MINERAL CO2 SEQUESTRATION IN ALKALINE SOLID RESIDUES

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Preface

Abstract

Mineral carbonation is a promising sequestration route for the permanent and safe storage of carbon dioxide. In addition to calcium- or magnesium-containing primary minerals, suitable alkaline solid residues can be used as feedstock. The use of alkaline residues has several advantages, such as their availability close to CO_2 sources and their higher reactivity for carbonation than primary minerals. In addition, the environmental quality of residues can potentially be improved by carbonation. In this study, key factors of the mineral CO_2 sequestration process are identified, their influence on the carbonation process is examined, and environmental properties of the reaction products with regard to their possible beneficial utilization are investigated. The use of alkaline solid residues forms a potentially attractive alternative for the first mineral sequestration plants.

1.   INTRODUCTION

CO_2 sequestration by mineral carbonation has been recognized as a promising route for the permanent and safe storage of carbon dioxide [1,2]. Various process routes have been proposed [2,3]. As feedstock, typically, calcium- or magnesium-containing primary minerals are used (*e.g.* wollastonite ($CaSiO_3$)). A possibly attractive alternative is the use of suitable alkaline solid residues, such as ashes from waste incineration, demolition waste and slags from steel production [1]. Using these alternative materials as feedstock has several advantages. The materials are often available in large amounts in industrial areas close to CO_2 sources. Thus, the need for transport of CO_2 is minimized. Sequestration costs are lowered because the mining of primary minerals can be avoided. In addition, due to their chemical instability, alkaline slags and ashes tend to be more reactive for carbonation than primary minerals. Less extreme reaction conditions (*i.e.* lower pressure and less grinding) are therefore needed to obtain a sufficient conversion. Finally, the environmental quality of alkaline solid residues has been shown to improve by carbonation [4], which can potentially facilitate the beneficial re-use of the carbonation products.

2.   CARBONATION PROCESS [5]

Steel slag was selected as feedstock for experimental work on mineral CO_2 sequestration because of its theoretically high specific CO_2 sequestration capacity (for the slag used 0.25kg/kg). The steel slag batch was dried, milled to pass a desired sieve class and split into representative sub-samples. Samples for carbonation experiments were mixed with nanopure-demineralised water to obtain a suspension with the desired liquid to solid ratio (L/S). The suspension was placed in an autoclave reactor and stirred continuously at a specific stirring rate (n). The autoclave was closed and heated until the reaction temperature (T) was reached. Carbon dioxide was added by means of a gas booster until the desired pressure (p) was reached. After the reaction time has passed, the reactor was cooled to 40°C and the pressure was released. The suspension was filtered and, subsequently, dried in an oven. The carbonate content and the conversion grade of the samples were measured by Thermogravimetric Analysis (TGA-MS).

In developing a cost-effective large-scale sequestration process it is important to determine the rate-determining step of the process. Therefore, process conditions were systemically varied and their influence on the carbonation process was determined. In principle, there are five potentially rate limiting reaction steps: diffusion of Ca towards the surface of the solid particles, leaching of Ca from the surface into the liquid, dissolution of $CO_2(g)$ in the liquid, conversion of dissolved $CO_2(aq)$ to the (bi-)carbonate-ion and precipitation of $CaCO_3$. A selection of obtained results (effect of particle size, reaction temperature, reaction time and CO_2 pressure on Ca-conversion) is shown in *Figure 1*.
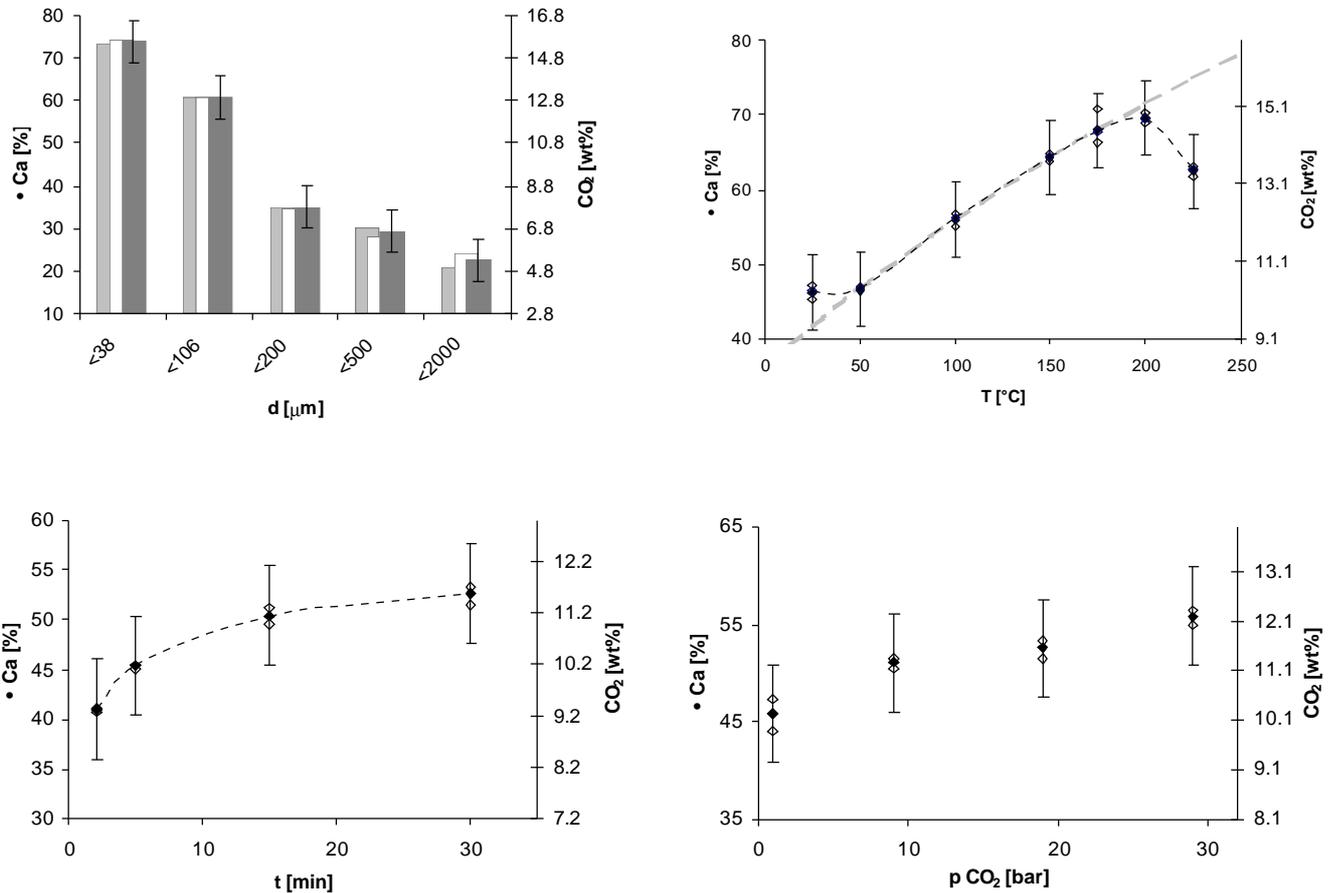
Figure 1 Effect of different process conditions on the carbonation of steel slag. (1) Particle size (p_{CO2}=19bar, T=100°C, t=30min, n=500rpm, L/S=10kg/kg). (2) Reaction temperature (p_{CO2}=20bar, t=30min, d<106•m, D[4,3]=32.6 •m, n=500rpm, L/S=10kg/kg). Bold grey line shows the Arrhenius-relationship. (3) Reaction time (p_{CO2}=19bar, T=100°C, d<106•m, D[4,3]=32.6•m, n=1000rpm, L/S=10kg/kg). (4) Carbon dioxide pressure (T=100°C, t=30min, d<106•m, D[4,3]=32.6•m, n=1000rpm, L/S=10kg/kg). Error bars are based on 5% Ca conversion standard deviation, corresponding to 2 times the standard deviation of a 8 times repeated carbonation experiment (p=20bar CO_2, T=150°C, d<106•m, n=500rpm, L/S=10kg/kg, t=30min).

Reduction of the particle size dramatically increases the conversion, which shows that a reaction step that involves the solid particle is rate determining. Grinding increases the reaction rate by either an increase of the specific surface (thus facilitating the Ca-leaching rate) or by a decrease of the diffusion length (enhancement of the Ca-diffusion). Fitting of particle size trends leads to the

relationship: $z_{Ca} \propto \dfrac{1}{\sqrt{D[4,3]}}$ (D[4,3]: volume based mean diameter). This finding suggests that the

Ca-diffusion through the matrix is the rate-determining process rather than Ca-leaching and is confirmed by the observation that calcium conversion is independent of the stirring rate. The diffusion rate also depends on the reactor temperature; increasing the temperature from 25°C to 175°C strongly increases the conversion. The data between 50 and 175 °C can be described by an Arrhenius-equation. The determined energy of activation is 3.6 kJ/mol, which is very low and consistent with solid-state diffusion control of the reaction rate. Above 175°C the measured conversions deviate from the Arrhenius-relationship, resulting in a reaction rate optimum around 200°C and a subsequent decline of the conversion at higher temperatures. This behaviour can be explained by a decreasing CO_2 solubility in the water phase at higher temperatures, suggesting that above 175°C, the Ca diffusion is no longer rate determining, due to a limitation of dissolved CO_2.

Both reaction time and CO_2 pressure at 100°C have a very limited effect on the obtained conversion. These characteristics would possibly enable substantial cost savings for mineral CO_2 sequestration when using steel slag. Scanning Electron Microscopy (SEM) analyses have confirmed the reaction phases and rate-limiting step (*Figure 2*). Combining the obtained process knowledge, it can be concluded that calcium conversions of over 70% are possible at relatively mild process conditions (d<106•m, T=200°C, p_{CO2}=10bar, t=15min) without any further pre-treatment or addition of chemicals. Preliminary experiments have shown that even higher conversions are possible when the slag is further ground or when higher reaction temperatures are combined with higher CO_2 pressures. However, in a further process optimisation study, the additional CO_2 sequestration needs to be balanced against the extra process costs and energy consumption.
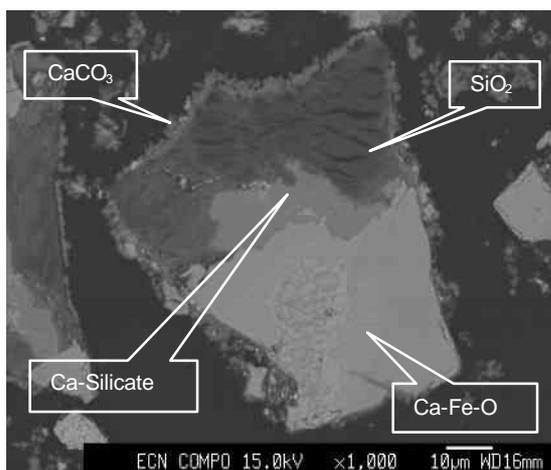

Figure 2   BSE-image of polished carbonated steel slag particle (p_{CO2}=20bar, T=150°C, t=30min, d<106•m, D[4,3]=32.6•m, n=500rpm, L/S=10kg/kg) (1000x, 15.0kV) with SEM-EDX analysis. Note the coating with $CaCO_3$ and the Ca-depleted SiO_2 phase (both absent in the non-carbonated sample).

3.   PRODUCT PROPERTIES

Another important part of the mineral CO_2 sequestration work performed at ECN is the environmental characterization of the carbonated products. The goal is to enable beneficial applications of the products in, for example, construction applications. Especially in densely populated countries such as the Netherlands, this forms a key-boundary condition for the possible large-scale implementation of mineral CO_2 sequestration. *Figure 3* shows some typical leaching characteristics for steel slag samples with varying carbonation grade, as obtained by pH-dependent (pH_{stat}) leaching experiments. On the one hand, the underlying processes during the carbonation process can be identified (*e.g.* Ca being converted from Ca-silicates/lime into calcium carbonate). On the other hand, the possibility of re-use applications can be evaluated. The environmental quality of the solid residues can be improved by carbonation, as is shown for the leaching of Barium. The concentration of Ba that is leached from steel slag at its native pH is critical relative to the limit of the Dutch Building Materials Decree. The leaching is significantly reduced by carbonation, probably by the formation of $BaCO_3$ or solid solutions with $(Ba,Ca)CO_3$. However, adverse effects have also been found, as is shown for Vanadium, which warrant further research and process optimisation.
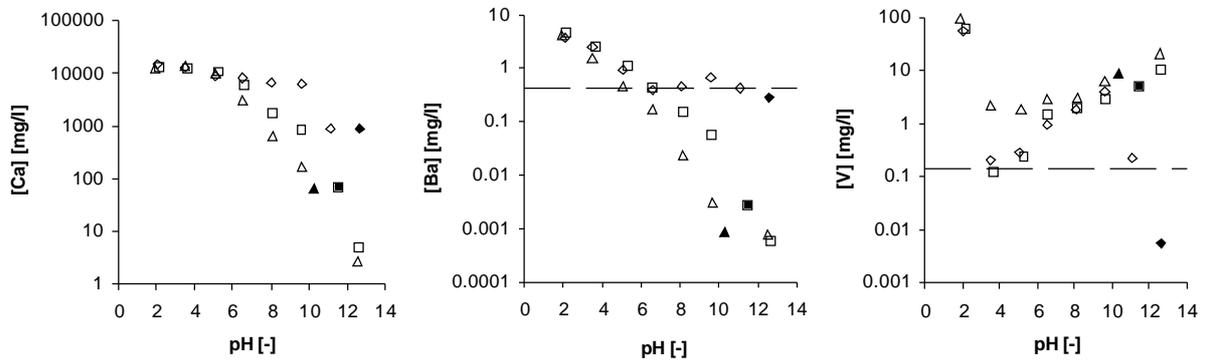
Figure 3 pH$_{stat}$ leaching characteristics of ground feedstock (diamond), ±30% carbonated product (square) and ±60% carbonated product (triangle). The filled symbols show the results at the native pH of the samples. Lines indicate the limits set by the Dutch Building Materials Decree.

4.   CONCLUSION

In this work we have shown that carbonation of steel slag is possible at relatively mild conditions. The calcium diffusion in the solid particles has been identified as the rate-determining step. Therefore, particle size and reaction temperature are key process parameters. Sequestration costs can be limited due to the short reaction time and low CO_2 pressure that are required to obtain a high (70%) degree of conversion. From an environmental point of view, beneficial application of the carbonated product seems possible. However, more research on the influence of carbonation on the leaching properties of solid residues is needed. Although their total sequestration capacity may be relatively limited compared to primary minerals, the use of alkaline solid residues is a promising option that can contribute to make the first mineral sequestration plants economically feasible.

5.   REFERENCES

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