

Chemical reduction of CO₂ to carbon at ambient conditions during artificial weathering of converter steel slag while improving environmental properties

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ABSTRACT – Converter slag and CO₂ are the predominant by-products of steel production. We investigated the accelerated weathering of steel slag derived from the converter process by treating it with synthetic combustion off-gas (20% CO₂, 80% Ar). Both water-saturated and under-saturated exposure for 8-200 hrs were studied at temperatures between 5-90°C. Primary justification was to look for improvement of environmental properties of the slag (pH and trace-element leaching). Secondary was the earning of some CO₂-credits.

INTRODUCTION

Any modern integrated steel plant nowadays will produce about 90-100 kg of steel slag per tonne of steel in its LD/converter process during the refining of hot metal from the blast furnace. With the annual steel production reaching 1 billion tonnes world-wide it should be clear that vast amounts of steel slag are being produced.

The steel (LD/converter) slag, is a stony material resembling basalt (after cooling). The cooling method (rapid/slow, with or without water) determines the surface quality of the stony aggregates obtained. The aggregates can be used in many applications as substitute for quarry materials but impose a high pH (12.5) and low Eh, which may exert adverse effects in aqueous environments with limited water flow. These specific environmental qualities are inherent to the mineralogy of this type of slag, consisting for over 50% of Ca₂SiO₄ (C2S, belite, the common cement clinker phase), 15-25% (Mg,Fe,Mn)O (MW, magnesio-wuestite) and 10-20% Ca₂(Fe₃₊,Ti,Al)₂O₃ (C2F). In addition accessory phases such as Fe₃O₄ (magnetite) and CaO (free-lime) can be present in amounts up to 10%. The hydration of the phases C2S+lime buffers the pH of interstitial water at the value of 12.5, while the presence of di-valent iron in wuestite gives rise to the highly reducing Eh values.

Steel slag is reactive with respect to CO₂, leading to the formation of CaCO₃ (calcite) and an amorphous Ca-bearing silicate residue at the expense of the C2S phase. Free-lime can be readily carbonated but the other phases, MW and C2F are inert to carbonation. An important observation is that calcite never occurs within slag grains. Phase equilibria calculations show that calcite is not stable at 1 atm CO₂ pressure at the pH/Eh of the C2S+lime+water+wuestite phase assemblage. Instead the hydration reaction is prevalent and forming Ca(OH)₂ (portlandite). During natural weathering of steel slag, calcite appears on the outside of aggregate grains as alteration.

A carbonation strategy of steel slag should always yield a product with increased value, either from CO₂ credits or from improved recycling properties. Complete reaction of steel slag with CO₂ (i.e. in practice only C2S) yields a fine grained (<100 micron) residue. As such it would create a large amount of by-product which potentially may be suitable as filler (e.g., in concrete, asphalt), but for which an application and market still need to be developed.

Instead we have opted for superficial carbonation of the slag, with the aim to amend the environmental pH problem, and hopefully improve the leaching properties of trace metals (viz. Vanadium). We have observed that under liquid-water absent conditions hardly any calcite formation occurs. Therefore the treatment runs at low slag to water ratios (L/S<0.3) leaving no residual water, but facilitating the build-up of a pH/Eh gradient between the CO₂-bearing gas-atmosphere and pH12.5 at the slag grain-surface. In this gradient calcite is expected to form as a coating around the aggregate grains. Combustion gas of almost any carbon source will be suitable for this carbonation treatment.

We studied the superficial mineralogical changes to understand how these processes affect the change in environmental properties. This is how we have noticed an additional process simultaneously operating with the carbonation which apparently leads to the deposition of carbon.

MATERIALS AND METHODS

Selected starting materials for carbonation experiments

The converter operates in a batch type process, and yields batches of 20-30 tonnes of slag that vary from heat-to-heat in modal mineralogy. We selected two types of converter slags for our studies, each derived from a single heat, representing the maximum difference in primary mineralogy - K1 slag (C2S + C2F + MW) and K3 slag (C3S + C2S + C2F + MW + free-lime). The C3S (Ca₃SiO₅) is a high-temperature phase which decomposes to C2S + lime during cooling, but leaves a characteristic intergrowth texture, possibly with a different reactivity for CO₂. Both slags were air-cooled and subsequently broken and sieved to obtain a representative 2-3.3 mm fraction of 25 kg starting material for the experiments. The modal mineralogy (Table 1) was determined using powder X-ray diffraction and Rietveld analysis to quantify the patterns (see section on characterisation)

Table 1: Modal mineralogy of slags used in experiments determined with powder-XRD.

heat nr.		Z1268		W8791		S6938	
mineral	formula	K1 (nw)	1σ	K3	1σ	K1(old)	1σ
MW	(Fe,Mg,Mn)O	23.7	3.0	29.2	3.5	37.0	5.0
Free lime	CaO	1.6	0.8	5.4	1.0	0.0	
Portlandite	Ca(OH) ₂			3.0	0.8		
C2F	2CaO.(Fe,Ti,Al,V) ₂ O ₃	25.6	3.0	25.7	3.0	13.2	2.0
C2S	2CaO.(Si,P,V)O ₄	49.2	5.0	36.6	5.0	49.1	5.0
magnetite	FeO.Fe ₂ O ₃					0.7	

Experimental set-up for carbonation

Carbonation experiments were performed in a glass column (5 cm ID, 20 cm length) with a thermostatic jacket. About 900 g steel slag was wetted and placed in the column. A CO₂/Ar gas mixture was water saturated at elevated temperature, to ensure the presence of water in the experiments, and was introduced in an upflow direction at a flowrate of about 400 ml/min. Experiments were performed at temperatures between 5 and 90 °C under water-saturated and under-saturated exposure for 8-200 h (van der Laan et al., in prep.).

Characterisation methods for starting materials and run products

Determination of carbonate content in steel slag

The carbonation efficiency was quantified by thermogravimetric analysis (Mettler-Toledo TGA/SDTA 851e) coupled to a Pfeiffer (thermostar) Quadrupole mass spectrometer (TGA-MS). 20-50 mg steel slag (<100 µm) was weighed in a ceramic cup and heated from 25-1100 °C under a nitrogen atmosphere at a heating rate of 40 °C/min. The weight loss was recorded by the TGA microbalance. The MS simultaneously monitored the evolved gases for CO₂. The CO₂ peak area was determined by integration, the amount of evolved CO₂ was calculated from a calibration line based on the decomposition of CaCO₃ standards. Separate samples were evaluated from top - middle - bottom of the reaction column (Van der laan et al., in prep.).

Column-leaching test

The column leaching tests were performed according to CEN/TS 14405. The steel slag was added to the column (borosilicate glass, inner diameter 5 cm) in layers of a few cm and packed by shaking and pushing gently with a rod until a filling height of ± 20 centimeters was reached. Demineralised water (nanopure) was used as the leachant. The packed columns were water saturated and pre-equilibrated for 72 hours, as prescribed by CEN/TS 14405, after which the influent was pumped in up-flow direction. Computer-controlled flow controllers were used assuring a constant flow velocity during the experiments. Fractions were collected automatically at cumulative liquid to solid ratio (L/S) values of 0.2, 0.5, 1, 2, 5 and 10 (l/kg). Effluent fractions were collected in acid-cleaned PE bottles. Shortly after collection of each effluent fraction, pH, redox potential and conductivity were determined, and sub-samples for chemical analysis were taken and filtered through 0.45 µm membrane filters. The leachates were analyzed by ICP-AES to obtain solution concentrations of Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, V, and Zn. Chloride and sulphate were determined by ion chromatography (IC) (Van der laan et al., in prep.).

SEM-EDS

Products were examined using a ZEISS Ultra55 Field Emission Gun Scanning Electron Microscope (FEG-SEM) equipped with a Thermo Fisher Scientific NORAN System SIX (NSS) microanalysis system. Imaging and micro-analysis was performed in high-vacuum mode at operating conditions of 15kV, working distance 12 mm. Initial data processing of elements with an atomic number higher than 10 was based on standardless quantification of the micro-analysis. Standardless quantification for Carbon and Oxygen containing phases in these type of specimens cannot be carried out for the following reasons:

- Specimens are carbon coated
- Phases of interest may contain structural water or carbonate groups
- Data is normalized to 100%
- K-ratio calculation of elements like Carbon, Nitrogen, and Oxygen is inaccurate (K-ratio being the intensity ratio of an element in an unknown material with respect to the same element in a standard)

To quantify carbon and oxygen the following processing steps were carried out with the X-ray spectra. 1) Spectra were corrected for carbon-coating by measurement of the net intensity of carbon on a "carbon-free" mineral (C2S) in the sample. The resulting carbon signal is a combination of carbon coating and carbon contamination. In the next step, this net intensity was subtracted from all collected spectra. 2) We calibrated on known pure minerals in the slag material (C2S and Calcite) and used these as internal standards to accurately determine the carbon, oxygen, calcium and silicon K-ratios and derive for all other elements theoretically calculated standard intensities. Finally, K-ratios were processed into atomic and weight percentage using Proza (Phi-Rho-Z) (Bastin and Heijligers, 1990) as a correction procedure, without normalizing to 100%.

IR-spectroscopy

FTIR microscopy (Nicolet) was used to investigate the presence of CO₂- and H₂O-bearing compounds in the reaction surface. FTIR was performed in Attenuated Total Reflexion (ATR) mode, bringing to contact a ZnSe crystal on the selected surface. All spectra were measured on a polished mount of K3 slag (carbonation at 90°C 24hrs, water-saturated).

XRD

The starting materials were ground to powder for X-ray diffraction. A Bruker D4 diffractometer was used with a position-sensitive detector, and patterns were quantified using the Topas 3 software package. Reacted material was mounted as whole grains and diffraction patterns were taken selectively of the grain surface using a Bruker D8 diffractometer equipped with a GADDS 2-D detector. Patterns were subsequently transformed to resemble ordinary 2 θ -intensity plots. The 2-D detector has the advantage of collecting the diffracted signal from many more grains compared to a conventional proportional counter or a 1-D position-sensitive detector. This procedure significantly improves counting statistics in the diffraction patterns, because the surface material itself cannot be prepared by grinding.

EXPERIMENTAL RESULTS

Degree and rate of carbonation

Given our aim to carbonate relatively large steel slag grains, with a limited surface area, only low degrees of carbonation are reached. In general the reaction proceeds fastest at higher temperature (50-90°C) in the presence of water. The K3-slag is more prone to carbonation (about 15 g CO₂/kg) than K1-slag (about 6 g CO₂/kg). The surface reaction strongly declines after about 24 h. The carbonation of K1 and K3 slag as a function of time (at 90°C) under water-saturated and unsaturated conditions is given in Figure 1. Details of the experiments are reported in van der Laan et al. (in prep.).

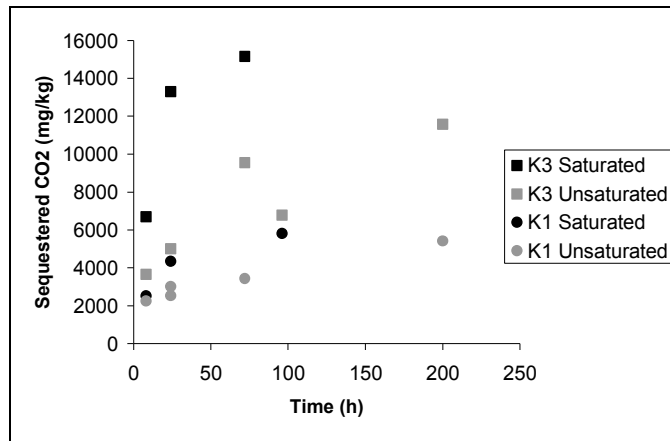


Figure 1: Captured CO₂ as a function of reaction time under water-saturated and unsaturated conditions for K1 and K3 slag (T=90°C).

Leaching behaviour of treated steel slag

The pH properties of the treated slag show a short lived improvement, starting at 9.5 but with a rebound to 10.5-11 for K1 and back to the original pH of 12.5 for K3 slag after 48 hrs of water contact. Initially, the surface reactions seem to be effective for neutralization of the pH, confirming earlier work from Huijgen and Comans (2005) and Huijgen et al. (2006).

Improved pH goes along with worsened V-leaching in both the batch-equilibrium test and the column test (CEN/TS 14405.) The K1 slag shows deterioration of the V-leaching (10-100 mg/kgDS) while the K3 slag remains within acceptable limits (<1 mg/kgDS). Figure 2 shows the pH and cumulative vanadium leaching as a function of the L/S ratio. A clear distinction is visible between the pH and vanadium leaching of the K1 and K3 slag. The K1 slag does not comply with the limit values for a category 1 application in the Dutch Building Materials Decree (open application without isolation measures), while the K3 slag does comply with these limit values. However, vanadium leaching does increase substantially after carbonation of K3 slag. Increase of the degree of carbonation leads to a further increase of vanadium leaching.

The pH of the untreated K1 slag as a function of L/S is substantially lower than the pH of the K3 slag. This observation is related to the absence of CaO in the K1 slag, whereas the K3 slag contains CaO. Carbonation of the K1 slag reduces the pH of the material. The pH of the K3 slag is not significantly influenced by the carbonation treatment. We observe that carbonation only takes place on the surface of the grains in both the K1 and K3 slags. During the carbonation treatment, portlandite is also partly formed from CaO inside the grains of K3 slag. This process results in the formation of cracks due to volume expansion, resulting in a slow (diffusive) release of alkalinity from unreacted portlandite in the inner grains. However, the K1 slag does not contain CaO and this material does not crack. In this case, the surface carbonation does cause a pH drop.

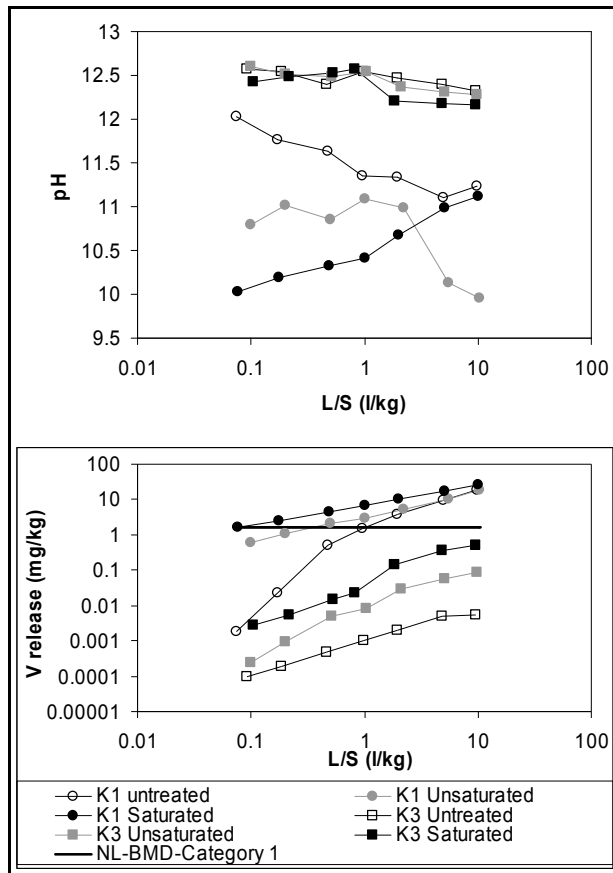


Figure 2: pH and vanadium leaching as a function of the L/S ratio in the column leaching test for untreated and carbonated K1 and K3 steel slag.

Microstructure and composition of reaction rims

The carbonation reactions were examined at the grain surface and in cross sections of grains. In the reaction, the C₂S appears converted to a silica-gel with complex zoning patterns of P, Ca and C, which only develop at the exposed outer surface of the slag. No secondary calcium silicate hydrate (CSH) phases were found (XRD, FTIR). Crystallisation of calcite occurs at seemingly random locations on the grain surface. The occurrence of carbon at the reacted surface was discovered with the SEM and quantified with EDS microanalysis after appropriate subtraction of the blank contribution. The carbon deposition is associated with calcite (Figure 3) and shows no relation with the mineral substrate. The carbon is found in amorphous, rounded morphology as well as in flaky, hexagonal platelets.

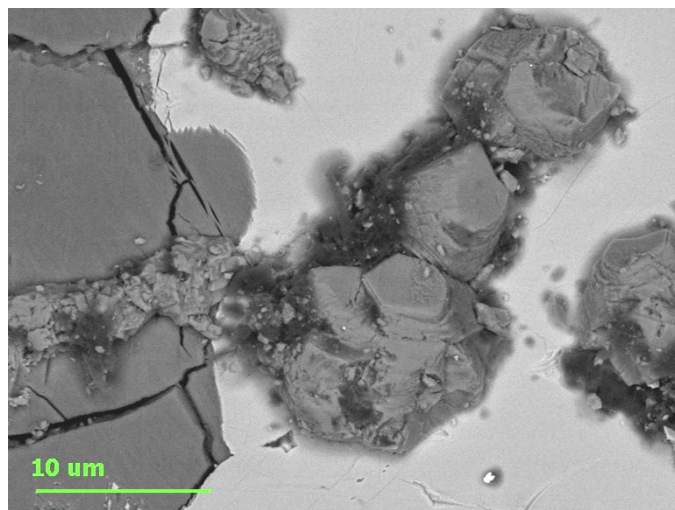
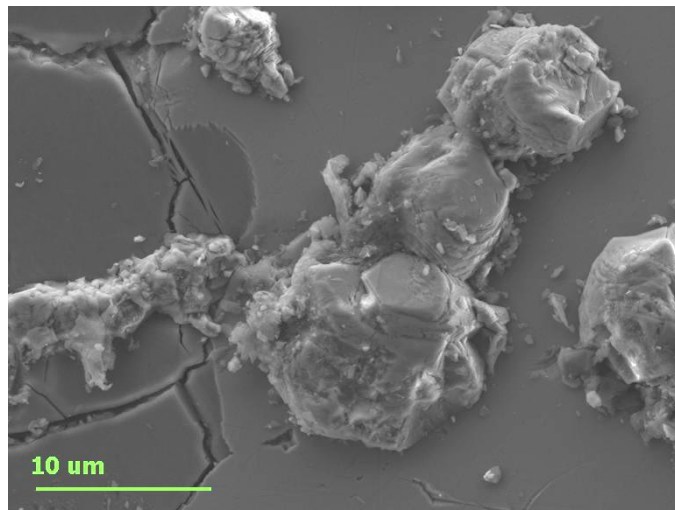


Figure 3: Calcite-carbon depositions in Secondary Electron Image (top) and Back Scatter Image (bottom) at 10keV. Dark areas in bottom image are carbon showing of platelets and rounded shape in top image. The carbon surrounds calcite the latter with characteristic crystal morphology. The substrate is partly C2S (grey with fractures) and C2F (light-grey).

Cross-sectional views and quantitative analysis of the reaction rinds clearly show that C2S is reactive and MW and C2F behave inertly (Fig. 4). Surprisingly the silicate residue of C2S is free from water based on FTIR, although it does contain excess oxygen (i.e. more oxygen than combined with the cations present assuming common oxidation states for Si, V and P) and no carbonate or CO₂ is present. Microanalyses are presented in Figure 5 for the corresponding spots in Figure 4. The outer zone most towards the surface of the slag grain in Figure 4 shows the highest free-carbon in the analyses. Although some excess-oxygen is found as well

in the analyses, this is clearly not enough to account for carbon present as carbonate. Analyses 6, 7, 8 of the reacted C2S occur in areas where porosity was observed. These analyses yield low analytical totals of between 80 and 90wt%. This deviation from 100% was plotted as pore%.

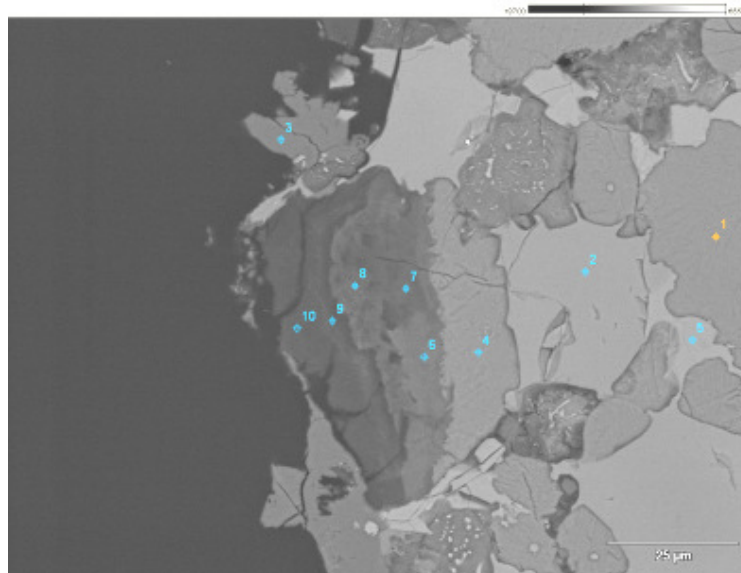


Figure 4: Cross sectional view of reaction rind as developed in C2S (with spot analyses 6-10). Pristine C2S (spot 4, 1), calcite (3), WM (2) and C2F (5). Corresponding analyses are given in Fig. 5. The dark grey at the left is the embedding medium, bordering at the grain surface.

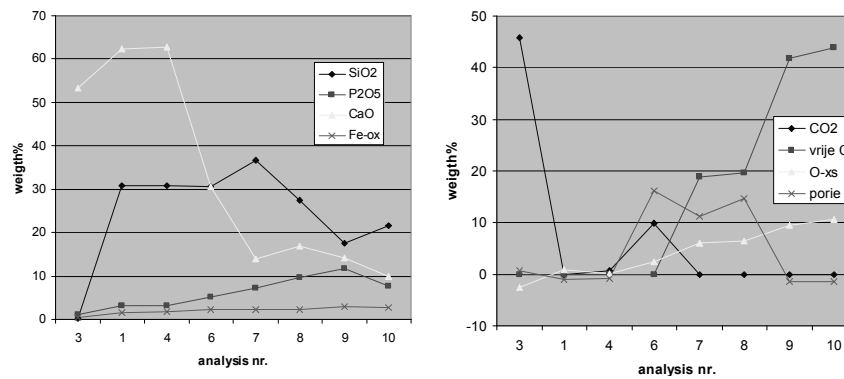


Figure 5: Microanalyses from SEM-EDS on selected points in Fig. 4.

From the analyses, it can be deduced that carbon is present in amounts up to 45wt% inside the residual silica from the C2S phase. Here CaO-contents have dropped from the original 62wt% to below 15wt%. The extracted CaO is supposed to have ended up in the calcite.

DISCUSSION AND CONCLUSIONS

Close examination of the microstructure and composition of the carbonation products surprisingly revealed the presence of large amounts of what is most likely elementary carbon. Carbon from CO₂, as in our experiments, is known to form in the presence of wuestite in grinding experiments at 200°C, the latter phase being transformed to magnetite (Zhang et al. 1999). Wuestite (MW) is available in the slag and likely to be also the reductor for our observed elemental carbon formation. The carbonation experiments here presented show that the reduction of CO₂ to elemental carbon can occur even at temperatures as low as 90°C. We estimate that the amount of carbon formation from CO₂ is comparable to the amount of CO₂ captured as carbonate in calcite. These results imply that the CO₂ sequestration in steel slag might be greater than currently assumed based on the formation of carbonate minerals alone. Further validation of this process using additional analytical techniques is in progress.

For calcite, the observed spatial pattern indicates that the Ca is derived from alteration of C2S but that external conditions determine where it precipitates. Although C2S at the surface is altered to amorphous silicate and not reactive with CO₂ anymore (reaction stops in the experiments after 24 hrs), the reaction products do not sufficiently envelope the grains to improve the environmental properties with respect to pH and V-leaching in a sustainable manner. The carbonation treatment of particularly K1 steel slag without CaO is judged insufficient to meet the legal standards of the Dutch Building Materials Decree.

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