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# High-temperature slag engineering in pursuit of effective mineral carbonation of pyroxene-rich ferronickel slag

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# ABSTRACT

The search for resources for low-carbon construction materials and valorization pathways for industrial residues go hand in hand. Mineral carbonation has been abundantly studied to strive for a net-zero  $CO_2$  construction sector. Ferronickel slags have been studied for the production of other cementitious materials, but have inferior carbonation potential due to their low Ca-content. This work shows that the reactivity of a pyroxene-rich ferronickel slag towards  $CO_2$  can be substantially increased using high-temperature slag engineering. Using a combination of CaCO<sub>3</sub> additions and slow cooling, the produced compacts made from synthesized slags acquire a compressive strength of 30–40 MPa after carbonation at 10 bar  $CO_2$  and 60 °C for 16 hours. The reactivity towards  $CO_2$  originates from the formation of akermanite (Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>) during slag modification with > 20 wt% CaCO<sub>3</sub>. The compressive strength is dependent on the particle size distribution of the modified slag and carbonation time. Although the reaction degree of akermanite is high after 6 hours of carbonation, a significant strength increase is still seen after carbonation for 16 and 48 hours. The carbonation process forms a binding phase composed of aragonite and a CaMg-carbonate which might be high Mg-calcite or protodolomite. The CO<sub>2</sub> balance of the overall process shows a substantially lower value compared to Portland clinker-based cements, but additional efforts are required to develop an optimum net-zero  $CO_2$  process.

# 1. Introduction

The construction sector is embracing low-carbon binders to become future-proof. A promising pathway is mineral carbonation, in which a carbonate binder is obtained by exposure of a pre-shaped compact to elevated concentrations of CO<sub>2</sub>, as its production process fixates more CO<sub>2</sub> in solid carbonates than it emits [9]. In other words, mineral carbonation is a subdivision of carbon capture and utilization techniques. Sector roadmaps towards net-zero CO<sub>2</sub> always mention carbon capture as the final process that can deliver zero CO<sub>2</sub> after avoiding emissions to the best possible extent [7,11]. While also using mineral carbonation as a hardening process to obtain a carbonate binder, the added benefit is the replacement of the current commercial alternative – Portland cement – and its related CO<sub>2</sub> emissions. The precursors for mineral carbonation are mostly alkaline waste streams derived from high-temperature metallurgical or combustion processes [22]. Globally, the mineral carbonation of alkaline solid wastes was estimated to have

the potential to reduce the anthropogenic  $\mathrm{CO}_2$  emissions by 12.5 % [25].

Mineral carbonation of Ca- and Mg-silicate minerals and waste streams containing them is well-known in literature. The carbonation of (stainless) steel slags can lead to the production of ultra-high compressive strength compacts (134 MPa) [28] or can be carried out using low CO<sub>2</sub> pressure and concentration (e.g. 17 % CO<sub>2</sub> at 1.5 bar) [14,23]. The ease of carbonation of steel slags is assisted by the presence of dicalcium silicates and sometimes calcium hydroxide [21], however, in some cases also the Mg, Fe, and Mn-bearing phases participate in the conversion to carbonates [4]. The carbonation of Mg-olivine (forsterite) has been studied extensively in view of carbon capture and storage (CCS), through injection in geological deposits. Its kinetics are limited due to the formation of an amorphous silica passivating layer [16]. This can be overcome partially by increasing the ionic strength of the pore solution by the addition of sodium salts [12] or potassium salts [35], but high temperatures and pressures are still needed to reach significant CO2 uptakes.

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High-temperature slag modification has been tested to increase the reactivity of slags [17,26,31]. Although literature is only found in view of its reactivity as supplementary cementitious or alkali-activated material, the general principles can be used for carbonation as well. During high-temperature slag modification, the cooling regime after slag-making is modified [26] or slight changes to the chemical composition are induced [17,31] to alter the overall phase composition or composition of slags is seen as one of the strength deciding parameters [21]. So, although high-temperature slag modification has not been applied for this purpose and the effects of e.g., cooling regime are unknown, it might be a promising tool for their use for carbonation curing.

The present paper targets to investigate the potential of hightemperature modification for optimizing the reactivity of ferronickel slag towards carbonation curing by studying (1) the effect of  $CaCO_3$ addition to modify its (chemical and phase) composition and (2) the effect of altering the cooling regime after slag-making to modify its phase composition while maintaining the same chemical composition. This is done through a combination of high-temperature modification of the slag and screening the mineral carbonation potential at moderate pressure. The study thereby brings novel insights by clearly revealing the candidate minerals for carbonation and on how to promote their formation by slag engineering.

## 2. Materials and methods

A slag originating from the processing of laterite ores into ferronickel was studied. The chemical composition of this ferronickel slag (FS) in Table 1 was obtained using X-ray fluorescence. Only the elements showing calculated oxide concentrations > 1 wt% are provided, the rest is cumulated in the "Others" column. The composition of the slag was used as input in the Equilib module of the FactSage software [5] to calculate the equilibrium phase compositions as a function of temperature. The "Others" from Table 1 were discarded from the composition for these simulations. The influence of additions of CaCO<sub>3</sub> on the equilibrium phase composition was explored. The FactPS and FTOxid databases were used, running calculations over all possible solid and gas phases, excluding the pure liquids (in other words only having a molten slag phase as liquid). Calculations were carried out from 1500  $^\circ C$  to 800  $^\circ C$ with 25 °C intervals at 1 atm pressure. The oxygen partial pressure was fixed at  $10^{-10}$  bar to ensure the elements were modeled in the oxidation state relevant to the ferronickel production process. The equilibrium was only calculated at the indicated intervals, not taking additional points at the transition temperatures.

Experimental modifications of the slag were carried out in a Nabertherm RHTV 120–600/18 vertical tube furnace modified to enable quenching of the crucible. A steel crucible filled with 40 g of sample is hung on a molybdenum wire and heated up to 1300 °C at a rate of 180 °C/h. Slow cooling at 180 °C/h inside the furnace was compared with water quenching by immersing the crucible in a bucket of water. The variable quantities of CaCO<sub>3</sub> addition resulted in the 7 samples listed in Table 2 to be studied in the carbonation process.

All samples were ball milled to a powder with a  $d_{50}$  of 6–12  $\mu m$  and pressed into a cylinder before carbonation. The cylinder consisted of 20–23 g of the modified slags from Table 2. Water was added to obtain a water/solids mass ratio of 0.08. Cylinders with a diameter of 23 mm were pressed using a force of 150 kg/cm² for 10 s, resulting in a height of 22–24 mm. The pellets were carbonated at a CO<sub>2</sub> pressure of 10 bar and 60 °C for 16 hours using a water container to maintain water saturation in a 3.25 L Premex reactor with continuous monitoring and steering of

Chemical	composition	of the	ferronickel	slag	(wt%).
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Element	FeO	SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	MgO	Others
wt%	15.2	50.1	2.6	5.0	24.7	2.4

Table 2

Overview of (modified) slag samples for carbonation	studies.
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Sample code	Additive	Cooling procedure
FS-0	No furnace treatment	
FS-0-w	/	Water quenching (w)
FS-0-f	/	Slow cooling in furnace 180°C/h (f)
FS-10Cc-w	10 wt% CaCO3	Water quenching (w)
FS-10Cc-f	10 wt% CaCO3	Slow cooling in furnace 180°C/h (f)
FS-20Cc-f	20 wt% CaCO3	Slow cooling in furnace 180°C/h (f)
FS-30Cc-f	30 wt% CaCO <sub>3</sub>	Slow cooling in furnace 180°C/h (f)

CO2 pressure and temperature. The reactor was not flushed before introducing CO<sub>2</sub> to build up the pressure. The compressive strength was measured on only 1 cylinder per experiment for screening of the samples, but triplicates were made in the final stage for comparing the strength values. The crushed samples were used for characterization; the total carbon content was measured and the phase composition was analyzed using X-ray diffraction (XRD) of the crushed carbonated samples and the powders before carbonation. The CO<sub>2</sub>-uptake was calculated from the difference in total carbon content before and after carbonation, measured using a multi EA 4000 device (analytikjena). Calculations were carried out as suggested by Nielsen and Quaghebeur [24], considering the mass gain during carbonation. XRD was carried out on a PANalytical Empyrean diffractometer with analysis using HighScore X'pert software and the PDF4 database. The diffractometer is equipped with a Co tube and was operated at 40 mA and 45 kV using a step size of 0.013°20 and 48.195 s measuring time per step from 5 to 120°20. Quantification was carried out using Rietveld refinement. An external rutile standard was used for determining the amorphous content. The external standard is measured within 1 week from the sample measurements. Raman analyses were obtained using a Horiba Jobin-Yvon LabRAM HR Evolution spectrometer. Samples were excited with a 532 nm wavelength laser (Nd:YAG, Oxxius, 100 mW power) via a 100x long working distance objective (Olympus LMPLFLN, NA 0.8) coupled to an Olympus BX41 confocal microscope. Spectra were acquired in a backscattered arrangement using a high spectral resolution 1800 grooves/mm grating, 10 % laser power, 25 µm confocal pinhole, and 40 s acquisition time with 10 repetitions.

# 3. Results and discussion

## 3.1. Thermodynamic simulations and choice of furnace conditions

FactSage equilibrium calculations provide an estimation of the phase composition of the slags without the need for experimentation, enabling to screen a wider range of compositions efficiently. The chemical composition of the slag is used as input and the phase composition is calculated as a function of temperature. Depending on the cooling speed, the phase composition of the experimentally synthesized slags will be comparable to the phase composition at the experimental temperature (for water quenching) or more closely related to a phase composition at lower temperature (for furnace cooling). In the latter case, the temperature from which the phase transformations are becoming kinetically hindered and therefore the exact temperature of comparison is difficult to unravel. The simulations of the phase compositions as a function of temperature are provided for the composition of FS-0 and FS-10Cc in Figs. 1 and 2, respectively. The composition of the phases is also provided by FactSage and mentioned in the discussion below, but not shown in the figures. The liquidus temperatures of FS-0 and FS-10Cc are approximately 1500 °C while the solidus temperatures are approximately 1200 °C in both cases. At the experiment temperature of 1300 °C, the phase composition is expected to have approximately 40 wt% of melt phase in FS-0 and 60 wt% of melt in FS-10Cc. The main phases are similar in both cases. An olivine phase which has a composition similar to the forsterite end-member is present, although it also contains approximately all Fe of the slag and is therefore a forsterite-fayalite solid



**Fig. 1.** Thermodynamic simulation of the phase composition as a function of temperature for FS-0.



**Fig. 2.** Thermodynamic simulation of the phase composition as a function of temperature for FS-10Cc.

solution. Due to its forsteritic composition, this phase persists at high temperatures (its fayalitic end-member usually melts already < 1300 °C [29,31]). Pyroxene phases are present in both cases. In the FS-0 this is mostly of enstatite composition, which precipitates < 1300–1400 °C and should – according to thermodynamics – transform from a clinopyroxene structure (cEnstatite) to an orthopyroxene structure (oEnstatite) between 1200 and 1000 °C. The pyroxenes in FS-10Cc are partially of diopside composition, which precipitate < 1200 °C and always have a clinopyroxene structure, also upon further cooling. The transformation from cEnstatite to oEnstatite is still noticeable at 1050–1000 °C. A minor quantity of anorthite collects the Al from the slag.

The slags are experimentally synthesized and cooled using the (fast) water quenching and slow furnace cooling. As the synthesis procedure at 1300 °C does not go above the liquidus temperature, the quenching will only slightly increase the amorphous nature of the slag. The resultant slags are milled, pressed into cylinders, and carbonated at 10 bars  $CO_2$  and 60 °C for 16 hours. The compressive strength of the carbonated cylinders is shown in Fig. 3. The strength values are very low in view of the application as construction materials and indicate that no substantial carbonation has occurred in any of the samples. Only one sample exhibited a significantly increased strength in comparison with the carbonation of the unmodified slag: i.e., FS-10Cc-f, the carbonated cylinder based on the slowly cooled slag with 10 wt% CaCO<sub>3</sub> addition.

# 3.2. Optimization of the slags for carbonation

Due to the positive effect of  $CaCO_3$  additions and slow cooling, despite the relatively low strength values obtained, further investigations of the impact of increased  $CaCO_3$  additions on the phase



**Fig. 3.** Compressive strength of carbonated slags with 0 and 10 wt% CaCO<sub>3</sub> addition using two cooling regimes.

composition, for the same cooling regime, are made. The phase composition at 1100 °C from thermodynamic simulations as a function of CaCO<sub>3</sub> addition is shown in Fig. 4 while the experimental phase compositions of the slowly cooled slags as a function of CaCO<sub>3</sub> addition is shown in Fig. 5. The full temperature-dependent thermodynamic simulated phase compositions of FS-20Cc and FS-30Cc are provided in the supplementary information, including the diffractograms and Rietveld fittings. A good agreement of the simulated with the experimental phase composition is observed - this is why the simulation at 1100 °C was selected. Minor differences in the experimental slags are (i) the appearance of a magnetite phase, (ii) the precipitation of monticellite, a second olivine phase, and (iii) the lower content of oEnstatite. Magnetite formation is caused by slight oxidation of the Fe, which was simulated to occur upon further cooling < 900 °C. Monticellite formation was not simulated, but monticellite can be a remnant of incomplete reaction of the raw meal. In other words, for longer reaction times at high temperature, more akermanite might form, replacing monticellite and diopside. The lower content of oEnstatite and its replacement by cEnstatite might be due to kinetic hindering during cooling. A minor amount of amorphous phase is present according to XRD, which can be glass from the solidification of the remaining melt during cooling from 1300 °C or poorly crystalline or unidentified phases.

The changes of the phase composition upon  $CaCO_3$  addition can be described in general terms based on simulations and experiments. These changes are mostly seen for the part of the initial phase composition of the pyroxenes. Upon  $CaCO_3$  addition, the enstatite pyroxene first transforms into diopside. After this conversion is complete, the formation of the melilite mineral akermanite is observed (or combination of akermanite and monticellite). The content of the forsterite-fayalite solid solution slightly increases and the anorthite phase slightly decreases



Fig. 4. Thermodynamic simulation of the phase composition at 1100  $^\circ C$  as a function of CaCO3 addition.

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**Fig. 5.** Experimental phase composition of the synthesized slags as a function of CaCO<sub>3</sub> addition.

upon higher CaCO<sub>3</sub> addition.

The compressive strength of slags after carbonation and  $CO_2$  uptake is shown as function of  $CaCO_3$  addition in Fig. 6. It is underlined that compressive strength values are larger by an order of magnitude in comparison with those shown in Fig. 3. The absolute values of strength have thus become more relevant for construction materials. For example, the compressive strength requirements for ceramic bricks according to EN 771–1 for use in houses  $\geq 3$  stories is > 13 MPa. The compressive strength of Portland cement pastes, however, is usually higher, mostly 50–90 MPa [8,13,30]. Overall, the data could suggest that the materials produced from FS-30Cc-f can be used for construction purposes. Comparing with Fig. 5, the strength increase might be explained in several ways, such as the increased content of akermanite and monticellite or an increased reactivity of the present diopside or forsterite. Which phase is the most important for the reactivity towards  $CO_2$  will be clarified in the next section.

## 3.3. Carbonation behavior of optimized ferronickel slag

The samples with significant strength gain and CO<sub>2</sub> uptake are investigated in more detail: FS-20Cc-f and FS-30Cc-f. The slag synthesis is replicated 6 times for testing the repeatability and the resultant slag was milled for 2 distinct milling times to obtain 2 particle size distributions (PSD). The full PSD curves are provided in the supplementary section; for the continuation of the discussion the 2 PSDs are referred to as L (large =  $d_{50} 11-12 \mu$ m) and S (small =  $d_{50} 6-8 \mu$ m). The slags from the first synthesis, the strength of which is shown in Fig. 6, have a similar PSD as the S samples. The two compositions (FS-20Cc-f and FS-30Cc-f) and 2 PSDs (L and S) are investigated for carbonation for 6, 16, and 48 hours. The compressive strength of the resultant hardened cylinders is shown in Fig. 7. A lower strength is noticeable in comparison with





Fig. 7. Compressive strength of carbonated furnace cooled slags with 20–30 wt % CaCO<sub>3</sub> addition as a function of carbonation time and particle size distribution of the slag (L = larger =  $d_{50}$  11–12 µm, S = smaller =  $d_{50}$  6–8 µm).

Fig. 6, for which an explanation is provided in the XRD discussion later in this section. The 30 Cc samples still have substantial strength gain. A gradual strength increase with carbonation time is observed, with higher strengths for the small PSD that results in increased carbonation kinetics due to the higher available surface area [20].

The phase assemblage as a function of carbonation time is studied in more detail for the sample FS-30Cc-S, which due to its highest strength is expected reach the highest reaction degree and will therefore provide the clearest view of the final phase assemblage. The phase composition is shown in Fig. 8. The inert phases stay approximately constant throughout the reaction: forsterite, diopside, and magnetite. Even monticellite, which may provide reactivity due to its higher dissolution rate in comparison with forsterite [33], did not react throughout the 48 hours of carbonation. The only phase with significant consumption is akermanite, making it clear that this is the phase providing sufficient carbonation reactivity to the slag. This also explains the lower strength observed in Fig. 7 vs. Fig. 6, since the akermanite content of the samples used to make Fig. 7 was lower. The importance of akermanite for providing reactivity to the modified slags is surprising in view of the current consensus in literature. Bodor et al. Bodor et al., [6], Librandi et al. Librandi et al., [21], and Wang et al. Wang et al., [32] consider the akermanite phase or phases from the melilite group in general as inert part of steel slags and carbonatable clinkers. Differences might be explained by the different carbonation conditions and the potential of akermanite to form solid solutions with gehlenite, which makes the melilite structure less soluble in most conditions [10]. The latter might be especially relevant in comparison with the steel slags, which contain a considerable amount of Al [6,21].

The crystalline reaction products are aragonite and at least one other



Fig. 6. Compressive strength and  $\rm CO_2$  uptake of carbonated furnace cooled slags with 0–30 wt%  $\rm CaCO_3$  addition.

Fig. 8. Phase composition of FS-30Cc-S as function of carbonation time.

carbonate phase. This other carbonate phase has similar peaks to calcite and dolomite in XRD, but only the main (104) diffraction peak is clearly observed and has a position which is situated between ideal calcite and dolomite. This suggests that it is a CaMg-carbonate phase where Mg partially substitutes Ca in calcite or Ca partially substitutes Mg in dolomite, and therefore is should be called a high Mg-calcite or protodolomite [15,19,27]. High Mg-calcite and protodolomite lack the Ca-Mg-ordering of the lattice structure [15] and therefore displays fewer XRD peaks than dolomite. Therefore, the XRD refinements use a Mg-calcite for the quantification. No Mg-carbonates have been observed. Other studies have also shown that the carbonation of CaMg-silicates results in limited precipitation of crystalline Mg-bearing carbonates [6,21]. Due to the deviation from ideal stoichiometry, a reaction formula is difficult to obtain. Future work with a more pure reaction product should allow the determination of the stoichiometry of the CaMg-carbonate to complete the reaction formula.

The CaCO<sub>3</sub> polymorph that is most stable in systems with high Mg concentrations is aragonite [1,2], especially considering that the experiments took place at higher temperature (60 °C), which also favors the formation of aragonite [18]. The CaCO<sub>3</sub> polymorph thus follows the general principles defined in the state-of-the-art. On the other hand, the presence of Mg-carbonates and mixed CaMg-carbonates is less common in carbonation cured CaMg-silicates and slag specimens [6]. The mineral carbonation of silicate minerals produces excess SiO<sub>2</sub> [3] and this is thus also expected from the reaction of akermanite. No crystalline reaction products are found, nor were they expected, as literature suggests that the carbonation of silicates results in the formation of silica-gel [3]. This gel does not provide additional benefits to the carbonated compacts, but might provide interesting properties when used as SCM, as exploited in carbonated recycled concrete fines [34]. The trend of akermanite consumption and carbonate formation in Fig. 8 is in line with the strength increase in Fig. 7, when considering the experimental errors introduced by the slag synthesis, carbonation, and XRD measurements.

### 3.4. Microstructure of modified and carbonated slags

The microstructure of the investigated materials is essential to understand the origin of the mechanical properties. More specifically, the link between the only minor akermanite content of the slag and the aragonite +  $Ca_xMg_{2-x}(CO_3)_2$  content in the carbonated samples with the high compressive strength value is investigated. All SEM images in this section are included in the supplementary information at higher resolution. As a reference point, the microstructure of the slag FS-30Cc-f is presented in Fig. 9 through a backscattered electron (BSE) image and

elemental maps of the major elements. The darkest grey shade has the largest concentration of Mg and also contains Fe and Si, indicating that this is the forsterite-fayalite solid solution. Diopside and akermanite are not easily distinguishable in the grey shade part or from their Mg or Si concentration. On the other hand, the Ca map suggests that the matrix phase on the right bottom of the image is akermanite (with the higher concentration of Ca) and in the middle-top-left is diopside (with the lower concentration of Ca). The diopside also seems to contain some Al. However, most of the Al should be attributed to anorthite, which is recognized from the highest intensities of Al and the lack of Mg. Some tiny bright spots indicate the presence of magnetite, which can also be seen in the Si map as spots without Si. The magnetite also seems to contain Al. It might be more correct to refer to the phase using the more general term "spinel". The akermanite seems to be present in quite large matrix-like grains in the slag. This is positive for the liberation of the akermanite after milling and might be one of the key phases that have led to the positive strength results.

The slag FS-30CC-f after milling to a  $d_{50}$  6–8 µm and after carbonation for 16 hours is used here as a sample for further investigation of the microstructure of the carbonated materials. BSE images are shown in Fig. 10 using various magnifications. A continuous network of a binding phase is observed between unreacted slag particles, as well as pores. The black pores are irregular in shape and size. The binding phase(s) are distinguished as a darker grey matrix between the particles. From the images provided here and in the supplementary information or during SEM imaging, it cannot be detected whether there is preferential growth of the binding phase(s) onto one of the slag phases.

Investigation of the Raman signal in the carbonated sample FS-30Ccf confirms that the binder is composed of a mixture of carbonates, aragonite and  $Ca_xMg_{2-x}(CO_3)_2$ , and the precursor akermanite (Fig. 11). Under reflected light, the binder shows slightly different reflective zones. Brighter zones and the bulk of the binder show a combination of 2 bands: (1) a thin band at around  $1087 \text{ cm}^{-1}$ , which is the characteristic wavenumber of the main vibrational band of aragonite. (2) The main band is shouldered by a broader band at a higher wavenumber. This higher wavenumber suggests the presence of a carbonate phase with higher Mg content than aragonite. A band at  $1097 \text{ cm}^{-1}$  would be characteristic for dolomite. The broader nature suggests a low crystallinity, while its position suggests that the composition is likely situated between dolomite and calcite/aragonite. Deconvolution to determine the exact position of the broad band could not provide a trustworthy result. The Raman spectrum thus merely confirms the presence of a mixed CaMg-carbonate that might be called high Mg-calcite or protodolomite. The zones of the binder that appear darker in reflective light



Fig. 9. SEM BSE image of FS-30Cc-f and elemental maps of the major elements. "D-matrix" refers to diopside; "A-matrix" refers to akermanite; "FF" refers to the forsterite-fayalite solid solution; "S" refers to the spinel phase.



Fig. 10. SEM BSE images of the carbonated FS-30Cc-f.



Fig. 11. Reflected light optical images (left) and Raman spectra (right) of the binder in sample FS-30Cc-f. The aragonite, dolomite, and akermanite reference spectra from the RRUFF database (respective codes between parenthesis) are presented for comparison.

do not show the shoulder band and only retain the main band of aragonite. The uncertainty on the actual structure of the CaMgcarbonate phase persists, partly due to its low concentration. Future work will provide more clarity using samples with a higher concentration of this phase.

# 3.5. A view on industrial implementation and carbon neutrality

High-temperature slag engineering at an industrial scale should for obvious economic/environmental reasons be carried out before cooling down to avoid the need for reheating the slag to 1300  $^{\circ}$ C as was done in the present lab experiments. Therefore, additives should be added in the

furnace during the metallurgical operation or in the slag pot immediately after tapping if the additive would endanger the stability of the metallurgical process. The investigated cooling procedures followed in the lab experiments correspond to the two most used cooling methods in industry: water quenching and slag pot cooling (the latter is the equivalent of the 180 °C/h furnace cooling). The results imply that for carbonation slag pot cooling is the most favorable. However, this is only the case if a substantial increase in Ca content is made as well. Such substantial additions to the slag chemistry might not be economically feasible for the metallurgical companies and the process would rather be a dedicated clinkering process requiring an additional furnace rather than a slag modification in the slag pot. Future work should investigate alternative routes, requiring fewer modifications in the current industrial processes, to increase the CO<sub>2</sub> uptake by fayalitic slags. Alternatively, other sources can be searched to obtain a similar phase assemblage of the precursor. A broader interpretation of the results teaches that any precursor with a substantial Mg-silicate content can be transformed in an akermanite-containing material upon the addition of a Ca-compound. The use of Mg-silicate tailings or virgin sourced pyroxene minerals can substantially increase the available feedstock for the technology, although these would require an additional heating stage – a kind of clinkering process – as there is no high temperature process where they originate from. Also, from the perspective of the Casource, a broader interpretation can be made and Ca-rich residues and by-products such as construction and demolition waste and steel slags could be considered in the further development.

In view of the carbon neutrality of the carbonated compacts, the addition of CaCO<sub>3</sub> is critically evaluated. For each kg of CaCO<sub>3</sub> added, 0.44 kg of CO<sub>2</sub> is emitted. A renormalization of the amount of modified slag resulted in the emissions in Table 3. The balance of these emissions and the CO<sub>2</sub> uptakes from Section 3.3 are shown in Table 3. In view of producing high-quality construction products the addition of 30 wt% CaCO3 to the ferronickel slag seems optimal, but a positive - i.e., emitting - CO2 balance of about 120 kg CO2/ton block is obtained (when not considering process emissions). Further optimization of the system should reveal whether a true CO2-negative effect can be obtained, as currently a large fraction of the Mg and part of the added Ca is still locked in unreactive phases such as forsterite, monticellite, and diopside. This may be done by approaching the process as clinkering instead of as slag modification (Peys and Pires Martins, under review). However, despite the low fraction of unreactive phases there (Peys and Pires Martins, under review), further optimization of the clinkering and carbonation process is needed to achieve a net absorbing CO<sub>2</sub> balance.

Nevertheless, the carbonated compacts target to replace Portland cement-based construction products, which have estimated embodied emissions of 400–800 kg  $CO_2$ /ton cement. The substitution of Portland cement with carbonated FS-30-f will thus result in a substantial decrease of the  $CO_2$  emissions related to construction products. Considering the impact of carbon credits on cement prices, economic incentives might become more pronounced in the future providing extra leverage to convince metallurgists that slags should be treated as a resource that should be altered for achieving optimal performance as feedstock for construction products.

#### 4. Conclusions

The results of the present study prove that mineral carbonation of a pyroxene-rich ferronickel slag is not straightforward. This study therefore provides novel insights in the carbonation potential of (Fe,Mg,Ca)-silicate minerals which can be applied for successful slag engineering. The original phase assemblage and slightly modified (< 20 wt% CaCO<sub>3</sub> additions) slags showed an insignificant reaction at 10 bar CO<sub>2</sub> and the produced cylinders acquired a compressive strength not exceeding 2 MPa. The addition of 30 wt% of CaCO<sub>3</sub> results in the production of a significant amount of akermanite (Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>), which after carbonated caused a compressive strength increase after carbonation up to

Table 3

CC	) <sub>2</sub>	bala	ance	to	prod	uce	moo	dified	slags	and	car	bonated	b	locł	ĸs.
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Slag	wt% CaCO <sub>3</sub> added to slag	Emissions (kg CO <sub>2</sub> /ton slag)	% TC measured in pellet	Uptake (kg CO <sub>2</sub> / ton slag)	Balance (kg CO <sub>2</sub> / ton slag)
FS-0-f	0	0.0	< 0.1	0.0	0.0
FS-10- f	10	48.9	0.2	7.4	41.5
FS-20- f	20	109.9	0.59	22.1	87.8
FS-30- f	30	188.4	1.72	67.3	121.1

20–40 MPa. The carbonation degree of akermanite is almost 70 % after 6 hours, although the compressive strength shows a significant increase even after 16 and 48 hours. A finer particle size also results in increased compressive strength. The carbonation of akermanite results in the formation of a binding phase composed of aragonite and a CaMg-carbonate which might be high Mg-calcite or protodolomite. The slag modification-carbonation process is slightly emitting  $CO_2$ , but poses a large decrease in emissions compared to Portland clinker-based cements. Future work should target to convert the Ca and Mg that was locked away in inert phases into reactive components to achieve a more beneficial net absorbing  $CO_2$  balance.

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## CRediT authorship contribution statement

**Peys Arne:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Pires Martins Natalia:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation. **Nielsen Peter:** Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Investigation, Formal analysis. **Prado Araujo Fernando:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation. **Komnitsas Konstantinos:** Writing – review & editing, Validation, Supervision, Project administration, Funding acquisition, Conceptualization.

## **Declaration of Competing Interest**

The authors from VITO declare that a patent was submitted comprising some of the slag compositions and carbonated products discussed in this paper.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jcou.2025.103077.

## **Data Availability**

Most datasets generated for this study are provided in the supplementary information. Other data can be made available on request.

#### References

- [1] J.-W. Ahn, K.-S. Choi, S.-H. Yoon, H. Kim, Synthesis of aragonite by the carbonation process, J. Am. Ceram. Soc. 87 (2) (2004) 286–288.
- [2] J.W. Ahn, W.K. Park, K.S. You, H.C. Cho, S.J. Ko, C. Han, Roles of additives on crystal growth rate of precipitated calcium carbonate, Solid State Phenom. 124 (126) (2007) 707–710.
- [3] W. Ashraf, J. Olek, Carbonation activated binders from pure calcium silicates: reaction kinetics and performance controlling factors, Cem. Concr. Compos. 93 (2018) 85–98.
- [4] R. Baciocchi, G. Costa, M. Di Gianfilippo, A. Polettini, R. Pomi, A. Stramazzo, Thinfilm versus slurry-phase carbonation of steel slag: CO2 uptake and effects on mineralogy, J. Hazard. Mater. 283 (2015) 302–313.
- [5] C.W. Bale, E. Bélisle, P. Chartrand, S.A. Decterov, G. Eriksson, A.E. Gheribi, K. Hack, I.H. Jung, Y.B. Kang, J. Melançon, A.D. Pelton, S. Petersen, C. Robelin, J. Sangster, P. Spencer, M.A. Van Ende, FactSage thermochemical software and databases, 2010–2016. Calphad 54 (2016) 35–53.
- [6] M. Bodor, R.M. Santos, L. Kriskova, J. Elsen, M. Vlad, T. Van Gerven, Susceptibility of mineral phases of steel slags towards carbonation: mineralogical, morphological and chemical assessment, Eur. J. Mineral. 25 (4) (2013) 533–549.
- [7] CEMBUREAU (2016). The role of cement in the 2050 low carbon economy. Brussels, The European Cement Association.
- [8] P. Chindaprasirt, C. Jaturapitakkul, T. Sinsiri, Effect of fly ash fineness on compressive strength and pore size of blended cement paste, Cem. Concr. Compos. 27 (4) (2005) 425–428.
- [9] A. Di Maria, R. Snellings, L. Alaert, M. Quaghebeur, K. Van Acker, Environmental assessment of CO2 mineralisation for sustainable construction materials, Int. J. Greenh. Gas. Control 93 (2020) 102882.
- [10] F. Engström, D. Adolfsson, C. Samuelsson, Å. Sandström, B. Björkman, A study of the solubility of pure slag minerals, Miner. Eng. 41 (2013) 46–52.
- [11] Eurofer (2019). Low carbon roadmap: Pathways to a CO2-neutral European steel industry. Brussels, Belgium.
- [12] Fei Wang, D. D, Mark Jarvis, Tony Hitchins, Kinetics and mechanism of mineral carbonation of olivine for CO2 sequestration, Miner. Eng. 131 (2019) 185–197.
- [13] I. Fischer, B. Pichler, E. Lach, C. Terner, E. Barraud, F. Britz, Compressive strength of cement paste as a function of loading rate: Experiments and engineering mechanics analysis, Cem. Concr. Res. 58 (2014) 186–200.
- [14] E. Georgakopoulos, R.M. Santos, Y.W. Chiang, V. Manovic, Influence of process parameters on carbonation rate and conversion of steelmaking slags – Introduction of the 'carbonation weathering rate, Greenh. Gases: Sci. Technol. 6 (4) (2016) 470–491.
- [15] D.L. Graf, J.R. Goldsmith, Some hydrothermal syntheses of dolomite and protodolomite, J. Geol. 64 (2) (1956) 173–186.
- [16] Béarat Hamdallah, M.J. M, Andrew V.G. Chizmeshya, Deirdre Gormley, Ryan Nunez, R.W. Carpenter, Kyle Squires, George H. Wolf, Carbon Sequestration

via Aqueous Olivine Mineral Carbonation: Role of Passivating Layer Formation, Environ. Sci. Technol. 40 (15) (2006) 4802–4808.

- [17] T. Hertel, A. Van den Bulck, B. Blanpain, Y. Pontikes, Correlating the amorphous phase structure of vitrified bauxite residue (red mud) to the initial reactivity in binder systems, Cem. Concr. Compos. 127 (2022) 104410.
- [18] Z. Hu, Y. Deng, Supersaturation control in aragonite synthesis using sparingly soluble calcium sulfate as reactants, J. Colloid Interface Sci. 266 (2) (2003) 359–365.
- [19] S.E. Kaczmarek, B.P. Thornton, The effect of temperature on stoichiometry, cation ordering, and reaction rate in high-temperature dolomitization experiments, Chem. Geol. 468 (2017) 32–41.
- [20] L. Li, M. Wu, An overview of utilizing CO2 for accelerated carbonation treatment in the concrete industry, J. CO2 Util. 60 (2022) 102000.
- [21] P. Librandi, P. Nielsen, G. Costa, R. Snellings, M. Quaghebeur, R. Baciocchi, Mechanical and environmental properties of carbonated steel slag compacts as a function of mineralogy and CO2 uptake, J. CO2 Util. 33 (2019) 201–214.
- [22] P. Nielsen, R. Baciocchi, G. Costa, M. Quaghebeur, R. Snellings, Carbonate-bonded construction materials from alkaline residues, RILEM Tech. Lett. 2 (2017) 53–58.
- [23] P. Nielsen, M.A. Boone, L. Horckmans, R. Snellings, M. Quaghebeur, Accelerated carbonation of steel slag monoliths at low CO2 pressure – microstructure and strength development, J. CO<sub>2</sub> Util. 36 (2020) 124–134.
- [24] P. Nielsen, M. Quaghebeur, Determination of the CO2 Uptake of Construction Products Manufactured by Mineral Carbonation, Minerals 13 (8) (2023) 1079.
- [25] S.-Y. Pan, Y.-H. Chen, L.-S. Fan, H. Kim, X. Gao, T.-C. Ling, P.-C. Chiang, S.-L. Pei, G. Gu, CO2 mineralization and utilization by alkaline solid wastes for potential carbon reduction, Nat. Sustain. 3 (5) (2020) 399–405.
- [26] Y. Pontikes, L. Machiels, S. Onisei, L. Pandelaers, D. Geysen, P.T. Jones, B. Blanpain, Slags with a high Al and Fe content as precursors for inorganic polymers, Appl. Clay Sci. 73 (2013) 93–102.
- [27] B. Purgstaller, V. Mavromatis, K.E. Goetschl, F.R. Steindl, M. Dietzel, Effect of temperature on the transformation of amorphous calcium magnesium carbonate with near-dolomite stoichiometry into high Mg-calcite, CrystEngComm 23 (9) (2021) 1969–1981.
- [28] M. Quaghebeur, P. Nielsen, L. Horckmans, D. Van Mechelen, Accelerated Carbonation of Steel Slag Compacts: Development of High-Strength Construction Materials, Front. Energy Res. 3 (52) (2015) 12.
- [29] C. Siakati, A.P. Douvalis, P. Ziogas, A. Peys, Y. Pontikes, Impact of the solidification path of FeOx-SiO2 slags on the resultant inorganic polymers, J. Am. Ceram. Soc. 103 (3) (2020) 2173–2184.
- [30] H.A. Toutanji, T. El-Korchi, The influence of silica fume on the compressive strength of cement paste and mortar, Cem. Concr. Res. 25 (7) (1995) 1591–1602.
- [31] J. Van De Sande, A. Peys, T. Hertel, H. Rahier, Y. Pontikes, Upcycling of nonferrous metallurgy slags: Identifying the most reactive slag for inorganic polymer construction materials, Resour., Conserv. Recycl. 154 (2020) 104627.
- [32] S. Wang, F. Gao, B. Li, Y. Liu, T. Deng, Y. Zhang, W. Chen, Clinkerization of carbonatable belite-melilite clinker using solid waste at low temperature, Constr. Build. Mater. 418 (2024).
- [33] H.R. Westrich, R.T. Cygan, W.H. Casey, C. Zemitis, G.W. Arnold, The dissolution kinetics of mixed-cation orthosilicate minerals, Am. J. Sci. 293 (9) (1993) 869–893.
- [34] M. Zajac, J. Song, P. Ullrich, J. Skocek, M. Ben Haha, J. Skibsted, High early pozzolanic reactivity of alumina-silica gel: A study of the hydration of composite cements with carbonated recycled concrete paste, Cem. Concr. Res. 175 (2024) 107345.
- [35] H. Zhen, Y. Mu, Z. Liu, F. Wang, Understanding the Impact of KNO3 on the Carbonation Behavior of &,#,x3b3;-C2S, J. Mater. Civ. Eng. 35 (6) (2023) 04023109.