# Mineral carbonation of a ferronickel slag-based clinker

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### Introduction

The production of alternative binders by mineral carbonation of metallurgical slags is a promising pathway to reduce anthropogenic CO<sub>2</sub> emissions and enhance environmental sustainability in the construction and metallurgical sectors<sup>1</sup>. As opposed to hydrated binders such as cement, carbonatable binders harden through mineral carbonation in a process that captures CO<sub>2</sub> while cementing particles together and achieving high mechanical strength<sup>2</sup>. Steel slags and clinkers containing nonhydraulic calcium silicate minerals are the main examples of such binders<sup>2</sup>.

Untreated ferronickel slags (FS) present limited carbonation reactivity at natural conditions, requiring higher temperatures/pressures and high liquid:solid ratios to react substantially<sup>3</sup>. According to a recent discovery<sup>4</sup>, when FS are co-clinkered with CaCO<sub>3</sub>, the change in chemical composition imposed by the addition of calcium results in the production of a clinker rich in akermanite (Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>) with enhanced reactivity towards CO<sub>2</sub>. The clinker can be carbonated after pressing the powder into a monolith, which favours its application as prefabricated blocks. However, previously, the carbonation step was carried out under fixed conditions, i.e., 10 bar CO<sub>2</sub> and 60 °C for 16 hours. Understanding the strength build-up at lower pressures is fundamental to improve the energy efficiency and economics of the process. Therefore, in the present study, the carbonation is further investigated at lower CO<sub>2</sub> pressures, i.e., 2-10 bar, and for different reaction times, i.e., 1-24 hours.

# Material and methods

The akermanitic clinker used in this study was produced from a raw blend that comprised 55 wt.% of a FS and 45 wt.% lab grade  $CaCO_3$ . The raw blend was pressed into pellets that were sintered in a box furnace for 30 minutes at 1300 °C, using a heating and cooling speed of 3 °C/min. After being cooled down, the clinkered pellets are milled to reach  $d_{50}$  of around 14  $\mu$ m. The chemical and phase compositions of the FS can be found elsewhere<sup>4</sup>, as well as more details about the clinker production process.

The clinker powder was mixed with distilled water (9.5 wt.% moisture) and pressed into 30 mm cubes using a force of 150 kg/cm<sup>2</sup>. This resulted in fixed values of dry density (1.92  $\pm$  0.02 g/cm<sup>3</sup>), porosity (38.2  $\pm$  0.6 %), and pore saturation (47.7  $\pm$  1.3 %) of the compacts before carbonation. Immediately after pressing, the compacts were carbonated in PARR autoclaves at 2-10 bar Pco<sub>2</sub>, at 60 °C, 100% CO<sub>2</sub>, > 90% relative

humidity, for 1-24 hours. The CO<sub>2</sub>-uptake was calculated based on the determination of the total mass of carbon in the carbonated samples by TC analysis. The compressive strength of the carbonated compacts was also measured after different reaction times. The phase composition of selected samples was determined by X-ray diffraction (XRD) using a PANalytical Empyrean diffractometer (Co-K $\alpha$ ) and applying the Rietveld method on the HighScore X'pert Plus software using the PDF-4 database. The amorphous content was determined using the external standard method.

#### **Results and discussion**

The compressive strength reached by clinker compacts carbonated at 2, 6, and 10 bar is shown in Figure 1, as a function of the CO<sub>2</sub>-uptake. The different data points plotted for each pressure were obtained after different carbonation times, i.e., 1- 24 hours at 6 and 10 bar, and 16-24 hours at 2 bar. A positive correlation between CO<sub>2</sub> uptake and compressive strength is found for the samples carbonated at 10 bar. Both properties are enhanced with the extension of the reaction time from 1 to 24 hours, as seen for steel slags<sup>5,6,7</sup>. This is an expected result of the microstructure densification caused by the increased formation of carbonated products after longer reaction times. However, at CO<sub>2</sub> pressures of 2 and 6 bar, the compressive strength of the compacts remains below 10 MPa even after prolonged reaction, i.e., 24 hours, and despite reaching considerable CO<sub>2</sub> uptake, i.e., up to 75 kg CO<sub>2</sub> per ton of clinker. At such pressures, the increase in reaction time is not linked to an increase in mechanical strength, although more CO<sub>2</sub> is bound in the solids. Hence, at the tested conditions, a CO<sub>2</sub> pressure of 10 bar was required for sufficient compressive strength build-up.



**Figure 1:** Relationship between compressive strength and CO<sub>2</sub> uptake of ferronickel slag-based clinker compacts (30 mm cubes) for different carbonation conditions, i.e., CO<sub>2</sub> pressures 2 bar, 6 bar, and 10 bar. Temperature: 60 °C; gas mixture: 100% CO<sub>2</sub>, reaction duration: 1-24 hours.

The compacts used in this study have the same initial moisture content and dry density. In such cases, the compressive strength obtained after carbonation is expected to correlate with the amount of carbonates formed during the carbonation process<sup>6,7</sup>. This correlation is, however, not maintained at lower values of CO<sub>2</sub> pressure, as shown in Figure 1. The results suggest that the use of lower CO<sub>2</sub> pressure disturbs certain steps of the carbonation process, which must be re-adjusted to enable the appropriate progress of the reactions. This might be achieved by tuning the other carbonation parameters and will be the subject of future investigations.

To obtain more insights into the carbonation reactions, the carbonated compacts were characterized by XRD. The phase composition of clinker compacts carbonated at 2, 6, and 10 bar for 16 hours is shown in Figure 2, next to the phase composition of the uncarbonated clinker.



Figure 2: Phase composition (rescaled to g/100 g of uncarbonated clinker) of clinkers before and after carbonation at 2, 6, and 10 bar  $CO_2$  pressure. Carbonation conditions: 60 °C; 100%  $CO_2$ , 16 hours.

Based on the rescaled results (to g/100 g of uncarbonated clinker), the presence of inert clinker phases is identified: forsterite (Mg<sub>2</sub>SiO<sub>4</sub>), diopside (CaMgSi<sub>2</sub>O<sub>6</sub>), and the phase(s) from the spinel group of minerals. Thus, although forsterite may react in certain systems carbonated under harsher conditions<sup>7,8</sup>, the reaction of this phase is not the target in the akermanitic clinker. In contrast, akermanite shows a clear decrease in phase content after carbonation, which is further reduced with the increase in the CO<sub>2</sub> pressure. In the samples investigated by XRD, akermanite reaches degrees of reaction (DoR) between 20 and 30% after 16 hours. A secondary reactive phase, merwinite (Ca<sub>3</sub>Mg(SiO<sub>4</sub>)<sub>2</sub>), is also identified in Figure 2. The initial content of merwinite is below 6 g/100g of clinker, and only 1-2 g remains after carbonation.

Identical carbonation products are identified in all samples: high Mg-calcite ((Ca, Mg)CO<sub>3</sub>), aragonite (CaCO<sub>3</sub>), and amorphous products. The amorphous products include amorphous carbonates and amorphous silica<sup>4</sup>. The total content of reaction products is higher at higher pressures, which is consistent with the higher DoR of akermanite. However, the carbonated phase composition does not correlate with the compressive strength reached by the compacts. In other words, although the carbonated compacts present similar phase compositions, there are striking differences in their compressive strength values (7.7 MPa, 7.3 MPa, and 30.3 MPa, for compacts carbonated at 2, 6, and 10 bar, respectively). These results indicate that the poor strength build-up observed at 2 and 6 bar is related to factor(s) other than the carbonate phase assemblage. Possible factors that are known to affect the strength of carbonate binders are related to the microstructure achieved after carbonated compacts and include the spatial distribution of carbonation products within the carbonated compacts and the morphology of said products<sup>7</sup>. Those factors will be evaluated in further investigations.

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