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Steel slag carbonation in a flow-through reactor system: The role of fluid-flux

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ABSTRACT

Steel production is currently the largest industrial source of atmospheric CO₂. As annual steel production continues to grow, the need for effective methods of reducing its carbon footprint increases correspondingly. The carbonation of the calcium-bearing phases in steel slag generated during basic oxygen furnace (BOF) steel production, in particular its major constituent, larnite {Ca₂SiO₄}, which is a structural analogue of olivine {(MgFe)₂SiO₄}, the main mineral subjected to natural carbonation in peridotites, offers the potential to offset some of these emissions. However, the controls on the nature and efficiency of steel slag carbonation are yet to be completely understood. Experiments were conducted exposing steel slag grains to a CO₂-H₂O mixture in both batch and flow-through reactors to investigate the impact of temperature, fluid flux, and reaction gradient on the dissolution and carbonation of steel slag. The results of these experiments show that dissolution and carbonation of BOF steel slag are more efficient in a flow-through reactor than in the batch reactors used in most previous studies. Moreover, they show that fluid flux needs to be optimized in addition to grain size, pressure, and temperature, in order to maximize the efficiency of carbonation. Based on these results, a two-stage reactor consisting of a high and a low fluid-flux chamber is proposed for CO₂ sequestration by steel slag carbonation, allowing dissolution of the slag and precipitation of calcium carbonate to occur within a single flow-through system.

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Introduction

The amount of steel produced globally has increased more than 76% over the past ten years with global outputs surpassing 1.5 billion tons in 2011 (World Steel Association, 2011). For every ton of steel produced, 1.9 tons of CO₂ is generated (World Steel Association, 2010). Cumulatively, these emissions place iron and steel production among the top industrial sources of anthropogenic CO₂, accounting for ~27% of global industrial emissions (International Energy Agency, IEA, 2007). In addition to CO₂, the basic oxygen furnace steel-making process generates approximately 400 kg of slag per ton

of steel (World Steel Association, 2010), comprising ~275 kg of slag from the iron-making stage (namely, blast furnace slag) and ~125 kg from the steel-making stage [namely, basic oxygen furnace (BOF) slag, converter slag, or, as used here, steel slag]. Whereas blast furnace slag is largely recycled, especially in construction materials, this is not the case for steel slag (World Steel Association, 2011). The major impediment to the recycling of steel slag is its relatively high free lime content, which causes considerable expansion of the slag during hydration (Renforth et al., 2011). Instead, steel slag collects in dumps and becomes a source of dust and harmful contaminants to the environment (Danilov, 2003).

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Although the high calcium content (typically ~45 wt.% CaO; Proctor et al., 2000) precludes the recycling of steel slag, combined with the abundance of this slag at locations of CO₂ emissions, it makes the slag an ideal candidate for CO₂ sequestration by mineral carbonation (Huijgen et al., 2005). Indeed, the most readily carbonated phase in steel slag, portlandite, if considered alone, can sequester 159.4 kg CO₂/ton of slag (Tian et al., 2013), translating to a global CO₂ sequestration potential of over 21 million ton CO₂/yr based on 2012 production statistics (World Steel Association, 2013). Less conservatively, assuming carbonation of all available Ca- and Mg-bearing phases, this figure increases to between 55 and 84 million tonnes of CO₂ (Renforth et al., 2011). Assuming complete carbonation of all Ca- and Mg-bearing phases, 6% to 11% of the CO₂ generated by basic oxygen furnace steel production could be sequestered in the co-produced steel slag (Richards et al., 2008). In addition, slag currently stored in dumpsites could provide an additional significant carbon sink (Renforth et al., 2014).

Previous studies have shown that carbonation of steel slag (electric arc furnace and ladle slag) can occur at ambient conditions (Bonenfant et al., 2008), but that it is more effective at high temperature and pressure (Huijgen et al., 2005; Bobicki et al., 2012). The same is true for carbonation of peridotite, a natural analogue to steel slag, in the sense that the main phases undergoing carbonation, olivine [(Mg,Fe)₂SiO₄] in peridotite and larnite [Ca₂SiO₄] in steel slag, have similar structures and reactivity (Lackner et al., 1995; Kelemen and Matter, 2008). These studies, which were based on the results of batch reactor experiments, emphasized the need for small grains (<100 μm) to overcome the rate-reducing effects of incongruent dissolution and grain-shielding by carbonate precipitation (Lackner et al., 1997; Huijgen et al., 2005; Rawlins et al., 2006; Lekakh et al., 2008; Bobicki et al., 2012). The use of finely-ground slag in these experiments prevented the reacted grains from being subjected to detailed petrographic study, and consequently these experiments provided limited information on the nature of reaction in polyminerallite slag.

In the batch-reactor systems employed in previous studies, the fluid composition evolves from being mildly acidic, dissolving the slag, to being saturated with respect to calcium carbonate, precluding further reaction. Here we report the results of a study that made use of a flow-through reactor to investigate steel slag dissolution and carbonation (the first to do so); batch experiments were also conducted for control purposes. By using a reactor of this type, the reaction was prevented from reaching equilibrium and instead moved towards a steady state. In addition, by employing a large grain-size, it was possible to investigate the progressive dissolution and carbonation of the steel slag. The study was also able to investigate the effect of varying fluid-flux (a variable neglected in previous studies) on the nature and progress of the reaction. Experiments of the type discussed in this paper are essential to develop strategies for the effective sequestration of CO₂ using steel slag, and to understand mineral carbonation in general, including *in situ* dissolution and carbonation of natural silicates (e.g., olivine).

1. Materials and methods

1.1. Characterization of steel slag

The steel slag used in this study was supplied by the Tata Steel plant in IJmuiden, The Netherlands. The 2–3.3 mm size fraction (sieved) of steel slag was collected from two basic oxygen furnace steel production cycles (samples 1 and 2 in Table 1). Although significantly larger than the size fractions used in previous studies (Huijgen et al., 2005), this large grain-size allowed the investigation of the textural changes occurring during progressive reaction of the slag. It should be noted, however, that smaller grains react more quickly because

of their greater specific surface area, thereby producing higher degrees of carbonation (Huijgen et al., 2005).

The bulk chemical composition of the steel slag, except for carbon, was analysed by AcmeLabs, Vancouver, using X-ray fluorescence (LiBO₂ fusion followed by XRF; the detection limit for all oxides was 0.01% except for Cr₂O₃, which had a detection limit of 0.001%) (Table 1). Carbon was analysed using the Leco method (0.02% detection limit; total carbon is 0.04 wt.% for slag sample 1 and 0.03 wt.% for slag sample 2), also by AcmeLabs, Vancouver. The identity and proportions of the major crystalline phases were determined by powder X-ray diffraction and Rietveld refinement, respectively (Table 2). Addition of a known amount (wt.%) of an internal silica standard to the powdered slag allowed the relative proportions of the phases, including amorphous phases, in the slag to be determined to a higher degree of accuracy than by conventional standardless Rietveld refinement (the accuracy was estimated to be within 1%). Scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDX) was used to identify and determine the textural relationships among the phases (Fig. 1), and wavelength-dispersive X-ray spectroscopy (WDS) electron microscopy to evaluate the composition of these phases (Table 3). The composition of the major phases (larnite, srebrodolskite, and wüstite) was determined using a JEOL JXA-8900 L electron microprobe equipped with five WDS and a Si(Li) energy-dispersive X-ray spectrometer. Quantitative analyses were made with a focused beam and an acceleration voltage of 15 kV, a 20 nA beam current, a beam diameter of 5 μm, and a 20 sec counting time. Standards used for each element analysed are described in the Supplementary material. Data reduction was performed using the ZAF correction procedure.

Calcium is the principal element of interest for slag carbonation. The steel slag used here contains 42.14 to 45.07 wt.% CaO distributed among two major phases, larnite [Ca₂SiO₄] and srebrodolskite [Ca₂Fe₂O₅], constituting ~50 and ~20 wt.% of the slag, respectively. The other major phase was Mg-wüstite [(Mg,Fe)O], constituting ~27 wt.% of the slag. Minerals in the steel slag display a variety of textural relationships but, in general, the larnite occurs as rounded to sub-rounded crystals of variable size (10–100 μm) surrounded by rounded crystals of Mg-wüstite (10–40 μm) within a srebrodolskite matrix (Fig. 1). Other textures include the occurrence of small crystals of larnite interfingered with small crystals of wüstite and domains dominated largely by wüstite. The latter texture was observed in very few grains, but where present, generally occurred in many parts of that grain.

The average composition of the major phases in a suite of unaltered slag grains is reported in cation units in Table 3. Based on these data and the stoichiometry of the three major phases, their average structural formulae are: larnite (Ca_{0.99}Fe_{0.01})₂(Si_{0.89}P_{0.09}Al_{0.02})O₄; srebrodolskite (Ca_{0.93}Mg_{0.03}Mn_{0.03})₂(Fe_{0.58}Al_{0.23}Ti_{0.13}Si_{0.04}Cr_{0.02})₂O₅; and wüstite (Mg_{0.49}Fe_{0.36}Mn_{0.11}Ca_{0.03})O.

1.2. Experimental method

Experiments were performed using both flow-through and batch reactors. The batch reactor experiments were run at 180°C for 5 days. They were prepared by placing 5 g of steel slag grains in a Teflon bag, punctured to ensure contact with

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