

# **Granulation-carbonation treatment of alkali activated steel slag for secondary aggregates production**

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## **Abstract**

In view of the EU's circular economy strategy, there is a need to develop treatments that may allow to improve the management of industrial residues such as steel manufacturing slag, for example by producing secondary products that may be used for different applications. This work evaluates the performance of a combined carbonation and granulation treatment applied to Basic Oxygen Furnace (BOF) steel slag with the aim of producing secondary aggregates and of storing CO<sub>2</sub> in a solid and stable form. In order to improve the mechanical properties of the product, a solution of sodium silicate and sodium hydroxide was tested as binder instead of water in both the granulation and combined granulation-carbonation tests. The results showed that the granules produced using the alkali activator with or without CO<sub>2</sub> addition, presented a mean size ranging from 1 to 5 mm and adequate mechanical properties for use in civil engineering applications. The maximum CO<sub>2</sub> uptake attained was of 4% wt. for the alkali activated and carbonated granules after 60 min of treatment and 7 days curing. As for the leaching behaviour of the produced granules, an increase in the release of Cr and V was found for the product of the granulation-carbonation treatment with alkali activation. Instead, granulation with alkali activation or granulation with carbonation showed to decrease the release of Ba and Cr with regard to the untreated residues.

*Keywords:* steel slag; granulation; carbonation; alkali activation; CO<sub>2</sub> storage; leaching behaviour

## **1 Introduction**

Manufacturing processes, such as steel production, are typically characterized by the generation of large amounts of solid residues, the recycling or reuse of which is not always feasible, due to the variability of the material's characteristics, the lack of a suitable national legislation on industrial by-product management, or the scarce availability of low-cost technologies for producing valuable secondary products. As a result, despite a growing awareness on the environmental impacts related to final disposal, for a relevant fraction of these residues no well-established management strategies apart from landfilling are currently applied.

Specifically, among the residues produced during steel manufacturing, Basic Oxygen Furnace (BOF) slag, a by-product of the conversion of iron into steel in BOF units, is the most abundant, amounting to 46% of the total European steel slag production in 2012[1]. BOF slag is typically ground for metal recovery at the steel plant and limitedly reused for low-end applications. However, a significant part of it, approximately 25% at a EU level but considerably more for Countries such as Italy, is landfilled [2]. These management practices need to be considerably improved in view of the EU's ambitious circular economy strategy, which includes the introduction of a binding landfill target to limit final disposal to a maximum of 10% of all waste by 2030 [3]. Several studies have focused on the possibility of using BOF slag as a replacement of natural aggregates in construction applications [4-6]; yet, some of BOF slag's characteristics constrain its potential use. In fact, in order to be employed in construction, secondary aggregates should exhibit a specific grain size distribution, a low free lime content (preferably below 4% [7]), and adequate mechanical strength. Due to the fact that BOF slag is ground at the plant for metal recovery, it generally presents an inadequate particle size and mechanical strength for use as aggregate. In addition, many EU Countries have established specific limits for the reuse of waste materials regarding the release of potential contaminants such as metals, metalloids or salts. In particular, in Italy, these limits have been issued by Ministerial Decree 186 (2006) [8]. Steel manufacturing slag generally presents a limited release of regulated elements; nevertheless, non negligible leaching of elements such as, such as Ba, Cr, V and Mo has been reported [9]. Furthermore according to Italian reuse criteria, the pH of the eluate of the waste material resulting from the leaching test should be lower than 12; this is typically not the case for alkaline industrial residues such as steelmaking slag [10]. The significant improvement of the technical (specifically grain size and mechanical strength) and environmental behaviour (leaching of metals and metalloids and pH) of BOF slag is hence the key to achieve its further valorisation as an aggregate in civil engineering applications.

Granulation is one of the most adopted particle size enlargement techniques. This process, generally applied in wet or dry mode [11], has numerous applications in several industrial sectors. Wet granulation is accomplished by contacting a mixture of a dry powder and a liquid binder in a dynamic

device, such as a disc granulator or a rotating drum [11-12]. The key parameters affecting the process are specific properties of the solid material (e.g. initial particle size distribution), of the liquid binder (i.e.: amount and viscosity) and of the equipment used (e.g. rotating speed and geometry) [13-14]. Several studies have started to focus on the application of disc granulation to waste materials, such as fly and bottom ash from waste incineration and contaminated soils, with the aim of producing aggregates to be used as filling material or for concrete manufacturing [15-18]. For these applications, binders such as lime or cement [18], as well as chemical additives, such as super-plasticizers [17], are typically added in order to improve the mechanical characteristics of the final product. It should be considered however, that these binders, cement in particular, typically present a high cost and significant CO<sub>2</sub> emissions associated to their production, hence their use for these types of applications may be considered questionable from both an environmental and economic point of view.

As for other types of treatments that may be applied to improve the technical and environmental properties of industrial by-products such as steel slag, several studies have indicated that accelerated carbonation may be effective for improving the environmental properties of alkaline residues [19], as well as their mechanical characteristics by increasing their density [20]. In addition, carbonation, which (see Eq. 1) involves the reaction of carbon dioxide in gaseous form with oxides of alkaline earth metals or metals (Me, i.e. Ca, Mg and Fe) contained in a mineral or alkaline residue, leads to the formation of the respective carbonate phase (MeCO<sub>3</sub>), permanently storing the reacted CO<sub>2</sub> in solid form [21-22]. This process is hence being investigated in the framework of Carbon dioxide Capture and Storage (CCS) techniques to reduce the emissions of this greenhouse gas from point-sources, such as fossil fuel-fired power plants, or cement or steel manufacturing plants [23].



Accelerated carbonation for CO<sub>2</sub> storage has been investigated using different process routes. The thin film route, which is performed wetting the residues employing liquid to solid ratios (L/S) between 0.1 and 0.5 l/kg, has been tested at mild operating conditions (30-50 °C and 1-10 bar CO<sub>2</sub>) as a CO<sub>2</sub> storage technique, but also to improve the leaching behaviour and mechanical properties of a wide range of residues [24], including stainless steel manufacturing slag [9, 25-27] and BOF slag [28].

Following the process proposed by [29], in a previous study our research group tested the combination of carbonation with wet granulation using water as binder with the aim of treating a BOF steel slag sample in order to produce aggregates to use in construction. The residues, initially presenting a fine particle size ( $d_{50}=0.4$  mm), showed to granulate readily and already after 30 min of reaction, coarse aggregates ( $d_{50}=4$  mm) and significant  $\text{CO}_2$  uptakes (120-144  $\text{gCO}_2/\text{kg}$ ) were attained [30]. In addition, the pH and Ba concentrations measured in the leachates of the uncrushed granules showed a noteworthy decrease compared to those resulting from the untreated slag, while conversely a slight increase of V leaching was obtained [30]. However, the mechanical strength of the granules, investigated applying the Aggregate Crushing Value (ACV) test [31], appeared to be quite poor and inadequate for meeting the requirements for use in civil engineering applications.

As for treatments that are effective in increasing the mechanical performance of a material, alkali activation has been widely investigated for those presenting high Ca and Si (or Al and Si) contents, such as blast furnace slag or pulverized coal fly ash [32]. In this process, the raw material, usually amorphous and/or metastable, is mixed with a solution containing sodium or potassium hydroxides, carbonates and/or silicates, in order to favour the dissolution of the reacting species so to enhance hydration reactions leading to the formation of a compact and strong product [33-34]. Recent studies tested the application of alkali activation also on dicalcium silicate [35] and crystalline non-hydraulic steel manufacturing residues (i.e. continuous casting slag and argon oxygen decarburisation slag) [36]. In particular, the work of Salman et al. showed that treating slag by alkali activation coupled with an initial period of steam curing at high temperature allowed to achieve a dense and strong solid, consisting of a calcium silicate hydrate matrix [36].

The objective of this study was to assess the performance of a combined carbonation and granulation treatment applied to Basic Oxygen Furnace (BOF) steel slag with the aim of producing secondary aggregates and of storing  $\text{CO}_2$  in a solid and stable form. In order to improve the mechanical properties of the product, the combination with alkali activation was also tested in both the granulation and combined granulation-carbonation tests. On the basis of the results of tests performed on BOF slag pastes and mortars employing different alkali activators [37], a sodium hydroxide (NaOH) and sodium

silicate ( $\text{Na}_2\text{SiO}_3$ ) solution was selected for the alkali activation experiments. The effects of the treatments were assessed in terms of the particle size distribution,  $\text{CO}_2$  uptake, mechanical strength (as ACV) and leaching behaviour at native pH of the produced granules. In addition, the reactivity of the BOF slag sample towards  $\text{CO}_2$  was investigated performing preliminary batch wet carbonation tests applying different operating conditions. Furthermore, key operating parameters such as the reaction time and the amount of liquid agent used were varied and tested for the combined process in order to investigate their effect on the final properties of the granules and assess the conditions that may allow to achieve the best technical and environmental performance.

## 2 Materials and methods

### 2.1 Materials

The slag sample employed in this study was collected just downstream of two different Basic Oxygen Furnaces (BOF) units of an integrated cycle steelmaking plant. The material was crushed and subjected to magnetic separation for iron and steel recovery at the plant. The particle size of the untreated material (around 20 kg) resulted lower than 1 mm, with a mean diameter equal to 0.2 mm.

The elemental composition of the BOF slag was determined by alkaline fusion of the dried sample with lithium metaborate ( $\text{LiBO}_2$ ) in platinum melting pots at 1050 °C for 1 h, followed by dissolution of the molten material with a 4%  $\text{HNO}_3$  solution and subsequent ICP-OES analysis of the obtained solution, employing an Agilent 710-ES spectrometer. This analysis was carried out in triplicate. The results, reported in Table 1, showed that Ca and Fe were the main constituents, with concentrations equal to 268 g/kg and 223 g/kg, respectively, followed by Mg (43 g/kg), Mn (31.3 g/kg) and Si (16 g/kg). As for trace constituents, similarly to what reported for other types of steelmaking slags, noteworthy concentrations of Cr (0.73 g/kg), Ba (0.7 g/kg) and V (0.47 g/kg) were retrieved. The mineralogy of the slag resulted very similar to that of samples analysed in a previous work, which were collected just downstream of the BOF units of the same plant (termed in that work as BOF1) [28]. The main phases detected were silicates, i.e. larnite ( $\text{Ca}_2\text{SiO}_4$ ) and hatrurite ( $\text{Ca}_3\text{SiO}_5$ ), and oxides, such as (MgO), tricalcium (hatrurite) and dicalcium (larnite) silicate, a mixed Ca–Al–Fe oxide ( $\text{Ca}_2\text{Fe}_{1.4}\text{Al}_{0.6}\text{O}_5$ ), a mixed Ca–Cr–Fe oxide ( $\text{Ca}_2\text{Cr}_{0.5}\text{Fe}_{1.5}\text{O}_5$ ), wüstite (FeO) and magnetite ( $\text{Fe}_2\text{O}_3$ ).

The activating solution used in this study was a 50:50 by weight mixture of a 2 M sodium hydroxide (NaOH) solution, prepared by dissolving NaOH pellets (Fisher Scientific, 99.4% purity) in deionized water, and a commercial sodium silicate solution in water (Sigma-Aldrich), the concentration of silicates of which, evaluated by ICP-OES analysis, resulted equal to 36%.

## 2.2 *Methods*

### 2.2.1 **Granulation and granulation-carbonation experiments**

Both the granulation and granulation-carbonation experiments were carried out in a lab scale disc granulator reactor presenting 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 [30].

In both types of tests, a sample of air-dried slag (approximately 500 g) was premixed in a plastic bag with either deionized water or the alkaline solution, at set liquid to solid ratios, following the procedure adopted in many previous studies on granulation [38-39]; then the mixture was inserted into the granulator and left to react for a set time. For the granulation-carbonation treatment a 100% CO<sub>2</sub> flow was maintained in the reactor for the entire duration of the experiment, placing a custom made Perspex lid equipped with a CO<sub>2</sub> feeding system over the reactor [30].

Table 2 reports a general overview of the performed experiments and of the operating conditions applied. Each test is identified with a code that is used to present and discuss the results in the next section. As it may be observed, the duration of the granulation tests was of 30 min, while for the combined granulation-carbonation tests also a reaction time of 60 min was adopted. The water to slag ratio (W/S) employed in most experiments was of 0.12 l/kg, which was experimentally proven to be the optimal value for granulating the analysed BOF slag sample; for the granulation-carbonation tests carried out on alkali activated slag a higher W/S (0.14 l/kg) was also tested. The ratios of alkali activation solution to slag (AA/S) employed were 0.16 l/kg (baseline condition) or 0.18 l/kg (for the 0.14 l/kg W/S). The product of each test was cured in a controlled environment (room temperature and 100% relative humidity) for 28 d in order to allow the completion of hydration reactions. Given the relatively large amount of slag treated in each test (500 g), not all experiments were carried out in

duplicate. However, the products resulting from duplicate tests carried out under the same operating conditions (e.g. GC60'\_AA\_W/S=0.14) presented quite similar properties in terms of particle size and CO<sub>2</sub> uptake, indicating a fair reproducibility of the experimental procedure adopted.

### **2.2.2 Batch carbonation experiments**

Batch accelerated carbonation tests were performed employing 100% CO<sub>2</sub> on the as-received BOF slag sample at mild operating conditions (T=20 °C, p=1 bar, L/S=0.3 l/kg), close to those applied in the granulation tests, in order to evaluate possible changes in the CO<sub>2</sub> uptake resulting from the different reaction mode adopted (batch or granulation-carbonation). In addition, carbonation tests were also performed applying the same operating conditions reported above but using the alkali solution tested in the granulation-carbonation experiments to wet the samples, in order to assess if the alkali solution employed in the granulation-carbonation tests may exert an effect on the CO<sub>2</sub> uptake of the residues.

Moreover, batch carbonation tests were carried out on the as received slag and on a milled sample (d< 0.125 mm), at enhanced operating conditions (T=50 °C, p=10 bar, L/S=0.3 l/kg). These specific conditions were selected since in previous works carried out on steelmaking slag they allowed to achieve significant CO<sub>2</sub> uptakes applying the wet carbonation route [25-26,28]. In this case, the aim of the test was to assess the maximum reactivity of this residue towards CO<sub>2</sub>, in order to compare it with those obtained in previous works and with the value obtained from the granulation-carbonation tests. In each test, 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 slag samples were mixed with water at the set L/S and exposed to a 100% CO<sub>2</sub> flow for different reaction times, ranging from 0.5 to 8 h. The humidity of the gas was maintained at 75% using a saturated NaCl solution in the reactor. Considering that for each set of operating conditions multiple reaction times were tested and that the results showed to be quite consistent, in agreement also with previous findings [26-29], one test was performed for each reaction time.



### 2.2.3 Characterization of treatment products

The particle size distribution, CO<sub>2</sub> uptake, mechanical strength and environmental behaviour of the cured samples were then assessed and compared (where applicable) to the properties of the untreated slag.

Specifically, the particle size distribution was determined by applying the ASTM D422 standard procedure. The CO<sub>2</sub> 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 analyser equipped with a SSM-5000A solid sampler. The CO<sub>2</sub> uptake was then calculated by applying Eq. 2, in which CO<sub>2final</sub> and CO<sub>2 initial</sub> represent respectively the CO<sub>2</sub> content of the treated and as received sample derived by the results the IC analysis. In particular, the initial IC content of the slag resulted equal to 0.03%, which corresponds to an initial CO<sub>2</sub> concentration of 0.1%. The CO<sub>2</sub> uptake of the granules was assessed immediately after the test and also after 7 and 28 d of curing to evaluate the degree of carbonation occurring during the curing treatment (performed under atmospheric air at ambient temperature).

$$\text{CO}_2 \text{ uptake (\%)} = \frac{\text{CO}_2 \text{ final (\%)} - \text{CO}_2 \text{ initial (\%)}}{100 - \text{CO}_2 \text{ final (\%)}} 100 \quad (2)$$

The mechanical strength of the granules was evaluated by performing the Aggregate Crushing Value (ACV) test, following the British standard BS 812-110 [31]. This test gives a relative measure of the resistance of an aggregate to crushing under a gradually applied compressive load. The ACV is the ratio (expressed in %) between the amount of fines formed upon crushing and the total mass of the test specimen.

The leaching behaviour of the granules 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. In addition, the leaching behaviour of the granules obtained after each treatment was also assessed by applying the EN 12457-2 procedure without grinding, so to analyse the behaviour of the material under more similar conditions to the foreseen application scenario. Specifically, for each experiment, the leaching test was performed on a subsample of the product presenting a particle size distribution representative

of the overall one of the granules reported in Fig. 1. The eluates obtained from each test were analyzed by ICP-OES analysis, employing an Agilent 710-ES spectrometer. Leaching tests were carried out in duplicate.

### **3 Results**

#### *3.1 Particle size distribution*

The particle size distribution (PSD) of the granules produced applying the different types of treatments is reported in Figure 1, together with that of the untreated BOF slag. As can be observed, the granules produced by granulation with water (G\_W) or the sodium silicate solution (G\_AA) presented a similar PSD with a mean diameter of 10 and 13 mm respectively, over 50 times greater than that of the untreated slag.

In accordance to the findings of our previous study on granulation-carbonation of BOF slag [30], the aggregates produced from the combined treatment applied using water (GC\_W) or the alkali activator (GC\_AA) as binder presented a smaller particle size compared to those resulting from granulation carried out under atmospheric air; this effect may be probably ascribed to the different conditions established in the reactor (e.g. temperature and relative humidity) under a continuous flux of CO<sub>2</sub>.

However, an increase in the reaction time from 30 to 60 minutes resulted in a decrease of the mean diameter of the water-based granules, passing from 3 to 2 mm, differently from what found in our previous work [30]. This slight decrease in mean particle size may be tentatively ascribed to a breakage phenomenon occurring during the granulation process as a result of friction between particles [40]. In the combined granulation-carbonation tests, mixing the slag with the activator produced smaller granules, with a mean diameter slightly above 1 mm. This behaviour is consistent with the results of a previous study [38] that indicated that a more viscous binder generally produces stronger granules that tend to deform less during the granulation process leading to a reduction of the consolidation rate and subsequently of their growth. For this type of test the W/S appeared to exert a stronger influence than reaction time. In particular, increasing the W/S value from 0.12 to 0.14 l/kg led to a maximum final mean diameter around four times higher than the one obtained at a lower liquid

content. For the W/S of 0.14 l/kg, a slight decrease of the mean diameter of the granules occurred for a reaction time of 60 min, in accordance to the results of the granulation-carbonation tests carried out with water, suggesting also in this case that breakage may occur during the treatment for prolonged reaction times.

### 3.2 *CO<sub>2</sub> uptake*

The CO<sub>2</sub> uptake obtained as a result of the different types of tested treatments is reported in Figure 2. It can be observed that regardless of the type of binder used the CO<sub>2</sub> uptake of the granules achieved after the granulation treatment was very low. The average CO<sub>2</sub> uptake of the granules produced by the combined granulation-carbonation treatment was significantly higher, with values equal to almost 2.3% and 3% for the granules containing water (GC\_W) and the alkali activator (GC\_AA), respectively. The CO<sub>2</sub> uptake of both types of tests showed to increase for a 60 min reaction time,. As for the influence of the W/S, for the tests carried out with the higher value (0.14 l/kg) a lower CO<sub>2</sub> uptake (especially for the 30 min test) was obtained.

To assess if there could be a possible effect of curing on the CO<sub>2</sub> sequestration yield of the material, the CO<sub>2</sub> uptake of the granules obtained from each of the performed tests after 7 and 28 days of curing was also analyzed and the results are reported in Figure 3. As can be noted, for all of the samples obtained after a treatment time of 30 min, including those from granulation tests carried out under atmospheric air (G\_W and \_AA), the CO<sub>2</sub> uptake showed to slightly increase after 7 days. For higher curing times instead, the CO<sub>2</sub> uptake showed not to increase. These results suggest that the BOF slag phases that can be carbonated under ambient conditions react completely either after a carbonation-granulation time of 60 min or after 30 min and a few days of curing at ambient conditions.

It should be noted that the BOF slag employed in this study presented a significantly lower CO<sub>2</sub> uptake at the operating conditions of the granulation reactor compared to that exhibited by the slag sampled from the same plant and tested in our previous work on granulation-carbonation [30]. The differences in the degree of reactivity with CO<sub>2</sub> were attributed to the different mineralogy of the two types of slag; as previously mentioned, the ones analyzed in this work were characterized by a

prevalence of Ca silicate-based phases, while the others presented a relevant content of portlandite, that is well known to present a high reactivity with CO<sub>2</sub> also at mild operating conditions.

In order to compare the CO<sub>2</sub> uptakes achieved for the BOF slag analyzed in this study with those reported previously for steel slag samples carbonated applying the wet route, batch carbonation tests were also carried out. The main results of these tests, reported in Figure 4, revealed low differences in the carbonation yield attained at mild and enhanced operating conditions for the as received slag (i.e. not milled). Grain size instead appeared to significantly affect the slag's reactivity with CO<sub>2</sub>, in agreement with findings reported in a previous work on stainless steel slag carbonation [41]. Indeed, the carbonation test carried out at enhanced conditions on the milled slag allowed to achieve a maximum uptake of almost 15% already after 2 hours of reaction, comparable to that reported for a similar type of BOF slag, milled below 0.15 mm [28]. In addition, it is interesting to observe, see Figure 4a, that the results of carbonation tests carried out at ambient conditions on milled slag using the alkaline solution as a wetting agent were similar to the ones obtained for the samples treated under the same conditions without the alkaline additives; however, the values obtained at low treatment times (up to 60 min) were slightly higher, in agreement with the results of granulation-carbonation tests. Comparing the results of the batch tests with those of granulation-carbonation, it can be noted that for the same operating conditions, the CO<sub>2</sub> uptake in the latter tests was almost double than that achieved in the former ones (around 3% compared to 1.5%). This is noteworthy, considering that in the granulation-carbonation tests a considerable amount of material ( $\approx 500$  g) was tested compared to the 1 g-BOF samples treated in the batch reactor. This difference may be due to the fact that the granulation-carbonation tests were carried out in a dynamic device, which may improve the kinetics of CO<sub>2</sub> diffusion and carbonation reactions, with respect to static conditions.

### ***3.3 Mechanical strength***

The results in terms of the ACV of the produced granules are shown in Figure 5, in which the average values typically reported for mixed gravel and blast furnace slag [31] are also indicated. The mechanical resistance of the granules showed to be affected both by the type of binder used and by

carbonation. Namely, the granulation treatment with alkali activation allowed to enhance the strength of the obtained granules, leading to an ACV value of 15%, considerably lower than the one obtained using only water as binder (around 45%) and also below the one for mixed gravel. Instead, for the granules resulting from the combined granulation-carbonation treatment with a W/S of 0.12 l/kg, the ACV remained above 35% even for the alkali activated slag, indicating a rather poor mechanical performance. However, an increase in the amount of alkali binder showed to significantly improve the resistance of the granules; in fact, the granules obtained from test GC\_AA\_W/S=0.14 were characterized by an ACV about half the value achieved using a W/S of 0.12 l/kg. It is also interesting to note that an increase of the reaction time showed to reduce the granules strength for both of the W/S tested for alkali activated slag and also for the tests carried out with water. The lower strength of the granules obtained at 60 minutes reaction time may explain their lower particle size compared to those obtained at 30 minutes, as they were more amenable to breakage due to friction. Hence, on the basis of the results achieved, also in comparison to the values reported for mixed gravel or blast furnace slag, it may be inferred that the granules produced with granulation and alkali activation, or granulation-carbonation and alkali activation at a W/S of 0.14 l/kg, exhibited adequate strength for use as aggregates for treatment times of 30 min.

### ***3.4 Leaching behaviour***

Table 3 reports the results of the leaching test performed according to the standardized EN 12457-2 leaching test (which foresees the crushing of material with a particle size > 4 mm) on the products attained from the different treatments tested in comparison to those of the untreated slag. Specifically, the table exhibits the pH values and eluate concentrations of major constituents (Al, Ca, Na and Si) and regulated elements that proved higher than instrumental quantification limits (Ba, Cr, V and Zn) along with the Italian limits for waste reuse [7]. For the granulation-carbonation with alkali activation treatment, based on the ACV results, it was decided to analyze the leaching behaviour of the granules obtained from the test carried out at a W/S of 0.14 l/kg, which appeared to be the most suitable for construction applications; in addition, to analyze the effect of the duration of the treatment, the product

obtained for the same conditions after 60 min (GC60'\_AA\_W/S=0.14) was also analyzed. As shown in Table 3, the untreated material was characterized by an alkaline pH (13.1), which exceeded the upper Italian limit for reuse, and limited leaching of regulated elements, which showed to comply with reuse requirements. The product of the granulation treatment carried out with water (G\_W) presented a similar leaching behaviour to the untreated slag. Instead, for the granules obtained from the test performed with the alkali solution (G\_AA), the pH slightly decreased (remaining above the Italian limit for reuse), Ca, Ba, and Cr release decreased, while Si and Na leaching increased. The higher concentration of Na was obviously due to the addition of the Na hydroxide/silicate solution, while the effects on both major and trace constituents' release may be related to the hydration reactions occurring in the material. As for the effects of carbonation, the treatment without alkali activation (GC\_W) appeared to exert a similar effect on pH, Ca, Ba and Cr release compared to G\_AA, although a higher mobilization of Al and Si was observed. The coupling of granulation-carbonation with alkali activation appeared to affect even greatly the leaching behaviour of the BOF slag. In particular, the effects noted for test GC\_W on major element release (i.e. Ca decrease and Si increase) were even more pronounced; regarding regulated elements, Ba release further decreased, while instead Cr and V leaching increased, exceeding the reuse limit values for the 60 min treatment.

As mentioned in section 2.2.3, the same type of leaching test was applied also to the uncrushed granules obtained after all of the tested treatments in order to evaluate the behaviour of the product at its final particle size (since this parameter is known to significantly affect leaching) and also to verify if, as indicated by the results of our previous study on granulation-carbonation, the effects of carbonation are more appreciable for unground samples due to the formation of a calcite layer on the treatment product. The results of these tests are reported in Figure 6. In terms of pH values, see Figure 6a, results were quite comparable to those obtained from the standard EN 12457-2 test. The influence of the carbonation-granulation treatment on the pH values was not relevant, except for the test carried out for 60 min, for which the pH was lower than 12, i.e. over one unit lower than the untreated slag and complying with the threshold value set by the Italian legislation for waste reuse.

As for major element release, see Figure 6b, the release of Al showed to increase after all the treatments tested with respect to the untreated slag. Moreover, it can be observed that after the carbonation-granulation treatment, the release of aluminium showed to decrease for increasing reaction time, regardless the type of binder used. With regard to the leaching of Ca, the alkali-based carbonated granules were characterized by a one order of magnitude lower concentration than the granules mixed with water; besides, increasing the amount of the alkaline binder further reduced the concentration of calcium in the eluates. The concentration of Na was obviously affected by alkali activation with a more than two orders of magnitude increase compared to experiments carried out using only water as binder. The concentration of Si in the eluates of the granules obtained from the granulation treatment in the presence of the alkali activator resulted over one order of magnitude higher than that of the untreated slag and also notably higher than that of the granules obtained with water. In addition Si release further increased after granulation-carbonation treatment of alkali activated slag. Previous studies that analysed the effects of carbonation on the leaching behaviour of steel slag by geochemical modelling also found similar effects on Ca and Si leaching and indicated calcite, the reaction product, and amorphous  $\text{SiO}_2$ , resulting from calcium silicate dissolution, as solubility controlling phases for the carbonated slag [9, 10]. Anyhow, in this case, we cannot rule out solubility control by hydration phases (e.g.: CSH).

As for the effects of the applied treatments on the leaching of regulated elements, see Figure 6c, it may be noted that for Ba, the alkali activated granules obtained from both granulation and granulation-carbonation, displayed a more than one order of magnitude lower release than the corresponding granules obtained at the same conditions by mixing the material with water; this effect appeared to be more remarkable for a 60 min reaction time. As far as Cr is concerned, it can be observed that while granulation, granulation with alkali activation or granulation-carbonation showed to reduce its release compared to the untreated slag, the coupling of alkali activation with carbonation led to an increase in concentration above the limit for reuse (0.05 mg/l) for all of the tested conditions. A similar behaviour was observed also for the release of vanadium, with the exception of the granules obtained from test GC\_AA\_W/S=0.14. It is interesting to note that the leaching pattern resulting for V for all of the

different experimental tests was very similar to that found for Si. In a previous study on BOF slag carbonation V was shown to be incorporated in Ca silicate phases such as larnite that react during carbonation leading to a significant increase in both Si and V release [42]. It is hence possible that also in this case V was bound to phases that react during the tested treatments, granulation-carbonation with alkali activation in particular.

### ***3.5 Assessment of the overall performance of the tested treatments for aggregate production***

The results of the different types of tests performed on BOF slag to produce secondary aggregates for use in construction applications are schematically reported in Figure 7. As can be noted, none of the treatment combinations investigated allowed to attain all of the 5 targeted conditions, related to requirements for use as aggregates (particle size, eluate pH, release of regulated elements and mechanical strength) and additional environmental benefits in terms of potential reductions of greenhouse gas emissions due to CO<sub>2</sub> storage. Specifically, while all of the tested treatments appeared to be effective in increasing the material's particle size, only the addition of alkali activation allowed to attain granules with a suitable mechanical strength. Carbonation proved necessary for achieving significant CO<sub>2</sub> uptakes and also for attaining a relevant reduction in eluate pH. Finally, the coupling of the three treatments appeared to exert positive effects for all of the analyzed properties of the product except for the leaching of regulated elements such as Cr and V.

However, considering only the requirements for use as secondary aggregates, the treatment that appears to be the most effective for the investigated BOF slag is granulation coupled with alkali activation, also considering that the requirement of eluate pH below 12 established by the Italian legislation may not be in force in other Countries.

## **4 Conclusions**

The main outcome of this work was that alkali activation proved to be an effective treatment for improving the mechanical properties of the granules obtained applying granulation or granulation-carbonation processes. In fact, differently from the tests performed using only water as binder, when a



Na hydroxide and silicate solution was employed, the ACV of the granules obtained at specific conditions was close to the one typically exhibited by natural aggregates such as gravel. Notably, the best performances were achieved for the granulation treatment and the combined granulation-carbonation process performed with a W/S of 0.14 l/kg for 30 min. The latter type of treatment allowed also to achieve a significant uptake of carbon dioxide, with a maximum value of 4% wt., achieved after 60 minutes and 7 days curing with the alkali activated slag at a W/S ratio of 0.12 l/kg. Moreover, the granules obtained from all of the tested treatments, and in particular granulation and granulation coupled with alkali activation, showed a remarkable increase in particle size with respect to the starting material. Finally, regarding the environmental behaviour of the produced granules, an increase in the release of Cr and V was observed for the product of the granulation-carbonation treatment with alkali activation. Instead, granulation with alkali activation or granulation with carbonation showed to decrease the release of Ba and Cr with regard to the untreated residues.

Hence, the results of these preliminary combined tests indicate the potential feasibility of applying the proposed treatments on BOF slag to obtain a product with enhanced mechanical properties. However, the amount and type of binder used, as well as treatment time appear to be critical parameters for the mechanical properties and also environmental behaviour of the product. Future studies will also need to assess the overall environmental, as well as economical, sustainability of these treatment processes for secondary aggregates production, since the production of chemical agents such as sodium hydroxide has non negligible environmental impacts. With this regard, it could be interesting to investigate the performance of alternative alkali activating reagents obtained from waste streams.

### **Acknowledgements**

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## References

1. Euroslag Statistics 2012. <http://www.euroslag.org/products/statistics/2012/>. Accessed in March 2015
2. Bohmer, S., Moser, G., Neubauer, C., Peltoniemi, M., Schachermayer, E., Tesar, M., Walter, B., Winter, B.: Aggregate case study, Final report (2008)
3. European Commission: Proposal for a Directive Of The European Parliament And Of The Council amending Directive 2008/98/EC on waste Brussels, 2.12.2015 COM (2015) 595 final 2015/0275 (COD) (2015)
4. Mahieux, P.Y., Aubert, J.E., Escadeillas, G.: Utilization of weathered Basic Oxygen Furnace slag in the production of hydraulic road binders. *Constr. Build. Mater.* 23, 742–747 (2009)
5. Shen, D.-H., Wu, C.-M., Du, J.-C.: Laboratory investigation of Basic Oxygen Furnace slag for substitution of aggregate in porous asphalt mixture. *Constr. Build. Mater.* 23, 453–461 (2009)
6. Herrmann, I., Andreas, L., Diener, S., Lind, L.: Steel slag used in landfill cover liners: laboratory and field tests. *Waste Manage. Res.* 28, 1114–1121 (2010)
7. Italian Ministerial Decree 186/2006: Regolamento recante modifiche al decreto ministeriale 5 febbraio 1998 Individuazione dei rifiuti non pericolosi sottoposti alle procedure semplificate di recupero, ai sensi degli articoli 31 e 33 del decreto legislativo 5 febbraio 1997, n. 22. *Gazzetta Ufficiale* 19 maggio 2006, n. 115 (in italian) (2006)
8. Wang, G., Wang, Y., Gao, Z.: Use of steel slag as a granular material: volume expansion prediction and usability criteria. *J. Hazard. Mater.* 184, 555–560 (2010)
9. Baciocchi, R., Costa, G., Polettini, A., Pomi, R.: Effects of thin-film accelerated carbonation on steel slag leaching. *J. Hazard. Mater.* 286, 369–378 (2015)

10. Huijgen, W.J., Comans, R.N.: Carbonation of steel slag for CO<sub>2</sub> sequestration: leaching of products and reaction mechanisms. *Environ. Sci. Technol.* 40, 2790–2796 (2006)
11. Litster, J., Ennis, B. :The science and engineering of granulation processes, Particle Technology Series, Kluwer Academic Publishers, Netherlands (2004)
12. Iveson, S.M., Litster, J.D., Hapgood, K., Ennis, B.J: Nucleation, growth and breakage phenomena in agitated wet granulation processes: a review. *Powder Technol.* 117, 3–39 (2001)
13. Adetayo, A.A., Litster, J.D., Desai, M.: The effect of process parameters on drum granulation of fertilizers with broad size distributors. *Chem. Eng. Sci.* 48, 3951–3961 (1993)
14. Tardos, G.I., Khan, M.I., Mort, P.R.: Critical parameters and limiting conditions in binder granulation of fine powders. *Powder Technol.*, 94, 245–258 (1997)
15. Medici, F., Piga, L., Rinaldi, G.: Behaviour of polyaminophenolic additives in the granulation of lime and fly-ash. *Waste Manage.* 20, 491–498 (2000)
16. Baykal, G., Döven, A.G.: Utilization of fly ash by pelletization process; theory, application areas and research results. *Resour., Conserv. Recy.*, 30 (1), 59–77 (2000)
17. Scanferla, P., Ferrari, G., Pellay, R., Volpi Ghirardini, A., Zanetto, G., Libralato, G.: An innovative stabilization/solidification treatment for contaminated soil remediation: demonstration project results. *J. Soils Sedim.*, 9, 229–236 (2009)
18. Cioffi, R., Colangelo, F., Montagnaro, F., Santoro, L: Manufacture of artificial aggregate using MSWI bottom ash. *Waste Manage.* 31, 281–288 (2011)
19. Bobicki, E.R., Liu, Q., Xu, Z., Zeng, H.: Carbon capture and storage using alkaline industrial wastes. *Prog. Energ. Combust.* 38, 302–320 (2012)
20. Lange, L.C., Hills, C.D., Poole, A.B.: The influence of mix parameters and binder choice on the carbonation of cement solidified wastes. *Waste Manage.* 16, 749–756 (1996).

21. Seifritz, W.: CO<sub>2</sub> disposal by means of silicates. *Nature* 345:486 (1990)
22. Lackner, K.S., Wendt, C.H., Butt, D., Joyce E.L. Jr., Sharp D.H.: Carbon dioxide disposal in carbonate minerals. *Energy* 20, 1153–1170 (1995)
23. Pan, S.Y., Chang, E.E., Chiang, P.C.: CO<sub>2</sub> capture by accelerated carbonation of alkaline wastes: a review on its principles and applications. *Aerosol Air Qual. Res.* 12, 770–791 (2012)
24. Baciocchi R, Costa G., Zingaretti D. Baciocchi R.: Accelerated carbonation processes for carbon dioxide capture, storage and utilization. In: Bhanage, B.M., Arai, M. (eds.) *Transformation and Utilization of Carbon Dioxide, Green Chemistry and Sustainable Technology*, pp. 263–299. (Berlin: Springer-Verlag, Berlin (2014).
25. Johnson, D.C., Macleod, C.L., Carey, P.J., Hills, C.D.: Solidification of stainless steel slag by accelerated carbonation. *Environ. Technol.* 24, 671–678 (2003)
26. Baciocchi, R., Costa, G., Di Bartolomeo, E., Poletini, A., Pomi, R.: Carbonation of stainless steel slag as a process for CO<sub>2</sub> storage and slag valorization. *Waste Biomass Valor.* 1, 467–477 (2010)
27. Santos, R.M., Van Bouwel, J., Vandeveld, E., Mertens, G., Elsen, J., Van Gerven, T.: Accelerated mineral carbonation of stainless steel slags for CO<sub>2</sub> storage and waste valorization: Effect of process parameters on geochemical properties. *Int. J. Greenh. Gas Con.* 17, 32–45 (2013)
28. Baciocchi, R., Costa, G., Di Gianfilippo, M., Poletini, A., Pomi, R., Stramazzo, A.: Thin-film versus slurry-phase carbonation of steel slag: CO<sub>2</sub> uptake and effects on mineralogy. *J. Hazard. Mater.* 283, 302–313 (2015).
29. Gunning, P.J., Hills, C.D., Carey, P.J.: Production of lightweight aggregate from industrial waste and carbon dioxide. *Waste Manage.* 29, 2722–2728 (2009)
30. Morone, M., Costa, G., Poletini, A., Pomi, R., Baciocchi, R.: Valorization of steel slag by a combined carbonation and granulation treatment. *Mineral. Eng.*, 59, 82–90 (2014)

31. British Standard 812 Testing aggregates – part 110: Methods for determination of aggregate crushing value (ACV). ISBN 0 580 18825 6 (1990).
32. Pacheco-Torgal, F., Castro-Gomes, J., Jalali, S.: Alkali-activated binders: a review. Part 2. About materials and binders manufacture. *Constr. Build. Mater.* 22, 1315–1322 (2008)
33. Song, S., Sohn, D., Jennings, H. M., Mason, T. O.: Hydration of alkali-activated ground granulated blast furnace slag. *J. Mater. Sci.*, 35, 249–257 (2000)
34. Rashad, Alaa M.: A comprehensive overview about the influence of different additives on the properties of alkali-activated slag—A guide for Civil Engineer. *Constr. Build. Mater.* 47, 29–55. (2013)
35. Kriskova, L., Pontikes, Y., Zhang, F., Cizer, Ö., Jones, P. T., Van Balen, K., Blanpain, B.: Influence of mechanical and chemical activation on the hydraulic properties of gamma dicalcium silicate. *Cement Concrete Res.*, 55, 59–68 (2014)
36. Salman, M., Cizer, Ö., Pontikes, Y., Vandewalle, L., Blanpain, B., Van Balen, K.: Effect of curing temperatures on the alkali activation of crystalline continuous casting stainless steel slag. *Constr. Build. Mater.* 71, 308–316 (2014)
37. Morone M., Cizer Ö., Costa G., Baciocchi R.: Alkali activation and CO<sub>2</sub> curing for BOF steel slag valorization. In preparation.
38. Iveson, S.M., Litster, J.D., Ennis, B.J. Fundamental studies of granule consolidation part 1: effects of bonder content and binder viscosity. *Powder Technol.* 88, 15–20 (1996)
39. Wauters, P.A.L., van de Water, R., Litster, J.D., Meesters, G.M.H., Scarlett, B.: Growth and compaction behaviour of copper concentrate granules in a rotating drum. *Powder Technol.* 124, 230–237 (2002)
40. Liu, L.X., Litster, J.D., Iveson, S.M., Ennis, B.J.: Coalescence of deformable granules in wet granulation processes. *AIChE J.* 46, 529–539 (2000)

41. Baciocchi, R., Costa, G., Poletini, A., Pomi, R.: Influence of particle size on the carbonation of stainless steel slag for CO<sub>2</sub> storage. *Energy Procedia* 1, 4859–4866 (2009)
42. van Zomeren, A., Van der Laan, S.R., Kobesen, H., Huijgen, W.J., Comans, R.N.: Changes in mineralogical and leaching properties of converter steel slag resulting from accelerated carbonation at low CO<sub>2</sub> pressure. *Waste Manage.* 31, 2236–2244 (2011)

## Figures

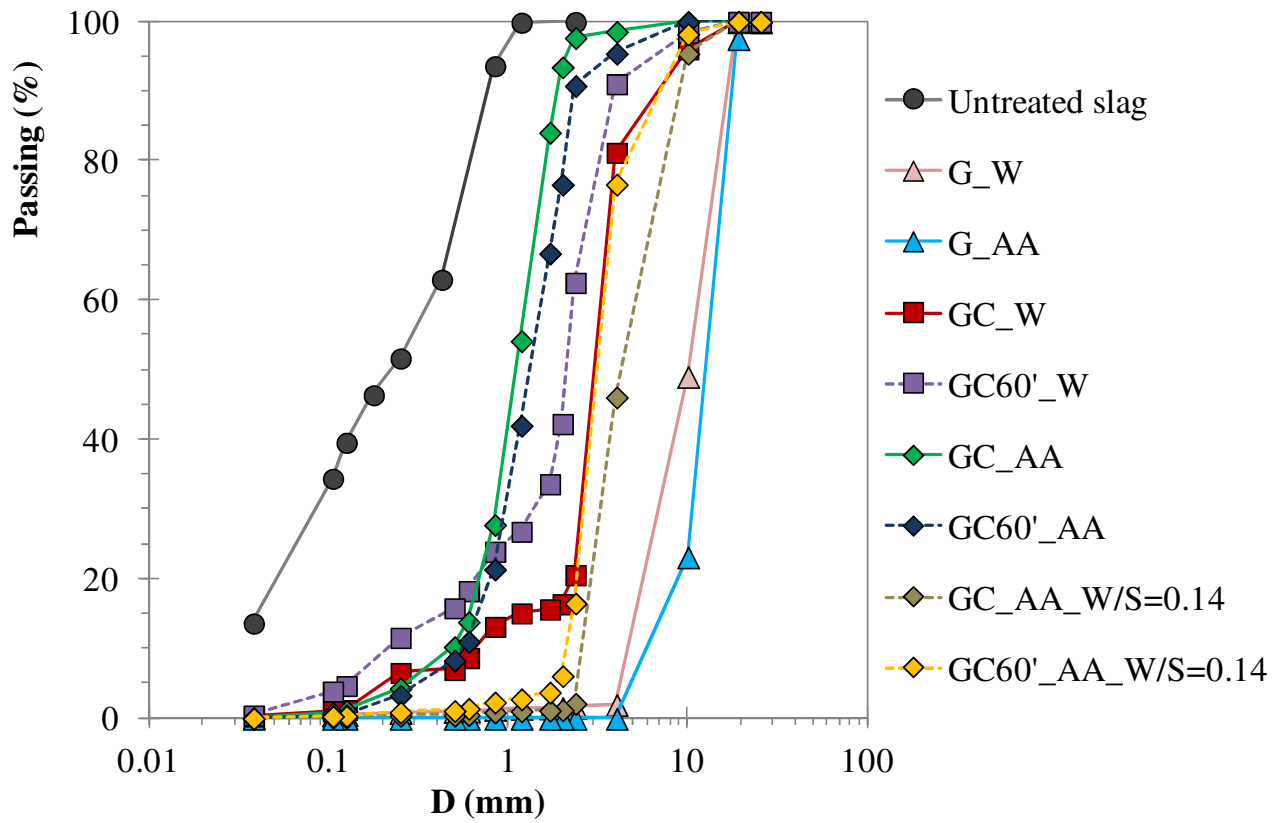


Figure 1. PSD of the untreated slag and of the granules obtained after the tested treatments (see Table 2 for the explanation of the experiment codes reported in the legend).

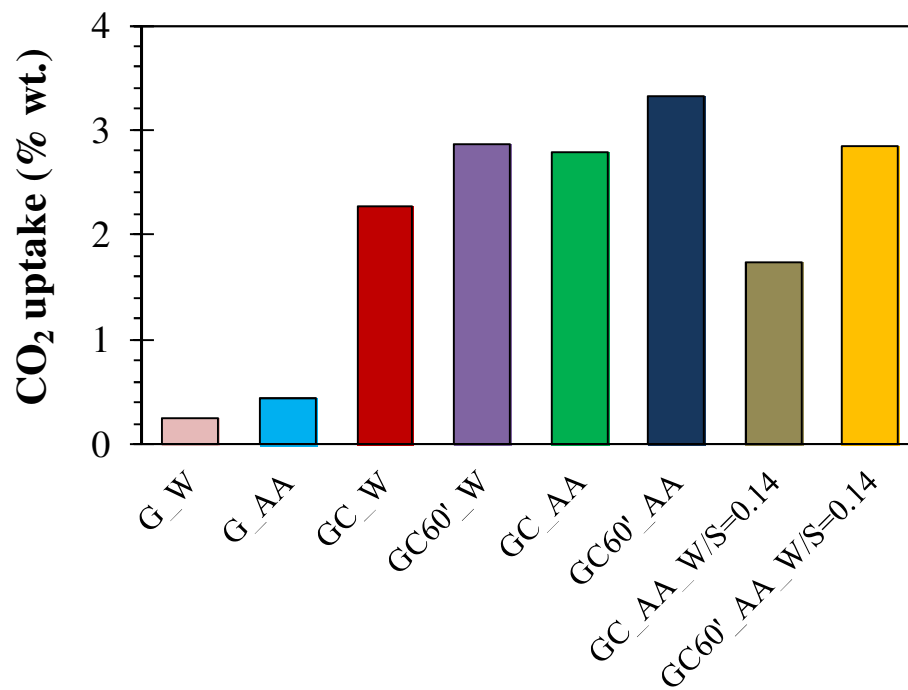


Figure 2. CO<sub>2</sub> uptake of the granules obtained after the tested treatments (see Table 2 for the explanation of the experiment codes reported on the x-axis).



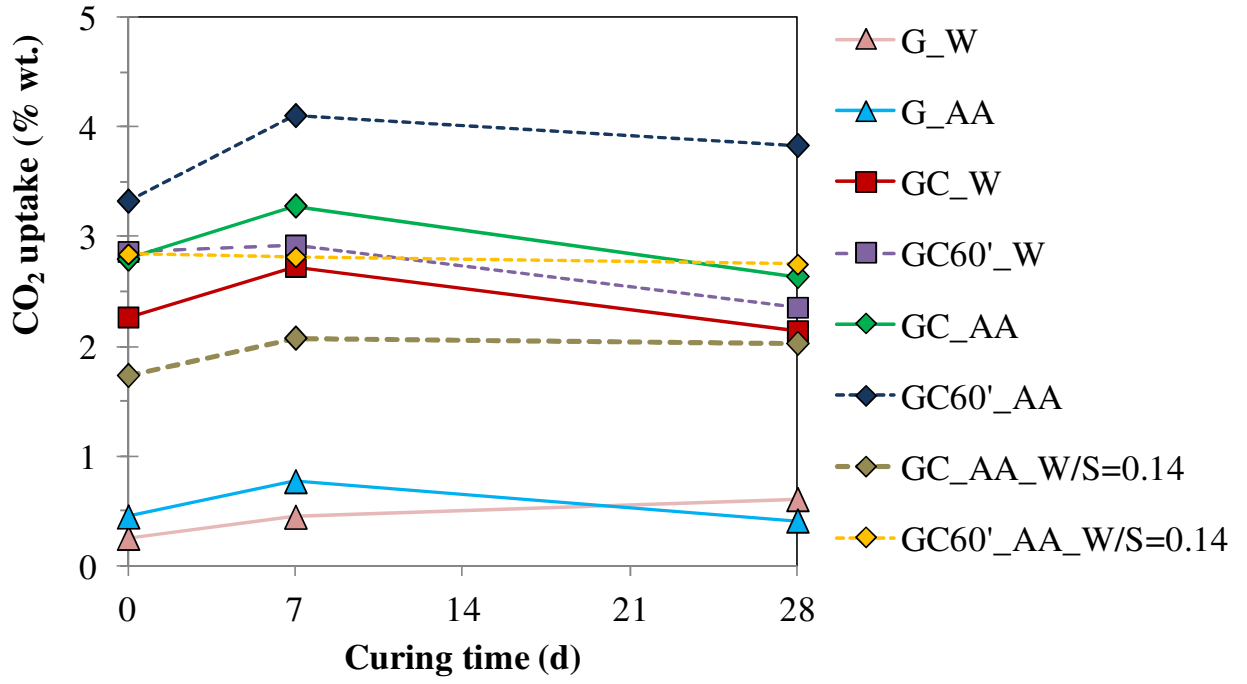


Figure 3. CO<sub>2</sub> uptake with curing time of the granules obtained applying the different types of treatments tested (see Table 2 for the explanation of the experiment codes reported in the legend).

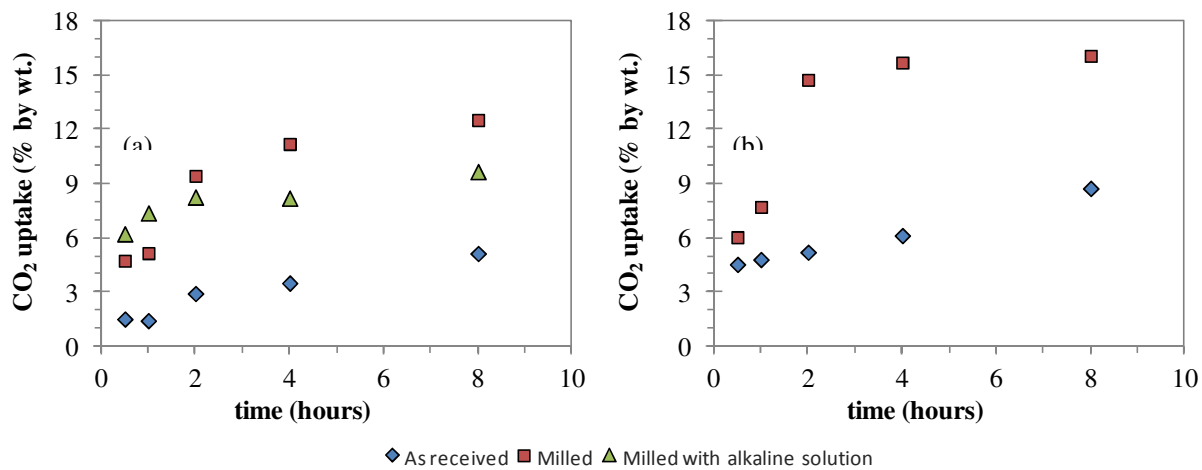


Figure 4. CO<sub>2</sub> uptake kinetics of BOF slag resulting from the batch tests: a) at ambient conditions (T=20 °C, p=1 bar, L/S=0.3 l/kg) and b) at enhanced conditions (T=50 °C, p=10 bar, L/S=0.3 l/kg).

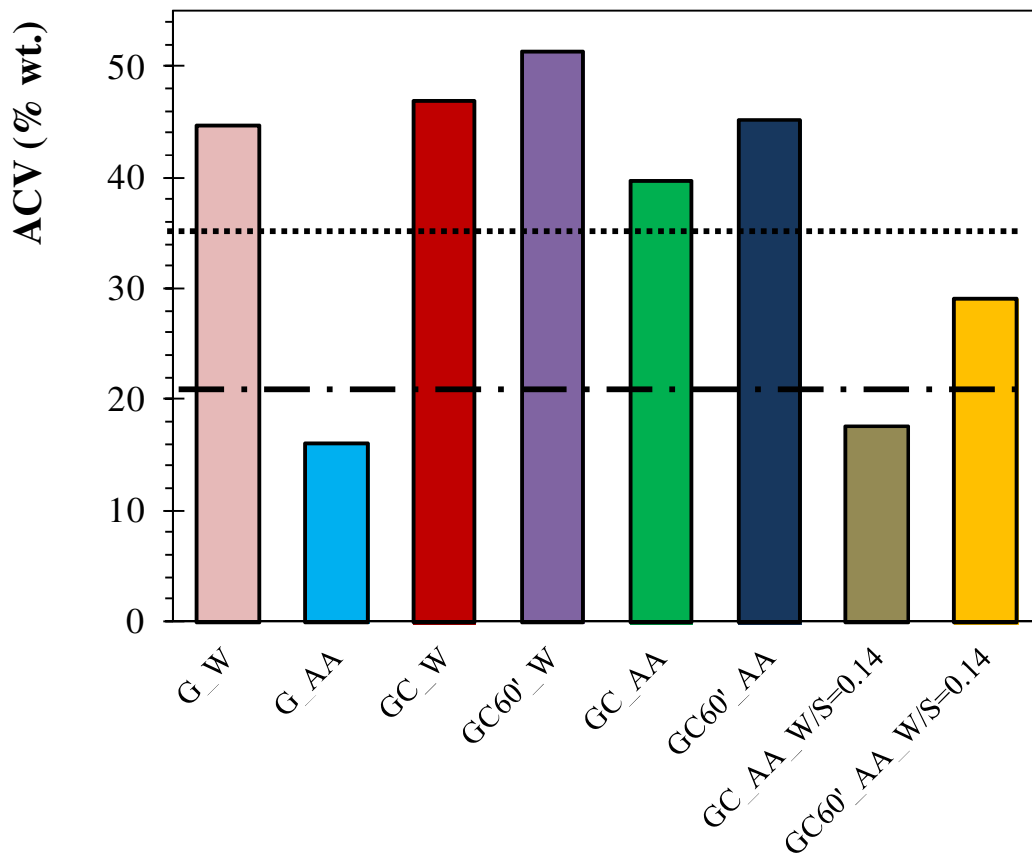


Figure 5. ACV of the granules obtained from the different treatments tested compared to the values reported for mixed gravel (21%) and blast furnace slag (35%) (British Standard, 1990), see Table 2 for the explanation of the experiment codes reported on the x-axis.

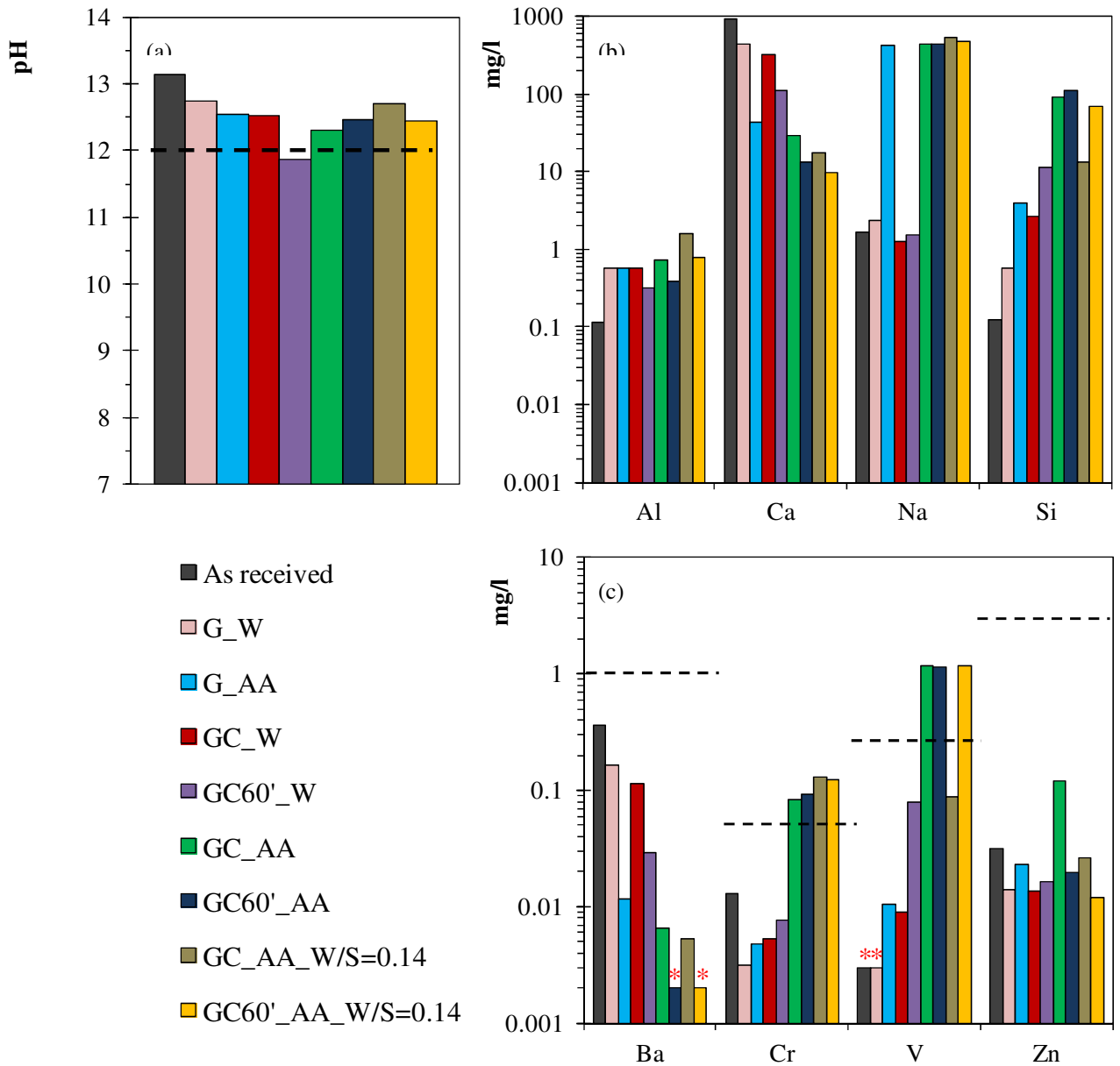


Figure 6. Results of the EN 12457-2 leaching test for the untreated slag and for the granules (without grinding the material) obtained after granulation-carbonation (see Table 2 for the explanation of the experiment codes reported in the legend). Red stars indicate concentrations below the instrumental quantification limit; dashed lines report the limits for reuse (It. MD 186/06).

		<b>Performance indicators</b>				
<b>Binder</b>	<b>Treatment</b>	Particle size	Potential GHG mitigation	Leaching pH	Leaching regulated elements	Mechanical strength
<b>Water</b>	Granulation	Green	Orange	Orange	Green	Orange
	Granulation-Carbonation	Green	Green	Green	Green	Orange
<b>Alkaline solution</b>	Granulation	Green	Orange	Orange	Green	Green
	Granulation-Carbonation	Green	Green	Orange	Orange	Green

Figure 7. Summary of the results achieved by each of the analyzed treatments in terms of obtaining a product with suitable properties for use as aggregate or presenting additional environmental benefits (potential GHG mitigation). Green: meets the requirement;

## Tables

Table 1. Elemental composition of the untreated BOF slag expressed on a dry weight basis.

<b>Element</b>	<b>(g/kg)</b>	<b>Element</b>	<b>(g/kg)</b>
Al	8	Fe	222.71
Ba	0.7	Mg	42.55
Ca	268.12	Mo	<0.003
Cd	0.17	Mn	31.31
Cr	0.73	Si	15.77
Cu	0.14	V	0.47
		Zn	0.15

Table 2. Summary of the main parameters adopted for the experiments (W/S: water to slag ratio; AA/S: alkali activation solution to slag ratio).

<b>Experiment code</b>	<b>Reaction time (min.)</b>	<b>Binder type</b>	<b>W/S ratio (l/kg)</b>	<b>AA/S ratio (l/kg)</b>
<i>Granulation tests</i>				
G_W	30	Deionized water	0.12	-
G_AA	30	Alkaline activator	0.12	0.16
<i>Granulation-Carbonation tests</i>				
GC_W	30	Deionized water	0.12	-
GC60'_W	60	Deionized water	0.12	-
GC_AA	30	Alkaline Activator	0.12	0.16
GC60'_AA	60	Alkaline Activator	0.12	0.16
GC_AA_W/S=0.14	30	Alkaline Activator	0.14	0.18
GC60'_AA_W/S=0.14	60	Alkaline Activator	0.14	0.18

Table 3. EN 12457-2 leaching test results for the untreated slag and the crushed granules obtained from the different tests compared to the Italian limits for reuse (Italian Ministerial Decree 186, 2006).

	<b>pH</b>	<b>Al</b> mg/l	<b>Ca</b> mg/l	<b>Na</b> mg/l	<b>Si</b> mg/l	<b>Ba</b> mg/l	<b>Cr</b> mg/l	<b>V</b> mg/l	<b>Zn</b> mg/l
untreated	13.13	0.11	915.2	1.67	0.13	0.36	0.01	<0.003	0.03
G_W	13.09	0.07	1001.3	2.97	0.24	0.4	0.01	<0.003	0.03
G_AA	12.85	0.11	480.62	510.2	0.35	0.18	0.003	<0.003	0.02
GC_W	12.75	0.48	401.39	2.02	1.11	0.17	0.004	<0.003	0.02
GC_AA_W/S=0.14	12.89	0.48	69.17	667	2.49	0.03	0.05	<0.003	0.03
GC60' _AA_W/S=0.14	12.29	0.52	14.59	503	101.8	0.003	0.11	1.26	0.07
Limit for reuse (It. D.M. 186/2006)	5.5-12	-	-	-	-	1	0.05	0.25	3