Thin-film versus slurry-phase carbonation of steel slag: CO₂ uptake and effects on mineralogy

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HIGHLIGHTS

- Batch thin-film and slurry-phase carbonation tests conducted on steelmaking slags.
- Max. CO₂ uptakes: 280–403 g CO₂/ kg slag (24-h slurry-phase carbonation).
- Theoretical expected sequestration potential: 2.2–4.2 Mt CO₂/y at a European level.
- Conversion of the original minerals into carbonates involved Ca, Mg, Fe and Mn.

ARTICLE INFO

ABSTRACT

The results of direct aqueous accelerated carbonation of three types of steel manufacturing residues, including an electric arc furnace (EAF) slag and two basic oxygen furnace (BOF) slags, are reported. Batch accelerated carbonation tests were conducted at different temperatures and CO₂ pressures applying the thin-film route (liquid to solid, L/S, ratio = 0.3 L/kg) or the slurry-phase route (L/S ratio = 5 L/kg). The CO₂ uptake strongly depended on both the slag characteristics and the process route; maximum yields of 280 (EAF), 325 (BOF1) and 403 (BOF2) g CO₂/kg slag were achieved in slurry phase at $T = 100 \,^\circ$C and $p_{CO2} = 10$ bar. Differently from previous studies, additional carbonates (other than Ca-based phases) were retrieved in the carbonated BOF slags, indicating that also Mg-, Fe- and Mn-containing phases partially reacted with CO₂ under the tested conditions. The results hence show that the effects of accelerated carbonation in terms of CO₂ uptake capacity, yield of mineral conversion into carbonates and mineralogy of the treated product, strongly rely on several factors. These include, above all, the mineralogy of the original material and the operating conditions adopted, which thus need specific case-by-case optimization to maximize the CO₂ sequestration yield.

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1. Introduction

Among the CO₂ capture and storage techniques, ex situ accelerated carbonation is the only option allowing permanent CO₂ sequestration in short timeframes. In this process, a material rich in alkaline earth metal oxides and/or silicates is contacted with CO₂ at optimized operating conditions, resulting in the formation of stable carbonate phases [1]. To maximize the CO₂ uptake achievable by minerals such as olivine, serpentine and wollastonite, several reaction routes (e.g., indirect, direct gas–solid or direct aqueous) have been tested (see e.g., [2]). The CO₂ sequestration capacity of several types of alkaline industrial residues (alkaline ashes from combustion processes [3–8], cement-based materials [9,10], cement kiln dust [7,11], steel manufacturing slag [12–22]) has also been recently evaluated. Such residues, although quantitatively limited, prove readily reactive toward CO₂ at significantly milder operating conditions than Mg or Ca silicate minerals, and could hence be used to sequester part of the CO₂ emitted from specific industrial facilities.

The most common carbonation route for alkaline residues is the direct aqueous route (see e.g., [6,8,23]), in which the dissolution of reactive phases and the precipitation of Ca carbonates occur in a single stage. Direct aqueous carbonation studies have been performed either in slurry phase at liquid to solid (L/S) ratios of 5–50 L/kg (especially for waste materials with high silicate contents [6,13,15]) or via the thin-film route, i.e., at L/S ratios <1.5 L/kg [3–5,7,8,11,12,23].

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Among the various alkaline industrial residues available, steel manufacturing slags are particularly interesting for mineral carbonation, on account of their widespread availability as well as chemical and mineralogical composition. Steel slags are produced either during the conversion of hot iron ores into crude steel in a basic oxygen furnace (BOF slag) in plants adopting the integrated manufacturing cycle, or during the melting of iron scrap in an electric arc furnace (slag from carbon steel – EAF-C – or stainless/high alloy steel production – EAF-S) [24–26]. Secondary metallurgical slags may also be generated in further secondary processing of crude steel [24–25].

A total crude steel production of 1.51×10^6 Mt was estimated worldwide in 2012, resulting in ~125.8 kg of BOF slag and ~168.6 kg of EAF slag per t of crude steel produced [27] The iron and steel industry is also recognized to be one of the largest industrial CO_2 emitters, with a total of 115.6 Mt CO_2 emitted by the EU-27 countries in 2007 [28], and a global annual emission of 1500–1600 Mt CO_2 [29].

Steel slag carbonation may contribute to the sequestration of CO_2 emissions while at the same time improving the technical and environmental behavior of the material, due to the mineralogical changes of thermodynamically unstable minerals produced by the process. Undesired alterations of steel slag minerals (e.g., hydration of CaO and MgO; C_2S transformation from the α- to the γ-polymorph) cause significant volume instability (see e.g., [26,30,31]) with swelling and cracking phenomena that may hinder slag utilization. Moreover, some types of steel slag may release non-negligible amounts of toxic metals (e.g., Cr, V, Mo [32]). Mineralogical alterations of steel slag resulting from carbonation lead to improved mineralogical stability and lower contaminant mobility.

Despite the fairly large amount of work that has been recently conducted in the field of accelerated carbonation of steelmaking residues, the individual mechanisms involved in the process and the resulting changes in the main physical, chemical and mineralogical characteristics of the materials have not been fully elucidated yet. With the present work we aimed at filling some of the existing gaps in the knowledge of accelerated carbonation of EAF and BOF slags applying the direct aqueous route by performing both slurry-phase and thin-film tests. Specifically, CO_2 sequestration yields and related mineralogical changes were investigated in detail to gain insights into the transformations occurring during the carbonation process.

2. Materials and methods

Slag samples were collected from a stainless steel plant after metals removal downstream the electric arc furnace unit (EAF slag), and from a steel plant employing the integrated steelmaking process both at the outlet of the basic oxygen furnace (BOF1 slag) and at the storage site after metals recovery (BOF2 slag). The samples were milled to pass the 150 μm sieve. The size distribution after milling was measured through laser particle size analysis (BT-9300S analyser).

Slag characterization included the determination of the elemental composition, carbonate content and mineralogy of the tested samples. The elemental composition was determined by alkaline digestion of triplicate slag 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) analyser. Mineralogy was analyzed by powder X-ray diffraction (XRD) with Cu $K\alpha$ radiation using a Philips Expert Pro diffractometer equipped with a copper tube operated at 40 kV and 40 mA. Fourier-transform infrared spectroscopy (FT-IR) analyses were performed using an Agilent 640 IR instrument operating in the mid-IR range. Scanning electron microscopy (SEM) analyses of polished thin sections were conducted with a GEMINI Supra 40 (Carl Zeiss) instrument.

Direct aqueous accelerated carbonation tests were performed at L/S = 0.3 L/kg (thin-film process: humidified material in contact with the gaseous phase) and L/S = 5 L/kg (slurry-phase treatment: aqueous suspension of the slag contacted by the gaseous phase). While the thin-film process was operated under relatively mild conditions to assess the applicability of a low energy-intensive carbonation treatment, the slurry-phase route was intended as a more severe treatment to assess the maximum practicable CO_2 sequestration yield. The values of pressure, temperature and L/S ratio adopted during the experiments were based on previous investigations [3–5,12,15]. The treatment was performed in a pressurized stainless steel reactor at 50 °C (thin-film route) or 100 °C (slurry-phase route), 100% CO_2 atmosphere and 10 bar pressure for 0.5–24 h.

After carbonation the samples were oven-dried at 105 °C and analyzed to determine their carbonate content and mineralogy (through XRD, FT-IR and SEM analyses), as specified above.

The process performance in terms of CO_2 uptake was calculated through Eq. (1):

$$CO_2 \text{ uptake}\,(\%) = \frac{CO_{2final}\,(\%) - CO_{2initial}\,(\%)}{100 - CO_{2final}\,(\%)} \times 100 \qquad (1)$$

where CO_2 uptake is expressed as g CO_2 sequestered by 100 g of as-received dry slag, while CO_{2final} and $CO_{2initial}$ are the CO_2 weight percent contents of carbonated and untreated samples as derived from their respective IC contents.

The conversion yield of reactive elements into carbonate forms, η, was also evaluated according to Eq. (2):

$$\eta\,(\%) = \frac{CO_2 \text{uptake}(\%)/44}{\sum\limits_k \left(Me_{in,k}(\%)/AW_k \right) - CO_{3in}(\%)/60} \times 100 \qquad (2)$$

where Me_{in} (Me generically indicating Ca, Fe, Mg or Mn) and CO_{3in} are the initial weight percent contents of metals and carbonate in the as-received untreated dry slag and AW is the atomic weight of Ca, Fe, Mg or Mn. In the present work, differently from our previous research [4,5] and other literature studies (e.g., [14,15,22,33,34]), the assumption that Ca only contributed to the formation of carbonate minerals appeared unreasonable, and explicit evidence was gained from XRD analyses (see below) of the conversion of Fe-, Mg- and Mn-bearing phases into carbonates. Eq. (2) is based on the implicit assumption that all the formed carbonate minerals had an equimolar Me/CO_3 ratio.

3. Results and discussion

3.1. Materials characterization

The main statistical parameters (10th, 50th and 90th percentiles, volume and surface mean diameters) of the grain size distribution of the milled materials are reported in Table 1. Although using identical milling conditions, the final grain size distributions were notably different, due to different initial dimensional characteristics and mechanical properties of the particles. The BOF2 slag displayed the largest amount of fine particles, with a final median diameter of 14.3 μm and a D_{90} of 50.2 μm. Conversely, the BOF1 slag contained significant proportions of larger particles (D_{90} = 208 μm); while physical aggregation may be excluded since a dispersant was used in the analysis, this finding may likely arise from particle hydration or cementation upon contact with the liquid medium used in the analysis. The actual grain size of the material when it comes in contact with water is important with a