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Whitfield, Pamela S.; Mitchell, Lyndon D.

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***In-situ* laboratory X-ray powder diffraction study of wollastonite carbonation using a high pressure stage.**

Pamela S. Whitfield^{1,*} and Lyndon D. Mitchell²

¹Institute for Chemical Process and Environmental Technology, National Research Council Canada, 1200 Montreal Road, Ottawa ON K1A 0R6, CANADA

²Institute for Research in Construction, National Research Council Canada, 1200 Montreal Road, Ottawa ON K1A 0R6, CANADA

*Corresponding author, Email: pamela.whitfield@nrc.gc.ca; Fax: +1 613 991 2384.

Abstract

A high-pressure gas stage, recently developed for *in-situ* X-ray powder diffraction studies of polymer crystallization under CO₂, has been used to observe the carbonation of wollastonite under various temperature/pressure conditions despite the fact that the stage was not designed for use with moisture-containing samples. The rate of carbonation of wollastonite at 60 °C was found to be pressure-independent. Additional experiments at 34.5 bar between 43 and 73 °C enabled an activation energy of 53 kJ mol⁻¹ to be determined for the rate-limiting step. This value agrees very well with a published value for the leaching of Ca from wollastonite in acidic conditions and suggests that Ca leaching is the rate-limiting step in wollastonite carbonation at these temperatures.

1. Introduction

Global warming has stimulated renewed interest in issues relating to C capture and storage in order to reduce CO₂ emissions from fossil-fuel power stations and other industrial facilities. There are currently two approaches under study, the first is to inject CO₂ into exhausted oil/gas wells or deep aquifers, and the second is to use a reactive mineral to permanently bind the CO₂ in the form of carbonates. Current studies on the impact of CO₂ well-injection rely heavily on geochemical modelling (Gaus et al., 2005). Long term predictions relying on such modelling are potentially unreliable due to very non-ideal behaviour of CO₂-containing mixtures (Weiss, 1974), and to the lack of experimental data on which to underpin the geochemical models. Indeed where data does exist it suggests that the chemical interactions are not as simple as previously assumed (Kaszuba et al., 2003). The scientific community needs to build experience of monitoring complex *in-situ* chemical reactions if it is to be able to design safe, leak-free, and functional CO₂ storage facilities that will survive on a geological timescale. A larger number of experimental studies on mineral sequestration have appeared and carbonation studies on a number of mineral systems including Mg silicates (Xu et al., 2004) and Ca silicates (Tai et al., 2006) have been

published recently. Magnesium silicates are quite common geologically, but their carbonation reactions are much slower than those of Ca silicates and require more severe reaction conditions.

X-ray powder diffraction is a powerful and common technique for the study of phase changes in solid materials, yielding phase information beyond the weight change and heatflow information accessible by thermal analysis techniques. Diffraction experiments under hydrostatic pressure are common in diamond-anvil cells, but experiments with high gas pressures are usually confined to facilities such as synchrotrons. The higher energy X-rays available at synchrotrons are better suited to penetrating sample environments, and the higher photon fluxes mean that reasonable diffracted intensities are obtained even with significant attenuation. However, one limiting factor with synchrotrons is the restricted beam time available to individual researchers. This makes synchrotrons ideal for fast reactions over a period of minutes or hours under extreme conditions, where experiments with time resolution of the order of seconds or less are required. In contrast, laboratory systems are better suited for longer experiments where less time resolution is required. The number of commercial instruments for *in-situ* laboratory studies under gas pressure is very limited, with relatively modest capabilities, due in part to often strict design criteria and differing pressure-vessel regulations in different jurisdictions. The lack of a suitable commercial gas pressure stage was the catalyst for the initial development of the stage described by Whitfield et al. (2008). The stage is a compact, ASME certified pressure vessel constructed from 304 stainless steel with 3.2 mm thick, coated Be windows. The maximum pressure rating is 125 bar with an allowable temperature range of -40 to 200 °C achieved using a recirculating fluid. The necessarily thick windows in such a pressure stage means that CuK α radiation isn't sufficiently penetrating and a MoK α X-ray tube has to be used to obtain a reasonable time resolution in experiments (Whitfield et al., 2008).

The objective of the study was to demonstrate the use of an *in-situ* pressure stage in a laboratory diffractometer for studying reactions relevant to CO₂ sequestration. Wollastonite was chosen for this proof-of-concept study because it carbonates relatively easily over a period of a few hours, and is readily available in a pure form. As such it is well suited for a series of laboratory-based experiments within a reasonable timescale. It also provided the opportunity to explore the chemistry of wollastonite as applied to mineral sequestration as the authors could find no *in-situ* study of wollastonite carbonation in the literature.

Wollastonite (CaSiO₃) is a white mineral with a silicate-chain structure (Ohashi, 1984). It has several industrial applications including building ceramics, low-voltage porcelain and facing tiles (Azarov et al., 1995). In the 1970s Ordinary Portland Cement (OPC) chemists studied calcination reactions of wollastonite (Klemm and Berger, 1972; Bukowski and Berger, 1979) and other hydraulic Ca silicates (Goodbrake et al., 1979; Young et al., 1974). Recently the study of wollastonite is re-gaining attention

due to its carbonation reaction and potential for CO₂ sequestration (Santos et al., 2007). The overall carbonation reaction of wollastonite is as follows:-

2. Experimental

The *in-situ* stage used for this study has been described previously (Whitfield et al., 2008) and fits on a laboratory-based diffractometer. The CO₂ gas used was a BOC supercritical grade which has negligible moisture content. The X-rays from the usual Cu X-ray tube (8 keV) have insufficient penetrating power in this instance. The attenuation of both the thick Be windows and the pressurized CO₂ are such that the more penetrating Mo radiation (17 keV) is necessary (Whitfield et al., 2008).

The material used in the experiment was a purified natural triclinic wollastonite from St. Onge, Quebec, Canada. After placing approximately 0.1 g of wollastonite into the sample holder 3 drops of 18 MΩ water were added, which was sufficient to produce a paste-like texture. Adding too much water formed a meniscus which severely attenuated the MoKα radiation. The stage was pre-heated before the sample was placed inside to reduce evaporation of the limited quantity of water prior to data collection. The first experiment (Table 1) was conducted at 60 °C with an applied pressure of 34.5 bar whilst X-ray diffraction data were collected. In experiments 2-4 different CO₂ gas pressures were applied at a constant temperature of 60 °C. In experiments 5-8 the pressure was constant at 34.5 bar and the temperature varied between 43 and 73 °C. The experiment at 60 °C and 34.5 bar CO₂ was not repeated.

The stage was mounted on a Bruker D8 Advance fitted with a Vantec position-sensitive detector (PSD) and a MoKα tube operated at 50 kV and 45 mA. Parafocussing geometry was used with a divergence slit of 0.1° and a radial Soller slit on the Vantec detector to reduce low angle background scatter. Scans were run using a 5° PSD window from 4° to 25° 2θ, with a step of 0.0285° 2θ and effective dwell time of 0.6 sec. Data collection started immediately after the application of CO₂ gas pressure. Scans were taken every 11 min for a period of 6 h. The phase composition was determined using quantitative Rietveld analysis (Hill and Howard, 1987) with version 4 of Bruker's *TOPAS* software (Bruker-AXS GmbH, 2008). A literature structure for triclinic wollastonite (Ohashi, 1984) was used in the quantitative analysis.

TGA data were obtained using a TA Instrument Q600 analyzer. Approximately 9 mg of sample were heated between room temperature and 950 °C at a heating rate of 10 °C min⁻¹. Scanning electron micrographs were obtained using a Hitachi S4800 FEG-SEM from powdered samples dispersed onto carbon tape.

3. Results and Discussion

Figure 1 shows the *in-situ* diffraction data collected during experiment 2 at 60 °C and 34.5 bar. The quality of these data is typical of all of the experiments. The wollastonite peak intensities diminish whilst the calcite peak intensities increase, which is consistent with the expected carbonation reaction. The increasing background and instability in the intensities during the first few datasets are due to fluctuating pressure and temperature on initial pressurization.

The collected data (Fig. 2) were suitable for quantitative analysis using the Rietveld method as the relative intensities of the wollastonite proved to be as expected and not distorted by the apparatus. The fits were respectable given the data quality, although the high background yields a misleadingly low R_{wp} value of 4.1% for the fit in Figure 2. In this case the background-subtracted R_{wp} , known as R_{wp}' , yields a more realistic measure of the fit quality, although in common with R_{wp} it is adversely affected by a noisy background.

Upon completion of experiment 1, the carbonated material was removed and analysed for calcite in a thermal gravimetric analyser (TGA), the result of which is shown in Figure 3. The results from experiments 1 to 4 are plotted in Figure 4, where the temperature was held at 60 °C and different gas pressures applied. The results are plotted in terms of the wt% CO₂ adsorbed by the reaction. These values are calculated using the reaction in equation 1. The wt% CO₂ derived for the sample subjected to TGA was calculated to be 16.2 wt%, which agrees well with the value of 15.7 wt% evolved CO₂ measured in Figure 3. This shows that the quantitative X-ray results can be consistent with thermal analysis results.

Figure 4 shows that the carbonation of wollastonite at 60 °C appears to be pressure independent, even with supercritical CO₂. The pressure independence of the reaction suggests that the rate limiting factor is not the availability of CO₂, but is rather linked to the solubility limits of CO₂ in water and to the leaching of Ca from the wollastonite as suggested by Huijgen et al. (2006).

The results from experiments 5 to 8 are plotted in Figure 5. The pressure was constant at 34.5 bar and the temperatures varied from 43 to 73 °C. The equivalent wt% of CO₂ was again calculated from the calcite content over a period of 6 h. Predictably, the results indicate a marked dependence on temperature, but appear to approach a plateau at just under 20 wt%, although only the 73 °C dataset reached a distinct plateau within 6 h.

The plateau around 17 wt% CO₂ for the 73 °C sample may be due to simple drying of the sample through evaporation or an amorphous silica surface layer on the wollastonite particles acting as a diffusion barrier. The loss of free water from the sample is obvious from the solid consistency of the sample on removal of the sample holder from the stage. An alternative option would involve the remaining amorphous silica after leaching acting as a diffusion barrier to prevent further leaching of Ca. The presence of the amorphous silica on the surface of the wollastonite grains could be confirmed by high

resolution electron microscopy, but it could not determine whether it forms an effective barrier against leaching. This question could be answered by supplying excess water and preventing sample drying by studying a flooded sample or possibly using a saturated steam environment.

Data collected from a reaction at different temperatures (Fig. 5) is particularly useful, as it allows an effective activation energy to be determined using the Arrhenius equation (Fig. 6). Pseudo-first order behaviour may be expected initially, assuming the water remains saturated with dissolved CO_2 (HCO_3^- (aq)). Only the first 3 datapoints for 73 °C yielded a straight line for the plot of $\ln[\text{wollastonite}]$ versus time, whereas 6 points could be used for the lower temperature data. Variable temperature studies at 34.5 bar yielded an activation energy of 53 kJ mol^{-1} for the carbonation of wollastonite. Comparison with literature values found to date: 72 kJ mol^{-1} , and 162.3 kJ mol^{-1} (38.8 kcal mol^{-1}) at 31 °C and 267.8 kJ mol^{-1} (64.0 kcal mol^{-1}) at 83 °C seems to indicate a change in the rate limiting step with temperature (Brady, 1991; Klemm and Berger, 1972). Pseudo-activation energies (no actual reaction rates were measured) of 22, 20, and 16 kJ mol^{-1} for <38, <106 and <500 μm batches respectively are also quoted in the literature (Huijgen et al., 2006).

Bailey measured the dissociation of wollastonite in terms of soluble Ca and silica and/or the diffusion through a surface layer of constant thickness, resulting in an estimated activation energy of 54.4 kJ mol^{-1} (13 kcal mol^{-1}) (Bailey, 1976). This agrees remarkably well with the present value of 53 kJ mol^{-1} , and is suggestive of a common mechanism of Ca leaching and dissolution to that studied by Bailey (1976).

The crystalline nature of the calcite formed is confirmed by the appearance of distinct rhombohedral crystallites as seen in Figure 7(a). The calcite can easily be distinguished from the needle-like wollastonite in the reacted material and unreacted material as shown in Figure 7(b). There was no discernable change in the refined wollastonite unit cell volume or crystallite size during the carbonation reaction.

This paper demonstrates the potential of using a laboratory based diffractometer for studying high pressure gas-mediated reactions *in-situ* at elevated temperatures and pressures. However, the conditions required for most experiments relevant to CO_2 sequestration reactions are too severe for the current design. For example, the conditions used by Kaszuba et al (2003) were 200 bar, 200 °C, 5 M Cl, 2 M Na, 1.4 M Mg, 0.8 M K, and smaller concentrations of Ca, Br, SO_4 , SiO_2 , Al, Fe, Mn and B. A new stage design capable of higher pressures and temperatures, acidic and corrosive, sour environments (geothermal brine solution), together with flammable gases would be required. Such a stage would be able to replicate the conditions for both industrial mineral CO_2 sequestration, and for down-well conditions to study gas-liquid-rock interactions inherent to CO_2 injection.

4. Conclusions

The carbonation of wollastonite under pressurized CO₂ has been studied between 43 and 73 °C using an *in-situ* pressure stage mounted on a laboratory diffractometer system. Quantitative Rietveld analysis was used to determine the calcite content in carbonating wollastonite samples with time under different temperature/pressure conditions. The calcite compositions were used to calculate the wt% of absorbed CO₂ in the samples. At 60 °C the carbonation reaction was shown to be pressure-independent. An activation energy of 53 kJ mol⁻¹ was derived from data collected at 34.5 bar between 43 and 73 °C.

It has been shown that carbonation reactions of interest to the C capture community can be monitored experimentally with the use of a laboratory based *in-situ* high-pressure X-ray diffraction stage. Such setups may be better suited than synchrotron-based setups to study the slower reactions often encountered in CO₂ sequestration. Further studies will require the construction of a stage capable of containing the correspondingly harsh chemical conditions.

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Figure captions

Figure 1. *In-situ* X-ray diffraction data of damp wollastonite during carbonation at 60 °C under 34.5 bar CO₂. The CaCO₃ reflections are marked with *, all other reflections belong to wollastonite.

Figure 2. Final difference plot from quantitative Rietveld analysis of XRD data from carbonating wollastonite at 34.5 bar and 73 °C after 6 h. In the plot the dots correspond to the experimental data, the overlaid solid line to the calculated pattern, the vertical tickmarks to the peak positions of the two phases and the lower continuous line to the difference curve. The background-subtracted R_{wp} is given in addition to the conventional R_{wp} residual.

Figure 3. Plot of the TGA results from wollastonite exposed to 13.8 bar (200 psi) CO₂ at 60 °C for 6.5 h. The solid line corresponds to the weight and the dashed line the derivative curve.

Figure 4. Plot of CO₂ content (wt% CO₂) versus reaction time determined by Rietveld analysis of the X-ray data for data at different pressures at 60 °C. The theoretical CO₂ content for 100% converted CaSiO₃ would be about 27 wt%.

Figure 5. Plot of CO₂ content (wt% CO₂) versus reaction time during the carbonation of wollastonite at 34.5 bar (500 psi) for several indicated temperatures.

Figure 6. Arrhenius plot for the carbonation of wollastonite at 34.5 bar (500 psi) pressure CO₂.

Figure 7. SEM of wollastonite (a) after exposure to 13.8 bar (200 psi) CO₂ at 60 °C for 6.5 h and (b) before reaction.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7(a).

Figure 7(b).

Table 1. Temperature/pressure conditions for each experiment.

Experiment number	Pressure	Temperature
1	13.8 bar (200 psi)	60 °C
2	34.5 bar (500 psi)	60 °C
3	56.5 bar (820 psi)	60 °C
4	79.2 bar (1150 psi)	60 °C
5	34.5 bar	43 °C
6	34.5 bar	52 °C
7 (= 2)	34.5 bar	60 °C
8	34.5 bar	73 °C