Slurry-phase carbonation of different types of steel slag: CO$_2$ uptake and effects on mineralogy

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Abstract

This paper reports the main results in terms of CO$_2$ uptake and conversion yield attained by three different types of residues from steel manufacturing subjected to accelerated carbonation. Electric arc furnace (EAF) slag and two basic oxygen furnace (BOF) slag samples were investigated. Both a wet (L/S = 0.3 l/kg) and a slurry-phase route (L/S = 10 l/kg) were applied for batch accelerated carbonation tests at controlled temperature and CO$_2$ pressure. The CO$_2$ uptake achieved upon the treatment varied significantly depending on the type of investigated slag and on the process route adopted; maximum values of 280, 325 and 404 g CO$_2$/kg slag were achieved for EAF, BOF1 and BOF2 slag, respectively, under slurry-phase conditions (T = 100 °C, pCO$_2$ = 10 bar). The results indicated that the effects of accelerated carbonation, assessed in terms of CO$_2$ uptake capacity and mineral conversion into carbonates, are strongly dependent, above all, on the mineralogy of the original material and the operating conditions adopted, which thus need specific case-by-case optimization.

Introduction

The CO$_2$ sequestration capacity of several types of industrial residues submitted to different accelerated carbonation processes has been recently the focus of various studies. The analysed residues include: alkaline ashes from combustion processes, cement-based materials, cement kiln dust and steel manufacturing slag. These waste materials, although quantitatively limited, prove readily reactive towards CO$_2$ at significantly milder operating conditions than Mg or Ca silicate minerals, and could hence be used in reduced-scale mineral carbonation demonstration projects to sequester part of the CO$_2$ emitted from specific industrial facilities.

The most commonly investigated process route for the carbonation of alkaline residues is the direct aqueous route, which involves the dissolution of the reactive phases and the precipitation of Ca carbonates in a single stage. For waste residues characterized by high contents of silicate phases, such as steel slag and cement waste, the indirect aqueous route, in which the dissolution and precipitation processes are carried out in separate steps, has also been tested to enhance Ca dissolution from the solid matrix and to produce a pure calcium carbonate product with specific properties.

Direct aqueous carbonation studies have been performed in two different modes, either in slurry phase at Liquid to Solid (L/S) ratios between 5 and 50 l/kg, in particular for waste materials with high silicate contents, or using L/S ratios <1.5 l/kg.

One of the types of alkaline industrial residues that appears most interesting for testing the mineral carbonation technology, based on its availability and typical chemical and mineralogical composition, is steel manufacturing slag. From current steel production data[1], it can be estimated that roughly 180 Mt of commingled slag were generated worldwide by the steel industry in 2009. The solid residues of steel manufacturing are commonly alkaline materials characterized by a prevalence of Ca-containing silicate phases and generally display relevant amounts of Mg, Al, Fe and Cr, among others, in the form of oxides and/or silicates.

In the present work, accelerated carbonation tests were carried out separately on milled EAF and BOF slag in order to maximize the CO_2 uptake achievable under relatively mild operating conditions, which were selected on the basis of the main findings of previous studies. The effects of the tested carbonation treatments on the mineralogy of the slag samples were also investigated to gain insights into the transformations occurring during the carbonation process.

Materials and methods

Slag samples were collected from different Italian steel manufacturing plants and specifically: from a stainless steel mill after metals removal directly downstream the electric arc furnace unit (EAF slag), from a steel mill employing the integrated steel-making process both directly at the outlet of the basic oxygen furnace (BOF1 slag) and from the BOF slag storage site after metals recovery (BOF2 slag). Given the critical influence exerted by particle size on carbonation[2] the slag samples, which had been pre-grinded at the plant of origin, were milled to a particle size below 150 μm.

The slag was characterized for elemental composition, calcite content and mineralogy. The elemental composition was determined by alkaline digestion of samples with $Li_2B_4O_7$ in platinum melting pots at 1050 °C, followed by dissolution of the molten material with 10% HNO_3 and analysis of element concentrations by atomic absorption spectrometry. The carbonate content was evaluated by a Shimadzu TOC analyzer for solid samples. The mineralogical composition was assessed by powder XRD analysis with Cu Kα radiation using a Philips Expert Pro diffractometer equipped with a copper tube operated at 40 kV and 40 mA. FT-IR analyses were also performed using an Agilent 640 IR instrument operating in the mid-IR range.

Accelerated carbonation tests were performed applying the direct aqueous route at two different L/S ratios: L/S = 0.3 l/kg (wet treatment) and L/S = 5 l/kg (slurry-phase treatment). The wet treatment was performed in a 150-ml pressurized stainless steel reactor placed in a thermostatic bath. The reaction temperature was set at 50 °C, while gas humidity was maintained at 75% using a saturated NaCl solution in the reactor. In each run, three 1 g samples of dry slag were mixed with deionized water to adjust the L/S ratio, placed in tin foil containers and exposed to 100% CO_2 for set times (from 0.3 to 24 h) at 10 bar pressure. The slurry-phase treatment was carried out in a 300-ml

pressurized stainless steel reactor equipped with magnetic stirring and a heating jacket. The reaction temperature was set at 100 °C. In each run, 20 g of sample were mixed with deionized water to adjust the L/S ratio and exposed to 100% CO_2 for set times (from 0.5 to 24 h) at 10 bar pressure.

After carbonation, the samples were oven-dried at 105 °C and analysed for carbonate content (through IC measurements) and mineralogy (through XRD and FT-IR analyses).

Results and discussion

The chemical composition of the EAF and BOF slag (see Figure 1) showed that the Ca concentration, accounting for 21-23% of the BOF samples mass and 35% of the EAF slag mass, was significantly higher than the Mg content (3.3-3.8% in the BOF samples and 2.4% in the EAF slag). Other elements displaying appreciable concentrations in the BOF slags were (in descending order of total content): Fe (20-25%), Si (4-6%), Al (0.7-1.1%), V (7800-9300 mg/kg) and Cr (1300-1800 mg/kg). In the EAF slag the concentrations for such elements were: Si (13%), Cr (3.7%), Fe (3.2%), Al (2%) and V (970 mg/kg). The initial carbonate content in the material accounted for 0.8, 6.7 and 3.5% of the BOF1, BOF2 and EAF slag, respectively. Among the minor elements, the most abundant toxic metals in BOF slags, besides V and Cr, were Zn (35-88 mg/kg), Pb (~60 mg/kg) and Cu (8-16 mg/kg); for the EAF slag, apart from Cr and V, Ni was the most abundant toxic element (480 mg/kg), followed by Mo (287 mg/kg), Zn (260 mg/kg), Cu (171 mg/kg) and Pb (91 mg/kg).
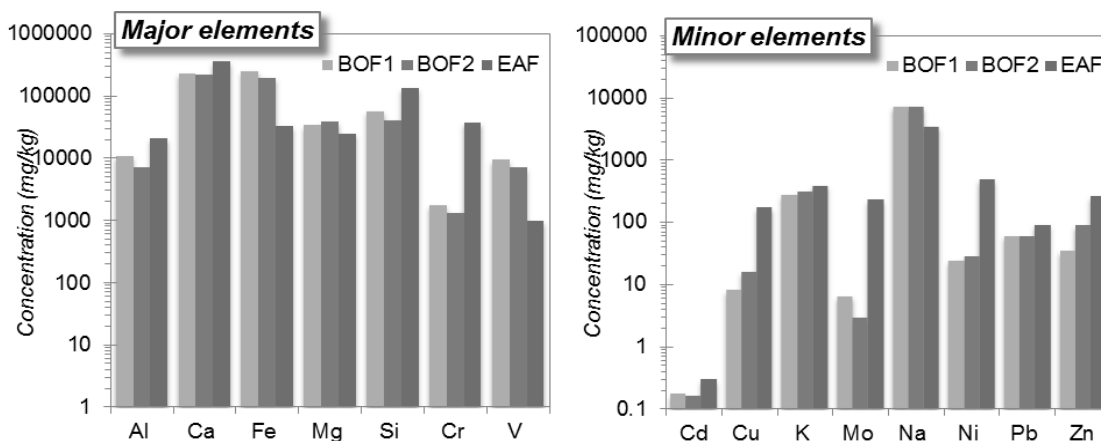

Figure 1. Content of major and minor elements in the slag samples

XRD analyses of the three slag samples investigated (see Figure 3 below) showed that for the BOF1 sample the main phases included silicate and oxide phases, namely tricalcium (hartrurite) and dicalcium (larnite) silicate, a mixed Ca-Al-Fe oxide ($Ca_2Fe_{1.4}Al_{0.6}O_5$), a mixed Ca-Cr-Fe oxide ($Ca_2Cr_{0.5}Fe_{1.5}O_5$), wüstite (FeO), magnetite (Fe_2O_3) as well as corundum (Al_2O_3); some small amounts of portlandite were also identified. The BOF2 sample showed a different mineralogical composition, with a largely prevalent presence of portlandite and smaller amounts of silicate and oxide

minerals, including Mg silicate, wüstite, mixed oxides ($(MgO)_{0.725}(MnO)_{0.275}$; $Ca_2Fe_{1.4}Al_{0.6}O_5$; $Ca_2Cr_{0.5}Fe_{1.5}O_5$), calcite and magnetite. The presence of portlandite was also indicated by FT-IR observations (results not shown here) from two sharp bands at 3610-3640 cm^{-1} (commonly associated to hydroxyl stretching modes) and ~950 cm^{-1} (related to hydroxyl deformation modes)[3]. The major presence of portlandite in BOF2 indicates a higher degree of hydration of the material compared to BOF1. For the EAF slag among the main Ca-containing silicate phases, dicalcium silicate, gehlenite ($Ca_2Al(AlSi)O_7$), akermanite ($Ca_2MgSi_2O_7$) and cuspidine ($Ca_4Si_2O_7(F,OH)$) were detected, whereas the main oxide phases retrieved were periclase, Ca-Al oxide, Cr oxides (CrO, $MgCr_2O_4$) and magnetite. The presence of fluorite (CaF_2), which is one of the additives used during steel production and refining, was also detected.

The main results of the carbonation experiments performed on BOF and EAF slag samples are summarized in Figure 2 a) and b). The CO_2 uptake obtained upon carbonation, reported on the left hand side y-axis, was calculated applying Equation (1), based on the results of IC analyses on carbonated (CO_2final) and untreated samples (CO_2initial) expressed as CO_2 weight percent contents.

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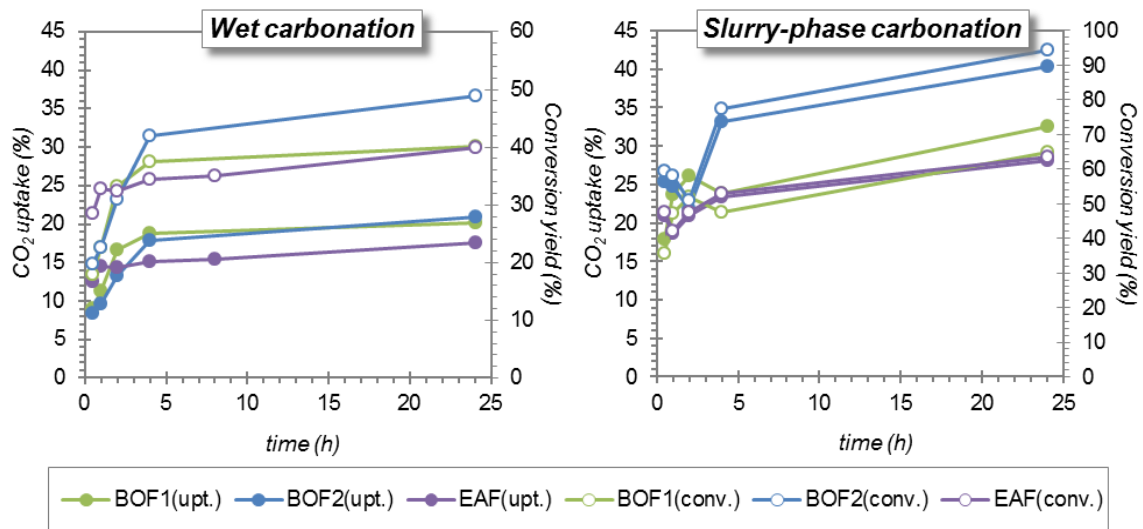

Figure 2. Results of a) wet and b) slurry-phase carbonation experiments

From CO_2 uptake data, large differences were evident in the carbonation yield between the wet and the slurry-phase process: while a maximum CO_2 uptake of ~21% was obtained after 24 hours using the wet route (BOF2 slag), the corresponding value attained for the slurry-phase route was ~40%. Differences between the two process routes were also observed as to process kinetics: expressing the 1-h CO_2 uptake as the percent fraction of the maximum yield attained after 24 hours, values of 56 (BOF1), 46

(BOF2) and 82% (EAF) were observed in the wet process, as opposed to 73, 61 and 66% in the slurry-phase treatment. Thus, in addition to displaying considerably higher CO_2 sequestration yields, for the BOF1 and BOF2 slags the slurry-phase treatment also showed faster carbonation kinetics; for the EAF slag – unexpectedly – the wet process resulted in more rapid carbonation in comparison to the other process route.

The CO_2 uptake yields obtained in the present study appear to be particularly promising when compared with the result (final CO_2 uptake of 48%) achieved by a previous study in which wet carbonation was applied in five cycles at ambient temperature and 2 bar CO_2 pressure to β–Ca_2SiO_4, re-milled after each cycle to remove the product coating acting as a diffusion barrier against the advancement of the carbonation front[4]. The uptake achieved in the present study is also deemed to be relevant on account of the fact that waste materials were employed for carbonation and no further mechanical treatment was applied during the process besides initial milling.

Additional considerations can be made with regard to the material conversion into carbonate minerals. The conversion yield, η, was calculated according to the following equation:

$$\eta[\%] = \frac{CO_2 uptake[\%]/44}{\dfrac{Ca_{in}[\%]}{40} + \dfrac{Fe_{in}[\%]}{55.8} + \dfrac{Mg_{in}[\%]}{24.3} + \dfrac{Mn_{in}[\%]}{54.9} - \dfrac{CO_{3in}[\%]}{60}} \times 100 \qquad (2)$$

where $Ca_{in}[\%]$, $Fe_{in}[\%]$, $Mg_{in}[\%]$, $Mn_{in}[\%]$ and $CO_{3in}[\%]$ are the initial contents of Ca, Fe, Mg, Mn and carbonate in the slag, expressed as weight percent. In the present study, differently from what observed in our previous research[5, 6], the assumption that Ca only contributed to the formation of carbonate minerals during carbonation appeared not to be reasonable. For the two BOF samples investigated, accounting only for Ca in the calculation of the conversion yield would have resulted in values above 100%. Given the significantly higher Fe content in the BOF slags compared to the EAF sample and considering the evidence of Fe and Mg conversion into carbonate minerals gained from XRD analyses (see below), accounting for the contribution of Fe and Mg to the carbonation process was deemed to be required to correctly calculate the conversion yield. The maximum values of η calculated according to Equation (2) were 40 (BOF1), 48 (BOF2) and 40% (EAF) for the wet process, while 65 (BOF1), 94 (BOF2) and 64% (EAF) for the slurry-phase process. It should be noted that, only for comparison purposes, the conversion yield was calculated using equation (2) also for the EAF slag, although for this sample no evidence of Fe and Mg conversion into carbonate could actually be gained; the conversion yield values calculated on the basis of carbonation of Ca minerals only would be as high as 47% and 75% for the wet and slurry processes, respectively.

The considerably high values for the conversion yield attained in the slurry process, especially for the BOF2 sample, indicate that even under relatively mild operating

conditions and a simple process configuration the carbonation process was virtually complete. The good conversion efficiencies attained also suggest the opportunity to explore the process performance at lower temperatures and/or lower CO_2 pressures.

The results of the mineralogical analyses conducted on the carbonated materials after a 4-hour treatment are reported in Figure 3 for the BOF1 and BOF2 slags. As for the EAF sample, the reader is referred to the results reported in a previous paper[5].
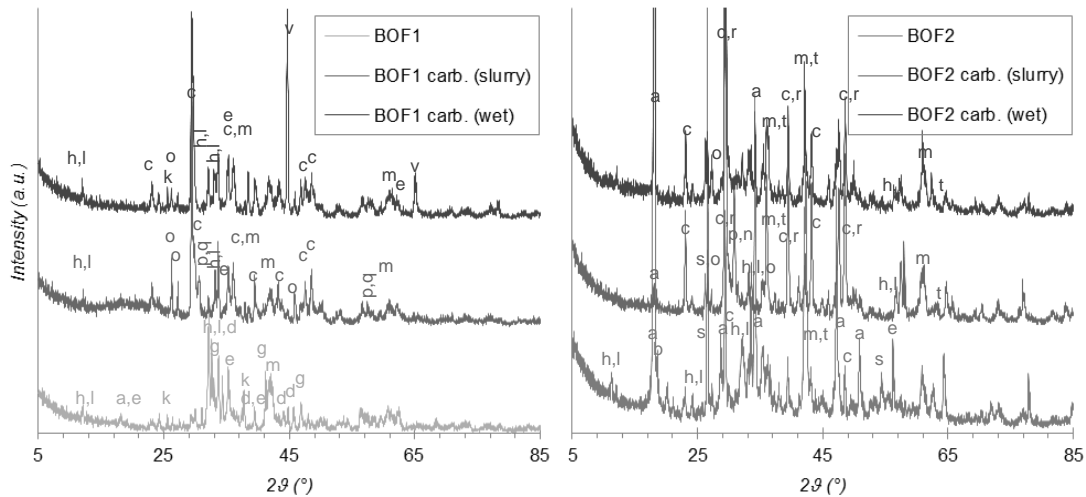

Figure 3. Mineralogical analyses of the carbonated slags: a) FT-IR spectra, BOF1; b) FT-IR spectra, BOF2; c) XRD patterns, BOF1; d) XRD patterns, BOF2. (Legend: (Legend: a) portlandite; b) brucite; c) calcite; d) larnite; e) magnetite; g) hatrurite; h) $Ca_2Fe_{1.4}Al_{0.6}O_5$); k) corundum; l) $Ca_2Cr_{0.5}Fe_{1.5}O_5$; m) wüstite; n) dolomite; o) aragonite; p) ankerite ($CaMg_{0.27}Fe_{0.73}(CO_3)_2$); q) kutnohorite ($(Ca_{0.86}Mn_{0.14})(Ca_{0.14}Mn_{0.5}Fe_{0.36})(CO_3)_4$); r) Mg-calcite ($(Mg_{0.064}Ca_{0.936}(CO_3))$; s) $MgSiO_3$; t) $(MgO)_{0.725}(MnO)_{0.275}$; v) $CrO_{0.87}$).

Both the FT-IR (not shown here) and XRD results showed appreciable changes in mineralogy as a result of the carbonation treatment. As explained further below, the content of some original minerals in the slags was found to variously decrease depending on their specific reactivity with CO_2, and concomitantly additional phases were observed to form upon carbonation. These included in particular new carbonate minerals of different type as well as new silicate minerals, which were likely present as poorly crystalline or amorphous phases. The latter aspect is suggested by the appearance of a broad band centered at 1010 and 990 cm^{-1} in the FT-IR spectra of carbonated BOF1 and BOF2, respectively, which was not visible in the untreated slag samples. This is interpreted as factual evidence that the original well-ordered silicate minerals took part to the carbonation reactions, that caused their partial dissolution with an associated release of alkaline elements thus made subsequently available for carbonate formation.

The different evolution of the process between the wet and the slurry-phase routes, macroscopically indicated by the CO_2 uptake yields discussed above, was also evident from the mineralogical observations. The XRD investigation indicated that for the BOF1

sample the main phases affected by the carbonation process included dicalcium and tricalcium silicate and some oxides ($Ca_2Fe_{1.4}Al_{0.6}O_5$, $Ca_2Cr_{0.5}Fe_{1.5}O_5$, wüstite). The decrease in the intensity of peaks for such phases was also more evident for the slurry-phase treatment compared to the wet process, thus confirming that the former favored to a larger extent the dissolution of reactive phases and their subsequent conversion into carbonate minerals. A notable feature for the BOF1 slag carbonated under wet conditions was the appearance of diffraction peaks associated to a Cr oxide phase having the composition $CrO_{0.87}$, which could not be detected in the slurry-phase carbonated slag. Although this issue deserves further investigation, it is tempting to hypothesize that $CrO_{0.87}$ is an unstable phase which is further converted into other minerals at later carbonation stages.

For BOF2, which showed the highest conversion yield upon carbonation, XRD results showed that the portlandite content, which was the main crystalline phase present, considerably decreased upon carbonation: however, after 4-hour treatment, while for the wet route a residual portlandite content was still detected, for the slurry-phase process no peak associated to this phase could be identified, indicating a more complete conversion of the original mineral structure into the final carbonated form. The presence of a highly reactive phase such as portlandite is also believed to explain the significantly higher CO_2 uptake attained for the BOF2 slag. Other minerals observed to be affected by the carbonation process included, as already noted for BOF1, the oxide phases $Ca_2Fe_{1.4}Al_{0.6}O_5$, $Ca_2Cr_{0.5}Fe_{1.5}O_5$ and wüstite, in addition to Mg silicate ($MgSiO_3$), Mg-Mn oxide ($(MgO)_{0.725}(MnO)_{0.275}$) and magnetite.

As for the newly formed mineral carbonates, the type and amount of phases produced was found to depend on both the type of slag investigated and the process conditions adopted. In general, the amount of carbonates in the slurry-phase carbonated material was appreciably higher than for the wet-treated slag for both BOF1 and BOF2. A wider variety of carbonate minerals was also found to be associated to the slurry-phase process for both slag samples, likely suggesting that more phases were involved in the carbonation reactions. For the BOF1 sample, in particular, while only calcite and aragonite could be detected by XRD analysis in the wet-carbonated material, additional carbonates including ankerite ($CaMg_{0.27}Fe_{0.73}(CO_3)_2$) and kutnhorite ($(Ca_{0.86}Mn_{0.14})(Ca_{0.14}Mn_{0.5}Fe_{0.36})(CO_3)_4$) could be identified in the slurry-phase carbonate slag. For BOF2, the newly formed carbonates included calcite and Mg-calcite ($(Mg_{0.064}Ca_{0.936})(CO_3)$) for the wet-treated slag; in addition to such phases, the slurry-phase carbonated sample was found to contain aragonite, dolomite ($CaMg(CO_3)_2$) and, again, ankerite.

For the EAF slag (see ref.[5] for details), the XRD analysis of the carbonated material indicated, for both the wet and the slurry-phase process, the disappearance of phases such as Ca-Al oxide and periclase, and a relevant reduction in peak intensities of dicalcium silicate, cuspidine and chromium oxide; on the other hand, no evident variations in the contents of akermanite, Cr-Mg oxide, magnetite and calcium fluoride could be detected. The only phase for which a significant increase in peak intensity could be retrieved after carbonation was calcite, indicating that, although MgO showed to decrease upon carbonation, for the EAF the chemical conditions of the

carbonation process were unfavorable to the formation of other carbonate species than calcium carbonate.

Conclusions

The study showed that steelmaking slag, when carbonated under suitable conditions, is capable of exhibiting a high CO_2 sequestration potential. Significant differences in the effects of the carbonation process in terms of CO_2 uptake yield and conversion of the original minerals into carbonates (as mirrored by the mineralogy of the carbonated material) were associated to the chemical properties of the original slag (with the mineralogical characteristics being far more relevant than the elemental composition) and to the treatment conditions adopted. As a result of this, maximum CO_2 uptake values of 18, 20 and 21% were attained after 24-h carbonation for EAF, BOF1 and BOF2, respectively, under wet conditions, as opposed to values of 28, 32 and 40% for the slurry-phase route. The corresponding values of the conversion yield also indicated that, especially for BOF2 carbonated adopting the slurry-phase route, a virtually complete conversion of the potentially reactive minerals into carbonates was attained. Unlike noted in previous studies, for the investigated BOF samples the carbonation reactions appeared to involve not only Ca, but also Fe, Mg and, to some extent, Mn. Considering that for BOF slags accelerated carbonation involved numerous mineral phases in the original material implying consistent rearrangement of the mineralogical structure, a further issue still to be investigated relates to the leaching behavior of metal contaminants (e.g., Cr, V) from the carbonated slag. Additional experiments are currently underway to clarify the effects of accelerated carbonation on the environmental behavior of the treated slag.

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