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## Influence of particle size on the carbonation of stainless steel slag for CO<sub>2</sub> storage

Renato Baciocchi<sup>a\*</sup>, Giulia Costa<sup>a</sup>, Alessandra Polettini<sup>b</sup>, Raffaella Pomi<sup>b</sup>

<sup>a</sup>Department of Civil Engineering, University of Rome "Tor Vergata", via del Politecnico 1, 00133 Rome, Italy

<sup>b</sup>Department of Hydraulics, Transportation and Roads, University of Rome "La Sapienza", via Eudossiana 18, Rome, Italy

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### Abstract

The main aims of this work were to assess the CO<sub>2</sub> storage capacity of different particle size fractions of stainless steel slag subjected to accelerated carbonation under mild operating conditions, to study the influence on reaction kinetics of some of the main operating parameters (temperature, pressure and liquid to solid ratio) and to determine the effects of the process on slag mineralogy and leaching behavior. Maximum CO<sub>2</sub> uptakes of 130 g CO<sub>2</sub>/kg residues were measured for the finest grain size and decreased with particle size owing to differences in reacting species availability and specific surface. Process kinetics proved relatively fast, achieving completion in around 2 hours with a CO<sub>2</sub> pressure of 3 bar and an optimal liquid to solid ratio of 0.4; temperature was the parameter that most influenced CO<sub>2</sub> uptake, due to its enhancement effect on silicates dissolution.

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### 1. Introduction

The steel industry is globally the largest energy consuming manufacturing sector, and accounts for 7-12 % of anthropogenic greenhouse gas emissions [1]. Several measures are hence being developed to improve energy efficiency and cut CO<sub>2</sub> emissions, such as scrap steel recycling for example, but more drastic measures are needed if reduction goals are to be met in a reasonable timeframe [2].

During steel manufacturing, a significant amount (10-15 % by weight of the produced steel [3]) of various types of slag are generated. These materials are mainly made up by CaO, SiO<sub>2</sub>, MgO, Al<sub>2</sub>O<sub>3</sub> and MnO [4]. Other alloy steel slags, such as Stainless Steel Slag (SSS) contain in general less Fe, more SiO<sub>2</sub>, high contents of Cr (2-5 %) and some Ni (0.02-0.55) [5]. The main mineral phases in steel slags are dicalcium and tricalcium silicates, calcium-aluminium silicates, calcium oxides and periclase (MgO); SSS in addition contain Mg and Ni chromites [5]. Steel slag is generally regarded as a non hazardous waste owing to low leachability of trace compounds [3]; however, SSS may be classified as hazardous, due to high Cr release [5]. Depending on its composition and particle size, steel slag can be employed for various uses, e.g. as an aggregate or as a filler in cement production [4]. The most important

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\* Corresponding author. Tel.: +39-06-72597022; fax: +39-06-72597021.

E-mail address: [baciocchi@uniroma2.it](mailto:baciocchi@uniroma2.it).

factor for the utilization of steel slag in engineering applications is its content of free CaO and MgO, since, due to hydration and natural carbonation, the slag volume increases causing disintegration of the construction material and hence strength loss [4].

Accelerated carbonation has been shown to improve the chemical stability and the leaching behavior of several types of industrial residues, such as Municipal Solid Waste Incineration (MSWI) residues [6], and to enhance the mechanical properties of materials to be reused as aggregates in civil works, such as steel slag [7-8]. Furthermore, accelerated carbonation of industrial alkaline residues has been also applied for permanent storage of CO<sub>2</sub> point source emissions, [9-14]. Alkaline waste residues, in fact, require a lower degree of pre-treatment and less energy intensive operating conditions than the minerals generally investigated (e.g.: olivine and serpentine) for CO<sub>2</sub> sequestration [12]. Furthermore, although their availability, when compared to silicate minerals, is quite limited, they are produced at CO<sub>2</sub> point source emissions generating plants, and hence could provide an effective and economically sustainable measure for selected industries to gain carbon credits.

Accelerated carbonation of steel slag consists of two sequential processes: the dissolution of alkaline elements (Ca and Mg) from the silicate minerals and the precipitation of the corresponding carbonates. The two processes can be performed in the same reactor (single stage process), or in two in-series reactors (2 step process). In the latter case dissolution and precipitation are optimized separately by selecting the proper pH with specific additives [14-16]. The single stage process has been carried out either in slurry phase, under high temperature (100-200 °C) and moderate CO<sub>2</sub> pressures (10-30 bar) [12], or with partially humidified slag at lower temperature and CO<sub>2</sub> pressure (30-50 °C and 1-10 bar respectively) [7-9]. For the slurry phase process, slag particle size was found to exert the most significant effects on the reaction, smaller grain sizes proving more reactive with CO<sub>2</sub>; temperature also was found to enhance silicates dissolution [12].

In this work accelerated carbonation tests were carried out on four particle size fractions of humidified SSS to assess the CO<sub>2</sub> uptake achievable by each fraction under mild operating conditions, to identify the reacting species and the influence of operating parameters on reaction kinetics and to analyze the effects of the treatment on the mineralogy and leaching behavior of the slag.

## 2. Materials and methods

The SSS analyzed in this study was a mixture of the main types of slag produced during stainless steel manufacturing, i.e. the residues generated from the Electric Arc Furnace (EAF) and from the Argon Oxygen Decarburization (AOD) converter units. A freshly produced 20 kg sample was collected from the slag deposit of the plant, homogenized and dried at 50 °C to constant weight. After determining its particle size distribution curve applying the ASTM D422 standard procedure, the slag was divided by sieving into the following size fractions: 2-0.425 mm (class A); 0.425-0.177 mm (class B); 0.177-0.105 mm (class C); < 0.105 mm (class D). Class A was then milled to < 0.425 mm prior to chemical composition analysis and CO<sub>2</sub> treatment. Each of the fractions was thoroughly characterized in terms of elemental composition, anion content, mineralogy and leaching behavior.

The water content and loss on ignition (LOI) of the slag samples were determined with the ASTM C25 and ASTM D2216 standard procedures respectively. The elemental composition of the SSS fractions was analyzed by atomic absorption spectrometry (AAS) after digestion of slag samples with Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> at 1050 °C and dissolution of the molten material in a 10% HNO<sub>3</sub> solution. Chloride and acid soluble sulphates were measured using the Italian standard test procedure UNI 8520, which involves dissolution with hot deionised water and titration with AgNO<sub>3</sub> for Cl<sup>-</sup> analysis and dissolution with 3% HCl followed by spectrophotometric analysis for acid soluble SO<sub>4</sub><sup>2-</sup> measurement. The carbonate content of untreated and carbonated SSS fractions was measured with a Dietrich-Frühling calcimeter. All chemical analyses were performed in triplicate. The mineralogy of both untreated and carbonated SSS samples was determined by X-ray diffraction (XRD) and Raman spectroscopy analyses. Variations in the leaching behavior of the slag were investigated by applying on a single replicate the EN 12457-2 standard compliance test and the CEN/TS 14429 pH-dependence leaching test to both untreated and carbonated SSS samples.

Batch accelerated carbonation tests were performed in a pressurized stainless steel reactor equipped with a 150 ml internal Teflon jacket and placed in a thermostatic bath for temperature control. Gas humidity was maintained at 75% by inserting a saturated NaCl solution in the reactor. In each run, three 1 g slag samples were mixed with distilled water at specific liquid to solid ratios (L/S), from 0 to 0.6 l/kg, placed in tin foil containers and exposed to a

100% CO<sub>2</sub> flow for set times, ranging from 0.5 to 24 h. Initial wet carbonation tests were carried out on class D to evaluate the influence of temperature, varied from 30 to 50 °C, pressure, from 1 to 10 bar, and the L/S, on the CO<sub>2</sub> uptake kinetics of the slag. Accelerated carbonation tests were then performed, under the optimal conditions determined for class D, on the other slag fractions and also on ungrinded class A to evaluate the influence of composition and specific surface on the carbonation yield. After treatment with CO<sub>2</sub>, the samples were oven dried at 50 °C and sample weight gain, which provides a first qualitative indication of carbonate formation, was recorded. The three samples treated in each run were grinded, since after treatment the slag exhibited a compact hardened structure, mixed together and analyzed by calcimetry testing, so to measure the CO<sub>2</sub> uptake of the slag during the carbonation treatment.

### 3. Results and discussion

The particle size distribution curve of the slag, see Figure 1, indicated that these residues could be classified as sandy granular material with a significant (above 15% wt.) amount of fines ( $d < 100 \mu\text{m}$ ), notably higher than values reported for steel slag [3]. Discarding the fraction with a  $d > 2 \text{ mm}$ , (less than 10% wt.), the weight distribution of the slag into the 4 classes chosen for testing was: class A = 45.9% wt., class B = 25.9% wt., class C = 12.8% wt., class D = 16.4% wt. The LOI values decreased consistently with particle size from 3.3 % wt. for class D to 0.6 % wt. for class A, but were anyhow quite low, indicating a reduced content of hydroxide and carbonate species, the only compounds for this type of residues likely to decompose at  $T < 1000 \text{ °C}$ . Comparing these results to the initial calcite content of the slag, see Table 1, it was inferred that only class D contained a small amount of hydroxide species (the LOI being higher than the CO<sub>2</sub> uptake of the material), whereas for classes A, B and C, the LOI values were ascribed entirely to the partial initial weathering of the slag.

The elemental composition and anion content of the four size fractions of the SSS are reported in Table 1. The calcium content was very significant (from 40 to 50 % wt.), in agreement with prior investigations on SSS [5, 7] and showed to decrease with particle size. The same trend, although with considerably lower concentrations, was observed for Mg (from 2.2 to 4.5 % wt.). Significant concentrations of Fe (4.3 to 6 % wt.), Cr (3 to 4.2 % wt.), Al (1.7 to 2.6 % wt.), Mn (0.76 to 1% wt.) and V (0.09 to 0.15 % wt.), were also measured and showed an increasing trend with particle size. Ni concentrations were quite lower than those found in prior studies on SSS [5] (0.04-0.075 as opposed to 0.2-0.45 % wt.), probably due to differences in the stainless steel manufacturing processes. The concentrations of other heavy metals and soluble salts, as expected, were very low.

The results of the EN 12457-2 compliance test on untreated slag, see Table 2, indicated that the pH of the eluates was high, above 12, and very similar for size fractions B, C and D, decreasing slightly for class A; a similar declining trend with particle size was also observed for Ca, Mg and Cr leaching. Cr in particular was the only trace compound that exhibited a higher eluate release than the Italian limit prescribed for inert waste landfilling (0.5 mg/l), but was nonetheless lower than values reported for AOD SSS [5].

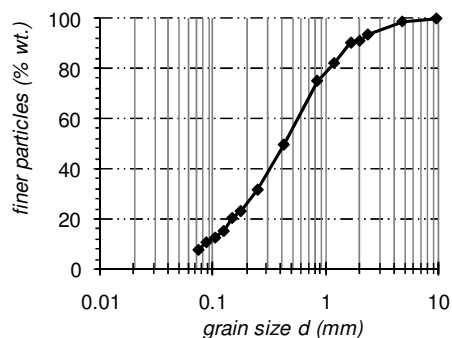


Figure 1: SSS particle size distribution curve

Table 1: Elemental composition (mg/kg dry wt.) and anion content (% dry wt.) of SSS

Element	Class A (2-0.425 mm)	Class B (0.425-0.177 mm)	Class C (0.177-0.105 mm)	Class D (<0.105 mm)
Al	26040	22080	17986.7	16840
As	3.5	3.1	4.1	6.2
Ca	432333.3	402000	445333.3	500333.3
Cd	51.7	1.8	14.3	3.5
Cr	42466.7	34066.7	29933.3	30466.7
Cu	228	234.7	145.3	166.7
Fe	59733.3	53000	43600	43266.7
K	310.7	334.7	313.3	356
Mg	22166.7	26466.7	29900	44600
Mn	10453.3	8773.3	7866.7	7600
Mo	230.7	186.7	168	225.3
Na	1960	1893.3	1738.7	1541.3
Ni	376	750.7	458.7	461.3
Pb	76	77.3	58	120
Sb	1.5	1.5	1.2	1.3
V	1520	1133.3	813.3	920
Zn	112.1	100.8	126.4	144.1
<b>Anion</b>				
Cl <sup>-</sup>	0.035	0.044	0.056	0.05
SO <sub>4</sub> <sup>2-</sup>	0.19	0.18	0.25	0.25
CO <sub>3</sub> <sup>2-</sup>	2.33	2.96	3.5	5.25

XRD analysis allowed to identify several crystalline oxides and silicate phases in the different particle size fractions of the slag, see Figure 2. The mineralogy of the SSS did not seem to vary significantly with particle size; in all fractions a predominance of silicate phases such as dicalcium silicate, merwinite, akermanite, anorthite, gehlenite and forsterite were found, confirming the results of other studies on SSS [5, 7]. Cuspidine, a typical species formed during SSS hydration after fluorine addition, silica and magnetite were also detected in all particle size classes. Even though CaO or Ca(OH)<sub>2</sub> were not identified by XRD analysis, Ca-Al-Fe oxide, Mg-Cr oxide, periclase (detected also in the above mentioned studies) as well as calcite, showed higher peak intensities in class D. Raman spectroscopy, results not shown, confirmed some of the results of elemental and XRD analyses, revealing the presence of Si, Fe and Al minerals including alumina (Al<sub>2</sub>O<sub>3</sub>), magnetite and olivine (Mg,Fe)<sub>2</sub>SiO<sub>4</sub> and also showed calcite presence in all fractions, but was not able to detect calcium silicate or oxide phases.

The main results of the accelerated carbonation tests are reported in Figure 3. Carbonation kinetics proved to be quite fast, reaching completion in 1 to 4 hours depending on operational conditions; in Figures 3a and 3b, the influence of CO<sub>2</sub> pressure and temperature on the kinetics of class D carbonation are shown respectively; similar trends were also found for the other particle size fractions, although the values of the achieved CO<sub>2</sub> uptakes were significantly lower (Figure 3d). Pressure did not appear to affect the CO<sub>2</sub> uptake or the kinetics of the reaction, in agreement with results of carbonation tests performed under similar operating conditions and 100 % CO<sub>2</sub> on other types of combustion residues [10, 13]. Temperature, other than grain size, was the parameter that seemed to mostly affect the reactivity of the slag towards CO<sub>2</sub>, allowing to achieve CO<sub>2</sub> uptakes of just below 13% wt. in 2 hours. This effect was ascribed to the enhancement of silicate dissolution, indicated as an important factor in slurry phase steel slag carbonation, for which optimal temperature values of 200 °C were reported [12]. The L/S ratio is also an important parameter for aqueous phase carbonation; while for slurry phase experiments optimal values of 2 were indicated [12], for partially humidified SSS, optimal values of 0.125 l/kg were reported [9]. In this study, the highest

CO<sub>2</sub> uptakes were achieved with L/S ratios ranging from 0.3 to 0.4, as shown in Figure 3c. This difference could be due to variations in the slag composition, since in Johnson’s study [9] portlandite was identified in the slag, whereas in the present study no hydrated compounds were detected, indicating that part of the water added to the slag was employed for hydration of the oxide and silicate phases, other than for solvation of CO<sub>2</sub> and Ca<sup>2+</sup> ions. CO<sub>2</sub> uptakes, as reported in other studies [12], varied considerably with particle size (see Figure 3.d); remarkable differences in elemental and mineralogical analysis however, were not detected, except for a slight increase of Ca and Mg oxides in class D, and therefore a reduction of the specific surface of the slag with increasing particle size was considered as the main mechanism behind the decrease in slag reactivity towards CO<sub>2</sub>. This supposition was confirmed by results of accelerated carbonation tests on milled (d<0.425 mm) class A slag, which presented CO<sub>2</sub> uptakes similar to class C (0.105<d<0.177 mm), indicating that, also under the operating conditions investigated in this study, as reported by Hujgen et al. [12], intensive milling could contribute in enhancing the carbonation yield considerably. Carbonated slag, particularly for L/S>0.2 l/kg and T=50 °C, exhibited a compact, hardened cement like structure, suggesting that through accelerated carbonation, aggregates of SSS with specific mechanical properties could be manufactured.

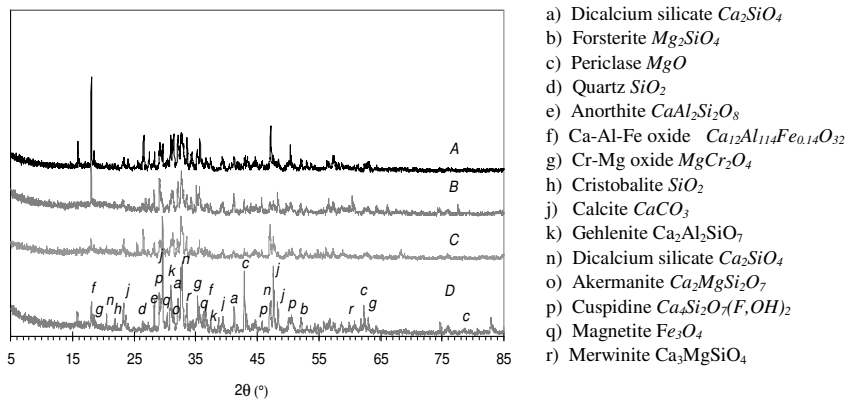


Figure 2: XRD pattern for the different particle size fractions of SSS

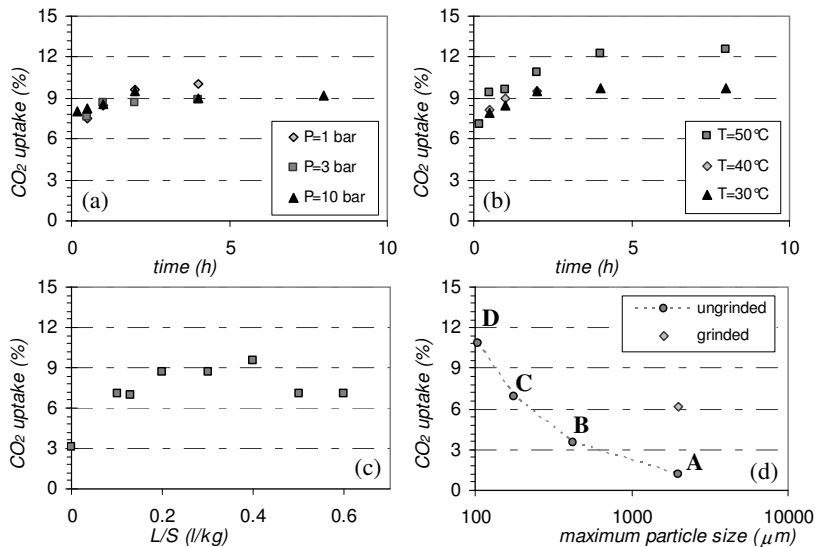


Figure 3: CO<sub>2</sub> uptake as a function of (a) pressure (for class D, at 30 °C and a L/S=0.3 l/kg); (b) temperature (for class D, at 3 bar and a L/S=0.3 l/kg); (c) the L/S (for class D, for a 2 h treatment with 3 bar CO<sub>2</sub> at 30 °C); (d) particle size (for a 2 h treatment at 50 °C, 3 bar and a L/S=0.4 l/kg)

Mineralogical transformations induced by carbonation reactions on class D samples are shown in Figure 4. The diffraction patterns of carbonated samples exhibited the disappearance of periclase, a significant reduction of the peaks associated to Mg-Cr and Ca-Al-Fe oxides, as well as a reduction of silicate phases such as dicalcium silicate, anorthite and cuspidine, accompanied by a significant increase in peak intensities for calcite and evidence of the formation of some dolomite; carbonates containing only Mg were not identified. Quartz and cristobalite peaks did not appear to increase after CO<sub>2</sub> treatment of the slag. These results are in good agreement with findings by Johnson et al. [7] that reported the increase of calcite peaks, the decrease of periclase, portlandite and partially also of dicalcium silicate, while an unmodified pattern for merwinite, akermanite and silica.

The results of the EN 12457-2 compliance leaching test (see Table 2) revealed a decrease in the natural pH for all the carbonated samples, which was more pronounced (almost 2 units) for class D, the fraction that exhibited the highest reactivity towards CO<sub>2</sub>. The only compounds whose leaching appeared to be significantly modified by the treatment were Ca and Si. Ca concentrations in the eluate were considerably reduced, up to 1 order of magnitude, in all particle size classes, indicating the formation of less soluble phases, such as calcite, than those making up the original slag. On the contrary, Si concentrations significantly increased in the eluates of all carbonated samples, except for class D, indicating that indeed part of the silicates reacted during the treatment, producing more soluble phases. These results are in good agreement with findings by Chen et al. [8] on steel slag carbonated under similar operating conditions. Cr release appeared to be slightly reduced only for class B and C samples, though it remained higher than the Italian regulatory limits for inert waste disposal (< 0.5 mg/l).

Figure 5 reports the acid titration curves obtained from the ANC test on untreated and carbonated class D samples. Both samples showed a significant (around 10 meq/g) acid buffering capacity in the pH range 8 to 10. The buffering capacity of treated slag at pH higher than 10 was reduced owing to the decrease in free oxides, whereas no significant increase compared to untreated samples in the pH range 7-8, typical of high calcite contents, of the buffering capacity of carbonated slag could be observed; this was probably due to the fact that partially reacted silicates buffer in similar pH ranges. Comparable results were reported by Johnson et al. [7].

The leaching of Ca, Mg, Si and Cr from class D slag as a function of pH, derived from the ANC tests is reported in Figure 6. The leaching curve for Ca confirmed the results of the EN 12457-2 test, showing a decrease in concentration for pH>8, due to calcite formation; for Mg a mobilization effect in the same pH range was observed, and could be attributed to the formation of hydrated soluble species, indicating that significant precipitation of Mg carbonates did not occur, as observed also by Huijgen and Comans [17]. Si leaching with pH did not show noteworthy variations after carbonation, probably owing to the low degree of reactivity of the silicates under mild operating conditions. The shape of the leaching curve for Cr was not appreciably modified by the carbonation process, probably due to solubility control by Cr<sup>+3</sup>, as also reported in the previously mentioned study [17].

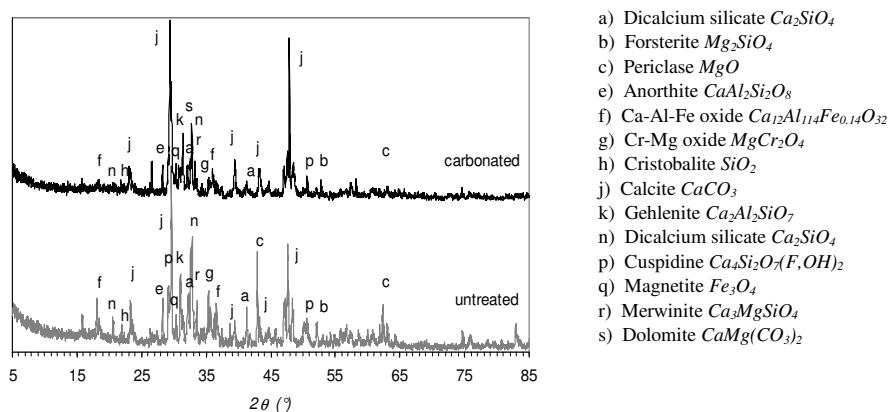


Figure 4: XRD pattern for the untreated and carbonated (2 h with a L/S=0.4 at 50 °C and P=3 bar) class D fraction

Table 2: Comparison of the EN 12457-2 leaching test results on different size fractions of SSS samples before and after treatment with CO<sub>2</sub> (2 h with a L/S=0.4 at 50 °C and P=3 bar)

	Class A		Class B		Class C		Class D	
	untr.	carb.	untr.	carb.	untr.	carb.	untr.	carb.
<b>pH</b>	12.43	11.38	12.82	11.18	12.81	11.29	12.87	10.59
<b>Ca (mg/l)</b>	399	67	882.5	105	1025	84	1050	23.1
<b>Cr (mg/l)</b>	0.04	0.06	0.15	0.06	0.16	0.08	0.18	0.17
<b>Fe (mg/l)</b>	0.07	0.03	0.06	0.01	0.06	0.09	0.13	0.03
<b>Mg (mg/l)</b>	0.08	0.08	0.2	0.17	0.19	0.23	0.43	0.24
<b>Si (mg/l)</b>	1.6	67.5	0.9	63.8	1.2	51.3	1.6	7.3

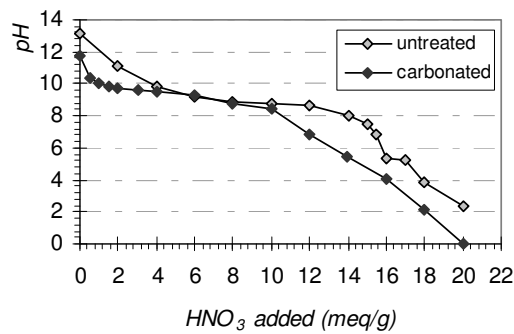


Figure 5: ANC curves for untreated and carbonated (2 h with a L/S=0.4 at 50 °C and P=3 bar) class D fraction

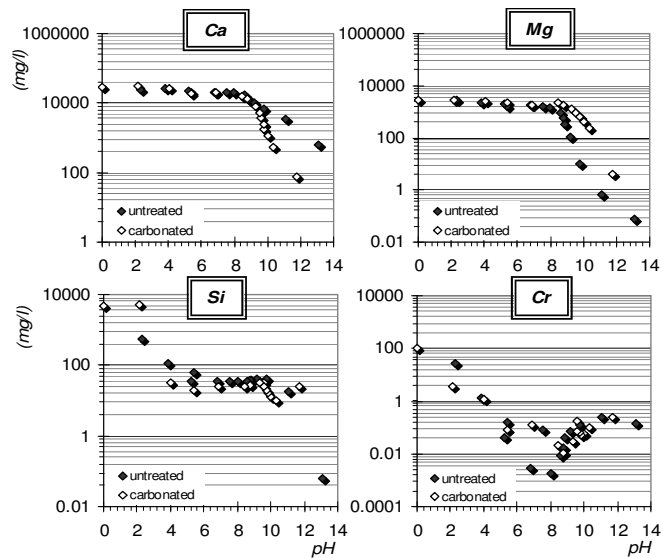


Figure 6: Leaching of Ca, Mg, Si and Cr as a function of pH for class D carbonated for 2h with a L/S=0.4 at 50 °C and P=3 bar

#### 4. Conclusions

The results of the present study indicated that the carbonation tests performed under mild operating conditions on different particle size fractions of SSS were able to affect several properties of this material. Chemical and mineralogical characterization showed that all size fractions had a high potential for reacting with CO<sub>2</sub>, owing to high Ca and Mg contents, mainly in the form of oxides and silicates. The results of the carbonation tests indicated that the parameter that most affected the CO<sub>2</sub> uptake of the slag was grain size, and in particular the specific surface of the particles. An increase in temperature had also a positive effect. The maximum CO<sub>2</sub> uptakes found in this study (13% wt.) were not significantly lower than those reported for slurry steel slag carbonation [12]; however the conversion of Ca and Mg reactive species to calcite was rather low (around 20% for class D) compared to that reported for the above mentioned study (75%), indicating the potential to achieve high reaction yields with these types of residues by slag milling or slurry phase carbonation with higher operating temperatures. Another aspect that needs to be further examined in order to identify the potential reuses of the treated slag in civil engineering applications is the influence of accelerated carbonation on the mechanical and structural properties of this specific type of industrial residue.

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