation at high pressure conditions, as well as the effect of steam addition and slag particle size. This method and the equipment used were adapted from the methodology applied in Larachi et al. [30] for the carbonation of chrysotile mining residues. The equipment is shown in Fig. SC-4 in the Supplementary Content. Approximately two grams of material was placed in a small stainless-steel mesh basket that allowed the process gas to creep into the sample material bed. The basket was slid coaxially and positioned midway in a steel cylindrical enclosure (1.65 cm internal diameter, 30 cm long) using a hollow metallic stem hosting a thermocouple driven in the middle of the bed. The cylindrical reactor was fit in an electrically-heated temperature-controlled ceramic furnace that could be operated up to 900 °C. Prior to carbonation, samples were first heated to 900 °C for calcination in argon atmosphere. Upon purging the reactor with argon flow and cooling to the desired reaction temperature (350-650 °C), carbon dioxide and steam were introduced up to the desired total pressure (up to 20 bar), consisting of 4 to 20 bar CO_2 and 0 to 8 bar steam partial pressures. Carbonation reaction was conducted for 30 minutes. Following carbonation, the reactor was immediately purged with nitrogen gas flow (300 ml/min) to preclude further carbonation.

Once purged, the reactor was heated up to 900 °C for calcination. During calcination the reactor outlet gas was directed to an infra-red (IR) detector (ABB AO2000 Uras14) for in-situ quantification of the released CO_2 amounts (i.e. integration of CO_2 gas content over time) and determination of the material CO_2 uptake. Several tests were performed in duplicate to ascertain the accuracy of the measured effects.

2.2.3 Atmospheric Furnace Carbonation

In order to produce larger amounts of high-temperature carbonated materials for XRD, basicity and leaching testing, a horizontal furnace was used. The carbonation methodology (depicted in Fig. SC-5) was analogous to the basket reactor methodology, except that up to 10 grams of material could be carbonated at a time in the furnace (it was possible to carbonate 3 grams of material in each of three alumina crucibles that could be placed simultaneously in the furnace to test different materials or particle sizes at identical process conditions, or 10 grams of a single material in a larger crucible). Carbonation experiments were conducted with 100% CO_2 gas flow at near atmospheric pressure (slight positive pressure to prevent infiltration) for varying reaction times (10 minutes to 6 hours) at fixed temperatures (200-800 °C). Following carbonation, samples were immediately withdrawn from the furnace to cease carbonation, and allowed to cool in air. The CO_2 uptake was quantified by ex-situ TGA; an amount of 30-50 mg carbonated sample was weighed in a sample pan heated from 25 to 900 °C under a nitrogen atmosphere at a heating rate of 15 °C/min. The weight loss was recorded by the microbalance and the amount of CO_2 uptake was quantified by the weight loss between 500-800 °C, which can be related to calcium carbonate decomposition [13]. Validation of the accuracy of CO_2 uptake determination via TGA and via calcination coupled to IR detection was performed by comparison of analysis results of identical samples examined with both methodologies; the average discrepancy between the two methods was 4% of the measured values (see Figs. SC-6 and SC-7 in the Supplementary Content).

2.3 Basicity and Leaching Tests

Batch leaching tests were performed on both carbonated and fresh slag samples to determine the effect of carbonation on the solubility of heavy metals and on the solution pH value. Determination of aqueous elemental concentration was performed in triplicate by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS, Thermo Electron X Series). An amount of two grams of solids was mixed with 100 ml MilliQ water (L/S = 50) in a sealed polyethylene bottle, and shaken on a vibration table for 24 hours. Solution pH was measured and the solution was filtered using 0.45 μm membrane filter prior to dilution for ICP-MS measurement. Solution matrix for ICP-MS measurement was 2% nitric acid. The following elements (in atomic weight order) were analyzed: V, Cr, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sn, Sb, Ba, and Pb. Table 1 presents leaching limits (in milligrams metal leached per kilogram dry solid) of the most pertinent heavy metals for the present work (i.e. those with notable measurable concentrations and that are affected by carbonation, as reported in section 3). It was verified using fresh slags that the liquid-to-solid ratio (L/S) of 50 (utilized for testing of carbonated slags due to limitation of material available) provides leaching values that are similar to, and in most cases exceeding, tests using lower L/S values (10 and 20; see Fig. SC-8 in the Supplementary Content); this is due to the solubility controlled (rather than availability controlled) equilibrium established. Therefore it is possible to compare results of tests using L/S = 50 to the leaching limits established for tests using L/S = 10 for assessment of material compliance.

3. Results and Discussion

3.1 Characterization of BOF slags

Average particle sizes by volume and specific surface areas of the two finest sieved fractions and the micronized samples are presented in Table 2. Specific densities of the slags were found to be 3.69 and 3.78 g/cm^3 for BOF$_I$ and BOF$_{II}$, respectively.

Table 3 presents the elemental composition of the slags determined by XRF. It can be inferred from the calcium content that the maximum theoretical CO$_2$ content (in the form of calcium carbonate) of a fully carbonated specimen would be 28.0 wt% CO_2 (equivalent to 0.39 g,CO_2/g,slag) for BOF_I and 31.2 wt% CO_2 (or 0.45 g,CO_2/g,slag) for BOF_{II}.

Table 4 shows the interpreted mineral composition determined by XRD. Samples were heated to 900°C in an argon atmosphere prior to analysis to decompose pre-existing hydroxides and carbonates formed due to exposure of the samples to ambient air (i.e. natural aging). The main mineral phases of the BOF slags were identified as srebrodolskite (C_2F), the beta polymorph of di-calcium silicate (β-C_2S), and free lime (CaO). The theoretical CO_2 uptake capacity of these materials based solely on their free lime content would be 7.7 wt% CO_2 (equivalent to 0.083 g,CO_2/g,slag) for BOF_I and 13.9 wt% CO_2 (or 0.162 g,CO_2/g,slag) for BOF_{II}.

Analysis of the polished cross-section of a millimetre-sized particle of BOF_I slag by SEM-BSE-EDX is shown in Fig. 1. The morphology and distribution of the major mineral phases quantified by XRD can be visualized in the image. Two types of free lime are observed: precipitated free lime and residual free lime. Precipitated free lime originates from the decomposition of tri-calcium silicate to di-calcium silicate during slag cooling [33]. Residual free lime is lime that was added during the steelmaking process as a flux, and either was added in excess or not allowed enough time to dissolve [34], as a means to increase steel productivity. The type of free lime is suspected to influence the slag reactivity and propensity for instability through volume expansion [35]. Wachsmuth et al. [34] pointed out that for BOF slag containing high amounts of free lime, residual free lime is the dominant form; this was confirmed for the present samples by inspection of several slag particles by SEM-BSE-EDX. In terms of the other minor elements detected by XRF analysis (Table 3), Mn and Mg were detected in the BOF slag in solid solution with iron oxides, while Al, Ti, V and Cr were found at the grain boundaries of C_2S and residual free lime phases. These interpretations are in accordance with reported observations of Waligora et al. [35] and van Zomeren et al. [15].

3.2 High Temperature Carbonation

The desire to attempt BOF slag carbonation at high temperature stems from the fact that the carbonation thermodynamics of the alkaline components of the slag are favorable (negative Gibbs free energy of reaction change) up to high temperatures (Table 5). Lime (CaO) carbonation (Eq. 1) is theoretically possible up to 861 ^{o}C at 1 atm CO_2 pressure, while other common slag minerals such as C_2S (Eq. 2), C_2F (Eq. 3), and periclase (Eq. 4) reach carbonation/calcination equilibrium at lower temperatures of 400, 664 and 400 ^{o}C, respectively. Beyond these temperatures the reactions reverse and CO_2 is released into the gas phase, a process commonly called calcination. Carbonation susceptibility is also affected by the partial pressure of carbon dioxide. In the case of lime, reducing the CO_2 partial pressure to levels present in the atmosphere (0.0003 atm), reduces the equilibrium temperature to 511 ^{o}C. However, at levels of CO_2 typically found in flue gases of thermal processes (e.g. 0.1 atm [22]) the equilibrium temperature is significantly higher at 732 ^{o}C. Thermodynamics also suggest that pressurization can be useful, as the equilibrium temperature at 5 atm CO_2 partial pressure rises to 971 ^{o}C (this condition could be achieved, for example, using a purified CO_2 stream from flue gas via capture and concentration processes).

$$CaO + CO_2 = CaCO_3 \quad (1)$$

$$Ca_2SiO_4 + 2CO_2 = 2CaCO_3 + SiO_2 \quad (2)$$

$$Ca_2Fe_2O_5 + 2CO_2 = 2CaCO_3 + Fe_2O_3 \quad (3)$$

$$MgO + CO_2 = MgCO_3 \quad (4)$$

However, favorable thermodynamics do not guarantee that these carbonation reactions will occur fast enough, as reaction kinetics also play an important role. Therefore it was the objective of this work to confirm the susceptibility of BOF slag carbonation at high temperature, both with regards to carbonation kinetics and CO_2 uptake, using three carbonation methodologies as will be detailed next.

3.2.1 In-situ TGA Carbonation

To gain insight on the interaction of BOF slag with CO_2 at high temperatures comparable to the conditions in the cooling path of the slag during metallurgical processing, in-situ TGA carbonation tests were performed. Fig. 2 presents experimental results applying the in-situ TGA carbonation methodologies for both hot-to-cold (subfigures a and b) and cold-to-hot (subfigure c) carbonation directions. For comparison, pure CaO, MgO and Fe_2O_3 as well as micronized BOF_I and BOF_{II} slag samples were tested. The hot-to-cold carbonation direction is meant to simulate the carbonation path BOF slag would undertake in the industrial setting when being reacted immediately after slag solidification from the molten stage. Carbonation was conducted from 900 to 400 ^oC, with 5 ^oC/min cooling rate. The cold-to-hot direction, though not representative of the envisioned hot-stage carbonation technique, was also utilized for comparison and to aid gaining insight on carbonation kinetics and mechanisms. In this case the heating rate was 5 ^oC/min, and carbonation took place from 80 to 1000 ^oC. Two CO_2 partial pressures were applied: 20 vol% (balanced with N_2) and 100 vol% CO_2 at atmospheric total pressure.

It is immediately possible to conclude from Fig. 2a that carbonation extent (sample mass gain due to CO_2 incorporation as carbonates) is directly proportional to the free lime content: pure CaO achieved significantly higher uptake than the slags, of which BOF_{II}, having greater free lime content (Table 4), and slightly higher specific surface area (Table 2), carbonated more than BOF_I. In contrast the other two oxides tested (MgO and Fe_2O_3) did not carbonate in the temperature range tested (Fig. 2b). Stainless steel slag samples containing mainly calcium silicates (including C_2S) and no free lime also did not exhibit reactivity to direct carbonation at these temperatures (see Fig. SC-9 in the Supplementary Content); in contrast these materials react well in aqueous carbonation [36]. Given the large content of calcium in BOF slags (Table 3), a major part being present as C_2F (Table 4), and the comparatively low CO_2 uptakes compared to pure CaO, it can be concluded that C_2F reactivity to direct carbonation is also low, despite favorable thermodynamics (Table 5). Available literature lacks extensive data on C_2F carbonation, but Schmidt [37] found it possible to carbonate a similar mineral, $Sr_2Fe_2O_5$, at 800 ^oC, though kinetics were slow (order of hours). C_2F likely suffers from too slow kinetics to influence CO_2 uptake in the time frame of the present experiments. Therefore it is concluded that free lime is the principal mineral in BOF slag responsible for CO_2 uptake during direct high temperature carbonation. Under this premise, the carbonation conversions of CaO to $CaCO_3$ for BOF_I and BOF_{II} are 32.4% and 45.7%, respectively. These conversions on the basis of the total Ca content of the slags are equivalent to 7.0% and 16.3%, respectively.

Furthermore, while for CaO there are two distinct carbonation regimes (one kinetically controlled and a second diffusion-controlled), for the slag samples a single regime dominates. From the CaO trends, it is observable that upon commencement of carbonation, the uptake rate is sharp and linear. After this linear region, carbonation of CaO continues at a reduced rate, which levels off over time (temperature decrease) until carbonation ceases. These trends are similar at both partial pressures of CO_2, except that at lower partial pressure CaO carbonation reaches lower final uptake level. In the case of slag samples, carbonation from the start behaves similar to the second stage of CaO carbonation, that is, it is gradual and declining in rate over time. These effects can be explained by the necessity of CO_2 to diffuse across a native inert layer into slag particles from the start of carbonation to achieve further uptake, and a second regime does not occur since emerging carbonates form a dispersed patchwork within the particle, rather than a dense shell. In the case of pure CaO, significant carbonation at the exposed outer surface occurs immediately, only later to be followed by diffusion through the reacted carbonate layer into the particle core.

It is also inferred that carbonation commences at approximately the same temperature for the three reacting materials at each partial pressure: 830-850 ^oC at 100% CO_2, and 750-770 ^oC at 20% CO_2. These carbonation temperatures as a function of CO_2 partial pressure correspond to predicted values from reaction thermodynamics presented earlier (Table 5). Distinctly from CaO, however, the slag samples reached the same final carbonation extent values at both CO_2 partial pressures. This signifies that CO_2 diffusion is hindered equally by the dense unreactive mineral phases of the slags regardless of diffusion driving force (partial pressure and temperature). In the case of CaO, higher driving forces (temperature and partial pressure) and higher CO_2 concentration aid further carbonation extent, possibly by better displacement of inert gas contained in the particle pores. The indifference of slag carbonation to CO_2 partial pressure is positive for industrial implementation as it means costly and energy intensive enrichment of flue gases may not be required. Further discussion on the benefit of CO_2 pressurization is given in section 3.2.2.

Fig. 2c demonstrates that carbonation in the cold-to-hot direction differs from the hot-to-cold trends. Most striking are the higher carbonation extents achieved with all three materials (CaO and micronized BOF_I and BOF_{II}). Also, CaO begins carbonating at a lower temperature (approx. 200 ^oC) than the slags

(> 400 ^{o}C). Maximum carbonation extent is reached slightly prior to reaching 900 ^{o}C for the three samples. After this point, in spite of the presence of CO_2, the carbonation reaction reverses, and $CaCO_3$ decomposition proceeds until the sample masses return to their initial values upon holding them at 1000 ^{o}C for several minutes. The higher carbonation extents may be explained by the ever increasing CO_2 solid-state diffusivity over time, opposite to the case of hot-to-cold carbonation. In addition, it can be expected that in the hot-to-cold case, due to the higher carbonation rates at higher temperatures (more data and discussion to follow), the carbonate layer formed at the outer particle surface quickly becomes denser and less permeable than when it is formed at lower temperatures, thus deterring carbonation continuance already at an early stage. Nevertheless, as mentioned earlier, this type of carbonation methodology has a major disadvantage, as it does not take advantage of the slag cooling path but rather would require external (thermal) energy input, therefore these results are meant to aid discussion only and are not deemed industrially feasible.

As the previously performed tests applied carbonation at varying temperatures, it was not possible to infer precisely the kinetics of the reaction. Therefore fixed temperature in-situ TGA carbonation experiments were performed with both micronized slag samples (BOF_I and BOF_{II}) and pure CaO as a reference material. Results are presented in Fig. 3 for five temperatures: 500, 575, 650, 725 and 800 ^{o}C. For all experimental runs, CO_2 was introduced at the two minute mark in these plots, hence all carbonation reactions can be deemed to have started at the same time. As can be observed, carbonation of all materials at all tested temperatures commences promptly after CO_2 introduction. It can also be noted from the vertical axes that BOF_I carbonation once again achieves lower extents compared to BOF_{II}, which itself achieves lower extents than CaO at comparable temperatures. For all materials, carbonation extent is greatest at the highest temperature, 800 ^{o}C.

Similar to trends observed in the hot-to-cold carbonation experiments, CaO demonstrates dual regimes of carbonation, a rapid linear stage followed by another of diminishing reactivity. The CaO carbonation rate during the first stage is independent of temperature, and is measured to be on average 58 ± 5 mg,CO_2/g,CaO/min. In contrast, BOF slags have a very short initial steep uptake as a result of surface/outer pore carbonation (< 1 min), thereafter transitioning into the decaying-rate-type trend during which CO_2 slowly penetrates deeper into the particle for the reaction, and thus mass gain, to continue. Because of this, temperature-controlled CO_2 diffusivity is a greater limiting factor for slag carbonation than reaction kinetics. This evidenced by the greater effect of temperature on BOF slag carbonation extent than for CaO. In the case of the latter, after 45 minutes the carbonation extent at 800 ^oC is 60% higher (expressed as percent mass gain) than at 500 ^oC. In comparison, for the slags, BOF_I achieves nearly five times greater mass gain and BOF_{II} more than four times greater mass gain at the highest temperature over the lowest temperature.

In comparison with literature reported carbonation values for CaO in direct high temperature carbonation, the carbonation conversions achieved in the experiments so far presented in this study were lower than some studies (for example, at 800 ^oC, CaO carbonation conversion was 27% of the theoretical maximum carbonation extent, compared to 60-80% reported values [27,38]). Other studies, however, have also found conversion in the 20-30% range [19,39,40]. For the other two experimental methods reported herein, pressurized basket reactor carbonation and atmospheric furnace carbonation, it was verified that CaO carbonation achieved conversions over 60% at optimized process conditions. The cause of these discrepancies was identified for the present experimental system as being due to the CO_2 flow rate utilized (100 ml/min). When the flow rate was increased to 300 ml/min, the carbonation conversion at 800 ^oC increased to 64% (Fig. SC-10a in the Supplementary Content), though the initial carbonation rates, within the first 2.5 minutes of CO_2 introduction, were identical. This suggests that in both cases, sufficient CO_2 initially contacts the free lime surface, which carbonates equally rapidly. As the reaction progress, nitrogen gas contained within the sample crucible and inside the particle pores must be displaced by CO_2 gas for the reaction to continue. However, when using a lower gas flow rate, sweeping of the displaced nitrogen is reduced, thereby CO_2 diffusion into the particles is slowed. Slower CO_2 diffusion leads to earlier occurrence of pore blockage due to carbonate formation close to the particle surface, and a limited final conversion compared to the high flow case. In the case of BOF slag, the effect of CO_2 flow rate was smaller and opposite (Fig. SC-10b in the Supplementary Content); 100 ml/min resulted in slightly higher carbonation extent. The micronized slag's relatively high surface area and presence of macropores compared to commercial CaO [40], and its dispersed free lime concentration likely attenuate the effect of nitrogen displacement, and pore narrowing/blockage is less dependent on CO_2 flow rate. Seeing the high variability of results in the literature, it is advisable future researchers consider the effect of flow rate on their in-situ TGA carbonation experiments.

3.2.2 Pressurized Basket Reactor Carbonation

Pressurized basket reactor carbonation experiments were conducted to investigate process effects that could not be assessed with the previously presented TGA methodology. These include the effect of CO_2 pressurization, up to 20 bar, the effect of steam addition (8 bar partial pressure), and the effect of particle size (up to 1.6 mm) on BOF slag carbonation extent. Fig. 4 presents results on the effect of three CO_2 pressures (4, 12 and 20 bar) on the carbonation of the 0.08-0.5 mm sieved fraction of BOF_{II} slag, performed at three temperatures (350, 500 and 650 ^oC) for 30 minutes reaction duration. These sets of conditions were chosen to ensure the effects of the process parameters could be observed (i.e. carbonation for longer duration or at higher temperature would mask the effect of pressure). It was found that the effect of CO_2 pressure on CO_2 uptake (reported as wt% CO_2 in the carbonated sample, determined by in-situ calcination and IR CO_2 detection) is more important at lower temperatures, having a significant effect at 350 ^oC (176% improvement at 20 bar over 4 bar), a much reduced effect at 500 ^oC (7% improvement), and no effect at 650 ^oC. The effect of temperature, at fixed CO_2 pressures, was more striking, as had been presented with the in-situ TGA carbonation methodology. At 4 bar CO_2 pressure there was a 400% improvement in CO_2 uptake at 650 ^oC over 350 ^oC; significant improvements were also measured at 12 bar (+130%) and 20 bar (+80%).

Fig. 5 presents pressurized basket reactor carbonation results on the effect of slag particle size for both types of BOF slag (BOF_I and BOF_{II}). Furthermore these experiments tested the effect of steam addition (8 bar partial pressure) on CO_2 uptake. The experimental temperature was fixed at 650 ^oC, the best value from the previous set of experiments presented, reaction time was 30 minutes, and total pressure was maintained at 20 bar (CO_2 + H_2O where applicable). Steam had a positive effect on CO_2 uptake for all particle size fractions, though the effect was reduced for the largest particles. Furthermore on a percent improvement basis, BOF_I benefited more from steam addition than the more reactive (due to greater free lime content) BOF_{II}. For reference, pure CaO was also carbonated in the pressurized basket reactor at 650 ^oC and 20 bar total pressure with and without steam. Steam addition allowed carbonation conversion to reach 100% of the theoretical value, compared to 64% in dry CO_2.

The effect of steam on lime carbonation has previously been reported in literature by Yang and Xiao [39] and Manovic and Anthony [38]; however the mechanism of action has not yet been fully characterized. Yang and Xiao [39] suggest steam introduces a 'catalytic effect', related to the adsorption of hydroxyl groups and the formation of bicarbonate intermediates, though no experimental data is provided to confirm this hypothesis. They claim $Ca(OH)_2$ is not likely formed since carbonation temperatures in their tests were above the decomposition temperature of $Ca(OH)_2$ at the utilized vapor pressures of water. Indeed, it would appear difficult to base the effect of steam on the hydration of free lime, given experimental conditions for hot-stage carbonation normally use temperatures beyond the decomposition temperature of calcium hydroxide at trace vapor pressure of water (i.e. condition within a TGA using inert carrier gas) of approximately 350-400 ^oC. However, in the present experiment the vapor pressure of water was 8 bar, which applying the model of Hartman and Martinovský [41] yields a decomposition temperature (dehydroxylation reaction $\Delta G = 0$) of 660 ^oC. Therefore it is plausible to assert that the presently observed steam-enhanced CO_2 uptakes may be related to an intermediate hydroxylation step prior to carbonation. This would be in agreement with reported results of Materic and Smedley [42], who found that hydration of lime prior to atmospheric carbonation can result in greater carbonation conversion when applying lime as a sorbent in calcium looping processes for CO_2 capture and concentration.

Manovic and Anthony [38], on the other hand, provide experimental evidence that the steam-enhancement of carbonation may be caused by improvement in solid state diffusion rather than hydroxylation. They show that steam does not improve carbonation kinetics during the initial fast (kinetically controlled) carbonation stage, but rather aids in carbonation extent improvement over prolonged time (i.e. during the diffusion controlled stage). The exact mechanism of how steam improves solid state diffusion, however, is not provided. In any case, regardless of the actual mechanism of steam assistance, the present experiments show that steam improvement of carbonation conversion of the slags is modest (i.e. coarse particles remain distant from theoretical maximum uptake). Therefore industrial application of steaming during hot-stage carbonation of BOF slag could be deemed optional, depending on process complexity and required or desired final product properties.

It is evident from Fig. 5 that particle size, and hence surface area, has a significant effect on CO_2 uptake. This is not surprising since direct carbonation is a surface based and diffusion controlled reaction. Moreover, BOF_I CO_2 uptake (Fig. 5a) was consistently lower than BOF_{II}, which is attributable to its lower free lime content (10.6 wt% versus 20.6 wt%). Converting CO_2 uptake into carbonation conversion of the free lime content of the slags (i.e. assuming, based on experimental evidence collected in this study, that free lime is the only mineral participating in BOF slag direct high-temperature carbonation), the difference between BOF_I and BOF_{II} diminishes (Fig. 5b). In fact, based on the shrinking core model, it would be expected that carbonation conversion of the two slag samples would be identical if: (i) solid state diffusivity of CO_2 in the two slags were equal; (ii) free lime was equally distributed within the particles of both slags (radially and concentrically); and (iii) the proportion of free lime present in each slag as precipitated free lime and residual free lime were equal. Fig. 5b indicates that the two finest fractions of BOF_{II} maintain an advantage with regards to carbonation conversion over BOF_I. This can be attributed to the moderately higher specific surface areas and lower average particle sizes of the two finest fractions of BOF_{II} compared to BOF_I (Table 2), and may also be due to differences in dispersion and morphology of free lime inclusions (precipitated and residual) in the two slags (for example, precipitated free lime may carbonate more/better than the residual variety). For the two coarser fractions, dry carbonation conversions were more similar, as it can be expected that carbonation of these samples is mainly controlled by solid state diffusion rather than their limited (not measured) surface areas. Still, the average percentage improvement in steam-assisted carbonation conversion for the two coarse fractions was similar to that of the two finest fractions (+46% and +40%, respectively). Therefore improvement of solid state diffusivity as proposed by Manovic and Anthony [38] appears to be a plausible explanation of the mechanism, though hydroxylation or another ‘catalytic’ effect cannot be entirely ruled out.

3.2.3 Atmospheric Furnace Carbonation

Subsequent to the two previously described experimental methods (in-situ TGA carbonation and pressurized basket reactor carbonation), atmospheric furnace carbonation experiments were conducted for two main reasons. Firstly, atmospheric carbonation appears to be a more feasible route for industrial implementation of hot-stage carbonation, as it appears from previous tests that pressure is not a critical parameter for satisfactory direct carbonation extent, and it should reduce technical complexity and thus processing cost. Secondly, with regards to the laboratory scale equipment used in this study, this methodology allowed production of larger quantities (up to 10 g) of carbonated material at one time (i.e. identical processing conditions), enabling detailed study on the mineralogy, basicity and heavy metal leaching properties of the carbonated products.

Similar to the previous methodologies, the effect of temperature on CO_2 uptake was studied to ensure furnace carbonation delivered equivalent results based on previous findings, and to elucidate unforeseen effects at atmospheric pressure. Furthermore, the effect of reaction time was studied, varied between 10 minutes (in-situ TGA carbonation indicated rapid CO_2 uptake in the first 10 minutes of reaction time) and 6 hours (longest reaction time tested thus far, to ensure cessation of CO_2 uptake). Fig. 6a shows that, in what appears to be the optimal temperature range of 650 to 750 ^oC, there is only a small increase in carbonation extent when increasing the reaction time from 10 minutes to 6 hours. At lower temperatures, such as 500 ^oC, the effect of time is more evident, but below this temperature, especially in the range of 200 to 400 ^oC, the carbonation extent is much smaller. Above 750 ^oC the stability of $CaCO_3$ decreases due to the low CO_2 pressure (Table 5), and at 800 ^oC the carbonation extent significantly decreases with 10 minutes reaction time (possibly the furnace is not completely purged of inert gas within 10 minutes of CO_2 introduction, hence the CO_2 partial pressure is somewhat lower than 1 atm, compromising $CaCO_3$ stability at this temperature). Results are very similar for both batches of BOF used, the difference being BOF_{II}, which contained more free lime, achieved greater CO_2 uptake amounts.

Quantitative XRD was also used to assess the carbonation extent of atmospheric furnace carbonated BOF_I slag samples (Fig. 6b). These analyses were conducted on unmilled 0.08-0.5 mm particle size fraction samples (i.e. not micronized to 5-10 μm as normally done for compositional analysis using XRD). The aim was to limit X-ray penetration into the particle to determine the conversion of free lime closer to the particle surface, which is the region that controls material basicity and heavy metal leaching. It is estimated that the X-ray penetration depth is limited to tens of microns up to 100 microns (depending on X-ray source and target material) [43], which is to some extent less than average particle radius based on D_{50} and D[4,3] values (Table 2). By comparing the calcite ($CaCO_3$) amounts to the remaining free lime (CaO) and portlandite ($Ca(OH)_2$) amounts, it was possible to determine carbonation conversion of the free lime present in the region penetrated by the X-rays. Values between 50-60% conversions are obtained in the optimal temperature range (600 to 750 ^{o}C), slightly higher than overall free lime conversions based on total CO_2 uptake (40-50%). Given that the carbonation depth may be smaller than the X-ray penetration depth, and/or that CaO grains are not fully carbonated due to formation of dense carbonated shell surrounding the unreacted core, detection by XRD of free lime present in regions of the particles that are not accessible to CO_2 is possible, therefore truly geometrical peripheral near-surface carbonation extent is likely to be higher.

The effect of particle size on CO_2 uptake by atmospheric furnace carbonation (Fig. 7a) was analogous to results obtained by pressurized basket reactor carbonation (Fig. 5a). The 1.0-1.6 mm particle size fraction of BOF_I slag achieved significantly lower CO_2 uptake than the finer 0.08-0.5 mm fraction after one hour carbonation at 700 ^{o}C. The reduction in basicity of the coarse samples, however, was very similar to the reduction obtained with the finer samples (Fig. 7b). This is explained by the fact that carbonation primarily occurs near the particle surface, which contacts the liquid phase and controls pH. Therefore reduction in basicity is not always directly proportional to CO_2 uptake, but rather depends on particle size and most importantly on surface area.

3.3 Basicity and Heavy Metal Leaching

The native basicity of BOF slag can be directly linked to its free lime content, which is detrimental to its valorization as a construction material. Furthermore, materials with high basicity when in contact with water produce alkaline solutions, which contribute to the leaching of several heavy metal contaminants [32,44,45]. For a specific slag particle size fraction, CO_2 uptake and basicity reduction are proportionally linked. Atmospheric furnace carbonation resulted in improvement of solution pH values of the 0.08-0.5 mm particle size fraction of BOF_I slag; the basicity reduction was proportional to CO_2 uptake, as presented in Fig. 8. BOF_I, having less free lime, achieved just under one pH unit reduction with 10 minutes reaction time (Fig. 8a), and reached incrementally better results after 6 hours reaction time (Fig. 8b). BOF_{II} benefitted more from increased reaction time, probably due to its significantly greater free lime content and moderately higher specific surface area. Nevertheless, at the optimal conditions (e.g. 700^{o}C) the final pH values for BOF_I and BOF_{II} after 10min/6hr carbonation were 11.6/11.6 and 12.1/11.7 respectively. This reduction in pH may be sufficient to increase the marketability of BOF slag into applications in the construction industry; however it remains to be tested whether swelling propensity sufficiently decreases given the incomplete free lime conversions achieved.

Positive effects on the leaching of heavy metals also resulted from carbonation of BOF slags. Leaching results as a function of atmospheric-furnace-carbonated sample pH are plotted in Fig. 9. For further insight, leaching results as a function of CO_2 uptake and reaction time are illustrated in Figs. SC-11 and SC-12 in the Supplementary Content, the former for 10 minutes reaction time, and the latter for 6 hours reaction time. The 0.08-0.5 mm particle size fraction carbonated samples were used to generate these data.

Carbonation was found to have a noticeable positive effect on reducing leaching of barium, nickel and cobalt. These results can be attributed to pH reduction (Fig. 9), which decreases the solubility and/or changes the speciation of some metals, and formation of less soluble compounds (e.g. $BaCO_3$, $BaSO_4$ [44]). Vanadium leaching, on the other hand, increases after carbonation, reaching 10 mg/kg (well above the regulatory limit of 0.8 mg/kg [32]) for three of the four sample sets. The only exception is 10 minutes carbonated BOF_{II} slag (Fig. SC-11), which remains below the limit. This can be explained by the lower reduction in basicity of this material (Fig. 8a), as vanadium is known to be more prone to solubilization at lower pH [15,45]. Chromium and molybdenum leaching also increase after carbonation (pH reduction), the former more than the latter; however their values remain below regulatory limits (Table 1). Chromium leaching, like vanadium, is also proportional to basicity reduction [45], as inferred from the 10 minutes carbonated BOF_{II} slag presenting marginal leaching increase (Fig. SC-11) compared to 6 hours reaction time (Fig. SC-12). Competition of carbonate ions with oxyanionic species can also play a role in controlling the solubility of chromate, molybdate and vanadate ions [32].

It can be concluded that the balance of basicity reduction and heavy metal leaching via carbonation is a challenge for the reutilization of BOF slag. While the solubility of some metals reduced after carbonation (barium, cobalt and nickel), vanadium and chromium leaching increased. With more moderate carbonation extent (10 minutes reaction time), the rate of solubility increase of these metals was lower, conforming to regulatory limits. Therefore, in view of industrial implementation of BOF slag carbonation, it should be considered whether a higher or lower carbonation extent is more interesting for commercialization of carbonated BOF slag. The increased solubility of vanadium (and to a smaller extent chromium) after carbonation can be used as a means to ease their recovery from the residues, in comparison to energy intensive traditional methods for vanadium recovery from waste materials [46], as these metals can be of commercial value. Alternatively, if the carbonated BOF slag is used as a fine aggregate in cement mortar/concrete, there are possibilities to introduce additives to the matrix (such as zeolitic sorbents) to contain leaching from the aggregate material. Moreover, the matrix itself can act as a sink for heavy metals, by incorporation of metalloids including Cr and V in hydration products [47], thereby suppressing leaching.

4. Conclusions

This work has investigated the hot-stage carbonation of Basic Oxygen Furnace (BOF) steel slag, with the objective of converting its high free lime content (10-20 wt%) to calcium carbonate and stabilizing its negative properties (high basicity and heavy metal leaching) that prevent material valorization. By performing hot-to-cold carbonation experiments in a TGA, it was observed that the optimum carbonation temperature lies just below the transition temperature between carbonation stability and carbonate decomposition: 830-850 ^{o}C at 1 atm CO_2, and 750-770 ^{o}C at 0.2 atm CO_2. Pressurization and steam addition were found not to contribute significantly to CO_2 uptake enhancement; for instance, diffusion limitations prevent free lime conversion from surpassing 50% for the 0.08-0.5 mm particle size fraction of the BOF_{II} slag batch. Instead, it appears feasible to apply flue gases from steel production plants directly (e.g. 0.2 atm CO_2 partial pressure) without need for additional and costly CO_2 separation/concentration processes. Improvement in basicity was independent of particle size; that is, even the coarser fractions achieved similar reduction in basicity despite significantly lower CO_2 uptake. However, the effect of carbonation on heavy metal leaching was mixed: while the solubility of some metals reduced after carbonation (barium, cobalt and nickel), vanadium and chromium leaching increased. Post-carbonation extraction of leachable components or mixing of carbonated slag with sorbent materials would be required for meeting hazardous materials regulations and enable slag commercialization. Otherwise, heavy metal leaching could be suppressed by applying carbonated BOF slag as a fine aggregate in cement mortar/concrete, where the encasing matrix could act as a sink for mobile metals.

Further optimization of hot-stage carbonation is still required prior to industrial implementation of this technology. Despite suitable reaction kinetics and enhanced CO_2 diffusivity at high temperatures, complete conversion of free lime is still limited by the ability of CO_2 to diffuse into the particle core, even for the 0.08-0.5 mm particle size fraction utilized. This size fraction is at the low-end of the expected particle size achieved by hot-stage granulation (as envisaged in Fig. SC-1 and reported in [10,25]). Therefore in order to achieve reasonably high levels of free lime conversion, development of granulation/hot-stage-milling technology capable of delivering sub-millimeter sized particles appears to be essential. Furthermore, investigation is warranted on finding the necessary level of free lime conversion needed to satisfactory stabilize BOF swelling in construction material applications. For instance, it should be assessed whether 50% conversion or more is required for complete stabilization, or if near-surface carbonation, which is enough to reduce basicity (as achieved in this work with 1.0-1.6 mm BOF particle size fraction), may be sufficient to improve material properties and enable its valorization.

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Appendix

[Supplementary Content]

List of Figures

Fig. 1. Major mineral phases of BOF_I slag identified via SEM-BSE-EDX.

Fig. 2. In-situ TGA carbonation of pure oxides (CaO, MgO and Fe_2O_3) and micronized slags (BOF_I and BOF_{II}): hot-to-cold (subfigures a and b) and cold-to-hot (subfigure c) methodologies; P_{CO2} = 1 atm, except where indicated.

Fig. 3. In-situ TGA carbonation of micronized slags (BOF_I (a) and BOF_{II} (b)) and pure CaO (c): fixed temperature (500, 575, 650, 725 and 800 ^oC) methodology; P_{CO2} = 1 atm.

Fig. 4. Pressurized basket reactor carbonation of 0.08-0.5 mm particle size fraction of BOF_{II} slag at multiple temperatures (350, 500 and 650 ^oC) and CO_2 pressures (4, 12 and 20 bar) for 30 minutes reaction time.

Fig. 5. Pressurized basket reactor carbonation of BOF_I and BOF_{II} slag samples of varying particle size fractions (< 0.08, 0.08-0.5, 0.5-1.0 and 1.0-1.6 mm) at 650 ^oC with dry or wet CO_2 at 20 bar total pressure and 30 minutes reaction time: results expressed as (a) wt% CO_2 uptake, and (b) carbonation conversion of free lime content.

Fig. 6. Atmospheric furnace carbonation results: (a) CO_2 uptake (determined by TGA analysis) and (b) peripheral near-surface free lime conversion (determined by unmilled XRD analysis with Rietveld refinement) for carbonation of 0.08-0.5 mm particle size fractions of BOF_I and BOF_{II} slags at varying fixed temperatures (200 to 800 ^oC) for 10 minutes and 6 hours reaction time.

Fig. 7. Atmospheric furnace carbonation results: (a) CO_2 uptake and (b) basicity for carbonation of two particle size fractions (0.08-0.5, 1.0-1.6 mm) of BOF_I slag at 700 ^oC for 1 hour reaction time.

Fig. 8. Atmospheric furnace carbonation results: basicity of 0.08-0.5 mm particle size fractions of BOF_I and BOF_{II} slags as a function of CO_2 uptake for 10 minutes (a) and 6 hours (b) carbonation reaction time. Varying CO_2 uptakes resultant from carbonation at multiple temperatures (i.e. same samples presented in Fig. 6a).

Fig. 9. Atmospheric furnace carbonation results: leaching of heavy metals (Ba, Ni, V (left-side); Cr, Co, Mo (right-side)) from 0.08-0.5 mm particle size fractions of BOF_I (top) and BOF_{II} (bottom) slags as a function of pH. Varying pH values resultant from carbonation at multiple temperatures and reaction times (i.e. same samples presented in Fig. 6a).

List of Tables

Table 1

Heavy metal leaching limits for waste material re-use in Belgium [31,32].

	V	Cr	Co	Ni	Mo	Ba
Limit [c] (mg/kg)	0.80 [a]	1.00 [b]	1.00 [b]	2.00 [b]	1.50 [b]	1.60 [a]

[a] Flemish/Dutch: NEN7343; [b] Walloon: DIN 38414/EN 12457-4/CEN TC 292.

[c] Walloon testing procedure uses batch extraction test at L/S = 10; Flemish testing procedure uses column leaching test at L/S = 10.

Table 2

Average particle sizes of prepared BOF slag fractions determined by laser diffraction and specific surface areas determined by nitrogen adsorption (BET).

Slag batch	BOF_I	BOF_{II}	BOF_I	BOF_{II}	BOF_I	BOF_{II}
Particle size range	micronized	micronized	< 0.08 mm	< 0.08 mm	0.08-0.5 mm	0.08-0.5 mm
D[4,3] (µm)	13.6	13.5	38.0	31.0	252.5	203.9
D[3,2] (µm)	1.7	1.3	2.9	2.5	68.4	49.7
D_{50} (µm)	10.7	7.3	30.5	23.5	224.7	179.5
S_{BET} (m^2/g)	8.2	10.5	5.4	7.8	1.6	1.7

Table 3

Elemental composition of BOF slag batches determined by XRF (measured as oxides, presented as elemental).

Elements (wt%)	Ca	Fe	Si	Mn	Al	Mg	Ti	Cr	V	Balance (H, C, O, trace…)
BOF_I slag	35.3	21.1	5.5	2.7	1.1	0.52	0.40	0.32	0.17	32.9
BOF_{II} slag	41.3	15.8	5.9	2.9	0.62	0.33	0.30	0.12	0.15	32.6

Table 4

Mineral composition (wt%) of BOF slag batches determined by XRD with Rietveld refinement (normalized to 100% of the identified crystalline phases).

Mineral	Chemical formula	BOF_I	BOF_{II}
Srebrodolskite (C_2F)	$Ca_2Fe_2O_5$	37.2	31.0
β-C_2S	Ca_2SiO_4	21.5	22.0
Lime	CaO	10.6	20.6
γ-C_2S	Ca_2SiO_4	7.3	7.9
Fayalite	Fe_2SiO_4	5.5	4.2
Hematite	Fe_2O_3	4.1	2.0
Enstatite	$MgSiO_3$	3.8	1.9
Ferrosilite	$FeSiO_3$	2.8	3.6
Quartz	SiO_2	2.8	1.4
Wollastonite	$CaSiO_3$	1.1	0.7
Wüstite	FeO	1.1	2.2
Magnetite	Fe_3O_4	0.8	0.4
Periclase	MgO	0.7	1.6
Iron	Fe	0.4	0.3

Table 5

Carbonation/calcination equilibrium temperatures (Gibbs free energy of reaction equal to zero) for alkaline mineral components of BOF slag (FactSage 6.2 modeling).

Mineral	Reaction Eq.	$P(CO_2)$ (atm)	T ($\Delta G = 0$) (^oC)
CaO	(1)	0.0003	511
CaO	(1)	0.01	627
CaO	(1)	0.1	732
CaO	(1)	1	861
CaO	(1)	5	971
Ca_2SiO_4	(2)	1	400
$Ca_2Fe_2O_5$	(3)	1	664
MgO	(4)	1	400

- Novel hot-stage carbonation approach to Basic Oxygen Furnace (BOF) slag presented.
- Optimum carbonation rate at boundary of equilibrium (830-850 ^oC at 1 atm CO_2).
- Limited effect of pressure (0.2 to 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.

Figure 1

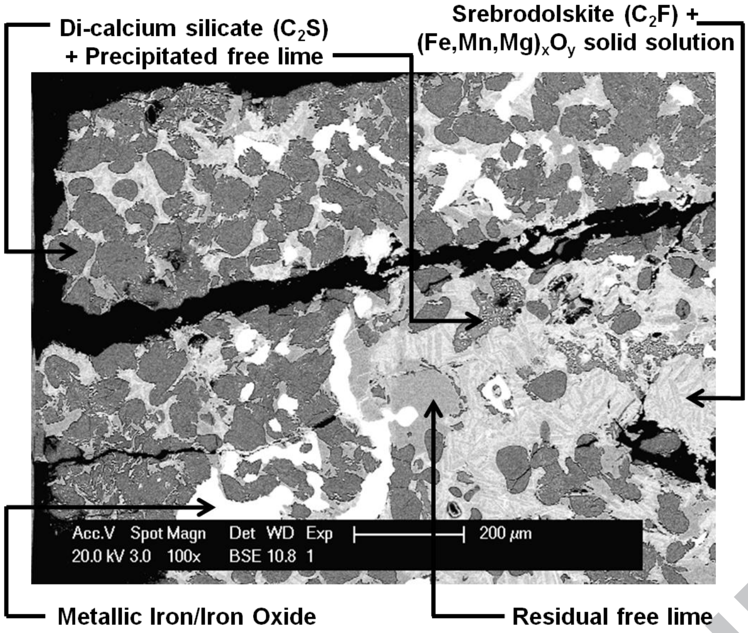

Di-calcium silicate (C_2S)
+ Precipitated free lime
Srebrodolskite (C_2F) +
$(Fe,Mn,Mg)_xO_y$ solid solution
Acc.V Spot Magn Det WD Exp
20.0 kV 3.0 100x BSE 10.8 1
200 µm
Metallic Iron/Iron Oxide
Residual free lime

Figure 2

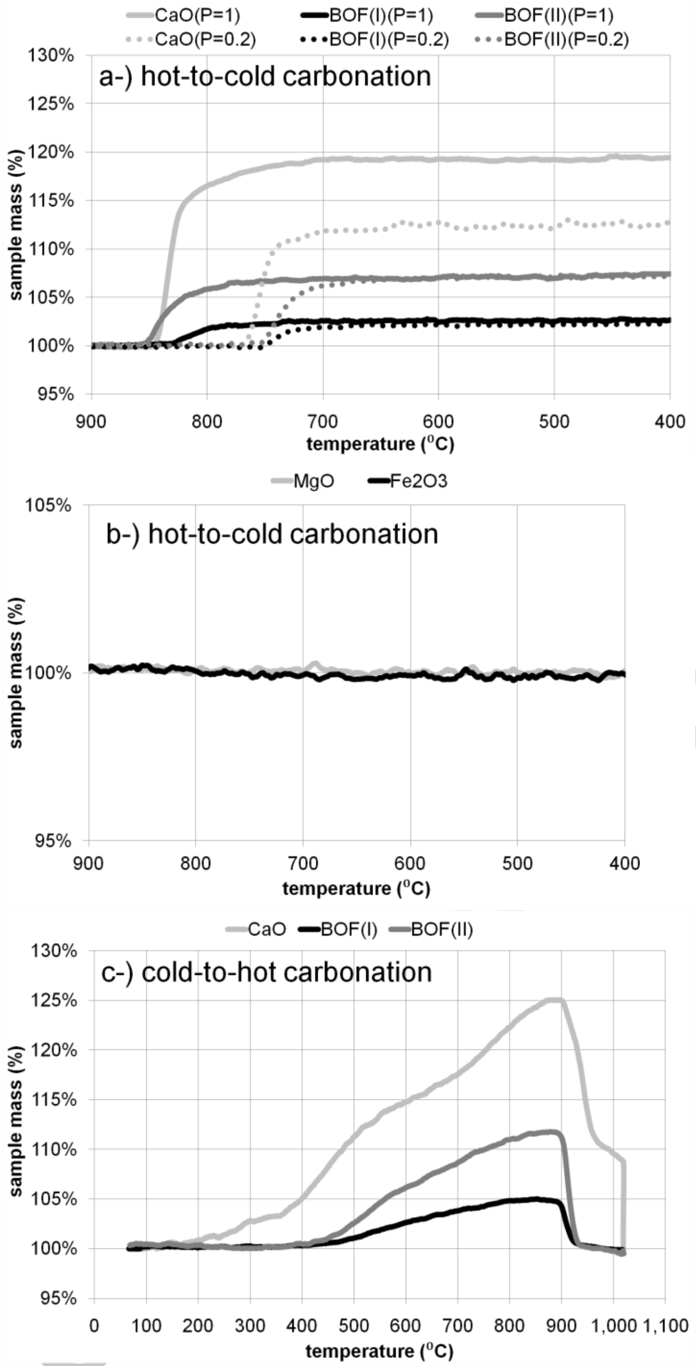

CaO(P=1)
BOF(I)(P=1)
BOF(II)(P=1)
CaO(P=0.2)
BOF(I)(P=0.2)
BOF(II)(P=0.2)
a-) hot-to-cold carbonation
sample mass (%)
130%
125%
120%
115%
110%
105%
100%
95%
900
800
700
600
500
400
temperature (°C)
MgO
Fe2O3
b-) hot-to-cold carbonation
sample mass (%)
105%
100%
95%
900
800
700
600
500
400
temperature (°C)
CaO
BOF(I)
BOF(II)
c-) cold-to-hot carbonation
sample mass (%)
130%
125%
120%
115%
110%
105%
100%
95%
0
100
200
300
400
500
600
700
800
900
1,000
1,100
temperature (°C)

Figure 3

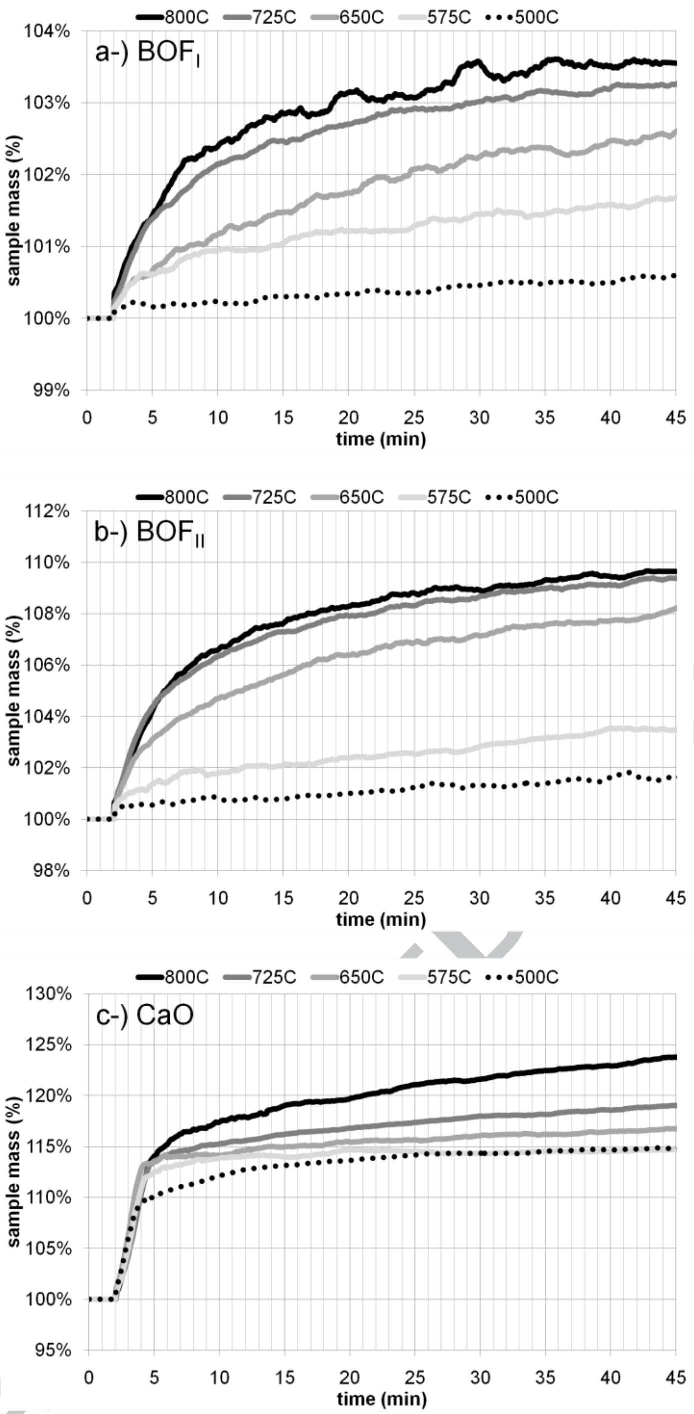

800C
725C
650C
575C
500C
a-) BOF$_I$
sample mass (%)
104%
103%
102%
101%
100%
99%
0
5
10
15
20
25
30
35
40
45
time (min)
b-) BOF$_{II}$
112%
110%
108%
106%
104%
102%
100%
98%
c-) CaO
130%
125%
120%
115%
110%
105%
100%
95%

Figure 4

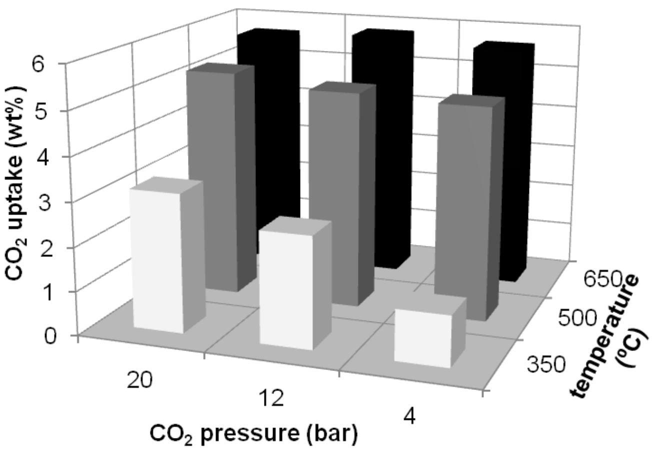

6
5
4
3
2
1
0
CO₂ uptake (wt%)
20
12
4
CO₂ pressure (bar)
650
500
350
temperature (ºC)

Figure 5

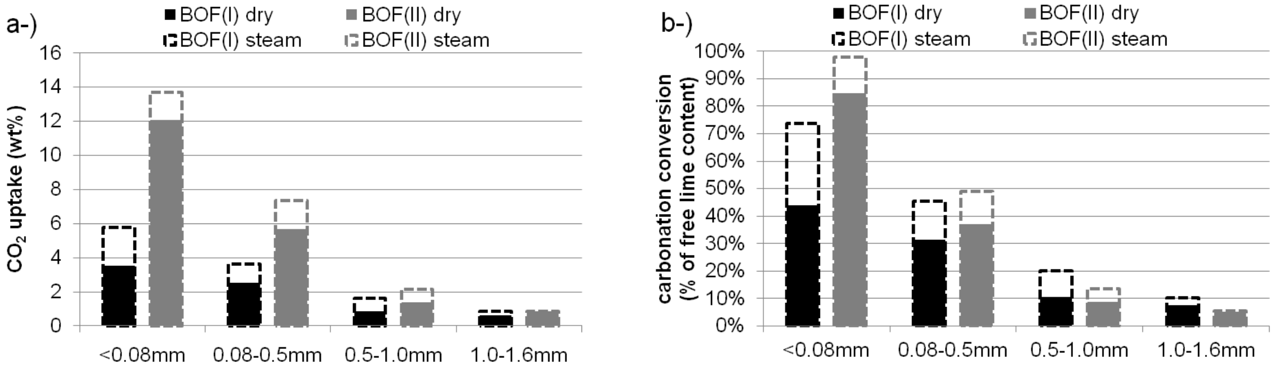

a-)
■ BOF(I) dry
■ BOF(II) dry
BOF(I) steam
BOF(II) steam
CO2 uptake (wt%)
16
14
12
10
8
6
4
2
0
<0.08mm
0.08-0.5mm
0.5-1.0mm
1.0-1.6mm
b-)
■ BOF(I) dry
■ BOF(II) dry
BOF(I) steam
BOF(II) steam
carbonation conversion (% of free lime content)
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
<0.08mm
0.08-0.5mm
0.5-1.0mm
1.0-1.6mm

Figure 6

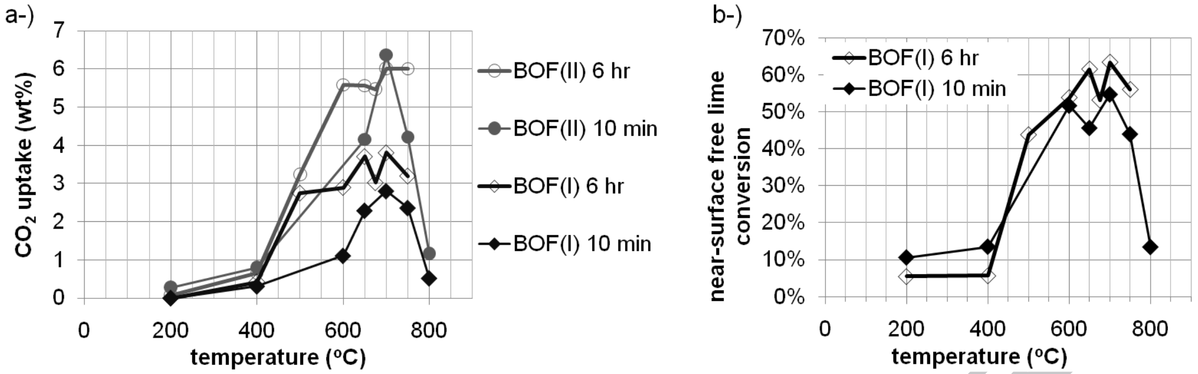

a-)
CO$_2$ uptake (wt%)
0
1
2
3
4
5
6
7
0
200
400
600
800
temperature (ºC)
BOF(II) 6 hr
BOF(II) 10 min
BOF(I) 6 hr
BOF(I) 10 min
b-)
near-surface free lime conversion
0%
10%
20%
30%
40%
50%
60%
70%
0
200
400
600
800
temperature (ºC)
BOF(I) 6 hr
BOF(I) 10 min

Figure 7

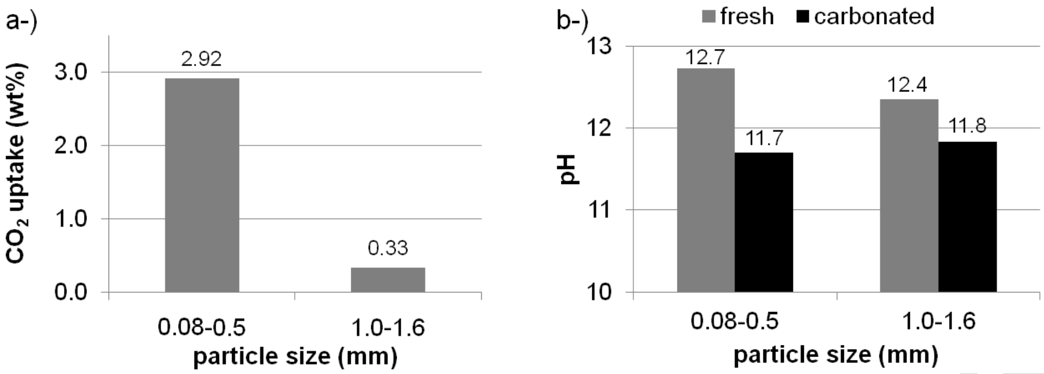

a-)
CO$_2$ uptake (wt%)
3.0
2.0
1.0
0.0
2.92
0.33
0.08-0.5
1.0-1.6
particle size (mm)
b-)
fresh
carbonated
pH
13
12
11
10
12.7
11.7
12.4
11.8
0.08-0.5
1.0-1.6
particle size (mm)

Figure 8

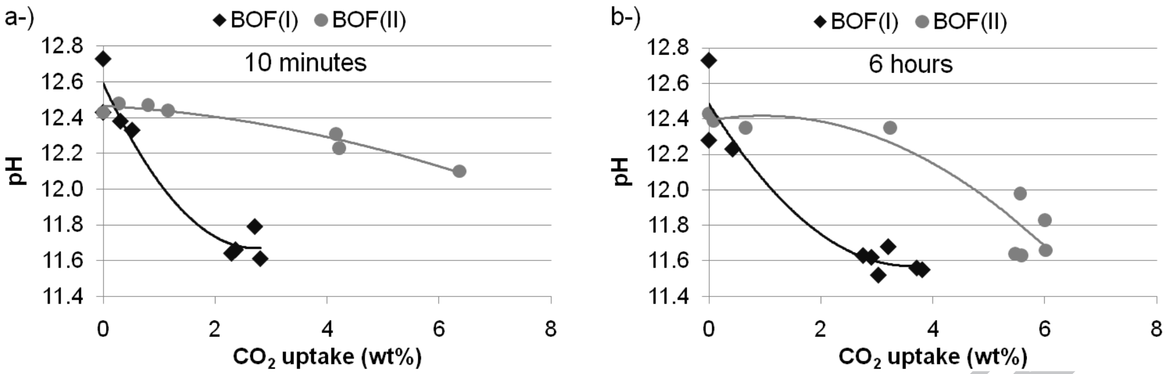
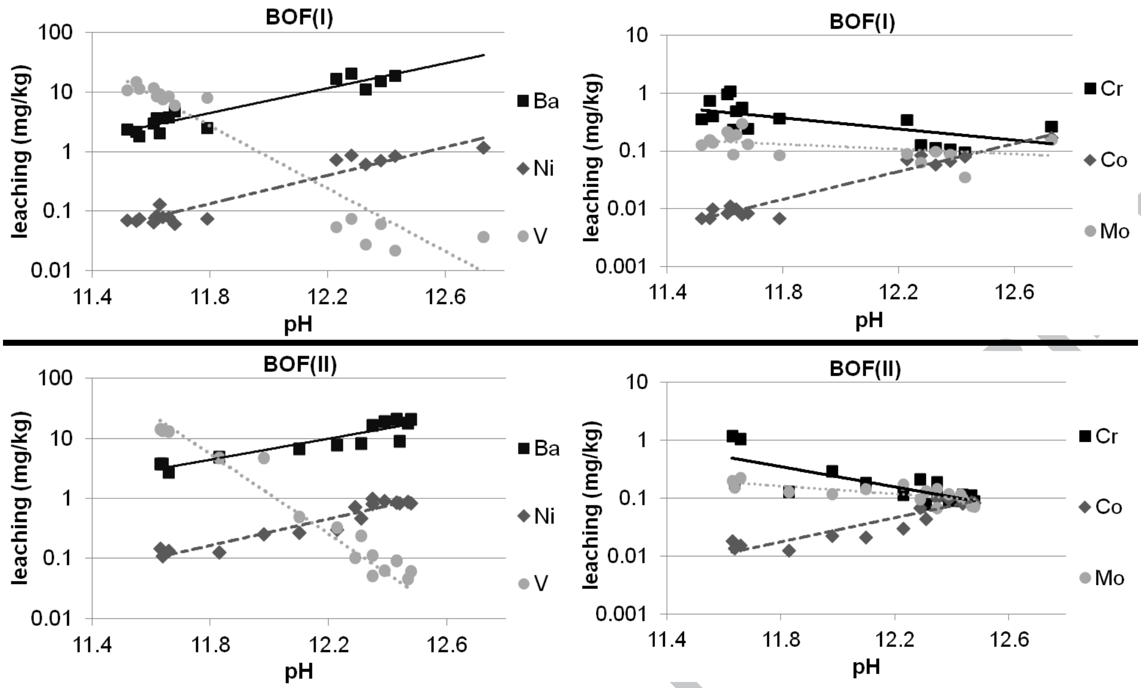

a-)
◆ BOF(I) ● BOF(II)
10 minutes
12.8
12.6
12.4
12.2
12.0
11.8
11.6
11.4
pH
0
2
4
6
8
CO₂ uptake (wt%)
b-)
◆ BOF(I) ● BOF(II)
6 hours
12.8
12.6
12.4
12.2
12.0
11.8
11.6
11.4
pH
0
2
4
6
8
CO₂ uptake (wt%)

Figure 9


BOF(I)
leaching (mg/kg)
100
10
1
0.1
0.01
11.4
11.8
12.2
12.6
pH
■ Ba
◆ Ni
● V
BOF(I)
leaching (mg/kg)
10
1
0.1
0.01
0.001
11.4
11.8
12.2
12.6
pH
■ Cr
◆ Co
● Mo
BOF(II)
leaching (mg/kg)
100
10
1
0.1
0.01
11.4
11.8
12.2
12.6
pH
■ Ba
◆ Ni
● V
BOF(II)
leaching (mg/kg)
10
1
0.1
0.01
0.001
11.4
11.8
12.2
12.6
pH
■ Cr
◆ Co
● Mo