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Carbon sequestration through accelerated carbonation of BOF slag: Influence of particle size characteristics

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HIGHLIGHTS

- CO_2 sequestration through slurry accelerated carbonation of steel slag was studied.
- The influence of particle size distribution was specifically investigated.
- CO_2 uptakes of 0.5–46% were observed depending on the grain size distribution.
- Various carbonate phases containing Ca, Ca, Mn, Mg, Fe and Zn were produced.
- Geochemical modeling revealed a carbonate-dominated slurry system for most elements.

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ABSTRACT

The paper reports the results of slurry-phase accelerated carbonation experiments using basic oxygen surface steel slag as the source of alkalinity for CO_2 sequestration. In particular, the effect of particle size distribution on the carbon sequestration performance was investigated in detail. To this aim, different size classes of the slag were separately subjected to accelerated carbonation, and the CO_2 uptake, the mineralogical changes, the final particle size distribution and the chemical equilibria in the liquid phase were studied. While the total content of potentially reactive elements in the different size fractions of the slag exerted only a minor influence on the carbonation performance, particle size was found to have a dramatic role during the process, in particular during the dissolution stage. Changes by up to two orders of magnitude in CO_2 sequestration (which varied in the range 4.7–465 g of CO_2 sequestered per kg of slag) were observed for the different size classes investigated. Geochemical modeling of the liquid phase after the carbonation treatment showed that the system was dominated by carbonate minerals of several elements including Ca, Mn, Mg, Fe and Zn, indicating the involvement of several components in the carbonation reactions. The presence of carbonate minerals containing not only Ca, but also Mn, Mg and Fe was also detected through XRD analyses. The analysis of the pore size distribution of the slag before and after carbonation revealed the competing effects of particle erosion/dissolution and pore clogging as a result of carbonate precipitation, the relative contribution of which was found to be related to the carbonation degree attained.

1. Introduction

The increase in carbon dioxide concentrations in the atmosphere is strongly related to anthropogenic activities including energy production from fossil fuels and manufacturing industry. The major proposed options for CO_2 sequestration include terrestrial (soil and vegetation), geological and ocean sequestration, as well as mineral carbonation. Carbon sequestration through accelerated carbonation of minerals is a promising alternative to other storage options and, in spite of its potential energy penalties, has a number of advantages that are mainly related to the spontaneous nature of the reactions involved and the absence of potential CO_2 leakages over time (see e.g. [1]). Mineral carbonation occurs spontaneously in nature and involves the reaction between atmospheric CO_2 and alkaline metals contained in rocks, with the formation of chemically stable carbonate forms. A wide variety of materials has been tested as alkaline feedstock for mineral carbonation, particularly naturally occurring minerals including olivine, serpentine and wollastonite, as well as a number of residual

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streams from a variety of thermal processes. The main types of solid residues from thermal processes investigated for CO_2 sequestration purposes include: steel slag [2–17], alkaline ashes from combustion processes [18–20], municipal solid waste ashes [19,21], cement kiln dust [19,22] and cement-based materials [23–25]). Industrial residues have been shown to be more reactive toward CO_2 compared to the silicate minerals contained in natural ores, which confers accelerated carbonation of alkaline waste materials the capability of achieving relevant CO_2 sequestration yields even under mild operating conditions.

Among the above mentioned industrial residues proposed for CO_2 sequestration purposes, steel manufacturing residues have in particular received considerable attention on account of the fact that they are generated in large amounts worldwide and their production is also associated to large CO_2 emission sources. It has been reported [26] that the 2014 world crude steel production was 1.67×10^3 Mt, with a major contribution of Asia (68.2%, mainly due to China [49.4%]); Europe accounted for 12.5% of the overall world production in 2014. The main technologies adopted are the basic oxygen furnace (BOF) and the electric arc furnace (EAF) processes, which account for 74.0 and 26% of the total amount of crude steel produced [26] and generate 125.8 and 168.6 kg of slag per tonne of steel, respectively [27].

In spite of the fact that accelerated carbonation of industrial residues has been the subject of numerous studies mainly over the past decade, a systematic assessment of the influence of the relevant operating parameters is still missing in the scientific literature. Several factors are recognized to play a role in one or more of the carbonation reactions (see e.g. [17,28] and references therein); they include both operating variables (temperature, total pressure and partial CO_2 pressure, liquid-to-solid [L/S] ratio, pH), and solid material properties (particle size, porosity and surface area, mineralogy). While a detailed review of the effects of the process variables on the carbonation mechanisms is beyond the scopes of the present paper and can be found elsewhere [17,28], Table 1 summarizes the relevant features of each factor during the process. A previous study [17] focused on the investigation of individual and joint effects of total pressure, temperature and CO_2 concentration in the gas phase on the CO_2 sequestration yield and carbonation mechanisms. On the other hand, the relevance of another relevant characteristic of the material subjected to accelerated carbonation, namely its particle size, has been mostly underrated so far. While it is commonly acknowledged that CO_2 uptake is inversely correlated with grain size (i.e., directly correlated with the specific surface) and a number of studies have focused on the CO_2 sequestration capacity of various size fractions of waste materials (see e.g. [4,7,9,29–32], to the authors' knowledge no specific in-depth study has been conducted so far about the influence of the particle size distribution on the carbon sequestration potential and reaction mechanisms of alkaline residues including steel slag. Since alkaline industrial residues such as steel slag are commonly characterized by a relatively broad particle size distribution, it would be extremely important for practical purposes to determine the particle size required to optimize their carbonation performance in view of maximizing the achievable CO_2 sequestration yield. This will serve as a relevant indication to evaluate the degree of material pre-treatment (and consequently the associated energy penalty) required ahead of the carbonation process. With the present study, we aimed at filling the existing gaps on this issue through a detailed investigation of the effects of particle size on CO_2 sequestration yield and carbonation reactions of basic oxygen furnace (BOF) steelmaking slag.

Table 1
Recognized effect of process parameters on carbonation.

Parameter	Reaction/mechanism/property affected
Temperature	• Mineral dissolution kinetics • Solubility of minerals (including carbonates) • CO_2 solvation into the liquid phase (→pH also indirectly affected) • CO_2 diffusion • Viscosity of the liquid phase • Nature of carbonate minerals formed
Pressure	• CO_2 solubility in the liquid phase (→pH also indirectly affected) • Formation and growth of carbonate crystals
pH	• Mineral dissolution • Mineral precipitation • Morphology of precipitated solid phases
L/S ratio	• Hydration and dissolution of minerals • CO_2 diffusion • Degree of mixing
Surface area	• Mineral dissolution/precipitation equilibria
Mineralogical composition of the solid material	• Mineral dissolution/precipitation equilibria • Nature of carbonate minerals formed

2. Materials and methods

Slag samples were collected at the outlet of the BOF of a steel plant employing the integrated steelmaking process. To investigate the influence of particle size on the carbonation degree and the final characteristics of the carbonated slag, the material was oven-dried at 60 °C to constant weight and separated into eight size classes through dry sieving. Specifically, the cut sizes for the different classes were as follows: 850–1000 μm (C1), 500–850 μm (C2), 250–500 μm (C3), 150–250 μm (C4), 100–150 μm (C5), 63–100 μm (C6), 38–63 μm (C7) and <38 μm (C8). The size distribution of the sieved materials was determined by laser particle size analysis.

Detailed characterization of the eight slag classes also included measurements of the elemental composition, carbonate content and mineralogy. The elemental composition was determined by alkaline digestion of triplicate samples with $Li_2B_4O_7$ in platinum melting pots at 1050 °C for 2 h, followed by dissolution of the molten material with 10% HNO_3 and analysis of element concentrations by atomic absorption spectrometry. Carbonate measurements were made in triplicate with a Shimadzu inorganic carbon (IC) analyzer. Mineralogy was analyzed by powder X-ray diffraction (XRD) with Cu Kα radiation using a Philips Expert Pro diffractometer equipped with a copper tube operated at 40 kV and 40 mA.

Direct slurry-phase accelerated carbonation tests were performed in duplicate in a pressurized stainless steel reactor equipped with an external magnetic stirring device and a heating jacket. The experimental conditions, selected on the basis of previous investigations [2–4,15,17,21], were: 50 °C temperature, 5 bar total gas pressure, 40% vol. CO_2 content in the gaseous phase (which was a mixture of CO_2 and N_2), 5 l/kg liquid-to-solids (L/S) ratio and 4 h contact time. At the end of the carbonation tests the reactor was immediately degassed and then rapidly cooled down to ambient temperature through immersion in a water bath. Liquid/solid separation was subsequently accomplished through