In Situ Mechanistic Observations of Serpentine Mineral Carbonation Reaction Processes: Facilitating the Engineering of Lower Cost Carbon Dioxide Sequestration Options

M. McKelvy,[1] J. Diefenbacher,[1] G. Wolf,[1] A. Chizmeshya,[1] H. Béarat,[1] D. Gormley,[1] B. Doss,[1] V. Prakapenka,[2] G. Shen[2]

[1]Arizona State University, Tempe, AZ, U.S.A.
[2]Advanced Photon Source (APS), Argonne National Laboratory, Argonne, IL, U.S.A.

Introduction

Above ground mineral carbonation is an emerging CO_2 sequestration candidate technology with large-scale sequestration potential. The process inherently produces environmentally benign and geologically stable materials and offers the added advantages of wide, low-cost feedstock availability and rapid mineral carbonation potential. The associated mineral carbonation processes are exothermic, so energy is not inherently required for carbonation to occur. The primary goal is cost-competitive process development.

Mineral carbonation is also an important factor associated with below-ground sequestration, as it can be utilized to enhance reservoir seal integrity and the carbonates that form can provide the long-term stability essential for effective sequestration. Investigating and evaluating candidate technologies that incorporate mineral sequestration, both above and below ground, is the primary focus of the CO_2 Mineral Sequestration Working Group, which is managed by DOE (Fossil Energy), and consists of members from the Albany Research Center, Arizona State University, Los Alamos National Laboratory, National Energy Technology Laboratory, and Science Applications International Corporation.

Serpentine [$Mg_3Si_2O_5(OH)_4$] carbonation is a particularly attractive sequestration technology candidate, due to the wide, large scale, low-cost availability of serpentine [1,2]. Recently, researchers at the Albany Research Center (ARC) have accelerated serpentine carbonation, which naturally occurs in geological time, to an industrial time scale via serpentine heat-activation [3]. However, the energy costs associated with the current serpentine heat-activation process are too high for process implementation [4]. Viable process development will require novel approaches to enhance carbonation reactivity. Although serpentine heat activation is presently too costly for process implementation, the associated materials characteristics and mechanisms that enhance carbonation are of keen interest for further reducing process cost. The goal is to develop the atomic-level understanding needed to engineer new materials and processes that can lower process cost.

The ARC mineral carbonation process uses water/CO_2 fluid reaction media under relatively modest conditions (e.g., 155 ^oC and 150 atm). Herein, we describe the progress made during 2003 in our ongoing investigations into the mechanisms and materials characteristics that control heat-activated serpentine mineral carbonation reactivity at the Advanced Photon Source. During 2003, we extended our initial investigations using lizardite feedstocks to probe the effects of serpentine mineral type, via studies of lizardite, antigorite and chrysotile heat-activation and the activated materials that form. We enhanced the capabilities of the novel microreaction system we developed last year to further our *in situ* observations of the mineral carbonation reaction process [5,6]. Initial system development and the first *in situ* observations of the mineral carbonation process are described in last year's report [7].

Methods and Materials

The microreaction system is suitable for a variety of X-ray synchrotron, visual and spectroscopic investigations and offers the ability to investigate both fluid-fluid and fluid-solid processes with full pressure and temperature control. During 2003 we extended the temperature and pressure range of the system from ambient to 300 atm and 400 ^oC [5,6]. The moissanite windows are transparent to X-ray radiation at energies above 25 keV [8], facilitating the X-ray synchrotron investigations described herein. In the present investigations, the reaction chamber is connected to an external high-pressure CO_2 supply system, which provides control and monitoring of the pressure during mineral carbonation. Temperature control utilizes an external thermocouple well in close proximity to the sample. Importantly, combining external pressure and temperature control can also provide reactant activity control throughout the reaction process. The relatively large volume of the reaction chamber (~0.1 cm^3) enables microscopic observation of both the fluid-fluid and fluid-solid reaction regions of interest [5,6,9].

Three serpentine samples, lizardite and chrysotile collected in Globe, Arizona, and antigorite donated by the Royal Ontario Museum, Canada, were used for the feedstock materials. A series of heat-activated materials were generated for each feedstock material with activation temperatures ranging from 550 to 1,100 ^oC. Samples were generally prepared by heating at 2 ^oC/min under helium during combined thermogravimetric and differential thermal analysis, followed by quenching from a select set of activation temperatures. Select heat-activated samples for *in situ* mineral carbonation studies were loaded into the moissanite sample holder in the microreactor cell, which was then sealed. Residual air was removed by evacuating to 10^{-3} torr. The cell was then injected with just enough solution (0.64 M $NaHCO_3$ + 1.0 M NaCl) to immerse the sample (~60% full) and reproduce the Albany Research Center's reaction process conditions as closely as possible [3]. The cell was then pressurized to 150 atm CO_2, inducing strong mixing of the aqueous and CO_2-rich fluid phases. After allowing time for equilibration, the microreactor was slowly heated. The ensuing reaction processes were monitored via *in situ* synchrotron X-ray diffraction using the GSECARS 13-BM beamline.

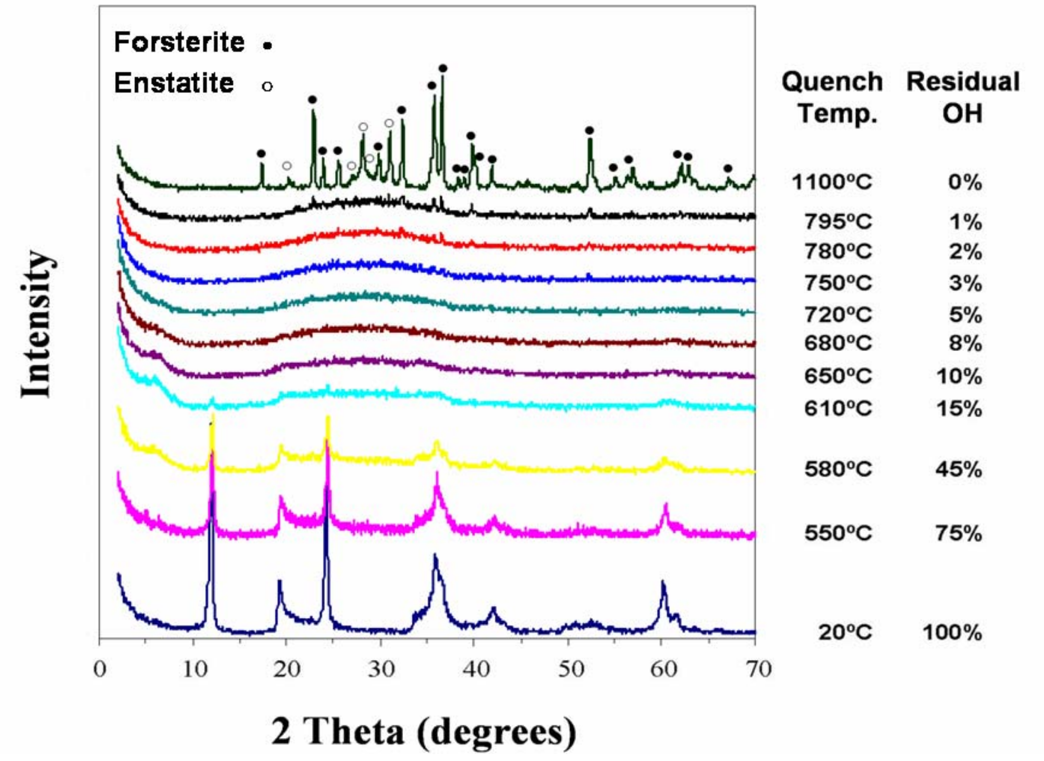

Fig. 1: X-ray powder diffraction patterns for the heat-activated lizardite samples [10]. Samples were heated at 2 ^{o}C/min. to the temperature shown (under He) and rapidly cooled. The residual hydroxyl concentrations shown are derived via thermogravimetric analysis.

Results and Discussion

Fig.1 shows X-ray powder diffraction patterns for the various materials that formed during lizardite heat-activation. They range, with increasing temperature, from crystalline lizardite-related materials that exhibit only minor dehydroxylation, to poorly ordered meta-serpentine materials, to materials that are almost completely dehydroxylated in which forsterite/enstatite nucleate and grow consuming the disordered meta-serpentine. The process and the materials observed to form during lizardite heat-activation were found to be reasonably representative of the processes and materials observed during antigorite and chrysotile activation [9-11]. Two poorly ordered meta-serpentine components are observed to form: an α component related to the broad feature observed at ~6^{o} 2Θ and an amorphous component related to the diffuse X-ray scatter observed from 18-38^{o} [10]. The α component, which can be associated with diffuse interlamellar order between alternate layers and intralamellar disorder, initially forms and grows along with the amorphous component, but yields to increasing levels of amorphous meta-serpentine at higher activation temperatures. Above ~780 ^{o}C, the amorphous component yields to the crystallization of forsterite and enstatite.

Utilizing the 13-BM beamline, we successfully observed the aqueous mineral carbonation reaction process *in situ* for select heat activated materials generated from lizardite, antigorite and chrysotile. The materials investigated were chosen to contain various levels of the host serpentine, the α and amorphous meta-serpentine components and the forsterite/enstatite generated during higher temperature activation, as well as varying residual hydroxide levels. Two fluids are present under the reaction conditions of interest: CO_2 rich and aqueous rich. The heat-activated reactant is immersed in the aqueous-rich phase, while fluid-fluid contact is maintained with the CO_2-rich phase to facilitate CO_2 transport and mimic mineral carbonation process conditions [5,6, 9-11].

The relative reactivity of the heat-activated materials observed was evaluated based on the carbonation onset temperature and reaction progression observed under 150 atm CO_2. The carbonation reactivity was generally observed to exhibit a strong correlation with the extent of meta-serpentine formation and structural disorder present for each series of heat-activated materials generated from the serpentine minerals lizardite, antigorite, and chrysotile.

Fig. 2 shows an example of the *in situ* observation of the aqueous mineral carbonation reaction process for the meta-serpentine-rich heat-activated material that formed during chrysotile heat-activation at 600 ^{o}C. The reaction temperature was gradually raised under 150 atm CO_2 until the onset of carbonation was observed at 110 ^{o}C via magnesite ($MgCO_3$) formation. Further heating led to reaction completion by 120 ^{o}C. Magnesite was generally observed to form directly, without intermediate crystalline phase formation, at mineral carbonation onset temperatures at or above 100 ^{o}C [11]. No other crystalline peaks are observed, indicating that the silica-containing species formed are generally amorphous in nature.

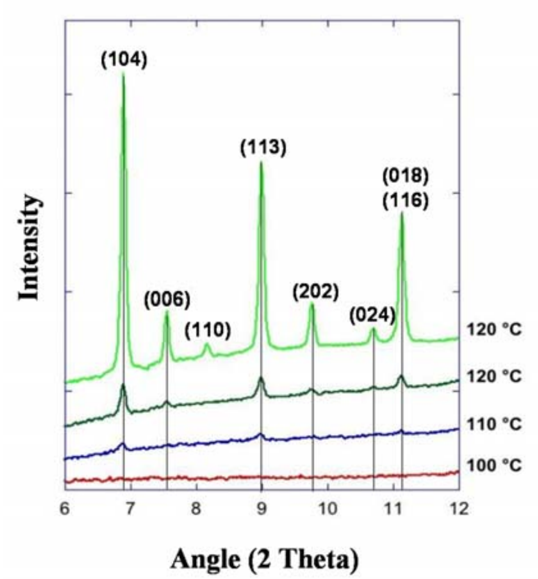

Fig. 2. X-ray diffraction patterns observed during in situ carbonation of the standard 600 ^{o}C heat-activated chrysotile as a function of reaction temperature. The reaction utilized the standard reaction solution and was pressurized to 150 atm CO_2 prior to heating. The onset of carbonation is apparent via the formation of magnesite at 110 ^{o}C, with the reaction reaching completion at 120 ^{o}C. The indices for the magnesite reflections observed are shown above the associated X-ray peaks. The X-ray wavelength is 0.3311Å.

The most reactive meta-serpentine materials discovered are being extensively investigated using a battery of high-resolution analytical techniques together with advanced computational modeling to better identify the materials characteristics that are most effective in enhancing carbonation reactivity.

Initial investigations of the relative reactivity of key fluid reactant species were also performed. The meta-serpentine rich material generated via 600 ^{o}C chrysotile heat-activation was utilized as a standard reference material, with reaction onset and completion observed at 110 ± 5 °C and 120 ± 5°C, respectively (Fig. 2) using the standard aqueous solution under 150 atm CO_2. Although these studies are preliminary at this point and need to be checked for reproducibility, some intriguing observations have emerged: (1) anhydrous CO_2 does not appear to react and (2) the standard bicarbonate solution (0.64M $NaHCO_3$ + 1.0M NaCl) only reacts weakly and at higher temperatures under similar helium pressures. Although these observations are preliminary, they suggest that the aqueous solution plays a critical role in enhancing mineral carbonation reactivity and the aqueous species CO_2(aq) associated with supercritical CO_2 may be critical to mineral carbonation reactivity.

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