



13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18
November 2016, Lausanne, Switzerland

Carbonation of steel slag: testing of the wet route in a pilot-scale reactor

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Abstract

This work reports the first results of an on-going activity aimed at the scale up of the wet-route carbonation of steel slag for storing CO₂ and generating a product with valorization potential. Two batches of Basic Oxygen Furnace slag (BOF1 and BOF2) collected at different times from a steelmaking plant downstream iron recovery were used to perform the tests in a pilot-scale rotary kiln unit part of ENEA's research infrastructure. The tests were carried out at ambient (25 °C- 37 °C) and enhanced temperature (45 °C-53 °C), under a 40-47% CO₂ flow, at atmospheric pressure for a reaction time of 30 min. In each experiment around 1000-1500 g of BOF slag was employed. The residues were humidified in order to achieve a liquid to solid ratio of 0.17 l/kg. This value was selected on the basis of the results of preliminary lab-scale static and dynamic experiments that are also presented in this paper. The product collected at the end of each test was cured at controlled conditions (T=25 °C e RH=100%) for 28 days and then characterized in terms of particle size, CO₂ uptake and environmental behavior. The mean diameter (D₅₀) of the obtained product was around 1 mm for the tests performed at room temperature and slightly lower for the test performed at 50 °C, i.e. around twice the size of the starting material. The CO₂ uptake measured for samples collected immediately after the tests was quite similar (4-6% wt.), whereas after curing a 50% increase was observed for all BOF1 slag samples, while only a slight increase was observed for BOF2 slag. These results are significantly higher than the ones of the lab-scale tests. The leaching behavior of the product appeared also to be significantly affected by the treatment performed in the pilot plant.

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Peer-review under responsibility of the organizing committee of GHGT-13.

Keywords: Accelerated carbonation; BOF slag; CO₂ uptake; granulation; leaching behavior; mineralogy; pilot-scale

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1. Introduction

CO₂ is the most important anthropogenic greenhouse gas, being responsible for about two thirds of the enhanced greenhouse effect [1]. The reduction of CO₂ emissions from key industrial sectors is hence one of the goals of the EU's climate mitigation policies for the next 10-15 years. In particular, steel manufacturing is one of the main industrial point sources of CO₂ emissions, which amount to around 1.6 Gt/year, i.e. 5% of global emissions [2]. In addition to CO₂ emissions, the steel sector is responsible for the production of large quantities of alkaline industrial waste, among which slag from Basic Oxygen Furnace (BOF) units. In the EU a production of about 21.4 million tons of steelmaking slag, 46% of which BOF slag was reported in 2012 [3]. Such residues are typically limitedly valorized, or reused only in low-end applications, due to their content of Ca and Mg (hydr)oxides or an inadequate environmental behavior. In Italy the availability of this type of residues can be estimated at about 2.75 Mt/year, considering that 100-150 kg of steel slag are generated per ton of steel produced [4] and assuming a current steel production of about 22 Mt/year [5]. The valorization of these residues would hence be important in a circular economy perspective, since it would lead on the one hand to a decrease of landfill disposal and its associated environmental burdens, and on the other to a reduction in the consumption of primary raw materials.

The goal of reducing CO₂ emissions can be combined with that of obtaining a product with suitable properties for reuse as secondary material by applying processes based on accelerated carbonation. Carbonation is a CO₂ mineralization process based on the reaction of solid phases containing alkaline earth metal oxides with gaseous CO₂ leading to the formation of thermodynamically and chemically stable carbonates [1]. This process, which applied to minerals such as Mg silicates has been proposed as CO₂ storage option, has been also investigated for the treatment of alkaline industrial residues, since the mineralogical and chemical transformations that take place within the solid matrix have been shown to modify their properties, especially with regard to the leaching of potential contaminants [1,2,4]. Hence, the application of carbonation processes to residues such as steel slag could allow to obtain a product with improved chemical, physical and environmental characteristics in view of reuse, as well as to store part of the CO₂ emitted by the steel plant. Different operating conditions and process routes have been tested for carbonation of residues and minerals [1]. In particular, most works have focused on aqueous process routes in which the reacting phases and CO₂ dissolve in water, followed by precipitation of the carbonate product. Among these, the wet (or thin film) route, applied contacting the residues with a small amount of water, applying liquid to solid ratios (L/S) below 0.5 l/kg, is particularly suitable for obtaining a potentially recyclable product. Generally, the operating conditions applied (30-50 °C and 1-10 bar CO₂) are typically milder than those employed in the slurry phase process [2]; in addition this process can be coupled with a granulation treatment, that can allow to obtain a product with a specific particle size distribution, that hence could find application as a secondary aggregate in construction applications [6].

A few studies focused on granulation-carbonation tests at laboratory scale [6-8]. However, to our knowledge, studies reporting data from pilot-scale applications of the wet carbonation route are currently missing. Pilot or bench-scale plants making use of the indirect carbonation route aimed at storing CO₂ and producing precipitated calcium carbonate of high purity have been reported; e.g. a bench-scale plant consisting of a calcium extraction reactor and a calcium carbonate crystallization unit has been built and tested for treating concrete sludge [9]. As for granulation-carbonation, the process described in [6] was actually recently developed up to full scale and commercialized [10], but data regarding the influence of operating conditions and other variables, such as for example variations in the composition of the residues are lacking.

The aim of this work was to analyze the performance of a wet carbonation process for CO₂ storage and BOF slag valorization carried out at pilot-scale in a rotary kiln reactor. In order to investigate possible variations both in the reactivity of the material and CO₂ uptake achieved, as well as in the properties of the product, preliminary static and dynamic lab-scale carbonation tests were also carried out. These allowed also to select the operating conditions to test in the pilot-scale device.

2. Materials and methods

2.1 Materials

The slag used in this study is a by-product of a steel making plant employing the Basic Oxygen Furnace (BOF) process. The sample was collected from the open air storage site after crushing and magnetic separation for iron and steel recovery. Two batches of steel slag (BOF1 and BOF2), sampled at different times, were analyzed and employed in the experiments. BOF1 was dried under a hood in order to reach a final humidity of 1%, while the BOF2 sample was already dry when it arrived at the laboratory.

Both samples were notably heterogeneous from a dimensional point of view. The fraction exceeding 2 mm was discarded, as it was considered not representative of a sample obtained downstream of a grinding plant for iron removal [7]. The particle size of the untreated material was lower than 2 mm with a D_{50} value of 0.5 mm for BOF1 and of 0.4 mm for the BOF2, slightly higher than that reported in [7]. The main chemical constituents in the BOF1 and BOF2 slag were determined by alkaline fusion with $\text{Li}_2\text{B}_4\text{O}_7$ at 1050 °C and ICP-OES analysis of the obtained solutions. As shown in Table 1, there were no significant differences in the chemical composition of the two slag samples, apart from the higher Ca and in Si content of BOF2. In general, the chemical composition of the samples resulted quite similar to the concentrations reported in other studies for this type of steelmaking slag [7,11,12]. The inorganic carbon content of BOF2 slag resulted more than twice the value measured for BOF1, as shown in Table 1.

Table 1. Elemental composition and carbon content of untreated BOF1 and BOF2 slag.

Element	Concentration (g/kg)	
	BOF1	BOF2
Al	21.23	17.59
Ba	0.07	0.06
Ca	212.42	319.08
Cd	0.1	0.4
Cr	2.5	0.73
Cu	0.18	0.048
Fe	178.68	153.96
K	1.77	2.07
Mg	44.11	57.90
Mn	15.5	16.62
Mo	0.01	0.02
Na	1.1	1.13
Si	39.1	59.01
V	0.38	0.45
Zn	0.27	0.27
TC (%)	1.26	1.78
IC (%)	0.64	1.36

The results of the leaching test performed on the as received material (see Table 2) showed a basic pH, equal to 12.6 and 12.5, respectively for the BOF1 and BOF2 slag, linked to the presence of calcium hydroxide and silicate phases, as indicated by mineralogical analysis performed on previous batches of the BOF slag generated by the same steel manufacturing plant. These residues showed to meet the limits established in Italy for reuse [13] and landfilling of

inert waste [14], except for pH which was higher than the limit for reuse. It should be noted however that Ba release in the case of BOF1 slag was exactly equal to the limit for reuse (1 mg/l).

Table 2. Results of the compliance leaching test (EN 12457-2) for the untreated BOF1 and BOF2 slag.

Element	Concentration (mg/l)		BOF1	BOF2
	Reuse limits (M.D. 186/2006)	Landfill limits - Inert waste (M.D. 27/09/2010)		
Al	-	-	0.159	0.12
Ba	1	2	1.003	0.26
Ca	-	-	923.3	1323.81
Cd	0.005	0.004	<0.001	<0.0004
Co	0.25	-	<0.004	<0.001
Cr	0.05	0.05	<0.003	<0.001
Cu	0.05	0.2	<0.02	<0.01
Fe	-	-	<0.007	<0.002
K	-	-	9.07	11.22
Mg	-	-	<0.06	<0.01
Mn	-	-	<0.002	<0.0003
Mo	-	0.05	<0.01	<0.002
Na	-	-	36.205	34.04
Pb	0.05	0.05	0.014	<0.002
Si	-	-	0.235	<0.005
V	0.25	-	<0.005	0.02
Zn	3	0.4	<0.01	<0.003
pH	5<12	-	12.61	12.53

2.2 Methods

The batch carbonation experiments were carried out in a pressurized stainless steel reactor equipped with a 150 ml internal Teflon jacket and placed in a thermostatic bath for temperature control; three 1 g samples of either the as received slag or a milled sample ($d < 0.177$ mm), were mixed with deionized water at the set liquid-solid (L/S) ratio (L/S=0.2 l/kg), exposed to a 40% or 100% CO₂ flow for different reaction times, ranging from 0.5 to 4 h. The total pressure was set at 1 or 10 bar, while the operating temperature of all the experiments was set at 50 °C. The humidity of the gas was maintained at 75% placing a saturated NaCl solution in the reactor.

A lab-scale disc granulator was used for the granulation-carbonation experiments. This reactor was characterized by a diameter of 0.3 m and a height of 0.23 m, equipped with a blade and operated at 24 rpm applying a tilt of 50° during all experiments [7]. The granulation-carbonation tests were performed by mixing the dry BOF1 slag (500 g) with deionized water, in a quantity such as to achieve a L/S suitable for obtaining an effective granulation, i.e. 0.17 l/kg, following the procedure adopted in many previous studies on granulation [15, 16]; the wet slag was screened through a sieve with an opening of 2 mm, then the mixture was inserted into the granulator and left to react for a set time. A CO₂ flow was maintained in the reactor for the entire duration of the experiment, placing a custom made Perspex lid equipped with a CO₂ feeding system over the reactor. The tests were carried out at room temperature for 30 min. Two different CO₂ concentrations of the gas flow were tested: 40% (GC40%) and 100% (GC100%). The granules obtained from each test were cured for 28 days under controlled conditions (room temperature and 100% relative humidity) to ensure the completion of hydration reactions. At the end of the curing period, the granules produced were characterized in terms of particle size distribution, CO₂ uptake and environmental behavior.

The pilot-scale unit consists of a steel rotary drum reactor (see Fig. 1). The rotary drum is a cylindrical shell rotating between two fixed flanges positioned at the two sides of the cylinder. It should be noted that in the reactor there are 8 baffles that run along its longitudinal axis (see Figure 1b). The main features of the pilot scale reactor are reported in Table 3. Granulation-carbonation tests were carried out in the pilot-scale reactor at ambient or enhanced operating temperature, setting the CO₂ percentage in the gas flow at around 40%, the reaction time at 30 min and the L/S at 0.17 l/kg, as reported in Table 4. In these tests it was not possible to control the values of the operating

parameters as rigorously as in laboratory scale; as a result the actual reaction temperature varied between 25 and 37 °C for the tests planned at 25 °C and between 45 and 53 °C for the test planned at 50 °C, while the percentage of CO₂ in the gas flow varied between 40 and 47%. During the tests carried out in pilot-scale, it was in fact possible to monitor the temperature and composition of the gas flow thanks to a gas chromatographer (3000A Agilent model), that allows to obtain an accurate analysis of main gas constituents, such as H₂, O₂, N₂, CO, CO₂, CH₄, C₂H₄, C₂H₆ in 6-7 minutes. The instrument is equipped with two columns operating in parallel (MolSieve 5A and Poraplot) and is equipped with a thermal conductivity detector (TCD); the carrier gas used was argon.

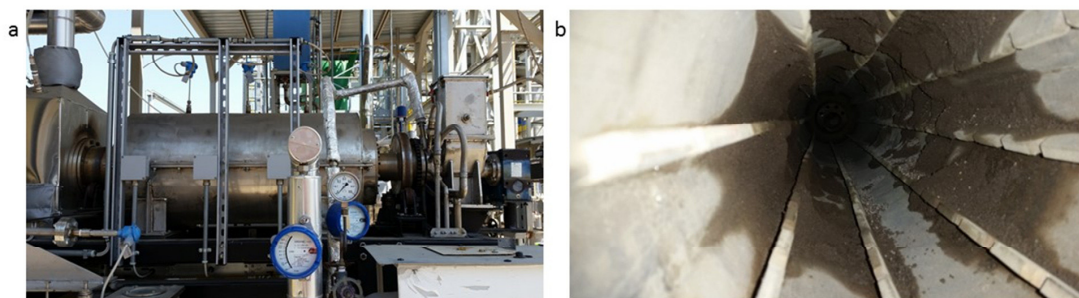


Fig. 1 (a) Side view and (b) inner section of the rotary drum reactor used as wet carbonation pilot plant.

Table 3 Main features of the rotary drum reactor

Furnace heating	Electric, three independent areas
Maximum power	9.2 kW
Maximum temperature	1600 °C
Max operating temperature	1550 °C
Heated zone length	600 mm
Length	1550 mm
Inner diameter	80 mm
Outside diameter	94 mm
Tilt	0-7°
Reactor volume	7.79 dm ³

Table 4 Summary of the experiments performed and main parameters adopted in the pilot scale reactor.

Experiment code	Target conditions	Material	Measured operative conditions	
			CO ₂ (%)	Temperature (°C)
E1 (30°C, BOF1)	GC40%_30°C_W	BOF1 slag	40	34
E2 (30°C, BOF1)	GC40%_30°C_W	BOF1 slag	46	37
E3 (30°C, BOF2)	GC40%_30°C_W	BOF2 slag	47	25
E4 (30°C, BOF2)	GC40%_30°C_W	BOF2 slag	47	27
E5 (50°C, BOF1)	GC40%_50°C_W	BOF1 slag	40	50
E6 (50°C, BOF2)	GC40%_50°C_W	BOF2 slag	42	45
E7 (50°C, BOF2)	GC40%_50°C_W	BOF2 slag	42	53

The tests were carried out by mixing the material with water at the L/S selected on the basis of the results of the lab-scale granulation tests. The speed of the rotating drum was set equal to 8 rpm, the maximum one reached by the system, while for these preliminary trials it was decided to keep the reactor in a horizontal position (i.e. to fix the inclination at 0°). The material was then introduced into the reactor and, after reaching the desired temperature and CO₂ content in the gas flow, the material was kept into the reactor for 30 min, the same reaction time adopted in the laboratory dynamic tests. Finally, the obtained material was subjected to curing for 28 days and characterized in terms of particle size distribution, CO₂ uptake and environmental behavior.

Specifically, the particle size distribution was determined by applying the ASTM D422 standard procedure. The CO₂ uptake of the treated slag was assessed on the basis of the results of Inorganic Carbon (IC) analysis that was performed with a Shimadzu TOC VCPH analyzer equipped with the SSM-5000A solid sampler. The CO₂ uptake was then calculated by applying Eq. 1, in which CO₂ final and CO₂ initial represent respectively the CO₂ content of the treated and as received sample derived by the results the IC analysis. The CO₂ uptake of the carbonated material was assessed immediately after the test and also after 28 d of curing to evaluate the degree of carbonation occurring during the curing treatment (performed under atmospheric air at ambient temperature).

$$CO_{2\text{uptake}}(\%) = \frac{(CO_{2\text{final}}(\%) - CO_{2\text{initial}}(\%)) \cdot 100}{100 - CO_{2\text{final}}(\%)} \quad (1)$$

These data were also used to evaluate the calcium conversion yield, defined as the ratio between the carbonated Ca, proportional to the measured CO₂ uptake, and the amount of potentially reactive Ca phases expressed in terms of Ca content (see Eq. 2).

$$R_x(\%) = \frac{\left(CO_{2\text{uptake}}(\%) \cdot \frac{40}{44} \right) \cdot 100}{Ca_{\text{tot}}(\%) - CaCO_{3\text{initial}}(\%) \cdot \frac{40}{100}} \quad (2)$$

The leaching behavior of the material was evaluated following the EN 12457-2 standard compliance test that involves grinding the fraction of the material presenting a grain size above 4 mm. Leaching tests were carried out in triplicate. The eluates obtained from each test were analyzed by ICP-OES analysis, employing an Agilent 710-ES spectrometer and by ion chromatography using an IC Thermo-Scientific ICS-1100 to determine the chloride, sulfate and fluoride concentrations in the eluates.

3. Results

The lab-scale experiments were performed only on the BOF1 slag in order to identify the optimal operating conditions to adopt in the pilot scale tests. In particular, these tests were conducted by setting the operating temperature (T=50 °C) and the liquid to solid ratio (L/S=0.2 l/kg), varying the total pressure of the gas (1 or 10 bar), the percentage of CO₂ in the gas (40 or 100%) and finally the size distribution of the particles (milled to d<0.177 mm or as received). As it can be seen from Fig. 2, the variation of these parameters showed no significant differences in the percentage of sequestered CO₂, with the exception of particle size, the increase of which caused a sharp decrease in CO₂ uptake with a maximum value of 5%, about one third of the maximum value obtained for the milled slag (above 15%, corresponding to a Ca conversion efficiency of 75%). As reported in previous studies [17, 18], particle size is a critical parameter for CO₂ uptake, which increases for an increasing specific surface area of the reacting material. The results of the carbonation test carried out with 40% CO₂ flows exhibited a quite constant CO₂ uptake over time, with a maximum value equal to 5.2% after a reaction time of 4 h and very similar values and overall trend to that resulting in an atmosphere of pure CO₂. Finally, the effect of the total pressure employed in the tests for 40% CO₂ flows was analyzed. For reaction times of up to 60 minutes, the decrease in pressure from 10 bar to 1 bar yielded a twofold reduction of the CO₂ uptake, which decreased from 4 to 2%. For higher reaction times, the values of CO₂ uptake were more comparable, varying between 4.3% and 5%.

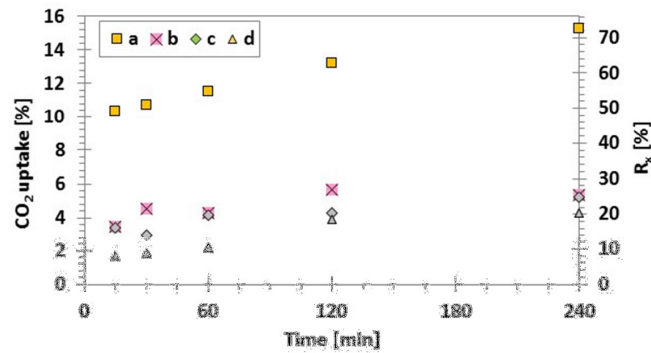


Fig. 2 Carbonation kinetics for BOF1 as a function of particle size (milled or as received), the gas mixture (40-100% CO₂) and the total pressure (p=1-10 bar). The operating conditions are as follows: a) milled slag, p=10 bar, 100% CO₂; b) untreated slag, p=10 bar, 100% CO₂; c) untreated slag, p=10 bar, 40% CO₂; d) untreated slag, p=1 bar, 40% CO₂.

The granulation-carbonation tests carried out at lab scale on BOF1 slag were performed varying the percentage of CO₂ in the gas flow. These tests led to similar particle size distributions (see Fig. 3a), with a mean diameter equal to 3.4 mm and 3.2 mm respectively in the tests conducted at 40% and 100% CO₂, about six times greater than the average diameter of the as received slag.

The CO₂ uptake of the granules obtained after the granulation-carbonation tests measured immediately at the end of the test (t=0 d) and after 28 days of curing is shown in Fig. 3b. It can be observed that the CO₂ uptakes obtained using 40% and 100% CO₂ gas flows were similar at the end of the tests, 2.5% and 3%, respectively. After 28 days curing a substantial increase of the CO₂ uptake was measured resulting in an average value of 5.5% for both types of tests. Similarly to what reported in a previous study [7], the uptake obtained for the granules was greater than that found in the lab scale tests performed at comparable operating conditions, probably due to the fact that this test was performed under dynamic conditions.

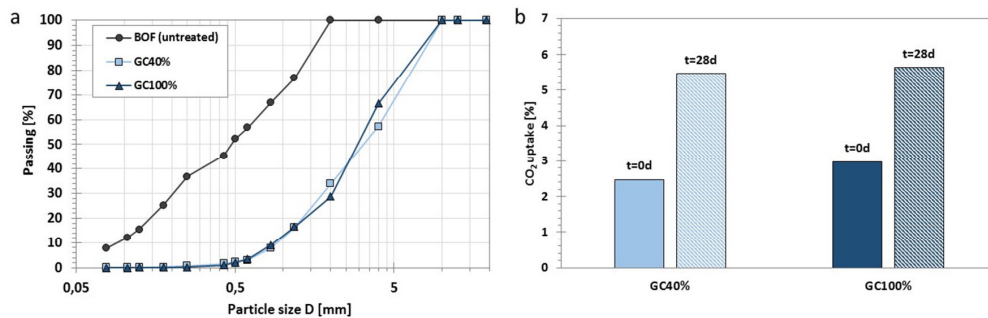


Fig. 3 (a) Particle size distribution of the as received BOF1 slag and the granules obtained from the granulation-carbonation tests varying the percentage of CO₂; (b) CO₂ uptake (%) of the granules obtained by the granulation-carbonation tests with 40% (GC40%_W) and 100% CO₂ (GC100%_W), immediately at the end of the test (t=0 d) and after 28 d of curing (t=28 d).

Fig. 4 shows the results of the leaching test, performed on granules obtained from the granulation-carbonation processes and untreated BOF1 slag. The elements not shown in the figure presented concentrations below the instrumental quantification limit.

The pH of the granules resulting for the GC40% and GC100% tests (12.5 and 12.44, respectively) was only slightly lower compared to that of the untreated BOF1 slag, remaining higher than the limit for reuse. As regards non-regulated elements (see Fig. 4a), a reduction of the leaching of Ca and Na was observed, as well as an increase of Al and Si release, with respect to the untreated BOF slag. In particular, a reduction in Ca leaching can be associated with the formation of less soluble Ca-phases such as calcite, while the increase of Si and, in a more accentuated manner, of Al, may be an indication of the formation of more soluble phases, such as amorphous SiO₂ or hydroxides containing aluminum [19]. As regards regulated elements (see Fig. 4b), Ba release was reduced up to 50% compared to the untreated slag, while Cr and V leaching remained below the instrumental quantification limit. As can be noted the effects on the leaching of both major and regulated elements were more significant for the slag treated under 100% CO₂, which may be partly related to the slightly lower pH of the eluate, but not to the CO₂ uptake which was practically the same for the two tests after curing.

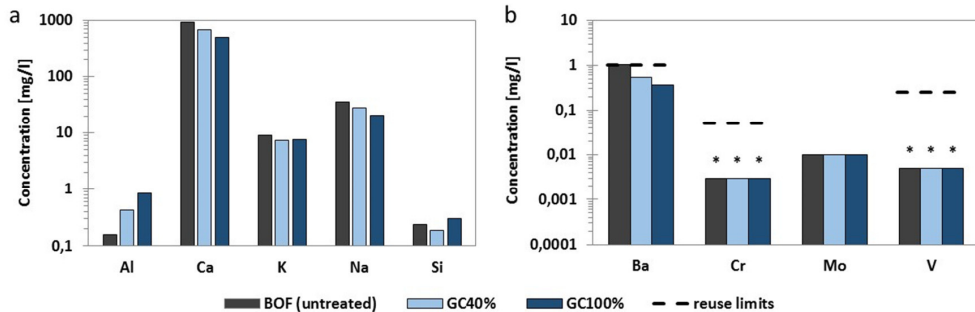


Fig. 4 Results of the leaching test (EN 12457-2) for the as received slag and for the granules obtained after the granulation-carbonation tests performed at lab scale. The starred bars indicate that the concentrations resulted below the instrumental quantification limit.

The product obtained after the granulation-carbonation process performed in the pilot scale rotary drum reactor was analyzed in terms of its particle size distribution, CO₂ uptake and environmental behavior.

Fig. 5 shows the particle size distribution curves of the product obtained as a result of the tests carried out in the rotary drum reactor, compared with those of the as received BOF slag samples. The results of the tests performed at ambient temperature are reported in tones of green, while those related to experiments carried out at 50 °C in tones of orange. As can be noted, for a lower operating temperature, a more significant increase in particle size was obtained compared to the tests performed at higher temperature, for both of the tested slag samples. In particular, the average diameter of the material obtained at ambient temperature was 1 mm, twice the average diameter of the untreated material; the average diameter of test E5_50°C_BOF1 did not increase, whereas it was equal to 0.8 mm for tests E6_50°C_BOF2 and E7_50°C_BOF2. This result is probably due to the higher evaporation of water occurring during the tests conducted at T=50 °C compared to that resulting at a lower temperature. Particle granulation is in fact known to be very sensitive to the L/S. Finally, it should be noted that the product obtained in the pilot-scale tests was significantly finer than that obtained in the experimental tests carried out at laboratory scale under similar conditions (see Fig. 3a). This difference is probably to be ascribed to the rotary drum reactor configuration, in which the presence of baffles along the longitudinal axis (see Fig. 1b) may have hindered particle aggregation or even caused breakage phenomena.

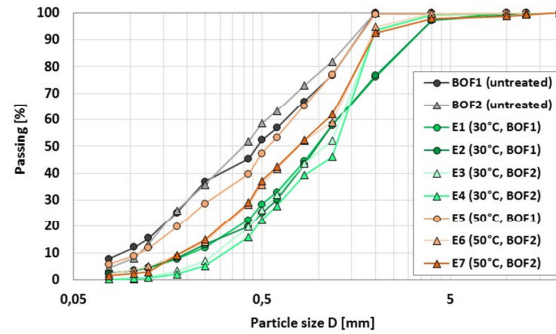


Fig. 5 Particle size distribution of the as received BOF1 and BOF2 slag and the granules obtained from the granulation-carbonation pilot-scale tests.

Fig. 6 shows the CO₂ uptake values obtained both immediately at the end of the treatment and after 28 days of curing. It can be observed that temperature did not appear to significantly affect the CO₂ uptake, in particular immediately after the treatment. The CO₂ uptakes measured immediately at the end of the tests carried out on the BOF1 and BOF2 slag were similar, varying between 4.4% and 6%. After the curing period, for the BOF1 slag, a twofold increase compared to the values measured immediately after the treatment was obtained, the same behavior found in the lab-scale tests carried out in dynamic conditions. This effect was not observed instead for the BOF2 slag. We can tentatively try to explain this behavior with a difference in the mineralogy of the samples, BOF1 containing phases that react readily during carbonation, but also others that hydrate and progressively carbonate during curing, even under atmospheric CO₂ concentration, opposed to BOF2 characterized mostly by phases that react only during carbonation. Further testing by XRD analysis will be carried out in order to elucidate this interesting finding. The maximum value of CO₂ uptake achieved after curing was equal to 10.4% and 7%, for E5_50°C_BOF1 and E3_30°C_BOF2 tests, respectively.

The CO₂ uptake obtained in the tests carried out in the pilot-scale reactor was about twice the one obtained in the static and dynamic tests carried out in laboratory scale. The difference respect to the results obtained in dynamic conditions in laboratory scale may be linked to the increased specific surface area (lower particle size) of the granules exposed to the CO₂ flow. The difference obtained with respect to the results obtained under static conditions at laboratory scale may instead be explained by a better contact between the treated material and CO₂ due to the dynamic conditions established in the rotary drum reactor.

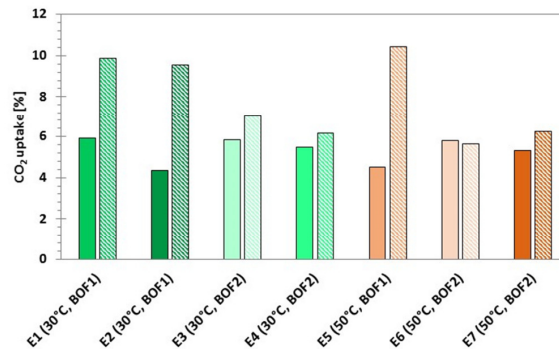


Fig. 6 CO₂ uptake (%) of the granules obtained from the granulation-carbonation tests carried out in the rotary drum reactor, immediately at the end of the test (t=0 d) and after 28 d of curing (t=28 d). The bars with the dotted filling indicate t=28 d.

The results of the UNI EN 12457-2 compliance test carried out on the slag obtained as a result of the tests conducted in the pilot-scale rotary drum reactor are shown in Fig. 7. Firstly, a decrease in pH respect to the as received slag, with values below the limit established for reuse only for E2_30°C_BOF1 and E5_50°C_BOF1, can be noted. As regards the effects of the treatment on the eluate concentrations of major elements (see Fig. 7a), an increase in Al and Si release was observed especially from the treated BOF 1 slag. Also Ca release appeared to decrease significantly only from the treated BOF1 granules, in accordance with the lower pH and higher CO₂ uptakes obtained after curing. Concerning the release of trace elements (see Fig. 7b), a marked reduction of Ba was obtained for both BOF1 and BOF2 samples. Cr leaching instead showed an up to three orders of magnitude increase for the treated BOF1 samples compared to the as received slag, exceeding the limit established for reuse. Even the leaching of Mo and V showed to increase, especially for the products of experiments carried out with BOF1 slag that showed a higher reactivity with CO₂.

The leachate of the BOF2 material treated in the rotary drum reactor was also analyzed by ion chromatography in order to determine concentrations of anions such as fluorides (F⁻), chlorides (Cl⁻) and sulfates (SO₄²⁻). The results obtained showed that the treatment resulted in a slight increase in sulfates (from 20 to over 35 mg/l), while the chloride concentration was quite constant (around 60 mg/l). The fluoride concentration was found to be below the instrumental quantification limit for all the tested samples. The measured concentrations of the analyzed anions proved anyhow well below the limits for reuse [13] before and after treatment.

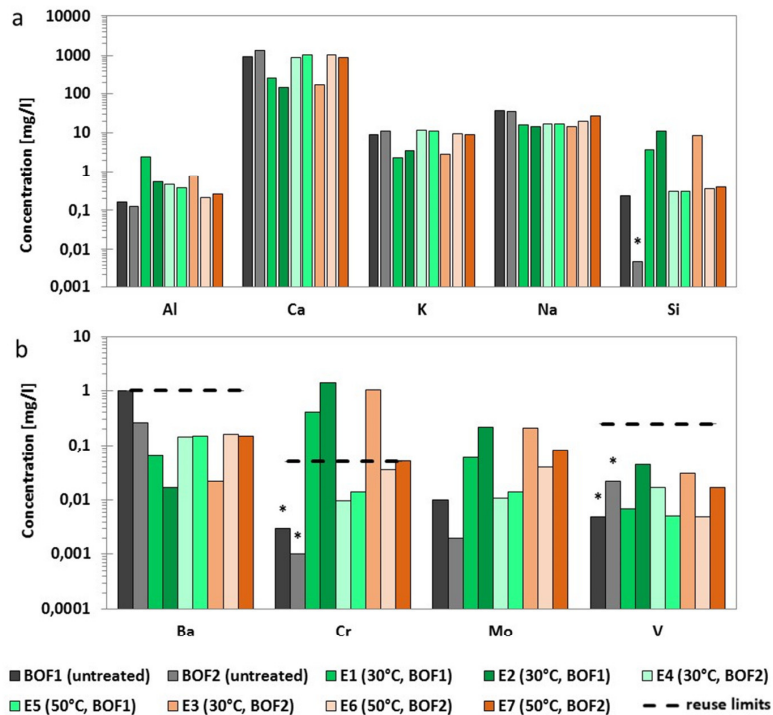


Fig. 7 Results of the leaching test (EN 12457-2) for the as received slag and for the granules obtained after the granulation-carbonation tests in the pilot-scale reactor. The starred bars indicate the concentrations resulting below the instrumental quantification limit.

4. Conclusions

The move from lab to pilot-scale testing may pose problems of reproducibility, since the operating conditions in pilot plant units are subject to a certain variability. Furthermore, due to a higher use of material, variations in residue composition may be more relevant and lead to very different results even in tests carried out under comparable operating conditions. In our study we found the above mentioned general considerations to hold true, but also that the differences in the results can be mostly explained also on the basis of findings of lab-scale work.

The results obtained in the pilot-scale carbonation tests showed that the treatment, especially after curing of the product, is effective for storing CO₂ employing BOF slag, with uptake values even higher than the ones obtained so far for the same type of residues in lab-scale tests. This is promising in view of the possible upscaling of the process to industrial applications. Nevertheless, in view of obtaining a product with valorization potential, such as aggregates for construction applications, a larger and more homogeneous particle size distribution should be achieved, possibly by employing a reactor with operating conditions (rotation speed, tilt) and internal configuration optimized to promote granulation. Finally, another critical aspect that must be addressed is that for increasing CO₂ uptakes, while pH and Ba leaching decrease, which may enhance the reuse potential of the product, a mobilization of Cr, Mo and V occurs.

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This work was financially supported by the Italian Ministry of Economic Development within the National Program on Electric System Research. The authors wish to express their gratitude and appreciation to Cassani S., Pagliari L. and Nobili M. from ENEA for sharing their expertise in running the experimental plant.

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