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Laboratory investigation of carbonated BOF slag used as partial replacement of natural aggregate in cement mortars

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Abstract

Direct mineral carbonation produces a material rich in carbonates and with reduced quantities of free oxides. The aim of this work was to show that such materials can be used in the construction domain. Basic Oxygen Furnace (BOF) slag from the steelmaking process has been traditionally seen as unfit for bounded applications due to its propensity to swelling, resulting from hydration of its high free lime content. Here, BOF slag was crushed to suitable particle sizes, carbonated in an aqueous solution of carbonic acid, and utilized to replace 50% of natural sand aggregate in cement mortars. The mechanical and chemical properties of these mortars were compared to mortars containing non-carbonated slags, and a standard cement mortar as a reference. Tests were conducted to determine mortar paste consistency and soundness, and cured mortar compressive strength and leaching tendencies. The results showed a satisfactory performance for all considered aspects (comparable with the reference) of the mortar sample containing 37.5 wt% (1.5 in 4 parts solids) carbonated BOF slag of <0.5 mm particle size.

Keywords: BOF slag; mineral carbonation; fine aggregate; cement mortar; soundness; leaching

1. Introduction

The development of various treatment routes for the valorization of steelmaking slags has resulted in these residues being withdrawn from the European Waste Catalogue [1]. With the purpose of using steelmaking slags in the construction domain, and after much research conducted internationally, different standards have been implemented regarding the conditions that should be met by these industrial wastes before utilization. When intending to use slags as binders, the hydraulic activity of the material is very important [2]. Several researches have shown that finely milled Basic Oxygen Furnace (BOF) slag can be used as a cement replacement in mortars and concretes [3-5]. Others have combined BOF slag with Blast Furnace (BF) slag [6, 7], where the BOF slag acts as basic activator due to its free lime content. However, with the use of BOF slag as a binder requiring intense grinding, and with the high metallic iron content of BOF slag, this processing step represents a high energy demand, and consequently a high cost.

Lower processing costs (due to at least halving the specific grinding energy requirement [8]) can be achieved when using BOF as an aggregate, as the extent of particle size reduction (from monolith to millimeter-sized grains, rather than to micron-sized powder) can be reduced. For this application, the main parameters that must meet stringent specifications are the volume stability, referred to as soundness, the basicity, and the leaching of regulated toxic heavy metals and metalloids [9]. Wang et al. [10] proposed a calculation method for volume expansion and the expansion forces of slag used, respectively, as an unbound or bound aggregate. A usability criterion was developed based on the free lime content, the specific gravity and the bulk relative gravity of the slag. The criteria can be used as guidance for the selection of steel slags as granular materials for use in highway construction, a field of extensive study [11-15]. Xie et al. [14] found that the failure mechanism in BOF dense-graded asphalt mixtures in moist environment is determined by the formation of portlandite ($\text{Ca}(\text{OH})_2$) and calcium-silicate-hydrates (C-S-H), which leads to partial structural failure and facilitates water infiltration.

To obtain acceptable values of hydraulicity and soundness, one solution has been to control the slag's cooling rate from the hot to cold stage. Gautier et al. [16] demonstrated the possibility to obtain low free lime (CaO) content in BOF slag (the main mineral component responsible for volume instability) with slow cooling (72 hours), and to obtain high C₃S (tricalcium silicate, the mineral responsible for hydraulicity) content by rapid cooling (3-5 seconds), thus obtaining materials potentially suitable for application in the construction domain. This approach, however, is less effective for slags containing high amounts of free lime, as much of this free lime will be present as residual (undissolved) rather than precipitated (originating from the decomposition of C₃S to dicalcium-silicate (C₂S)) lime [17], and thus will be inert to changes in cooling rate. Another hot-stage approach is to modify the slag's chemical composition prior to cooling. Li et al. [18] showed that by adding EAF and coal bottom ash to BOF slag, it is possible to reduce free lime content and improve soundness and cementitious properties. A disadvantage of this approach is the added process complexity of controlling slag chemistry (typically undesirable as this is a secondary product of steelmaking) and ensuring sufficient residual process heat to drive the dissolution and reaction of the additives (waste heat from the BOF process is limited [1]).

An alternate route is the reaction of the alkaline oxides in BOF slag with CO₂, a process called mineral carbonation that leads to the formation of geochemically stable carbonates (e.g. CaCO₃), thus preventing the formation of expansive hydroxides and implicitly obtaining a stable material [19]. An advantage of this method over hot-stage treatments is that it is applicable to the existing storage heaps of these wastes, which are significant worldwide (e.g. in Turkey [20]). Another advantage is that both forms of free lime found in BOF slag (residual and precipitated) can be made to react with CO₂, thus substantially reducing basicity [9] and likely propensity for swelling, although the latter has not been reported in literature. The noble purpose of sequestering carbon dioxide, however, is insufficient for extending the process of mineral carbonation to an industrial scale if the economical balance is not a positive one. For this reason, the materials obtained after mineral carbonation must be valorized by utilizing them in large-scale commercial applications. Recently, Kirchofer et al. [21] calculated the CO₂ sequestration capacity through mineral carbonation of alkaline industrial wastes that can be subsequently used as aggregates in the construction domain at 7.6 Mt,CO₂/year (for the USA). Out of that quantity, 0.6 Mt,CO₂/year represents the amount of emissions avoided by reducing the exploitation of natural sand, gravel, granite and limestone.

Besides capture of CO₂, desirable for emissions reduction, mineral carbonation has also been reported to yield positive effects in terms of basicity and the leaching behavior of alkaline earth metals, heavy metals and metalloids from steelmaking slags [22]. Van Gerven et al. [23], however, observed that the leaching evolution of some metals, from blocks obtained by mixing cement with municipal solid waste incineration ashes, increases at high carbonation degrees, compared to lower leaching levels for partially carbonated specimens. This was suggested to result from leachate-induced transformation of carbonates into more soluble bicarbonates once the pH drops below 10. This means that an optimal level of carbonation might exist that minimizes leaching.

In the case of carbonated Basic Oxygen Furnace (BOF) steelmaking slag, vanadium and chromium leaching are reported to be the most problematic elements at low pH values. Chaurand et al. [24] found that chromium is present at octahedral coordination in the trivalent form, the less mobile and less toxic form of Cr, and that its speciation does not evolve during natural ageing (the reaction of slags with CO₂-containing air and moisture). Vanadium, on the other hand, was found to be highly mobile; it was found to be present predominantly in the +4 oxidation state, and became oxidized to the pentavalent form (the most toxic form) during natural ageing. After carbonation, Santos et al. [9] observed increased leaching of chromium and vanadium from BOF slag, and like Van Gerven et al. [23] observed a minimum to occur at intermediate levels of carbonation extent and basicity reduction.

Monkman et al. [25] demonstrated that mortars with carbonated BOF slag as fine aggregate can reach 28-day strengths comparable to the strengths of typical river sand mortars, though this study did not present results regarding soundness nor heavy metals leaching. Saikia et al. [26, 27] tested heavy metal leaching from mortars containing different industrial wastes as partial replacement of natural fine aggregate, and found that the leaching effect is considerably reduced in comparison to leaching from the unbound industrial wastes. Formation of expansive products like ettringite, aluminium hydroxide and H₂ gas, due to the reaction of some constituents of the wastes with alkali, created cracks in the pastes and the cement mortars, which lowered the compressive strength of those mortars. Manso et al. [28] termed as 'cloistering' the effect of the cementitious matrix on the leaching reduction of contaminant elements from non-carbonated Electric Arc Furnace (EAF) slag aggregates bound in concrete.

The purpose of this work was to assess the mechanical and chemical properties of cement mortars containing non-carbonated or carbonated BOF slag as a fine aggregate. This work complements those previously described by applying a more complete set of testing methods, including consistency of fresh mortar pastes, soundness, compressive strength, basicity and contaminant leaching. This is the first work to report values of soundness, determined by the Le Chatelier test, for carbonated BOF slag-containing mortars. This work also aimed at evaluating the effect of slag particle size on the carbonation extent, and the effects of slag particle size and carbonation degree on the mortar properties.

2. Materials and methods

2.1. BOF slag characterization

The BOF slag used in this study was acquired from a steelmaking plant in Belgium. Prior to analyses or experimentation, the material was first crushed using a jaw-crusher (Retsch BB100) to obtain particles smaller than 1.6 mm. The obtained material was further divided into three particle size classes using standard sieves: <0.08 mm, 0.08-0.5 mm, and 0.5-1.6 mm. These three particle size classes were chosen based on the values reported in literature for BOF slag dry granulation [29] and in accordance to our group's previous researches regarding BOF slag carbonation [9, 30].

The chemical composition of the slag was determined by X-ray Fluorescence (XRF, Panalytical PW 2400) analysis; results are presented in Table 1. High concentration of calcium was detected, which imparts this material its alkaline properties and high reactivity towards mineral carbonation. Also, BOF slag contains large quantities of iron, an undesirable loss of product from the steelmaking process, and a significant quantity of silicon, important for the formation of silicate minerals.

The mineralogical composition of the slag was determined by Quantitative X-Ray Diffraction (QXRD) on a Philips PW1830 equipped with a graphite monochromator and a gas proportional detector, using Cu K α radiation at 30 mA and 45 kV, step size of 0.03° 2 θ and counting time 2 s per step, over 5–70° 2 θ range. Mineral identification was done in Diffrac-Plus EVA (Bruker) and mineral quantification was performed by Rietveld refinement

technique using Topas Academic v4.1 (Coelho Software). The quantification results are presented in Table 2. Predominant minerals detected consist of Ca–ferrite and Ca–silicates, with Srebrodolskite and β –polymorph of dicalcium silicate (C_2S) being present in the largest quantities. Also observed are significant quantities of calcium and magnesium oxides, which are the minerals detrimental to soundness.

2.2. Pressurized slurry carbonation

Each particle size class of the slag was individually carbonated under pressure and elevated temperature in a 1.1 L stirred batch autoclave reactor (Buchi Ecoclave 300 type 3E). For all the experiments, 200 g of material was added to 800 ml ultrapure water ($18.2 \text{ M}\Omega\cdot\text{cm}$); the slurry was stirred by a turbine impeller rotating at 1000 rpm. Carbonation was conducted at $90 \text{ }^\circ\text{C}$ and 20 bar, gauge CO_2 partial pressure, for 2 hours duration. The carbonated slurry was filtered and the recovered solids were dried for 24 hours at $105 \text{ }^\circ\text{C}$ prior to analyses and further utilization. Several identical carbonation batches were run to produce sufficient material for mortar preparation. Carbonation degree of BOF slag was determined by using Thermogravimetric Analysis (TGA), measuring the mass loss between $400\text{--}900 \text{ }^\circ\text{C}$, which corresponds to the temperature interval where carbonates decompose and CO_2 is released. The instrument used for this purpose was a NETZSCH STA 409 PC, operated in nitrogen atmosphere, at a heating rate of $15 \text{ }^\circ\text{C}/\text{minute}$. After mineral carbonation experiments, visualization of trapped carbon and of other elements within a carbonated BOF slag sample was realized through elemental mapping, performed based on Wavelength Dispersive Spectroscopy (WDS) by means of an Electron Probe Micro-Analyzer (EPMA) equipped with a Field Emission Gun (FEG) (JEOL JXA-8530F). The sample was embedded in resin and polished to produce smooth sections for analysis.

2.3. Preparation and testing of mortar samples

In order to test the possibility of using BOF slag as partial replacement of fine aggregate in building materials, it was necessary to obtain representative specimens that could be used for testing. These specimens were prepared according to the standard EN 196-1:1994, by using a binder/aggregate ratio of 1/3 and a binder/water mass ratio of 0.625. The natural aggregate used was standard quartz sand (CEN 196-1, at 0-2 mm particle diameter), and the binder used was cement CEM I 42,5 R HES (CCB Italcementi Group). The same mix ratios were also

used when carbonated or non-carbonated BOF slag were used as replacement for half of the aggregate amount by weight. When one of the two finest slag classes (<0.08 mm and 0.08-0.5 mm) was used to replace the finer half of the natural aggregate, natural aggregate having particle size >0.5 mm (separated by sieving) was used as the other half. When the coarsest slag class was used (0.5-1.6 mm), an equal amount of natural aggregate having particle size <0.5 mm was used.

Mortars were prepared in accordance to EN 196-1. Consistency of the fresh mortar mixes was tested using a flow table (according to EN 1015-3:1998) in quadruplicate measurements, and then cast in a mould that permitted four specimens (with dimensions 20x20x160 mm) of the same mortar sample to be obtained. These reduced dimensions, in comparison with standard moulds of 40x40x160 mm, were required due to the limited amount of slag obtained from each carbonation batch. After 60 cycles of shock compaction, the material was kept in the mould for 24 hours, and the demoulded specimens were placed in a moist room at $\geq 93\%$ humidity and at constant temperature of 20 °C. Different curing durations (1 to 28 days) were used to assess their effect on the compressive strength. Also, some samples were subjected to accelerated curing in boiling water, as described by Rao et al. [31], to assess the effect of this curing condition on compressive strength. The intention was to magnify the effect of unhydrated oxides on volumetric expansion and compressive strength by boiling in water for an extended period. From the four specimens of one mortar sample, one specimen was maintained in the moist room for 1 day and then boiled for 6 hours, the second specimen was kept for 7 days in the moist room and then boiled for 6 hours, the third specimen was simply kept for 7 days in the moist room, and the fourth specimen was simply kept for 28 days in the moist room. After curing, specimens were dried for 48 hours at a temperature of 40 °C to remove excess pore water, which can cause detrimental effects during compressive strength testing. After drying, each specimen was cut into four cubes (20x20x20 mm), and each cube was tested for compressive strength (according to EN 196-1) in a Schenk Trebel screw tester at a compression rate of 0.2 mm/s, to obtain quadruplicate data.

Each mortar paste was also used for soundness testing (Le Chatelier test, according to EN 196-3, realized in duplicate). Samples mounted in the appropriate moulds and under load were kept in a water bath at 20 °C for 24 hours, and then boiled for 3 hours. Distances between indicator arms before and after boiling were measured by caliper and the difference (equivalent to sample expansion/swelling) was recorded; a difference greater than 5 mm is

considered inappropriate for use as construction material [18], although an expansion of 30 mm is allowable for hydraulic road binders [6].

Basicity and leaching behavior of the non-carbonated and carbonated slag powders, and that of the mortar samples, were tested using batch leaching test methodology (EN 12457-4). The crushed samples from compressive strength tests were first jaw-crushed and sieved to <1.6 mm. This methodology was chosen to assess the geochemical properties of the material rather than the effect of physical containment (in which case monolith leaching methodology would be applied). This methodology is also valid from the point of view of the material's life cycle, since a greater risk of leaching is found at the end of their lifetime, when demolished materials can end up stored in waste storage sites as CDW (construction and demolition waste). The solids were added to sealed bottles containing ultrapure water at a ratio of 10 g/100 ml and shaken for 24 hours at 160 rpm and 25 °C on a shaking table (Gerhardt Laboshake). Basicity was determined by pH measurement of the final slurry. The slurry was then centrifuged for 5 minutes at 4000 rpm (Heraeus Labofuge 400) to separate the supernatant, which was then diluted in 0.3 M nitric acid solution and analyzed in triplicates for metal and metalloid content by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Thermo Electron X Series).

Water absorption of non-carbonated and carbonated slag powders, and of the standard sand, was measured using an adapted methodology based on norms EN 1097-6 and BS:812 Part 2. Dry samples of the materials were mixed with DI water, at a mass-to-volume ratio of 25 g to 100 ml, in sealed bottles. The samples were allowed to hydrate statically for 24 hours. The resulting slurry was then vacuum-filtered on Whatman paper 5 to recover the moist solids. The difference in mass between the wet solids and the initially dry solids is taken as the total water absorption. The moist solids were then dried in an oven at 105 °C for 24 hours and re-weighed. The difference in mass between the moist and the dried solids is taken as physically absorbed water, while the difference in mass between the dried and the initially dry solids is taken as chemically absorbed water (i.e. water that is consumed by the formation of hydroxides and hydrates).

3. Results and discussion

3.1. CO₂ uptake

The CO₂ uptake of carbonated materials was determined by TGA analysis, and thus the evolution of CO₂ uptake based on particle size distribution was obtained. Figure 1 presents this evolution, where an increase of CO₂ uptake is observed once the particle size is reduced (10.0 wt% uptake for BOF slag <1.6 mm, compared with 16.2 wt% uptake for BOF slag <0.08 mm). This trend is easily explainable by the material's exposed surface increase that occurs when particle size is diminished, thus promoting contact between carbonic acid from the solution and the reactive minerals on the particle surfaces. Once the carbonation extent increases, the formation of passivating layers prevents access of the carbonic acid to the unreacted particle core [32]. Greater mineral conversion is thus obtained for finer particles. Based on the calcium content of the fresh BOF slag (35.0 wt%, Table 1), the maximum theoretical CO₂ uptake of the slag is 27.8 wt%. Accordingly, the Ca-conversion of the finest sample is 58.3 %, compared to 36.0 % for the coarsest sample.

EPMA analysis allowed insight on the distribution of the main constituent elements and mineral phases in the carbonated BOF slag <0.5 mm sample. The mineral distribution can be observed in Figure 2 in the form of backscattered electron microscopy analysis. Here, minerals containing heavier elements (e.g. Fe) appear in lighter shades of grey, while minerals containing only lighter elements (Ca, Mg, Si, C) appear in darker shades. The main point to take from these images is the heterogeneity of the material, both in terms of mineralogy as well as particle morphology. Better identification of the mineral phases can be made with aid of elemental mapping, shown in Figures 3 and 4. These images correspond to the higher magnification section shown in subfigure b of Figure 2. Figure 3 shows single element distributions, while Figure 4 shows composite (overlaid) elemental compositions for easier identification of minerals and chemical speciation of minor elements (phosphorus and vanadium shown).

The elemental distribution presented in Figure 3 offers details regarding the location and relative concentrations (with respect to the maximum concentration of each element in the sample) of nine different elements within the sample. The greatest quantities of calcium (magenta color scale) are present in the same places where silicon is found, meaning these are regions of calcium silicate. According to Table 2 this should be β -C₂S. As seen in Figure 4a, Ca and Si are co-located (cyan color) in large, relatively free grains, as well as in small grains within Fe-containing minerals (magenta regions). The mass concentration of calcium in C₂S

is 46.5 wt%. This is why the areas corresponding to calcium carbonate are shown in red (lower on the scale than magenta), since CaCO_3 contains 40.0 wt% Ca. This was also confirmed by means of energy-dispersive X-ray spectroscopy (EDS) point analysis, which detected only calcium and carbon in meaningful quantities in these areas, with calcium mass concentrations in the range of 40.5-42.6 wt%. It should be noted that the embedding resin contains primarily carbon; thus carbonate regions, where carbonate content is moderate, are seen mainly as blue. The elemental C content in CaCO_3 is only 12 wt%; in comparison the carbon content of bisphenol A, a typical component of epoxies, is 79 wt%.

Notably, no particle containing calcium but absent in other elements, which would correspond to free lime, is found. This signifies extensive free lime conversion. This result is corroborated by the elimination of chemical water absorption by the carbonated slags, according to Figure 5, which occurs in non-carbonated slag due to the hydration of free CaO into Ca(OH)_2 . Evidence was found by EPMA (see large CaCO_3 crystal on Figure 2b, and additional crystals on Figure 2a) that lime may readily dissolve in the carbonation medium, and precipitates in the bulk solution as large crystals. In contrast, CaCO_3 originating from silicates precipitates immediately on the silicate surfaces. Evidence of this is that all C_2S grains are enveloped by CaCO_3 layers (red rims around magenta areas in Figure 3 Ca map), including those C_2S grains inside Fe-containing minerals. This suggests that carbonic acid is able to access these interior grains, and that carbonation conversion limitation is mainly due to passivation of the reactive grains by dense carbonate layers rather than their blockage by less reactive or unreactive surrounding minerals. This confirms that a higher specific surface area of the powder material is beneficial to obtain a greater conversion through mineral carbonation. Simultaneously, a water-rich environment and proper mixing are essential for enhanced CO_2 uptake.

Lower on the Ca scale in Figure 3, orange regions are attributable to calcium-ferrite, due to the presence of Fe and absence of Si in these regions. This is confirmed in Figure 4a by the co-placement of Ca and Fe. The existence of darker and lighter 'CaFe' regions in Figure 4a may suggest that Ca has been removed from the lighter regions due to carbonation, leaving behind Fe-enriched regions compared to the darker areas. Still, seeing how there are more of the darker magenta regions in Figure 4a, it appears that C_2S reacts more extensively than srebrodolskite. This would be in accordance with the results of Bodor et al. [30], where QXRD was used to quantify mineral conversions.

Looking at magnesium, regions where Mg is not co-located with other elements can be found (blue in Figure 4b), which correspond to unreacted MgO; periclase is known to require more intense conditions for carbonation than calcium minerals [33]. Regions can also be found where Mg is co-located with srebrodolskite. This is visible by inspecting Figure 3, as the tri-elemental set of Ca-Mg-Fe is not plotted in Figure 4. It is possible that Mg is present in solid-solution with srebrodolskite, substituting partially for Fe. Doucet et al. [34] suggested this occurrence, but also suggested Si substitution, resulting in the chemical formula $\text{Ca}_2\text{Fe}_{1.4}\text{Mg}_{0.3}\text{Si}_{0.3}\text{O}_5$. Looking at Figure 3 and Figure 4a, silicon is not observable in srebrodolskite regions; thus srebrodolskite in the present material is more likely to have a formula such as $\text{Ca}_{(2-x)}\text{Fe}_{(2-y)}\text{Mg}_{(x+y)}\text{O}_{(5-0.5y)}$.

In the case of silicon, green regions (absent of Ca co-placement) are observable in Figure 4a that can be associated with residual silica from the carbonation of C_2S . In Figure 4c it is seen that phosphorous is strongly associated with these regions. Phosphorous is also found in the carbonate regions and the C_2S regions. It thus appears that after carbonation of C_2S , P containing in this phase remains with the carbonation products. On the other hand, looking at Figures 4a and 4c, vanadium is mainly co-placed with Fe-rich regions, which can correspond to srebrodolskite or iron compounds (metallic iron and iron oxides, visible as magenta regions on the Fe map in Figure 3). Van Zomeren et al. [35] suggested that V is attached to surfaces of C_2F (srebrodolskite) and C_2S in BOF slag, and when these phases react it is redistributed, thus partially explaining the increased leaching of V after carbonation (leaching of V also increases due to pH reduction). The regions richest in Cr and Al also contain V, low concentrations of Fe and Ca, and no Si (Figure 3). They thus appear to be unique ferrite inclusions. Chromium and vanadium represent two of the important metalloids regarding the leaching effect, due to their toxicity and their tendency to leach at less alkaline pH [9, 33]. Their leaching results, alongside other controlled elements, are presented in Section 3.5.

3.2. Mortar paste consistency

For all mortar samples, a constant water/cement weight ratio was used (0.625); hence, consistency of mortar pastes was not controlled but rather was a response variable. In the cases of replacing 50% of natural aggregate with BOF slags, sieving of standard sand was done with a <0.5 mm mesh sieve, with the fine fraction being replaced by one of the two

finest BOF slag materials (<0.08 mm and <0.5 mm), while the coarse (> 0.5 mm) sand fraction was replaced by <1.6 mm BOF slags. This was done to minimize the impact of aggregate replacement (sand by slag) on the particle size distribution of the aggregate fraction, which has important implications on mortar consistency and strength properties. However, the particle size distribution of the slags also varied based on its type: carbonated or non-carbonated. This happened due to modification of particle size (namely, size reduction) during the carbonation process, resulting from the intense mixing (1000 rpm) in the reactor that promotes particle attrition, and the leaching and precipitation effects that occur during aqueous carbonation. In some cases, very small sized particles formed, the quantities of which exceeded the maximum accepted by standard EN 196-1:1994 [36]. This phenomenon occurred when both carbonated and non-carbonated BOF slag <0.08 mm were used, and also occurred for the <1.6 mm carbonated BOF slag sample.

The presence of small sized aggregate particles in an excess amount leads to increased physical water absorption, as shown in Figure 5. It is seen that physical water absorption is higher when aggregate particles are smaller, and is higher for the carbonated slags compared to the non-carbonated slags. The latter is a consequence of the particle size reduction that occurs during carbonation. Increase in physical water absorption can lead to a decrease in mortar consistency, and can further affect its density through formation of larger voids that reduce compressive strength.

The average values (four values for each sample) of flow table results, which measures mortar paste consistency, are presented in Figure 6. When the average value is equal to 110 mm, the flow table value of the mortar paste is considered to be zero, implying its lack of flow behavior. This phenomenon is recorded in Figure 6 for some mortars that contained BOF slag. Although for some mortar samples the flow table value was zero, the water/cement ratio was not adjusted in this study, so that a single variable could exist throughout the experiments, namely aggregate replacement. As suggested by Martínez-Lage et al. [37] regarding the use of recycled fired clay aggregates for partial or total replacement of natural aggregate, more water must be added to conventional concrete pastes to obtain the same workability (flow behavior). Thomas et al. [38] related the greater water demands of concrete pastes prepared using CDW as aggregate to their greater intrinsic porosity, which increases water absorption. This is also reflected in the significantly smaller water absorption value of the standard sand used in the present study (Figure 5). However, according to Thomas et al.

[38], considering the mechanical properties, the influence of the recycled aggregate is worse for the case of high water-to-cement ratios. Thus the benefits of increasing water content are limited. Optimization of mortar paste consistency represents an aim for future research on the use of BOF slags as aggregates.

Density dependence on mortar paste consistency is demonstrated by the similarity between Figures 6 and 7. Figure 7 presents the average values of specimen densities (four specimens were obtained from the casting of each paste) for all mortar compositions. Since sample volumes were constant, sample densities are proportional to masses. Good agreement between paste consistency and mortar density was observed for samples containing non-carbonated or carbonated BOF slag <0.08 mm, and for that containing carbonated <1.6 mm BOF slag. For these samples, results from flow table (110 mm, which signifies no flow) and density (1.5-2.2 g/cm³) measurements were the smallest. Small specimen density is a consequence of higher void volume, which is a direct result of poor flow behavior of the mortar paste. The smaller average value of the reference specimen density compared to the other samples is explained by the higher specific density of BOF slag (3.69 g/cm³ [9]) compared to that of natural sand (2.65 g/cm³).

Flow table values obtained for mortar samples containing non-carbonated <1.6 mm BOF slag or non-carbonated/carbonated <0.5 mm BOF slag (123-136 mm, compared to 161 mm for the reference specimen) were reasonable for mortar applications. These specimens had densities of 2.4 g/cm³, compared to 2.3 g/cm³ for the reference. These results have important effects on a specimen's compressive strength (see Section 3.4).

3.3. Soundness of mortars

Volumetric expansion of BOF slag, mainly due to hydration of free alkaline oxides [19], has restricted its use in the construction domain. This implies the necessity of treatment methods before its utilization. Mineral carbonation of BOF slag also has as an outcome, besides the sequestration of CO₂, the improvement of the material's volumetric stability. This is due to the formation of geochemically stable carbonates, which prevents the formation of hydroxides when exposing the material to a humid or aqueous environment (as observed from the chemical water absorption values in Figure 5). To confirm this theory, samples of

the prepared mortar pastes were used to perform the Le Chatelier test. Results of this test are shown in Figure 8.

For a material to be considered stable, the difference between the value read before boiling and the value read after boiling, during the Le Chatelier test, should not be greater than 5 mm [18]. In this study, the reference mortar sample (with a content of 100% standard quartz sand as aggregate) indicated a swelling expansion of only 0.9 mm. Other samples that remained under 5 mm variation were the mortar samples with 50% aggregate replaced by carbonated BOF slags of particle sizes <0.08 mm (-0.3 mm contraction) and <0.5 mm (1.1 mm swelling). All remaining mortar samples, including all which contained non-carbonated slag, registered swelling values substantially greater than 5 mm (11.4 to 91.7 mm swelling), placing them in the category of materials unsuited for use in the construction domain.

A variation of the distance between Le Chatelier test indicators greater than 5 mm was registered for all mortar samples containing non-carbonated BOF slag as replacement of 50% of the aggregate, regardless of the slag's particle size. Notably, the coarser slags had greater swelling. It had been rather expected that smaller particle size of the untreated BOF slag would conduce to greater swelling, since greater contact surface would be available for reaction with the aqueous solution. Instead, it appears that the finer slag becomes extensively hydrated, but not completely, already during paste preparation, and thus it suffers diminished delayed hydration (i.e. during curing). These results confirm the theory that free oxides (particularly lime since not all periclase was carbonated according to the EPMA results, discussed in Section 3.1) have a detrimental effect regarding volume stability.

A swelling value of 15.7 mm was obtained for the mortar sample containing carbonated <1.6 mm BOF slag. In this case, the reason for volume instability can be attributed to insufficient carbonation extent of slag, as observed in Figure 1. This means that a more intense process should be used for carbonation of materials with larger particle sizes, or further comminution should be done prior to or during carbonation. It should be pointed out that mineral carbonation not only reduces the near-term instability of BOF slag caused by the formation of hydroxides, but also reduces the long-term weathering of a slag-containing building material caused by reaction with atmospheric CO₂.

3.4. Compressive strength of mortars

Each of the four specimens belonging to one mortar sample was cured differently, as described in Section 2.3. The main variables were curing time (24 h, 7 d, and 28 d) and boiling or no boiling after curing (for the purpose of accelerated curing). The compressive strengths of 4 cubes cut from the same mortar specimen were averaged to obtain the compressive strength value of that specimen. No significant statistical difference was observed between the curing conditions. This is thought to be a result of the accelerated curing performed on the samples cured for shorter durations (24 h and 7 d), which diminished the difference in their strength compared to the samples cured for 28 days. The small sample sizes used (20 mm sides, compared to typical 40 mm) contributed to measurement variability due to greater influence of defects on the sample's strength. On the other hand, significant differences were observed between mortars of different compositions. Therefore, the compressive strengths data from each mortar composition were averaged as presented in Figure 9.

The main objective of the compressive strength test was to assess the effect of aggregate replacement relative to the reference composition. From Figure 9 it is observed that the smallest values of compressive strength belong to the fairly dry mortar pastes that showed insufficient flow (i.e. 110 mm value in the flow table test), which included the two samples prepared with the finest BOF slag fractions (<0.08 mm). At the same time, the mortar samples prepared with the coarsest BOF slags (<1.6 mm) had compressive strengths significantly lower than the reference. This is in agreement with their volume instability being greater than that of samples prepared with the finer BOF slag fractions (Figure 8). Hence, the only mortar specimen that obtained similar consistency, soundness and compressive strength values as the reference mortar specimen, was the one with carbonated BOF slag of <0.5 mm particle size. For this mortar, the compressive strength value was averaged at 27.3 N/mm², even higher than the value obtained for the reference mortar (23.4 N/mm²). These results are in accordance with those obtained by Monkman et al. [25], who reported that mortars made with a blend of carbonated <0.6 mm BOF slag and river sand had comparable 28 days compressive strengths (~14.5–22.5 MPa) to mortars made with only river sand when subjected to conventional moist curing. This result seems to be due to the fact that mortars with carbonated slag as aggregate possess less pore water, as indicated by their flow table values (Figure 6), which in turn can be attributed to higher water absorption

of the carbonated slag particles when compared to that of sand particles (Figure 5). This will also influence the porosity of the mortar specimens.

Results from compressive strength test, supported by the other tests (consistency and soundness), demonstrate the utility of the carbonation process as a treatment method for BOF slag towards its use as aggregate in the construction domain. Also, it can be concluded that if BOF slag is used as stated, this material should possess a particle size distribution according to the standard EN 196-1:1994, and the free lime conversion after mineral carbonation should be high enough to ensure an acceptable value of soundness for the final building material.

3.5. Leaching from mortars

Based on the abovementioned results, the only BOF slag fraction (carbonated and non-carbonated) used in leaching tests was that with particle size <0.5 mm, along with the crushed and ground mortar samples containing this type of slag, and the crushed and ground reference mortar sample used for comparison. The aim was to compare the leaching tendency of some regulated metalloids and heavy metals from the slag, and assess the effect played by both mineral carbonation and partial containment in a cementitious matrix on this tendency. At the same time, by comparing the leaching results from the reference mortar sample with those from the slag-containing mortar samples, the differential influence on leaching tendency by including the BOF slag in the mortar composition can be deduced.

It was found (Figure 10) that after mineral carbonation the leaching tendency of several elements drops, namely barium, nickel and lead, while it remains nearly unchanged for chromium and copper, and it increases substantially for vanadium. The leaching tendencies of cobalt and molybdenum remained below the detection limit (0.1 mg/kg). These findings are in agreement with previous work of our group on hot-stage carbonation of BOF slags [9]. As previously reported, the important increase of V leaching, from 0.06 mg/kg to 9.17 mg/kg here, represents one of the main reasons for which BOF slag mineral carbonation is considered unfavorable in the context of waste reuse. Santos et al. [39] attributed the competition of carbonate ions with vanadate ions for chemical bonding sites (e.g. BaO, CaO and PbO) as the mechanism for vanadium mobility from carbonated municipal solid waste incineration bottom ashes. However, as seen in Figure 10, including the BOF slags in a

cementitious mortar matrix led to full containment of the metalloid's leaching tendency. Leaching of lead and nickel similarly decreased for the slags contained in mortars.

Looking at the leaching results of other elements, in some instances leaching increased from the slag-containing mortar compared to the pure slag. This was the case for barium and copper. In both cases, leaching from the reference mortar sample was substantial, which indicates contribution from the other materials of the mortar (sand and cement) to the leaching of these elements. This means that placing BOF slags in a cementitious matrix is not detrimental to its Ba and Cu leaching tendencies. On the other hand, the only result of concern was that of chromium leaching from the carbonated BOF slag-containing mortar. Its Cr leaching tendency was the highest of all tested materials. Yet, the leaching extent from this material (3.9 mg/kg) is still comparatively low; the Belgian-Walloon limit for Cr^(VI) leaching from re-used waste materials is 20 mg/kg [40]. According to Fernández-Bertos et al. [41] and Cornelis et al. [42], leaching of chromium at high pH in alkaline materials is controlled by Cr substitution in calcium-silicate-hydrates (CSH), the main component of hydrated cement. Thus, over time, it is possible that chromium leached from BOF slag can become chemically bonded to the surrounding matrix, thus minimizing the leaching risk from the construction material for the duration of its life cycle, including the CDW phase.

Differing leaching tendencies from slag-containing mortar samples compared to leaching values of the same elements from the pure slags are linked to the basicity of the materials, and thus the pH values of the leaching solutions. Figure 11 presents the pH values that correspond to the leaching tests presented in Figure 10. In the figure, a decrease of approximately one pH unit was registered for the carbonated BOF slag compared to the non-carbonated slag. The mortar samples, however, had elevated pH, ranging from 12.4 for the reference sample to 12.7 for the mortar containing non-carbonated BOF slag. The high pH values of the mortars represents the reason for which vanadium leaching was kept low, since V is known to mobilize in response to pH reduction [24].

The results regarding leaching from mortar samples containing carbonated BOF slag as partial replacement of natural sand aggregate provide further confirmation that mineral carbonation process can be considered an effective treatment method for metallurgical slags prior to utilization of this material in the construction domain. A further research direction that can be investigated is the inclusion of sorbent materials as partial aggregate replacement

to further attenuate the leaching tendency of elements of concern, such as chromium in the present case.

4. Conclusions

The research presented in this paper aimed to demonstrate that mineral carbonation can be considered a route to treat steelmaking converter slags in order to further use this residual material as a partial aggregate replacement in the domain of civil constructions. In this respect, the CO₂ uptake of BOF slag was studied, and it was observed that its value is inversely proportional with the size of slag particles. At the same time, particle size had an important influence on consistency of the fresh mortar paste and, implicitly, on compressive strength of the hardened mortar specimens. From this point of view, it can be concluded that maintaining the particle size distribution of the aggregate mixture according to the standard norms is critical for ensuring suitable consistency and mechanical strength.

Mineral carbonation of BOF slags leads to the sequestration of meaningful amounts of CO₂, 0.11–0.19 kg,CO₂/kg,slag at the conversions achieved herein. Taking into account a 50% replacement ratio of natural aggregate, and an aggregate-to-binder ratio of 3, the prepared mortars contained up to 74 g,CO₂/kg; this categorizes it as a carbon sink. The mineral carbonation process also represents a means of treatment by forming stable carbonates through reaction of calcium and magnesium oxides with CO₂. This is especially important for the stabilization of free lime, which was shown to have detrimental effects on the hydration-driven volume expansion of mortars prepared with non-carbonated BOF slag. In contrast, for mortar samples containing carbonated slag, soundness increased in proportion to the carbonation conversion, reaching values similar to the soundness of the reference cement mortar.

The best result obtained in terms of the combination of all tested parameters (consistency via flow table test, soundness, compressive strength and leaching of toxic elements) corresponded to the mortar mixture prepared with carbonated BOF slag of <0.5 mm particle size. In light of these results, it is possible to conclude that BOF slag utilization as partial aggregate replacement in the construction domain can be a realistic method to valorize and recycle this kind of industrial residue. Future research directions could be undertaken by: (i) using a constant particle size distribution of the aggregate mixture, thus allowing better

control of water content and absorption, and consequently mortar consistency; (ii) using sorbent materials in the aggregate mixture to further reduce the leaching behavior of certain elements, particularly metalloids, that originate from the carbonated slag content; and (iii) testing the long-term durability of building materials containing carbonated slag.

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List of figures:

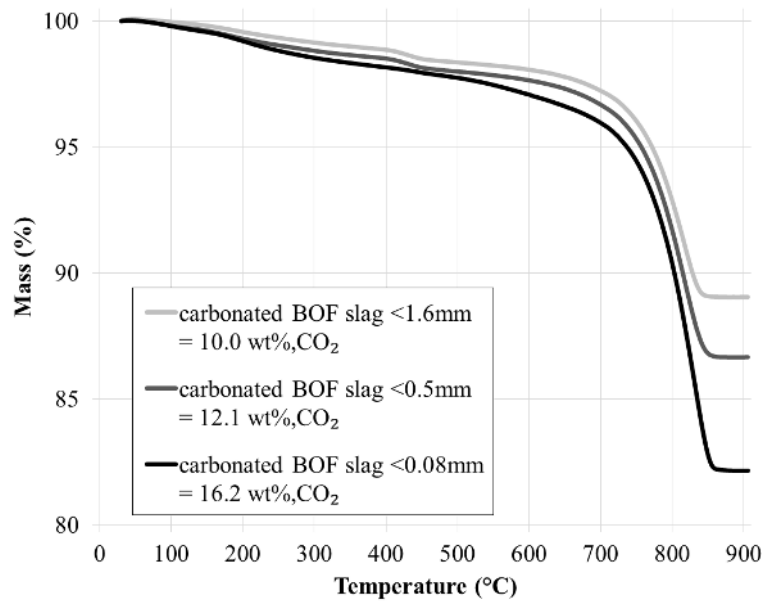


Fig. 1 – CO₂ uptake of carbonated BOF slags as a function of particle size, determined by TGA analysis.

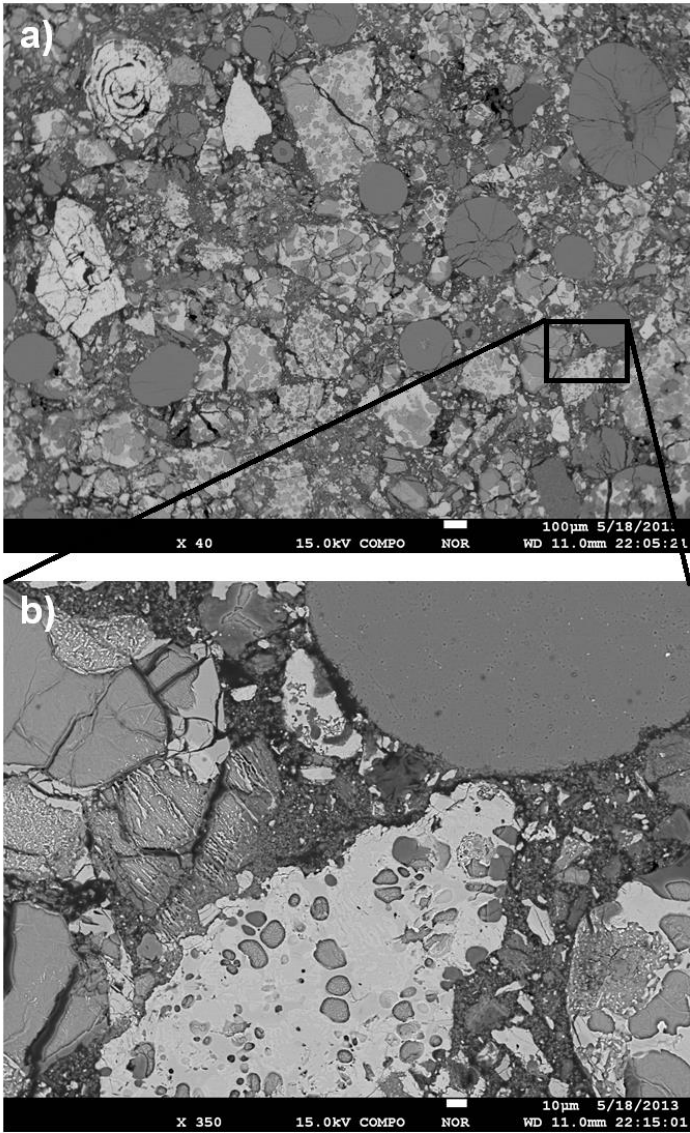


Fig. 2 – Backscattered scanning electron microscopy image of a polished section of carbonated BOF slag <0.5 mm embedded in resin, obtained by EPMA analysis; lower (a) and higher (b) magnifications.

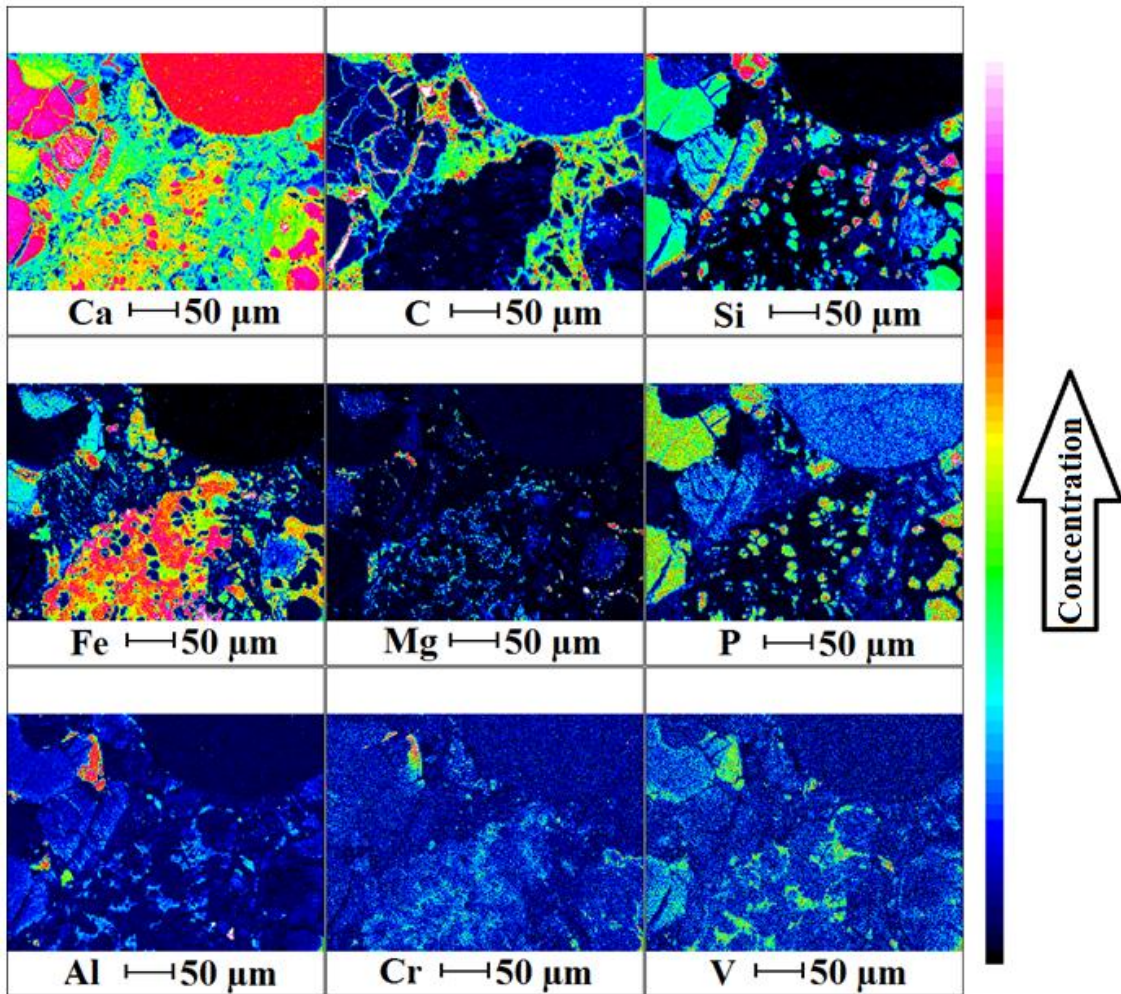


Fig. 3 – Distribution of elemental components in a polished section of a carbonated BOF slag <0.5 mm sample embedded in resin, obtained by EPMA analysis; color scale is proportional to mass concentration of each element relative to its highest detected concentration, and is semi-quantitative.

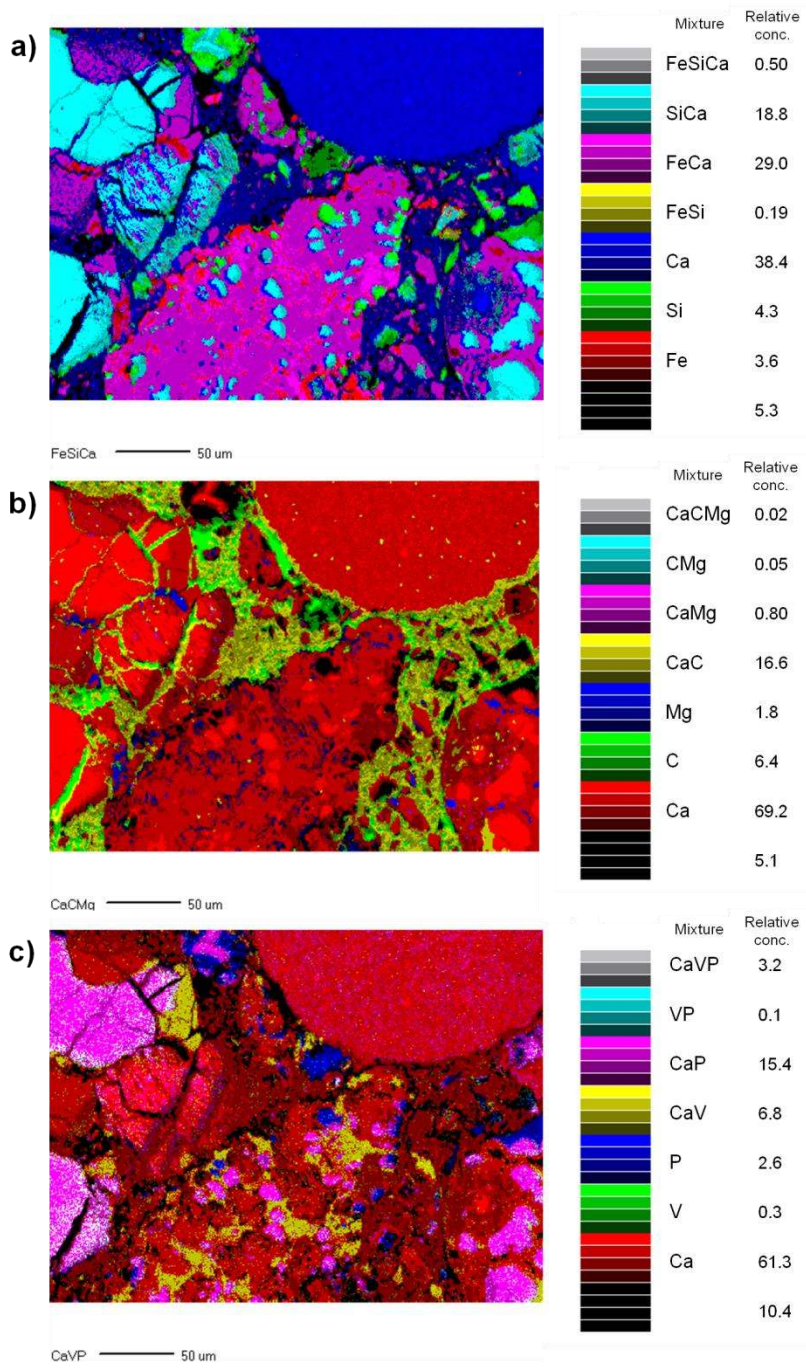


Fig. 4 – Distribution of elemental components in a polished section of a carbonated BOF slag <0.5 mm sample embedded in resin, obtained by EPMA analysis; indicated concentrations (mass %) are relative to tri-elemental mixtures (a. Fe, Si, Ca; b. Ca, C, Mg; c. Ca, V, P), not material total, and are semi-quantitative.

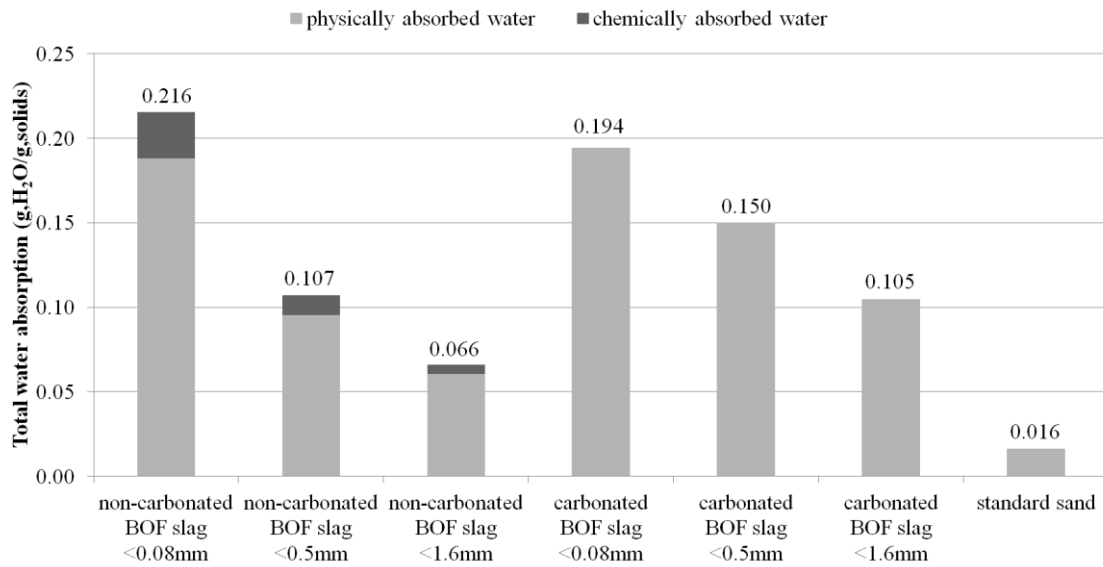


Fig. 5 – Water absorption (physical, chemical and total) of non-carbonated and carbonated BOF slags and of standard sand.

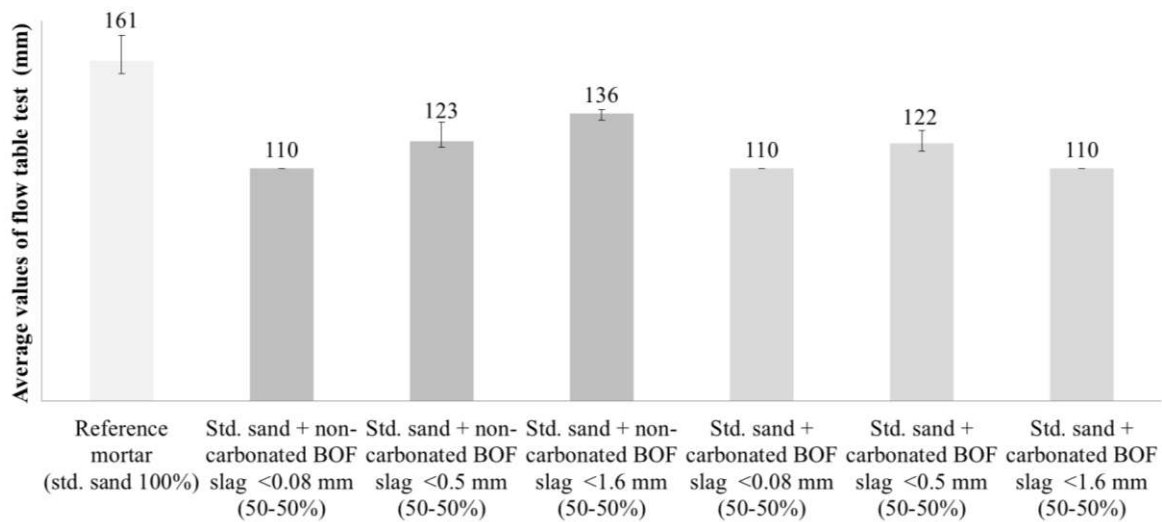


Fig. 6 – Average values of flow table tests for all mortar pastes prepared (reference, non-carbonated BOF slag aggregate replacement, and carbonated BOF slag aggregate replacement); error bars based on quadruplicates.

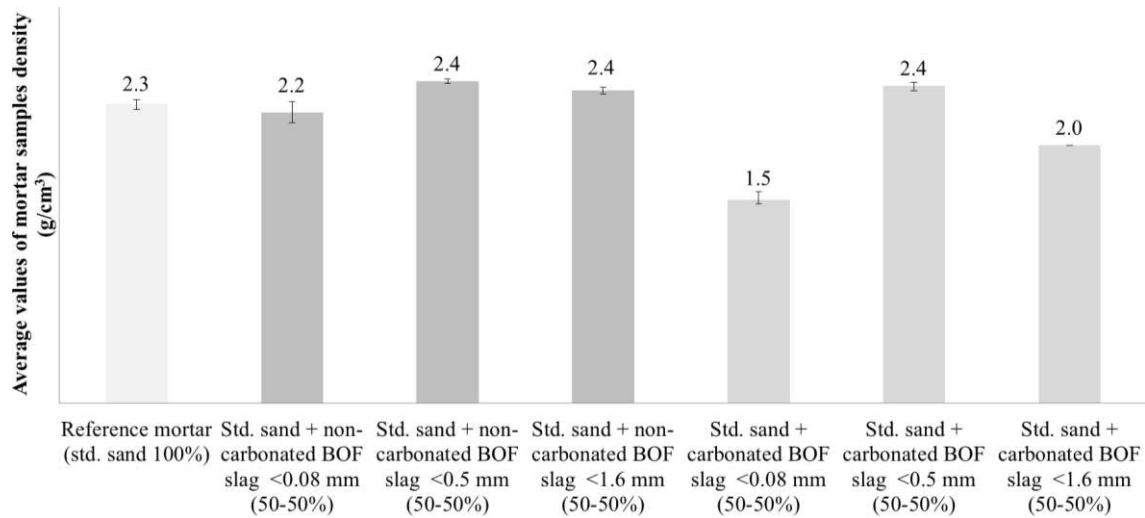


Fig. 7 – Average values of density for all mortar pastes prepared (reference, non-carbonated BOF slag aggregate replacement, and carbonated BOF slag aggregate replacement); error bars based on quadruplicates.

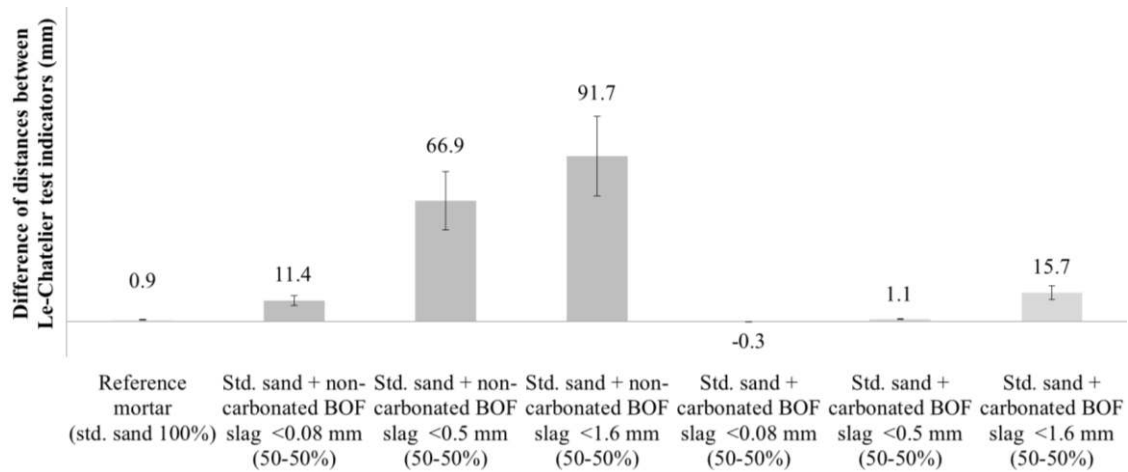


Fig. 8 – Difference of distances between Le Chatelier test indicators for all mortar mixtures, before and after boiling for 3 hours; average of duplicate measurements.

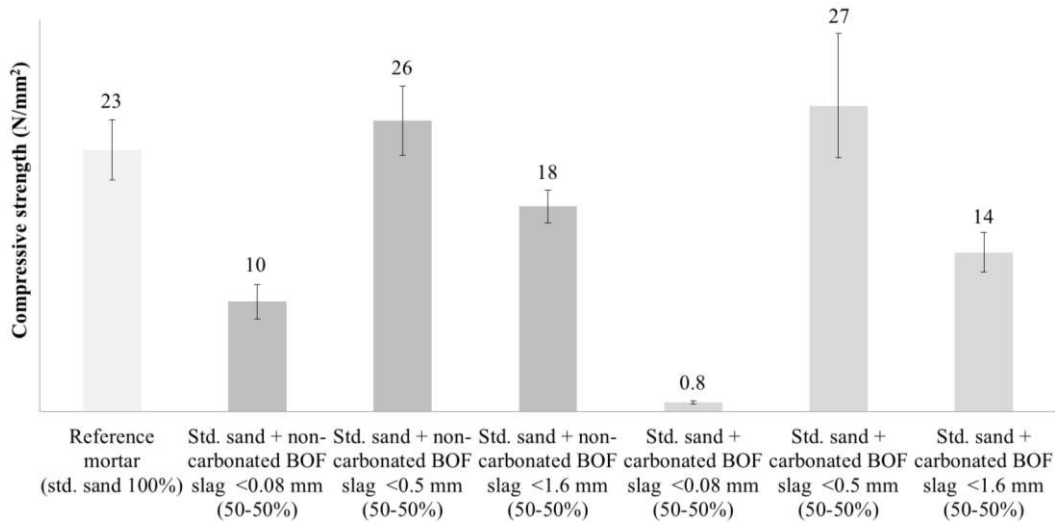


Fig. 9 – Average values of compressive strength for all mortar specimens (reference, non-carbonated BOF slag aggregate replacement, and carbonated BOF slag aggregate replacement); error bars are based on data from samples treated under different curing conditions (1 and 7 days followed by boiling, and 7 and 28 days without boiling) and quadruplicates of each measurement.

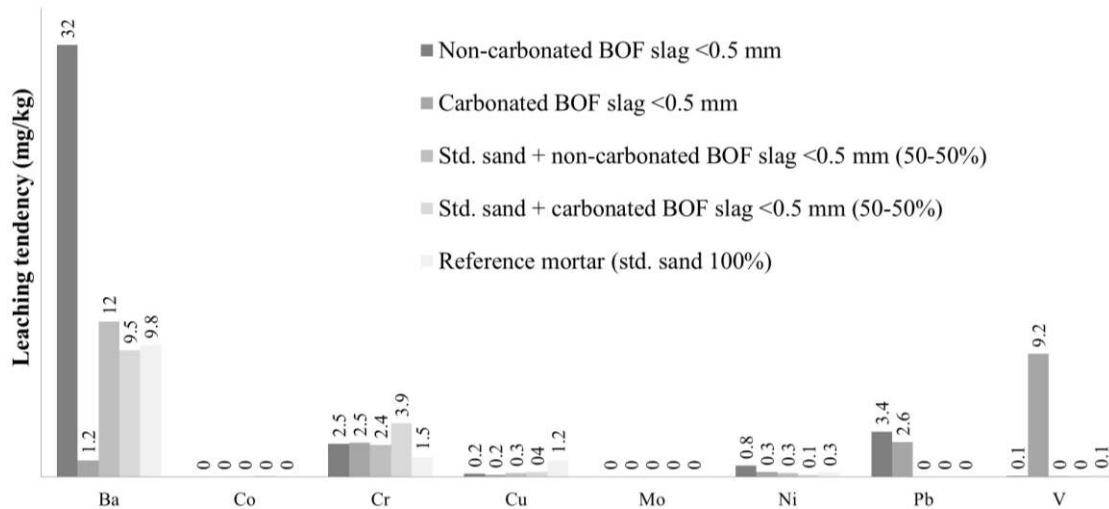


Fig. 10 – Leaching tendency of eight metalloids and heavy metals from <0.5 mm BOF slags before and after carbonation, from mortar samples containing <0.5 mm BOF slag (carbonated or non-carbonated) as partial aggregate replacement, and from reference mortar sample; value of ‘0’ means <0.1 mg/kg.

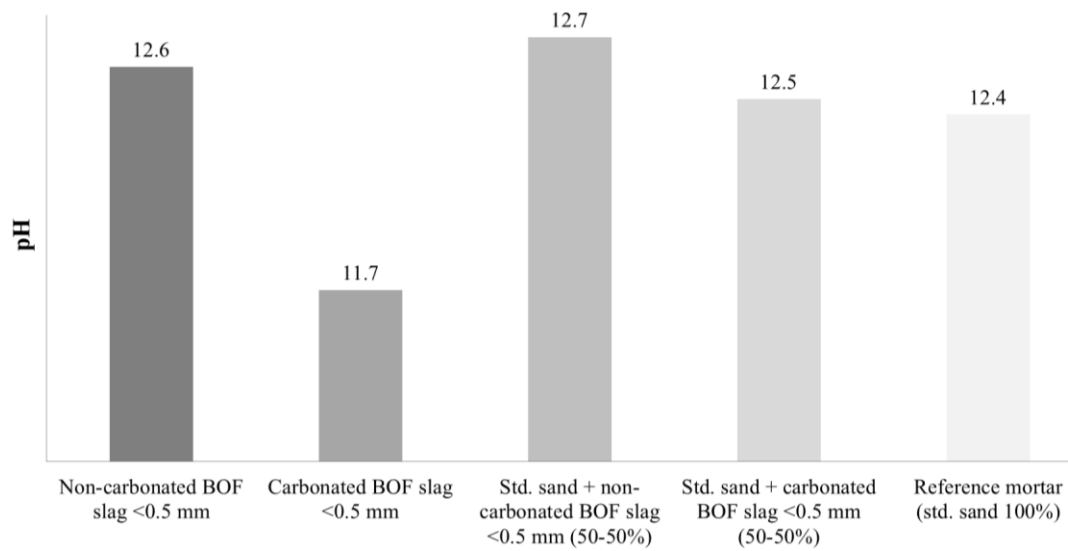


Fig. 11 – pH values from batch leaching solutions of <0.5 mm BOF slags before and after carbonation, of mortar samples containing <0.5 mm BOF slag (carbonated or non-carbonated) as partial aggregate replacement, and of reference mortar sample.

List of tables:**Table 1** – Chemical composition of BOF slag, determined by XRF, in wt%.

Element	wt%
Al	1.3
Ca	35.0
Cr	0.27
Fe	20.6
Mg	0.61
Mn	2.8
Ni	0.08
Si	5.8
Ti	0.40
Balance	
(H, C, O, trace)	33.1

Table 2 – Mineralogical composition of BOF slag, determined by QXRD, in wt%.

Mineral name	Chemical formula	wt%
Srebrodolskite	$\text{Ca}_2\text{Fe}_2\text{O}_5$	32.3
β - C_2S	Ca_2SiO_4	30.8
Lime	CaO	8.8
Wuestite	FeO	6.7
Fayalite	Fe_2SiO_4	3.8
Portlandite	$\text{Ca}(\text{OH})_2$	3.1
Wollastonite	CaSiO_3	2.9
Brucite	$\text{Mg}(\text{OH})_2$	2.4
Ferrosilite	$(\text{Fe}^{(\text{II})}, \text{Mg})_2\text{Si}_2\text{O}_6$	2.2
Clinoenstatite	$\text{Mg}_2\text{Si}_2\text{O}_6$	1.9
Periclase	MgO	1.1
Other (< 1 wt%)	-	4.0