

Changes in mineralogical and leaching properties of converter steel slag resulting from accelerated carbonation at low CO² pressure

André van Zomeren ^a Sieger R. van der Laan ^b Hans B.A. Kobesen ^c Wouter J.J. Huijgen ^a Rob N.J. Comans ^{a,d}

^a Energy Research Centre of the Netherlands (ECN), The Netherlands
 ^b Tata Steel RD&T, Ceramics Research Centre, The Netherlands
 ^c Tata Steel Strip Products, OSF2, The Netherlands
 ^d Wageningen University, Department of Soil Quality, The Netherlands

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André van Zomeren^a, Sieger R. van der Laan^b, Hans B.A. Kobesen^c, Wouter J.J. Huijgen^a, Rob N.J. Comans^{a,d,*}

^a Energy Research Centre of the Netherlands (ECN), P.O. Box 1, 1755 ZG Petten, The Netherlands ^b Tata Steel RD&T, Ceramics Research Centre, P.O. Box 10000, 1970 CA IJmuiden, The Netherlands ^c Tata Steel Strip Products, OSF2, P.O. Box 10000, 1970 CA IJmuiden, The Netherlands ^d Wageningen University, Department of Soil Quality, P.O. Box 47, 6700 AA Wageningen, The Netherlands

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ABSTRACT

Steel slag can be applied as substitute for natural aggregates in construction applications. The material imposes a high pH (typically 12.5) and low redox potential (Eh), which may lead to environmental problems in specific application scenarios. The aim of this study is to investigate the potential of accelerated steel slag carbonation, at relatively low pCO₂ pressure (0.2 bar), to improve the environmental pH and the leaching properties of steel slag, with specific focus on the leaching of vanadium. Carbonation experiments are performed in laboratory columns with steel slag under water-saturated and -unsaturated conditions and temperatures between 5 and 90 °C. Two types of steel slag are tested; free lime containing (K3) slag and K1 slag with a very low free lime content. The fresh and carbonated slag samples are investigated using a combination of leaching experiments, geochemical modelling of leaching mechanisms and microscopic/mineralogical analysis, in order to identify the major processes that control the slag pH and resulting V leaching. The major changes in the amount of sequestered CO₂ and the resulting pH reduction occurred within 24 h, the free lime containing slag (K3-slag) being more prone to carbonation than the slag with lower free lime content (K1-slag). While carbonation at these conditions was found to occur predominantly at the surface of the slag grains, the formation of cracks was observed in carbonated K3 slag, suggesting that free lime in the interior of slag grains had also reacted. The pH of the K3 slag (originally pH ± 12.5) was reduced by about 1.5 units, while the K1 slag showed a smaller decrease in pH from about 11.7 to 11.1. However, the pH reduction after carbonation of the K3 slag was observed to lead to an increased V-leaching. Vanadium leaching from the K1 slag resulted in levels above the limit values of the Dutch Soil Quality Decree, for both the untreated and carbonated slag. V-leaching from the carbonated K3 slag remained below these limit values at the relatively high pH that remained after carbonation. The V-bearing di-Ca silicate (C2S) phase has been identified as the major source of the V-leaching. It is shown that the dissolution of this mineral is limited in fresh steel slag, but strongly enhanced by carbonation, which causes the observed enhanced release of V from the K3 slag. The obtained insights in the mineral transformation reactions and their effect on pH and V-leaching provide guidance for further improvement of an accelerated carbonation technology.

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1. Introduction

The annual steel production reaches about 1.3 billion tonnes world-wide (Worldsteel, 2010). Since modern integrated LD/converter steelplants produce about 90–100 kg of steel slag per tonne of steel, vast amounts of steel slag are being co-produced (Worldsteel, 2010). The steel (LD/converter) slag is a stony material that,

after cooling, resembles basalt. The cooling method (rapid/slow, with or without water), together with the mineralogy, determines the properties of the obtained stony aggregates, such as surface quality, (major- and minor-element) leachability and the volume expansion behaviour. It is well established that free lime in converter slag is a major determinant regarding the material properties (Shi, 2004). The aggregates can be used in many applications as substitute for natural aggregate materials, but impose a high pH (typically between 11.5 and 12.5) and low redox potential (Eh). While the materials generally comply with current regulatory limit values, e.g. in the Netherlands, the high pH and/or reducing properties can lead to environmental problems in specific applica-



^{*} Corresponding author at: Energy Research Centre of the Netherlands (ECN), P.O. Box 1, 1755 ZG Petten, The Netherlands. Tel.: +31 224 56 4218; fax: +31 224 56 8163.

E-mail address: comans@ecn.nl (R.N.J. Comans).

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tion scenarios with limited water flow and/or limited access of CO_2 and O_2 to the material, which hampers the carbonation and oxidation of the slag that would normally occur in contact with the atmosphere. Currently, there are no specific environmental criteria in the Netherlands for (re)use of (secondary) construction materials with regard to pH and Eh or the associated buffering capacities. Therefore, a decision scheme is being developed based on rules for the acceptance of construction materials in these specific applications.

A possible technology to reduce the pH of alkaline slags is carbonation. Carbonation of steel slag has been studied using a wide range of process conditions from ambient to elevated pressure and temperature (Baciocchi et al., 2009; Bonenfant et al., 2008; Huijgen et al., 2005; Lekakh et al., 2008). The aim of this study is to apply (enhanced) carbonation for the purpose of improving the environmental pH and leaching properties of converter steel slag. Two types/qualities of slags are considered that cover the full range of typical compositions of converter slag. Our optimisation of the process conditions is not aimed at maximising the CO₂ sequestration, but rather at reaching a substantial reduction of the alkaline slag pH while complying with regulatory limit values for contaminant leaching. Special attention is paid to the leaching of vanadium that is of specific concern with respect to the environmental quality of specific types of steel slags (Presslinger and Klepp, 2002). Accelerated carbonation of steel slag is performed at relatively low pCO_2 pressure (0.2 bar) at about the same concentrations as present in the process gasses of the steel plant. Experiments were performed under water-saturated and unsaturated conditions. The fresh and carbonated steel slag samples are studied for their mineralogical composition and controlling leaching processes, in order to evaluate the nature and sustainability of the observed changes in slag properties.

2. Materials and methods

2.1. Steel slag feedstock

Two qualities of rapid air-cooled slag from the basic oxygen steelmaking process, differing in free lime content, were used in this study to cover the full range of typical converter/LD slag compositions. Type K1 slag contains 0–3 wt.% free lime forming by minor free lime (CaO) crystallization at the solidus. Type K3 contains more than 6 wt.% free lime and the lime crystallizes at temperatures above the solidus (Geiseler, 1995). These type indications K1, K3 are slag definitions used at the production site of TATA Steel IJmuiden, The Netherlands. All slags represent single converter heats, and were air-cooled and subsequently broken and sieved to obtain a representative 2–3.3 mm fraction of starting material for the experiments. Samples were stored dry in a closed container under a N₂ atmosphere. The native pH of the K1 and K3 steel slag batches was 11.7–11.8 and 12.4–12.7, respectively.

2.2. Mineralogical characterisation

Mineralogy of the slag samples was determined using powder X-ray diffraction (XRD), reflected light microscopy and scanning electron microscopy (SEM) with microanalysis (EDS). For XRD, a few grams of the starting material was ground in a tungsten-carbide ball mill to below 15 μ m, no internal standard was used. XRD-patterns were acquired from 10° to 130° 2-theta with a Bruker D4 diffractometer using Co–K α radiation and a Vantec detector. The software package Topas (Bruker) was used to perform Rietveld quantification. To fit the pattern we used two types of wuestite (Fe-wuestite and Mg-wuestite) two polymorphs of di-Ca silicate (larnite and α -C2S), srebrodolskite, portlandite, calcite, aragonite

and lime. Lime was detected on the basis of two free-lying peaks at near 44° and 64° 2-theta, related to its cubic crystal structure, which allows reliable quantification down to 0.5 wt.%.

In addition to the XRD analyses to determine the structure, SEM–EDS was used to quantify the amounts of elements incorporated in the different minerals. For reflected light microscopy and SEM–EDS, polished grain-mounts were prepared of slag before and after carbonation. SEM–EDS was carried out with a JEOL 7001 operating at 15 kV and 10 nA, equipped with dual Silicon Drift Detectors with a Noran System 7 (NS7) platform. Spectra (EDS) were interpreted using NS7 software.

2.3. Carbonation experiments

Carbonation experiments at atmospheric pressure were performed in a glass column (Pharmacia XK-50/30, inner diameter 5 cm, 20 cm height) with a thermostatic jacket. About 900 g steel slag was wetted (see below) and placed in the column. A CO₂/Ar gas mixture (20% CO₂, 80% Ar) was water-saturated at elevated temperature, to ensure the presence of water in the experiments, and was introduced in an up-flow direction at a flow rate of about 400 mL/min. Experiments were performed at 5, 20, 50, 70 and 90 °C under water-saturated and unsaturated exposure for mostly 24 h. The effect of time (8-200 h) on carbonation was studied under water-saturated and unsaturated exposure at 90 °C. The experiments with unsaturated water conditions were performed by wetting the steel slag to an L/S ratio of about 0.01–0.1 L/kg. Based on preliminary experiments, the moisture content was increased to an L/S ratio of about 0.4 L/kg for experiments with reaction times greater than 24 h to avoid drying of the steel slag during the test. Water was added, and the amounts registered (usually between 5 and 10 mL per addition), in several steps during the course of the experiment to prevent drying of the material while keeping the conditions unsaturated (moisture content ranged from 2% to 10% during the experiments). In the water-saturated experiments the total free volume between the slag grains was occupied by water and surplus water was added during the experiment to compensate for evaporation due to the gas flow and/or the elevated temperatures of the carbonation. As a result, the corresponding L/S ratio in the columns varied between 0.4 and 2 L/kg during the carbonation experiments.

The carbonation efficiency was quantified by thermogravimetrical analysis (Mettler-Toledo TGA/SDTA 851e) coupled to a Pfeiffer (thermostar) Quadrupole mass spectrometer (TGA-MS). About 20– 50 mg of finely ground (<106 μ m) steel slag (Huijgen et al., 2005) was weighed in a ceramic cup and heated from 25 to 1000 °C under a nitrogen atmosphere at a heating rate of 40 °C/min. The weight loss was recorded by the TGA microbalance and the amount of carbonate was quantified by the weight loss observed between 500 and 1000 °C, which was verified by the MS detection of only CO₂ in that temperature range. Further details on the TGA-MS method are provided in Huijgen et al. (2005).

2.4. Leaching tests and characterisation

2.4.1. Batch pH-static leaching experiments

Both the K1 and K3 type steel slag samples were leached at a liquid to solid (L/S) ratio of 10 L/kg for 48 h in acid-cleaned 300 mL PTFE vessels at eight different pH values. The pH values of the suspension were adjusted (between 2 and 12) using a computerized pH-stat system. The pH of one of the suspensions was not adjusted in order to assess the leaching at the 'native' pH value of the suspension. Solutions of 1 M HNO₃ and NaOH (analytical grade) were used to adjust the pH of the suspensions which were in contact with the atmosphere, continuously stirred and kept at a constant temperature of 20 °C. After the equilibration period, the

suspensions were filtered through pre-washed 0.45 μ m membrane filters. The filtrates were preserved with concentrated HNO₃ (suprapure) and analysed by ICP-AES to obtain solution concentrations of 29 major and minor elements.

2.4.2. Column leaching test

Column leaching (percolation) tests were performed according to CEN/TS 14405 (2005) on the K1 and K3 type steel slag. The steel slag was added to a borosilicate glass column (inner diameter 5 cm) in layers of a few cm and packed by shaking and pushing gently with a rod to a filling height of ±20 cm. Nanopure demineralised water was used as the leachant. The packed columns were water-saturated and pre-equilibrated for 72 h, after which the influent was pumped in up-flow direction. Computer-controlled flow controllers assured a constant flow velocity during the experiments. Fractions were collected automatically at cumulative L/S values of 0.1, 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 (Eh) and conductivity were determined, and sub-samples for chemical analysis were taken and filtered through 0.45 μ m membrane filters. The filtered leachates were preserved with concentrated HNO₃ (suprapure) and analysed for 29 major and minor elements by ICP-AES.

2.4.3. Geochemical modelling

Geochemical modelling was performed on the pH_{stat} leachates from fresh and carbonated (K1 and K3) steel slag to identify the leaching processes and inferred changes in mineral composition. The database/expert system LeachXS (van der Sloot et al., 2003) in combination with the geochemical modelling framework ORCHESTRA (Meeussen, 2003) was used for this purpose. Potential solubility control was evaluated by calculation of mineral saturation indices (SI) of the minerals portlandite, CSH and calcite. The SI is defined here as $log(\frac{IAP}{K_{sn}})$ with IAP = ion activity product and $K_{\rm sp}$ = solubility product. The thermodynamic database used consisted of the MINTEQA2 database version 3.11 (Allison et al., 1991), extended with minor modifications as described by Dijkstra et al. (2002) and with solubility constants for Ca-silicates (i.e. CSHphases) (Gaucher et al., 2004). The total element concentration in solution corresponding with solubility control by a selected mineral was calculated as explained in detail by Meima and Comans (1997).

The dissolved carbonate concentrations were not analysed in the leachates. It was assumed that the eluates from fresh steel slag samples contained no dissolved carbonate. For the eluates from carbonated steel slag, total dissolved carbonate was assumed to be 10 mg/L over the whole pH range based on analyses of leachates from pH-static leaching experiments with carbonated converter slag from the same steel plant (Huijgen and Comans, 2006).

3. Results and discussion

3.1. Mineralogy of slag feedstock

Since the primary mineralogy of the slag is being altered in the carbonation process it is important to characterise the starting materials in some detail. Mineralogy of the starting materials from Rietveld-XRD is presented in Table 1 and Fig. 1a and b. Mineral compositions determined with SEM–EDS are reported in Table 2 and form the basis for the formulas of Table 1. In all fresh steel slags, Ca is mainly present in phases like free lime-portlandite (CaO– Ca(OH)₂), Ca-silicate (C2S), and Ca-ferrite (C2F). Two K1-slags are mentioned in Table 1. The K1-a was lowest in CaO-content resulting in high magnesio-wuestite (MW) and low Ca-ferrite (C2F), with no free-lime and a small amount of magnetite. When

we ran out of K1-a slag a replacement batch, K1-b, was prepared. This batch appeared to be more calcic, as expressed in the mineralogy with the presence of some free-lime and higher Ca-ferrite contents. The K3 slag sample contains about 8% free-lime when portlandite is counted as hydrated free-lime. It is similar in Ca-ferrite content to K1-b but lower in di-Ca silicate (C2S), as a consequence of its lower bulk silica content. Optical examination reveals that K3 contained considerable tri-Ca silicate (C3S), which exsolved to form C2S + free-lime. The latter exsolution minerals are detected with XRD, however the outline of C3S crystals are clearly recognized optically and their composition was analysed with SEM–EDS (Table 2).

The elemental composition of the major mineral phases among the three samples are similar, with the exception of C2F which has high Ti-contents in K1-a (Table 2). This is again an effect of Ca-deficiency, causing only small amounts of C2F to form, which preferentially accommodates the Ti of the slag. The element V is preferentially concentrated in the C2S and C2F phases.

3.2. Carbonation of steel slag

Carbonation processes and their effect on the leaching properties of steel slag are related to the mineralogy of the two slag types and alteration processes as a result of reaction with CO₂. Fig. 1 shows the amount of sequestered CO₂ and the development of the pH (L/S = 10, 48 h) at a number of stages during the carbonation of K1 and K3 steel slag at a partial CO₂ pressure of 0.2 bar, as a function of time (at 90 °C) and under both water-saturated and unsaturated conditions. Consistent with its content of free lime, the K3-slag is more prone to carbonation (about $15 \text{ g CO}_2/\text{kg}$) than K1-slag (about 6 g CO₂/kg). Assuming that the vast majority of sequestered CO₂ has reacted with the (rapidly carbonating) free lime (Huijgen et al., 2005), the maximum CO₂ uptake measured in the carbonation experiments (under conditions as outlined in Fig. 1) would correspond to 48% and 35% conversion of the free lime content of the K1 and K3 steel slags, respectively. Huijgen et al. (2005) have reported CO₂ sequestration capacities of about 100–150 g CO₂/kg with ground (<38 μ m) steel slag under high temperature and pressure conditions. Given our aim to carbonate relatively large steel slag grains (2-3 mm), with a limited surface area, only low degrees of carbonation are reached. The surface area of the grains is known to be an important process parameter (Baciocchi et al., 2009; Huijgen et al., 2005).

The carbonation as a function of the reaction temperature was examined with the K1 slag and the results are presented in Fig. 2. After 24 h of carbonation with K1 slag under saturated conditions at higher temperatures (50–90 °C), the amount of sequestered CO₂ was generally about a factor of 2 greater than that at room temperature. The experiments under unsaturated conditions did not show a significant effect of temperature (Fig. 2). In addition, the resulting pH showed no correlation with the reaction temperature in either the experiments under unsaturated or saturated conditions, as can be seen in Fig. 2.

Fig. 1 shows that the carbonation rate is fastest at water-saturated conditions and the rate declines strongly after about 24 h under these conditions. In addition, the observed changes in the pH of the steel slag also take place within the first 24 h of reaction time. The pH of the K3 slag is lowered by about 1.5 units, suggesting that the material is substantially improved with respect to its alkalinity. This decrease is very similar to that observed earlier by Huijgen et al. (2005) for this (K3) type of steel slag at corresponding Caconversion. The K1 slag shows a smaller decrease in pH from about 11.7 to 11.1 within the first 24 h reaction time. The pH values after carbonation seem to stabilise around 11.0–11.3 for both slag types. It is concluded that the major changes in the material take place within the first 24 h of carbonation and that the resulting pH and

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Table 1

Modal mineralogy of steel slag feedstock as determined with Rietveld-XRD. Indicated substituting elements were taken from SEM-EDS analyses shown in Table 2.

Slag batch nr.	S6938		Z1268		W8791		
Phase	Formula	K1(a)	1σ	K1 (b)	1σ	К3	1σ
Magnesio wuestite (MW)	(Fe,Mg,Mn)O	37.0	5.0	23.7	3.0	29.2	3.5
Free lime	CaO	0.0		1.6	0.8	5.4	1.0
Portlandite	Ca(OH) ₂					3.0	0.8
Di calcium ferrite (C2F)	2CaO (Fe, Ti, Al, V) ₂ O ₃	13.2	2.0	25.6	3.0	25.7	3.0
Di calcium silicate (C2S)	2CaO (Si,P,V)O ₄	49.1	5.0	49.2	5.0	36.6	5.0
Magnetite	FeO·Fe ₂ O ₃	0.7					



Fig. 1. Sequestered CO₂ and resulting pH (at *L/S* = 10 L/kg, 48 h equilibration) in K1 and K3 steel slag particles (2–3.3 mm) as a function of reaction time during watersaturated and under-saturated conditions at 0.2 bar *p*CO₂ and *T* = 90 °C.

Table 2 Mineral composition of steel slag feedstock samples based on SEM-EDS analyses (%wt.).

Phase	MgO	Al_2O3	SiO ₂	P_2O_5	CaO	TiO ₂	V_2O_5	MnO	FeO
K1-a, C2S	0.1	0.5	30.1	2.6	62.4	1.4	1.4	0.2	1.5
K1-a, MW	31.2	0.0	0.4	0.0	1.5	0.0	0.2	17.7	48.9
K1-a, C2F	0.8	6.6	2.3	0.1	44.3	10.2	2.0	2.0	31.9
K1-b, C2S	0.2	0.9	28.0	3.0	61.0	1.1	1.7	0.4	2.5
K1-b, MW	33.0	0.1	0.8	0.0	2.9	0.0	0.3	16.0	47.0
K1-b, C2F	0.9	10.0	1.6	0.2	44.0	5.0	1.4	2.0	34.0
K1-b, Lime	1.0	0.8	0.9	0.1	68.0	0.3	0.6	9.6	19.0
K3, C2S	0.3	0.7	29.2	2.6	60.6	0.8	0.9	1.1	3.7
K3, MW	30.2	0.0	0.3	0.0	2.8	0.0	0.1	12.5	54.1
K3, C2F	0.7	4.0	1.1	0.1	43.5	4.6	2.0	1.5	42.5
K3, C3S ^a	0.1	0.5	22.7	1.5	70.1	0.6	0.2	2.4	2.0
K3, lime	0.8	0.1	0.3	0.2	79.7	0.2	0.0	7.6	11.0

^a Exsolved into C2S and lime.

amount of sequestered CO_2 under these conditions should be feasible targets for further improvement of this technology. Based on these results, subsequent leaching tests to evaluate changes in the environmental quality of steel slag have been performed on fresh samples of the two steel slag types and corresponding samples carbonated during 24 h at 90 °C.

3.3. Mineralogical characterisation of carbonation products

As mentioned above, we hypothesised the environmental quality of carbonated steel slag to be related to mineralogical alterations at the steel slag surface, as a result of the reaction with CO₂. When determining the alteration phases on the surfaces of reacted grains, calcite was detected by XRD as the only newly formed (crystalline) mineral. The diffraction intensity of the original mineralogy was suppressed by the calcite encrustation. and, consequently, no quantitative phase portions were obtained from these measurements.

Reflected light microscopy of the K1 slag grains (Fig. 3) showed that calcite formation occurs mainly on the outside of grains, but that not all surfaces are equally overgrown. The grain at the bottom of Fig. 3 has developed a thick layer of calcite without signs of mineralogical alteration at the exposed surface. The other grain (top) shows some alteration (dark rim) of C2S, but no calcite deposition. These observations imply that calcite deposition was not related to the degree of alteration of the underlying slag mineralogy within a particle but seems to be controlled by external conditions imposed by the fluid covering the grain surfaces during the carbonation experiments. Hence, the carbonation reaction appears to take place in two subsequent steps, rather than by solid-state conversion; calcium is first leached from the Ca-minerals and subsequently reacts with dissolved carbonate to form calcite that precipitates on the surface of the steel slag particles. This sequence has also been observed (Huijgen et al., 2005) to occur during the carbonation of steel slag in an autoclave at high temperature and pressure $(T = 150 \circ C/pCO_2 = 20 \text{ bar}).$

Results from reflected light microscopy of the carbonated K3 slag are given in Fig. 4. The carbonated K3 slag shows severe fracturing in contrast to the observations for K1 slag. This phenomenon is caused by volume expansion of the reacting free lime, resulting in more extensive development of alteration rims on both C3S-relicts and C2S (Fig. 4). The large C3S grains have a cloudy appearance from lime exsolution while the C2S grains are clear. Dusty material surrounding the grain is largely calcite. The formation of the calcite layer on these mineral phases of the K1 slag (Fig. 3) has been reported to hinder the further leaching and subsequent reaction of Ca from the coated particles (Huijgen et al., 2005; Lekakh et al., 2008).

The leaching of vanadium from (carbonated) steel slag is known to be important with respect to the environmental quality of this material (Presslinger and Klepp, 2002). Therefore, the A. van Zomeren et al./Waste Management 31 (2011) 2236-2244



Fig. 2. Sequestered CO₂ and resulting pH (at *L/S* = 10 L/kg, 48 h equilibration) in K1 steel slag particles (2–3.3 mm) as a function of reaction temperature during water-saturated (solid circles) and under-saturated (open circles) conditions at 0.2 bar *p*CO₂ and 24 h reaction time.



Fig. 3. Two grains of K1-a from a water-saturated carbonation experiment after exposure for 24 h to a humid CO_2 -Ar atmosphere at 50 °C (pCO_2 = 0.2 bar).

mineralogical phases and element distribution patterns of vanadium were determined for carbonated K1-a (Fig. 5) and K3 slag (Fig. 6). The top left image in these Figures represent the backscatter images of the carbonated K1-a and K3 grains. The arrows with the label "alt." point to various alteration areas (darker grey) of the C2S grains. The top right images show the distribution of V, the bottom left images show the distribution of Ca and the bottom right images represent the distribution of Fe. The alteration rims represent a residue containing phosphate and silica. The element distribution patterns clearly show V-enrichment at the rims of the C2S-crystal and on the borders of C2F phases for both slag qualities. The dark areas in the backscatter image (alteration rims) correspond to the brighter red areas in the V-distribution image.

The MW-phases and the lime phases (for K3 slag) contain no V. The alteration rims on the C3S phases in the K3 slag are V-enriched (see top-left corner grain in Fig. 6). The top right facet of the large C2F grain in the centre of Fig. 6 is also clearly altered and enriched in both Fe and V.

Fig. 5 and Fig. 6 show that unaltered C2S and C2F phases at the inside of the slag grains contain the highest V-concentrations in their outer zones. This zoning is related to the primary solidification process of molten slag where cores of phases are solidified at higher temperatures than their outer zones that appear to be enriched in V. Calcite, C3S and MW do not contain V. Therefore, the observed V enrichment of C3S alteration rims appears to be a secondary process, caused by sorption or precipitation of V that was previously leached from C2S and C2F phases. It can also be seen



Fig. 4. A heavily fractured grain of K3 slag after 24 h exposure to a CO_2 -Ar gas atmosphere at 95 °C under water-saturated conditions ($pCO_2 = 0.2$ bar). The indicated C3S phase is exsolved into C2S and lime.

that there is Ca-loss from altered C2S (for both slag types), with possibly some additional, secondary, V-enrichment at the mineral surface (e.g., top right edge of the C2S grain shown at the top left corner of Fig. 5).

The mineralogical characterisation clearly shows that the carbonation process results in (incongruent) dissolution of Ca from C2S (Fig. 5, top left corner of Ca image) and, to a lesser extent, C2F and subsequent reaction with dissolved carbonate, followed by calcite precipitation on the surface of the steel slag particles (calcite particles on the alteration layer in Fig. 5). The calciumbearing phases C2S and C2F are also shown to be the primary Vcontaining minerals in the steel slag. In the process of their partial dissolution, V is partly redistributed and enriched in alteration rims, particularly on C3S. The effect of these mineralogical alterations on the leaching properties of steel slag is addressed in the next section.

3.4. Leaching behaviour of fresh and carbonated steel slag

Fig. 7 shows the leaching of Ca, Si and V from fresh and carbonated steel slag as a function of pH. The solubility and leaching of Calcium increases strongly and consistently towards low pH and this pattern is likely to originate from the (partial) dissolution of the alkaline lime and Ca- (and V) bearing C2S and C2F phases. Si has previously been observed (Zinngrebe et al., 2004) to be released primarily from C2S, and simultaneously with V. The

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Fig. 5. SEM backscatter image and element distribution of carbonated K1-a slag (24 h, 50 °C, water saturated conditions), top left: SEM Backscatter Image in which grey levels correspond to the three slag phases, magnesio-wuestite (marked MW) and Srebrodolskite (marked C2F) are equally bright; Larniet (C2S) is distinctly darker grey. Alteration (marked alt.) occurs only in C2S grains and is even darker and patchy grey; top right: V-distribution; bottom left; Ca-distribution, bottom right: Fe-distribution.



Fig. 6. SEM backscatter image and element distribution of carbonated K3-slag (24 h, 95 °C, water saturated conditions). Top left: SEM Backscatter Image; top right: Vdistribution; bottom left; Ca-distribution, bottom right: Fe-distribution. The indicated C3S phase is exsolved into C2S and lime. Alteration products are marked with "alt".

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Fig. 7. Leaching of Ca, Si and V from fresh and carbonated (90 °C for 24 h) steel slag as a function of pH. Lines represent the calculated Ca and Si leaching assuming solubility control by mineral phases. The native pH of the fresh slag samples was 11.7 (K1) and 12.4 (K3). After carbonation, the native pH of the samples was 11.2 (K1) and 11.4 (K3).

optical microscopic analysis of the carbonated steel slag has shown that C2S phases have been altered to a much higher degree than C2F. Given these findings and the rather similar V content of these phases (Table 2), leached V is, therefore, believed to originate largely from the partial dissolution of C2S. Fig. 7 does also show that the leaching of Ca is substantially reduced after carbonation of both slag types.

The processes behind the observed differences in the pH-dependent leaching of Ca from the different steel slag samples have been further examined by geochemical modelling. This approach contributes to bridge the mineralogical observations with the leaching data, particularly with regard to the major mineral phases that control the Ca solubility. Potential mineral phases involved in the leaching of Ca were selected based on the mineralogical characterisation (Table 1). For the fresh materials, solubility products of portlandite (Ca(OH)₂) and CSH (Ca_{1.1}SiO₇H_{7.8}) (Gaucher et al., 2004) were selected as proxies for free lime and C2S, respectively. The mineral Ca₁₁SiO₇H_{7.8} was chosen based on previous work (Huijgen and Comans, 2006), where it was observed that this mineral phase adequately described the leaching behaviour of Si in fresh steel slag. Although we note that the selection of this mineral phase, and particularly its stoichiometrical composition remains somewhat subjective, the solubility of Ca and Si is reasonably well approximated by CSH between pH 11 and the native pH of the fresh K3 slag (=12.4 for K3 slag after 48 h of water contact). At this native pH, Ca is also close to equilibrium with co-existing portlandite (Fig. 7; see also Eq. (1) below).

For the carbonated steel slags, the pH-dependent Ca concentration in equilibrium with calcite was calculated. The lower Ca concentration in the leachates of the carbonated slags (pH interval 6– 10) tend towards the values predicted in equilibrium with calcite, which has a significantly lower solubility than the original Caphases. The carbonated K3 slag still contains portlandite but this mineral is present inside the grains and protected from leaching by the unaltered minerals, the alteration rims and the calcite layer around the grains (Fig. 6). The leaching pattern of V is qualitatively identical to the leaching of Si. This observation suggests that the leaching of V and Si is governed by the same mineralogical changes during carbonation. As indicated by the above mineralogical analysis, the observed partial dissolution of the V-bearing C2S phase is most probably responsible for these effects. It has been suggested that V is incorporated as vanadate (VO_4^{3-}) in the C2S phase of fresh steel slag (Presslinger and Klepp, 2002).

The fresh K3 steel slag contains free lime, leading to its native pH of 12.4. At these alkaline conditions V is relatively immobile. However, as Fig. 7 shows, the V leaching drastically increases when the pH is lowered (as a result of acid addition in the pH-stat) to values of about 11 or less. This leaching pattern is consistent with the dissolution of (V-bearing) C2S and subsequent formation of CSH and portlandite, which can be represented by the general equation:

$$C2S + mH_2O = CSH_{m-1} + Ca(OH)_2$$
⁽¹⁾

Eq. (1) shows that the dissolution of C2S is limited by the presence of portlandite, particularly in case of a free lime buffer such as in K3 slag. Hence, the leaching of V from dissolving C2S is strongly reduced when portlandite is present (i.e. at the native pH of K3 slag; Fig. 7). Carbonation of K3 slag clearly shows that V leaching also increases as a result of this treatment, due to the transformation of portlandite to calcite and subsequent partial dissolution of C2S, with more intensive carbonation of the slag leading to higher V mobility, as will be shown below.

The fresh K1 steel slag shows a relatively high V leaching at high pH, probably as a result of the absent (or very limited) portlandite buffer, allowing greater C2S dissolution. When the pH of this slag is decreased by carbonation and/or by addition of acid in the pH-static leaching test, the C2S dissolution and V leaching increase. These results are consistent with those of Huijgen and Comans (2006), although the severe carbonation at elevated temperature and pressure in that study does result in even higher V emissions between pH 11 and 13. The effects of carbonation on pH and the leaching of V was further tested with the upflow percolation test to verify

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Fig. 8. Cumulative release of V (top) and leachate pH (bottom) as a function of liquid/solid (L/S) ratio for untreated and carbonated K1 and K3 slag, under both water-saturated and unsaturated conditions. NL-SQD refers to the limit value for V leaching as specified in the Dutch Soil Quality Decree.

compliance with limit values specified in the Dutch Soil Quality Decree (SQD; as published in 2008).

Fig. 8 shows the cumulative release of V and the leachate pH in the percolation tests with K1 and K3 slag, before and after carbonation using water-saturated and -unsaturated conditions. The pH of the treated slag showed a short-lived improvement, starting at around 10 (K1-b saturated) to 10.8 (K1-b unsaturated) but with a rebound to around 11 for K1-b saturated (original pH of the K1 slag was 11.7). However, the K1-b slag that was carbonated under unsaturated conditions does not show a pH rebound effect, for reasons that we were unable to identify. The K3 slag does not show any differences in the pH between the fresh and carbonated samples. This large difference in the leachate pH development of K1 and K3 slag is in agreement with the presence of a larger amount of free lime in the K3 steel slag (Table 1), i.e., the pH determining phase in the fresh slag (Fig. 7). Huijgen et al. (2005) showed that portlandite is the Ca-phase most susceptible to carbonation of the three phases present. The results in Fig. 8 indicate that the surface reactions seem to be effective for neutralisation of the pH, confirming earlier work (Huijgen et al., 2005). We have observed that carbonation only takes place on the surface of the grains in both the K1 and K3 slags, as shown in Fig. 3. During the carbonation treatment, portlandite is partly formed from CaO inside the grains of K3 slag. This process results in the formation of cracks due to volume expansion (Fig. 4), resulting in a slow (diffusive) release of alkalinity from unreacted portlandite in the inner grains. This effect was not observed for K1 slag due to its limited CaO content.

The carbonation was observed to lead to an increased V-leaching in both the pH-stat test (Fig. 7) and the column test (Fig. 8) for the K3 slag. The leaching of vanadium from the K3 slag remained below the Dutch limit values (<1 mg/kg), although it was found to increase substantially after carbonation. Both the fresh and the carbonated K1 slag were found to exceed the limit values of the Dutch SQD for an open application without isolation measures. Comparing samples carbonated under unsaturated conditions (lower degree of carbonation; see Fig. 1) with those carbonated under water-saturated conditions (higher degree of carbonation), shows that increasing the degree of carbonation is paralleled with further increasing vanadium leaching. This effect is most likely the result of the more extensive dissolution of C2S and subsequent V release.

Improvement of the K1 steel slag pH by carbonation appears incompatible with an acceptable leaching of V (leaching of V from untreated material was already higher than limit value). The results in Fig. 8 imply that a further improvement of the pH of K3 slag would be needed to substantially lower this parameter to an acceptable value. However, our findings strongly suggest that the V leaching in the K3 slag would then also increase beyond the criteria specified in the SQD.

4. Conclusions

Accelerated carbonation of steel slag at relatively low pCO₂ pressure (0.2 bar) and water-saturated and under-saturated conditions was investigated as a potential method to improve the environmental properties of steel slag. In general the reaction was found to proceed fastest at higher temperature (50-90 °C) in the presence of water. Carbonation at these conditions was found to occur predominantly at the surface of the slag grains, the free lime containing slag (K3-slag) being more prone to carbonation (about 15 g CO_2/kg) than the slag with lower free lime content (K1-slag) (about 6 g CO₂/kg). The major changes in the amount of sequestered CO₂ and the resulting pH reduction occurred within 24 h. The formation of cracks was observed after carbonation of the K3 slag, suggesting that free lime in the interior of slag grains had also reacted. The pH of the K3 slag was reduced by about 1.5 units, suggesting that the material is substantially improved with respect to its alkalinity. The K1 slag showed a smaller decrease in pH from about 11.7 to 11.1 within 24 h reaction time. For both slag types, the pH values after carbonation seem to stabilise around 11.0-11.3. The pH reduction after carbonation was observed to lead to an increased V-leaching. In parallel to the pH reduction, the K1 slag showed a relatively high V-leaching (10-100 mg/kg slag) at levels above the limit values of the Dutch Soil Quality Decree (for untreated and treated slag), while the K3 slag remained within acceptable limits (<1 mg/kg slag) at the relatively high pH that remained after carbonation. It is concluded that improvement of the steel slag pH by carbonation is largely incompatible with maintaining an acceptable leaching of V. Combined geochemical modelling of the leaching mechanisms and microscopic/mineralogical analysis of fresh and carbonated slag grains have proven to constitute a consistent and valuable approach to identify the major processes that control the slag pH and resulting V leaching. The di-Ca silicate (C2S) phase has been found to contain a substantial level of V and its dissolution has been identified as the major source of the Vleaching. In fresh steel slag, particularly K3 slag, the dissolution of C2S and the resulting V-leaching are limited by the presence of portlandite. Carbonation of the slag leads, however, to transformation of portlandite to calcite, the subsequent partial dissolution of C2S and release of V. Given that this V-bearing C2S phase is (partially) dissolved during carbonation, further improvement of an accelerated carbonation technology should focus on stimulation of a secondary binding mechanism for V in the carbonated slag matrix.

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