

Mineral CO₂ Sequestration by Steel Slag Carbonation

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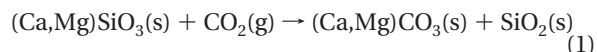
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Mineral CO₂ sequestration, i.e., carbonation of alkaline silicate Ca/Mg minerals, analogous to natural weathering processes, is a possible technology for the reduction of carbon dioxide emissions to the atmosphere. In this paper, alkaline Ca-rich industrial residues are presented as a possible feedstock for mineral CO₂ sequestration. These materials are cheap, available near large point sources of CO₂, and tend to react relatively rapidly with CO₂ due to their chemical instability. Ground steel slag was carbonated in aqueous suspensions to study its reaction mechanisms. Process variables, such as particle size, temperature, carbon dioxide pressure, and reaction time, were systematically varied, and their influence on the carbonation rate was investigated. The maximum carbonation degree reached was 74% of the Ca content in 30 min at 19 bar CO₂ pressure, 100 °C, and a particle size of <38 μm. The two most important factors determining the reaction rate are particle size (<2 mm to <38 μm) and reaction temperature (25–225 °C). The carbonation reaction was found to occur in two steps: (1) leaching of calcium from the steel slag particles into the solution; (2) precipitation of calcite on the surface of these particles. The first step and, more in particular, the diffusion of calcium through the solid matrix toward the surface appeared to be the rate-determining reaction step. The Ca diffusion was found to be hindered by the formation of a CaCO₃-coating and a Ca-depleted silicate zone during the carbonation process. Research on further enhancement of the reaction rate, which would contribute to the development of a cost-effective CO₂-sequestration process, should focus particularly on this mechanism.

Introduction

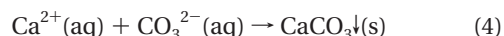
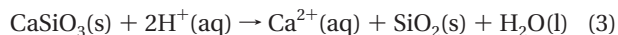
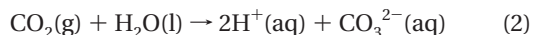
The increasing atmospheric CO₂ concentration, mainly caused by fossil fuel combustion, has led to concerns about global warming. A possible technology that can contribute to the reduction of carbon dioxide emissions is CO₂ sequestration by mineral carbonation, as originally proposed by Seifritz (1) and first studied in more detail by Lackner et al. (2). The basic concept behind mineral CO₂ sequestration is

to mimic natural weathering processes in which calcium- or magnesium-containing minerals are converted into calcium or magnesium carbonates:



Compared to other CO₂ storage options, such as storage in empty gas fields, oceans, and aquifers, mineral CO₂ sequestration has some potential advantages. First, mineral sequestration is a chemical sequestration route of which the products are thermodynamically stable. Therefore, the storage of CO₂ is permanent and inherently safe. In addition, the energy consumption and costs of carbon sequestration may be limited by the exothermic nature of the carbonation reaction. A disadvantage of mineral CO₂ sequestration is that large amounts of Ca/Mg minerals are required to sequester a significant fraction of the CO₂ emitted from fossil fuel combustion, although sufficient suitable ores are available on a global scale (2).

Natural weathering proceeds too slowly to effectively mitigate global warming. Therefore, mineral sequestration research aims at accelerating the reaction to obtain a viable industrial process. For this purpose, many process routes have been developed for mineral CO₂ sequestration (3–5) of which the aqueous carbonation route (6) was selected for experiments on the basis of technological and economical considerations, which are outlined in more detail in ref 4. In a simplified form, the aqueous carbonation of a calcium silicate can be written as



Research on the aqueous carbonation route has focused mainly on Mg silicates so far. Typical process conditions reported to obtain a sufficient reaction rate include either an energy-consuming pretreatment step or high CO₂ pressures (typically >100 bar) (4).

A possible feedstock for mineral CO₂ sequestration, which has not attained much attention so far, is industrial solid waste, such as combustion residues, slags, and fly ashes. These materials are generally alkaline and rich in calcium. Major advantages compared to ores are their low costs and widespread availability in industrial areas, i.e., near large point sources of CO₂. No mining is needed and consumption of raw materials is avoided. Moreover, these residues tend to be more reactive for carbonation than primary minerals due to their chemical instability and thus their use might enable a reduction of the energy consumption and costs of mineral CO₂ sequestration (7). In addition to advantages from a CO₂ sequestration perspective, research has shown that carbonation of alkaline solid residues can lead to an improvement of their environmental quality (e.g. 7, 8). Although their total CO₂ sequestration capacity is limited compared to primary minerals, the use of alkaline solid residues could facilitate the realization of the first cost-effective mineral CO₂ sequestration plants. In addition, this alternative route could be of interest at sites where both large quantities of CO₂ and suitable solid residues are produced, such as steel production facilities and municipal waste incineration plants. Various alkaline solid waste streams can be used as feedstock for mineral CO₂ sequestration. Steel

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slag was selected for the experiments presented in this paper because of its high specific sequestration capacity.

Research on the carbonation of industrial residues published so far has focused mainly on improvement of their environmental quality (e.g. 8–11) and their mechanical properties with regard to utilization in construction (e.g. 12, 13). Some of these earlier studies have suggested that the carbonation of alkaline residues may also contribute to the minimization of atmospheric CO₂ emissions (9, 10). However, very limited research has been published in this area for the specific purposes of carbon sequestration (e.g. 14, 15). This paper presents a first systematic study of the reaction mechanisms of CO₂ sequestration by carbonation of an alkaline solid residue. The rate-determining reaction steps are identified, and routes for further process optimization are indicated.

Experimental Section

Materials Processing. Linz Donawitz steel slag (size class 0–20 mm) was dried at 60 °C in an oven and stored in containers under a nitrogen atmosphere. Representative samples were taken from the steel slag and ground until all material passed predetermined sieve sizes (d , <38 μm to <2 mm). Homogeneous subsamples of the prepared batches were taken for the carbonation experiments with a sample splitter.

Carbonation experiments were performed in a 450 mL AISI316 autoclave reactor (Limbo 350, Büchi Glas Uster). A suspension of steel slag and Nanopure-demineralized water, at a desired liquid-to-solid ratio (L/S , 2–20 kg/kg), was stirred at a specific stirring rate (n , 100–2000 rpm) using a Rushton turbine. The reactor was closed and heated to the reaction temperature (T , 25–225 °C) and maintained at that temperature during the reaction time (t , 2–30 min). When the temperature had reached the set point, CO₂ was added directly into the solution using a gas booster (Haskel AG75) until a specific CO₂ pressure was established (p_{CO_2} , 1–30 bar). During the reaction time, the CO₂ pressure was kept constant within ±0.2 bar of its set point by replenishment of the consumed CO₂. A hollow stirring axis was used to enhance mass transfer of CO₂ by transporting the gas through the axis from the gas phase into the solution by the underpressure caused by the stirrer. When the reaction time had elapsed, the addition of CO₂ was stopped and the autoclave was cooled to 40 °C, depressurized, and opened. The suspension was immediately filtered quantitatively over a 0.2 μm membrane filter, and the solid was dried overnight at 50 °C in an oven. Finally, the product was analyzed to determine the conversion of the reaction.

The heating and cooling times were approximately 11 and 8 min, respectively, for a set of typical conditions used ($T = 100$ °C, $n = 1000$ rpm, $L/S = 10$ kg/kg). During the experiment, the temperature of the reactor and the heating jacket and the total pressure inside the reactor were recorded with a data acquisition unit (Agilent 34970A). The partial CO₂ pressure was calculated from the total pressure and the water vapor and air pressure corresponding with the temperature inside the reactor.

At one carbonation experiment, the chemical composition was measured of the aqueous phase, sampled directly in the autoclave reactor at typical process conditions (i.e., $d < 106$ μm, $T = 100$ °C, $p_{CO_2} = 19$ bar, $L/S = 10$ kg/kg, $n = 1000$ rpm, $t = 30$ min). For this purpose, the reactor was equipped with a dedicated sampling device, which included an in-line filter that allowed instantaneous filtration of the steel slag suspension.

Materials Characterization. The carbonate content of the fresh and carbonated samples was determined with two different analytical methods: (1) thermal decomposition (TGA-MS); (2) acidification (C-analyzer).

TGA-MS analyses were performed in duplicate in a thermal gravimetric analysis system (Mettler-Toledo TGA/SDTA 851e) coupled with a mass spectrometer (Pfeiffer, ThermoStar) (TGA-MS). Samples (10–20 mg) (<106 μm) were heated in aluminum oxide ceramic cups under an oxygen atmosphere at 40 °C/min from 25 to 1000 °C. Weight loss was measured by the TGA, while the evolved gas was analyzed for CO₂ and H₂O by the MS. Three weight fractions were distinguished: (1) 25–105 °C; (2) 105–500 °C; (3) 500–1000 °C. These fractions represent (1) moisture, (2) organic, elemental carbon and (if present) MgCO₃, and (3) CaCO₃ (inorganic carbon), respectively. During heating of the samples, samples were kept isothermally at 105 and 500 °C for 15 min to obtain a good discrimination between the weight fractions. The third weight fraction of the TGA curve ($\Delta m_{500-1000^\circ C}$) based on dry weight ($m_{105^\circ C}$) was used as the calcium carbonate content, expressed in terms of CO₂ (wt %):

$$CO_2 \text{ (wt \%)} = \frac{\Delta m_{500-1000^\circ C}}{m_{105^\circ C}} \times 100 \quad (5)$$

Total inorganic carbon (TIC) was determined with the solid sample module of a Shimadzu TOC 5000A C-analyzer (TOC-SSM). A 0.75 mL volume of 1:1 diluted HCl was added to a 50–100 mg sample (<106 μm) and heated to 200 °C. The evolved gas was analyzed for CO₂ with a nondispersive infrared detector (NDIR). Since the C-analyzer measures total inorganic carbon and TGA-MS determines CaCO₃, the difference between the two measurements was used to verify that no carbonates other than CaCO₃ had formed.

For determination of the total composition, a fresh steel slag sample was ground (<106 μm) and, subsequently, digested and analyzed with inductively coupled plasma atomic emission spectrometry (ICP-AES) for Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Ge, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Sn, Sr, V, W, Y, and Zn (digestion with HNO₃/HClO₄) and Si and Ti (HNO₃/HClO₄/HF). In addition, Cl was determined coulometrically after heating of a solid steel slag sample at 1200 °C in an oven and subsequent trapping of the evolved gases.

The carbonation degree (ζ_{Ca}) can be determined from the total Ca content of the fresh steel slag (Ca_{total}), the molar weights of Ca (MW_{Ca}) and CO₂ (MW_{CO_2}), and the carbonate content measured with TGA-MS, corrected for the weight increase due to carbonation. In eq 6, it is assumed that only Ca is carbonated during the carbonation process, that the initial carbonate content of the (fresh) steel slag is negligible, and that no significant mass is lost due to leaching in the autoclave reactor:

$$\zeta_{Ca} \text{ (\%)} = \frac{\frac{CO_2 \text{ (wt \%)}}{100 - CO_2 \text{ (wt \%)}} \times \frac{MW_{Ca} \text{ (kg/mol)}}{MW_{CO_2} \text{ (kg/mol)}}}{Ca_{total} \text{ (kg/kg)}} \times 100 \quad (6)$$

Significant formation of other carbonates (mainly MgCO₃) is improbable because of the relatively low Mg content of steel slag and the very limited Mg conversion expected due to the relatively low CO₂ pressure and short reaction times (4) applied in the experiments (see below for verification). Typical process conditions needed to carbonate Mg silicates via the aqueous carbonation route, without addition of extra chemicals or additional pretreatment steps other than grinding, include $p_{CO_2} > 100$ bar and a reaction time in the order of hours (6).

The leaching characteristics of Ca and Si from the original steel slag were determined in a pH_{stat} system, to obtain additional information on the available Ca species in the

TABLE 1. Composition of Fresh Steel Slag Expressed in Terms of Oxides^a

element	composn (wt %)	element	composn (wt %)
Fe ₂ O ₃	35.5	MnO	3.4
CaO	31.7	Al ₂ O ₃	1.6
SiO ₂	9.1	TiO ₂	1.3
MgO	6.0		

^a Only elements present at >1 wt % are shown.

steel slag. Eight suspensions of a ground steel slag sample ($d < 106 \mu\text{m}$) and Nanopure-demineralized water at a liquid-to-solid ratio of 10 kg/kg were stirred in closed Teflon reaction vessels for 48 h at room temperature. For seven vessels, the pH was controlled automatically at a preset pH value by the addition of 1 or 5 M HNO₃ and 1 M NaOH. One vessel was left at the native pH of the sample. After 48 h, the pH of the suspensions was measured and the suspensions were filtered through 0.2 μm membrane filters. The clear filtrates were acidified with concentrated HNO₃ and, subsequently, analyzed for Ca and Si by ICP-AES. The leaching of other elements was also measured. These data and geochemical modeling of the pH_{stat} leaching curves are the subject of a subsequent paper (16).

To determine the native pH of samples that had been carbonated in the autoclave, $L/S = 10 \text{ kg/kg}$ suspensions in Nanopure-demineralized water were prepared and stirred open to the atmosphere for 24 h. The pH was recorded continuously, and the pH value reached after stabilization was reported. Particle size distribution and volume-based mean particle size ($D[4,3]$) of samples were measured by laser diffraction (Malvern Mastersizer 2000) using ethanol (96%) as dispersing agent. The BET single point method with N₂ was used to measure the specific surface area. Mineralogical composition was determined using powder X-ray diffraction (XRD) (Bruker, D8 advance). Samples were studied with a scanning electron microscope (SEM) with energy-dispersive X-ray (EDX) spot analysis. Finally, geochemical equilibrium calculations were performed with The Geochemist's Workbench 4.0 (GWB) (17).

Results and Discussion

Feedstock Analysis. The bulk total composition of the steel slag used is shown in Table 1. The slag is rich in Fe originating from the processed iron ore and Ca from the addition of limestone in the steel production process to remove impurities (e.g. Si and P). The slag is very suitable for mineral CO₂ sequestration because of its high Ca content and high alkalinity (pH = 12.6). The maximal CO₂ sequestration capacity is 0.25 kg of CO₂/kg of steel slag on the basis of the total Ca content, which would be equivalent to a carbonate content of the product of 20 wt % CO₂. The native pH of the fresh slag is in good agreement with the theoretical pH of a saturated portlandite (Ca(OH)₂) solution (pH 12.4 calculated with GWB), the presence of which was confirmed by XRD analysis. The acid neutralizing capacity of the fresh slag is 4.0 mol of HNO₃/kg on the basis of the total acid consumption in the pH_{stat} at pH = 8 (i.e., approximating the pH of a calcium carbonate saturated system in equilibrium with the atmosphere). This value corresponds to a CO₂ sequestration capacity of 0.09 kg/kg. Since this value is based on the amount of Ca that is available for leaching at 25 °C, it is lower than the capacity based on the total composition.

The size distribution, mean particle size, and carbonate content of the different batches of fresh steel slag that were used for the carbonation experiments are shown in the Supporting Information. All samples show a wide size distribution, which includes very small particles (<1 μm).

TABLE 2. Identified Minerals in Fresh and Carbonated Steel Slag ($\zeta_{\text{Ca}} = 60\%$, $p_{\text{CO}_2} = 20 \text{ bar}$, $T = 150 \text{ }^\circ\text{C}$, $t = 30 \text{ min}$, $d < 106 \mu\text{m}$ (batch 3), $n = 500 \text{ rpm}$, $L/S = 10 \text{ kg/kg}$) with Analysis Method

element	phase	fresh steel slag	carbonated steel slag
Ca	Ca(OH) ₂ (portlandite)	XRD	ND ^a
	Ca-(Fe)-silicates	SEM	SEM
	Ca-Fe-O	SEM	SEM
	CaCO ₃ (calcite)	TGA-MS	XRD, TGA-MS, (traces) SEM
Mg	Mg-Fe-O	SEM	SEM
	MgCO ₃ (magnesite)	ND	XRD (traces)
other	SiO ₂	ND	SEM
	FeO	SEM	SEM

^a ND = not detected.

The initial calcium carbonate content of the steel slag is significantly higher for the small size fractions and varies between 1.5 and 5.1 wt % CO₂, corresponding to a Ca conversion (eq 6) of 6 and 22%.

Mineralogy. Table 2 shows the mineralogical phases that were identified in a representative fresh and carbonated steel slag sample. Element mappings of Ca, Si, O, Fe, and Mg by SEM-EDX are shown in the Supporting Information. Calcite and traces of MgCO₃ (magnesite) were the only carbonates identified by XRD in the carbonated product. Comparison of the TGA-MS and TOC-SSM results (not shown) indicated that no significant amount of MgCO₃ was formed during the carbonation process, which confirmed that reaction conditions (i.e., particularly pressure) were insufficient to significantly carbonate Mg minerals. The same result was obtained for other degrees of carbonation. Therefore, the Ca conversion as defined by eq 6 can be applied to quantify the sequestration of CO₂ by the steel slag. For the further carbonation results presented in this paper only the TGA-MS results will be used.

Calcium Speciation. Three major phases of calcium in the fresh steel slag have been identified (Table 2): Ca(OH)₂; Ca-(Fe)-silicates and Ca-Fe-O. The first two phases have been reported as minerals reacting with CO₂ in other alkaline solid residues (8, 10). A lower carbonation rate is expected for Ca silicates relative to Ca (hydr)oxides, on the basis of their solubility and previous carbonation experiments (4, 18). Portlandite was converted completely to calcite at the applied carbonation conditions (Table 2).

Figure 1 shows the pH-dependent leaching of Ca and Si in a pH_{stat} system. At two pH values the leached amount of calcium shows a steep increase. The first step occurs between pH 11.1 and 9.6, and the calcium concentration at pH 9.6 is 6450.2 mg/L or 29.6% of the total calcium content. We define this part of the calcium as fraction I. The second step occurs between pH 5.1 and 3.5. At pH 3.5, 61.6% of the total Ca has been dissolved. Fraction II is defined as the increase in the second step (i.e., 32.0% of the total calcium content). This fraction includes the amount leached between pH 9.6 and 5.1. The rest (Ca fraction III, 38.4% of the total Ca) consists of Ca that is virtually insoluble or physically not available for leaching at this particular particle size and leaching time. Possibly, fraction III corresponds with the identified Ca-Fe-O phase.

Solubility products of Ca(OH)₂ (portlandite), amorphous SiO₂ (19), and CSH (Ca_{1.1}SiO₇H_{7.8}) (20) were used to calculate the solubility curves of these minerals, as shown in Figure 1. Ca fraction I probably consists mainly of portlandite and Ca silicates (similar to CSH) that are relatively easily leachable. Fraction II is assumed to consist of Ca silicates that are more difficult to dissolve, on the basis of the observed slight increase in Si leaching below pH 9.6.

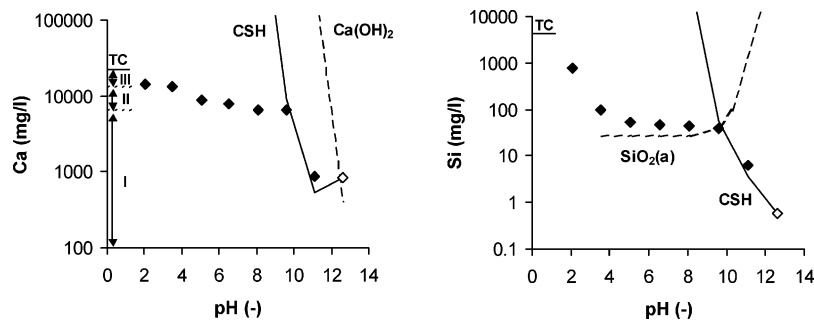


FIGURE 1. Ca- and Si-leaching characteristics of fresh steel slag feedstock (<106 μm) and geochemical modeling of solubility control by specific minerals. Total content (TC) and Ca fractions I–III are indicated. Open symbols indicate the native pH of the sample.

Process Variables. Process conditions in the autoclave reactor were varied systematically to determine their influence on the Ca conversion and to identify the rate-limiting step in the carbonation of steel slag. Given eqs 2–4, five different process steps can be distinguished: (1) diffusion of Ca toward the surface of the solid steel slag particles; (2) dissolution of Ca from the surface into the solution; (3) dissolution of gaseous CO₂; (4) conversion of dissolved CO₂(aq) to the (bi)carbonate ion; (5) precipitation of CaCO₃. The main process variables are (1) reaction time (*t*), (2) temperature (*T*), (3) CO₂ pressure (*p*_{CO₂}), (4) particle size (*d*), (5) stirring speed (*n*), and (6) liquid-to-solid ratio (*L/S*). These process variables were varied individually in six series of experiments. Ranges of process conditions were chosen such that a wide variation of conversions was obtained (20–80%). Because Ca fraction I was found to be carbonated very rapidly (see below), this study focuses particularly on the reaction mechanisms involved in the carbonation of Ca fraction II, and process conditions were selected accordingly. The results of the six series of experiments are shown in Figure 2 and will be discussed below.

In the following discussion, it is assumed that precipitation only occurs during the reaction at elevated temperature and pressure and that any possible formation of calcite upon depressurization of the reactor is negligible. This assumption was tested by analyzing a sample taken directly from the reactor at typical process conditions. Only 3% of Ca in the suspension was found to be dissolved just before depressurization. It is unlikely that significant amounts of additional Ca are leached during the short depressurization time (typically 1–2 min) and given the increasing pH. Therefore, no more than approximately 3% of the measured Ca conversion can be attributed to calcite formed during the depressurization of the reactor.

Reaction Time. In the first 2 min over 40% of the calcium is carbonated (i.e., fraction I and 36% of fraction II), while only an extra 13% (or 39% of fraction II) reacts when the reaction time is increased to 30 min. This pattern is consistent with the observed calcium speciation in the fresh steel slag; first, a Ca fraction that is carbonated relatively easily (I), followed by a more difficult to convert fraction (II). Carbonation of fraction II is initially rapid and then declines gradually. The declining reaction rate shows that the precipitation of calcite is not rate-determining for this process. In that case, precipitated calcium carbonate would have enhanced further precipitation by serving as precipitation nuclei and a progressive increase of the conversion with reaction time would have resulted.

Particle Size. Reduction of particle size from <2 mm to <38 μm results in a large increase of the conversion from 24 to 74%. This observation suggests that reactions involving the solid particles contribute to the overall reaction rate. BET analyses performed on fresh steel slag samples 2 and 3 showed that steel slag particles are nonporous and, therefore, the specific surface area can be calculated directly from the

D[4,3] value obtained from particle size analysis if we assume spheric particles. The conversion-particle size (*D*[4,3]) dependence measured at various reaction temperatures shows an exponential relation with a power of between –0.7 and –0.4. Thus, reducing the mean particle size by a factor of 2 increases the conversion relatively by 32 to 62%.

Temperature. The reaction temperature has two opposite effects on the carbonation rate. At higher temperatures leaching of Ca from the matrix is likely to proceed faster, but the solubility of carbon dioxide in the solution decreases. As shown in Figure 2, the carbonation increases toward higher temperatures between 25 and 175 °C. At temperatures above the optimum of around 200 °C, the conversion decreases when the temperature is increased further. Apparently, the lower carbon dioxide solubility limits the conversion at high temperatures. The observed temperature pattern and optimum correspond well with the reported pattern and optimal temperature (185 °C) for the aqueous carbonation of olivine (6). The calcium conversion between 50 and 150 °C shows an Arrhenius-type temperature dependence with ζ_{Ca}/t as pseudo-reaction rate for the carbonation of Ca fraction II. The temperature influence shows that leaching of Ca is probably the rate-determining reaction step between 25 and 150 °C and that at temperatures above the optimum (i.e., >200 °C) a reaction step involving CO₂ becomes rate limiting.

Carbon Dioxide Pressure and Stirring Rate. At a reaction temperature below the temperature optimum, CO₂ pressure and stirring rate have a very limited influence on the reaction rate above a specific threshold value (i.e., 500 rpm and around 9 bar, respectively, as observed in preliminary experiments). These trends are also visible in Figure 2. Below this threshold, the Ca conversion decreases significantly due to inadequate mixing and a deficiency of dissolved CO₂, respectively. The presented carbonation experiments were typically conducted at conditions above these threshold values, and the reaction rate can, therefore, be considered independent of the stirring rate and CO₂ pressure. The insignificant effect of the CO₂ pressure shows that CO₂ mass transfer is not rate-determining and confirms that it is the leaching of Ca that controls the reaction rate. The leaching of Ca consists of two steps: (1) diffusion of Ca toward the surface of a particle; (2) dissolution of Ca from the surface into the solution. The negligible influence of the stirring rate on the conversion suggests that mass transfer from the particle's surface into the solution is relatively fast. Therefore, the diffusion of calcium from the particle interior toward its surface is the likely reaction step that determines the overall carbonation rate.

Liquid-to-Solid Ratio. A decrease of the liquid-to-solid ratio results in a slight increase of the conversion, which might be explained by the higher ionic strength and, consequently, higher solubility of calcium. O'Connor et al. have shown that addition of salts could enhance the carbonation of Mg silicates (6). *L/S* ratios lower than two cannot be stirred sufficiently in the autoclave reactor that was used in this study and would result in poor CO₂ gas–

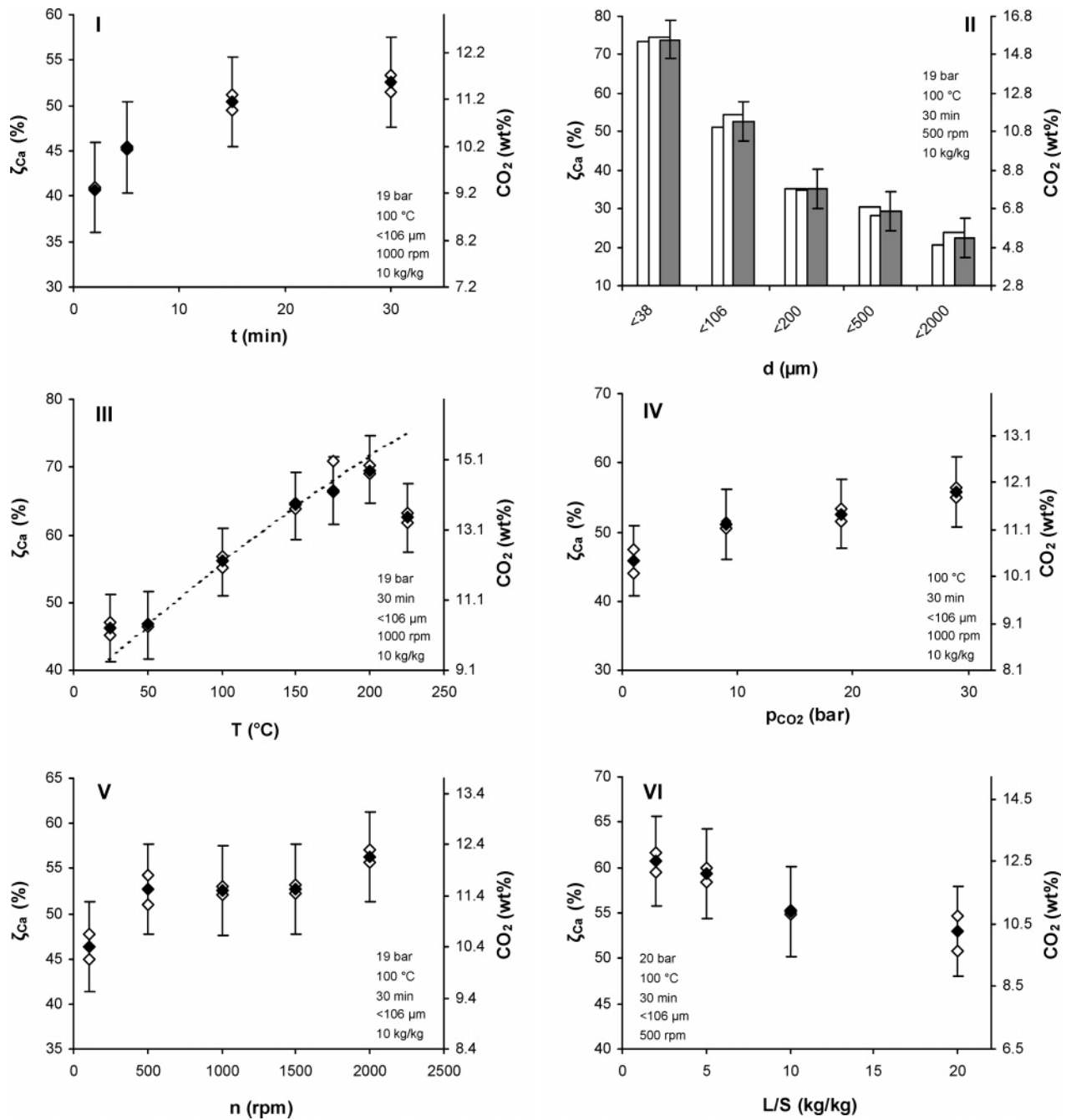


FIGURE 2. Calcium conversion (ζ_{Ca}) and carbonate content (CO_2) as a function of various process variables. For each carbonation experiment the duplicate TGA analyses (open symbol) and the resulting mean conversion (solid symbol) are shown. Error bars are based on 5% absolute deviation of the Ca conversion (as calculated in ref 16): (I) reaction time, feedstock batch 2; (II) particle size, sample <106 μm = batch 2; (III) reaction temperature including Arrhenius plot (dotted line) with $A = 6.0\%$ Ca/min and $E_a = 3.6$ kJ/mol, batch 3; (IV) carbon dioxide pressure, batch 2; (V) stirring rate, batch 2; (VI) liquid-to-solid ratio, batch 3.

liquid and Ca solid-liquid mass transfer rates. Therefore, we conclude that the optimal liquid-to-solid ratio in this type of reactor is 2 kg/kg.

Reaction Mechanisms. Figure 3 shows SEM micrographs of fresh and carbonated steel slag. Notable is the change in morphology of particle surfaces when comparing micrographs I and II. The carbonated particles contain a porous coating that is absent in the noncarbonated particles. The composition of this coating was identified as $CaCO_3$ by SEM/EDX analysis of polished samples embedded in resin (micrograph III). No separate calcium carbonate particles were identified in the carbonated sample. Further examination of the polished samples has revealed three other phases: (1) an iron-rich phase (indicated as Ca-Fe-O, Ca

fraction III); (2) a calcium silicate phase (Ca fraction II); (3) a SiO_2 phase with traces of Ca. The first two phases are present in both the noncarbonated and the carbonated slag (Table 2). SiO_2 and $CaCO_3$ were only identified in the carbonated material. The formation of a carbonate coating and SiO_2 rim has also been reported for the carbonation of Mg ores (21).

The mineralogical changes taking place during carbonation resulted in a neutralization of the pH value. Figure 4 shows how the native pH of steel slag samples, measured after 24 h stabilization, decreases with increasing carbonation degree for selected carbonation experiments at $L/S = 10$ kg/kg. The pH of the 74% carbonated slag (9.4) is still significantly higher than the pH of a solution saturated with calcite (8.3 calculated with GWB). Similar changes in mineralogy and

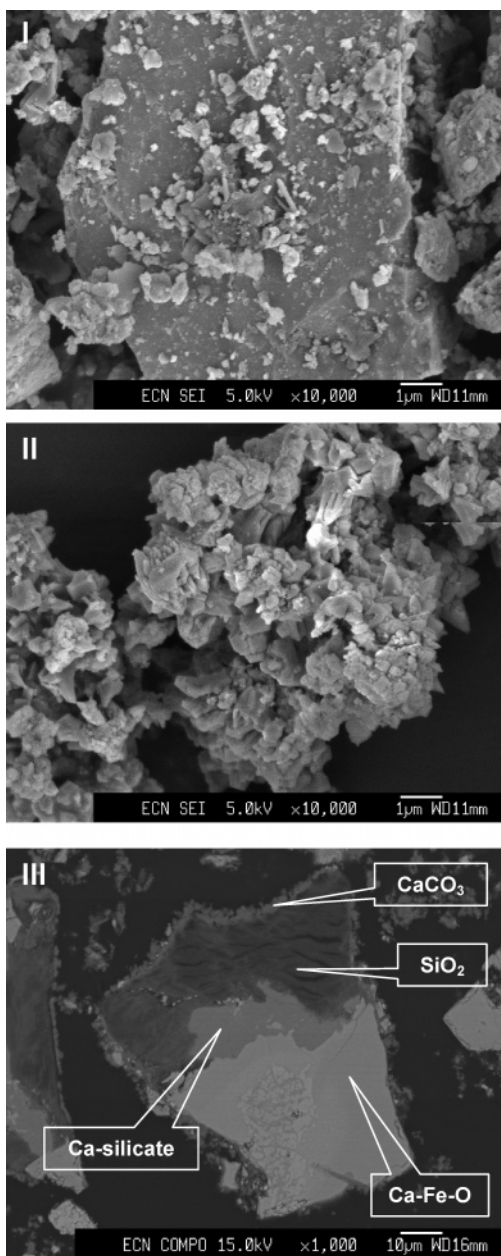


FIGURE 3. SEM micrographs of fresh (I) and carbonated (II) steel slag ($p_{\text{CO}_2} = 20$ bar, $T = 150$ °C, $t = 30$ min, $d < 106$ µm (batch 3), $n = 500$ rpm, $L/S = 10$ kg/kg) and SEM-BSE (backscatter electron) micrograph of polished carbonated steel slag particles embedded in resin with SEM-EDX analysis (III).

pH values after carbonation have been reported for other alkaline residues (e.g. 8–10). During the 24 h pH measurement, the pH of carbonated steel slag suspensions was found to start around 8 after which it increased regressively before stabilizing. This behavior suggests that the pH is controlled initially by calcite and at longer equilibration times by diffusion of residual alkalinity through the porous CaCO₃ coating.

These observations and the influences of the process variables discussed above lead to the following conclusions on the carbonation mechanisms of steel slag: (1) The carbonation of Ca takes place in two subsequent steps (i.e., dissolution and precipitation) rather than by solid-state conversion. After the initial rapid carbonation of the Ca(OH)₂ present in the fresh steel slag, calcium from the Ca silicate phase diffuses toward the surface of the particle and is

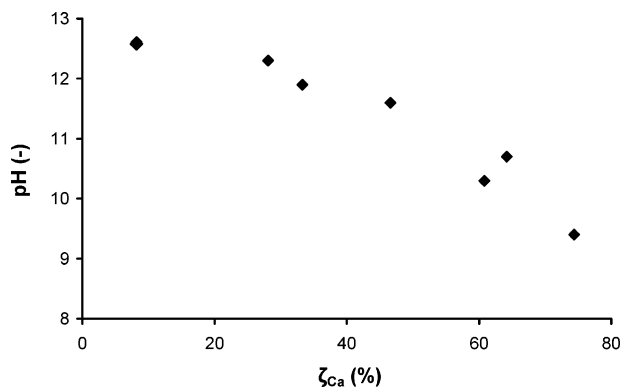


FIGURE 4. Native pH of carbonated steel slag as a function of the degree of carbonation ($L/S = 10$ kg/kg, 24 h).

subsequently leached (eq 3). The Ca in solution is carbonated and precipitates as calcite on the outer surface of the steel slag particles (eq 4). (2) Among the various process steps, the diffusion of Ca toward the surface of steel slag particles probably determines the overall reaction rate at temperatures below an optimal conversion temperature (i.e., 200 °C for the conditions presented). At higher temperatures or lower CO₂ pressures, a deficiency of dissolved CO₂ results in a decrease of the conversion. (3) The leaching of Ca results in a withdrawing Ca silicate core surrounded by a Ca-depleted SiO₂ rim apparently hindering the diffusion of Ca from the particle interior resulting in a declining reaction rate.

Further enhancement of the carbonation rate could contribute to the development of a cost-effective CO₂ sequestration process, and research efforts should focus particularly on the identified rate-controlling mechanisms.

Acknowledgments

This work was funded by the Dutch Ministry of Economic Affairs as part of the Clean Fossil Fuels program of ECN and the CATO research program on CO₂ capture, transport, and storage.

Supporting Information Available

Particle size distribution, mean particle size, and carbonate content of fresh steel slag batches used in carbonation experiments and SEM-EDX mapping of noncarbonated and carbonated steel slag samples. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Received for review April 26, 2005. Revised manuscript received October 13, 2005. Accepted October 13, 2005.

ES050795F