

# DEVELOPMENT OF A CO<sub>2</sub> SEQUESTRATION MODULE BY INTEGRATING MINERAL ACTIVATION AND AQUEOUS CARBONATION

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## OBJECTIVES

Carbon dioxide is a greenhouse gas that contributes to global climate warming. Mean annual concentrations of gaseous CO<sub>2</sub> have increased by 19.4% from 315.98 parts per million by volume (ppmv) of dry air in 1959 to 377.38 ppmv in 2004<sup>1</sup>. To limit the risk of a climate change to acceptable levels, the emission of CO<sub>2</sub> and other greenhouse gases should be reduced. Mineral carbonation can provide benign and long-term storage capabilities. The formation of stable mineral carbonates can occur by the reaction of carbon dioxide with metals such as calcium and magnesium. Research has focused on calcium and magnesium silicates due to favorable thermodynamics for carbonation and their relative abundance and availability (Goff and Lackner, 1998). The natural weathering process is unfortunately limited in extent by slow reaction kinetics; in an effort to expedite the reaction, the use of sulfuric acid as an accelerating medium has been investigated. According to current CO<sub>2</sub> emission levels, the serpentine requirements for a mineral carbonation plant are not trivial. Therefore a better understanding of the dissolution of serpentine is warranted. In addition to dissolution studies, the reaction of the magnesium-rich leachate with carbon dioxide provides its own challenges.

The overall objective of the proposed research program is to optimize the active carbonation process in order to design an integrated CO<sub>2</sub> sequestration module for Vision 21 plants. This research program can be divided into the following four tasks, as described in the research proposal. Task 1 ‘Mineral activation’ will conduct a parametric study to optimize the operation conditions for the mineral activation, where serpentine and sulfuric acid are reacted. The optimization of these processing parameters will yield a maximum dissolution of magnesium cations and also produce a high surface SiO<sub>2</sub> solid. Under Task 2 ‘‘Aqueous carbonation’’ the extracted Mg<sup>2+</sup> will then be reacted with CO<sub>2</sub> at various temperatures and pressures in a CSTR to optimize the variables (temperature, pressure, pH, and stirring speed) that predominantly affect the carbonation reactions. Task 3 ‘‘Integration of the activation and carbonation units into a CO<sub>2</sub> sequestration module’’ will involve the integration of the two CSTR reactors and their optimum operating conditions into a module. Finally, Task 4 ‘‘Economic assessment’’ will be conducted to evaluate the economic viability of the proposed CO<sub>2</sub> sequestration module<sup>2</sup>.

## ACCOMPLISHMENTS TO DATE

The mineral dissolution study samples consisted of serpentine from the Cedar Hills quarry in SE Pennsylvania. The sample was provided by the Department of Energy - Albany Research Center (ARC) and consisted of an 80% passing 400 mesh (-37 μm) ground sample that underwent magnetic separation from a separation pilot-plant study (O’Connor, 2003). Analyses of chemical composition, solutions and solids, were carried out on a Leeman Labs PS3000UV Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES). Carbonation experiments were carried out in a 300 ml Parr – 4651 stirred high pressure/high temperature reactor. X-ray diffraction analyses were conducted with a Philips Analytical 1050 XRD with a Hilton Brooks x-ray generator and scanning electron microscopy images were obtained on an FEI Quanta 600.

The treatment of serpentine with sulfuric acid has shown to be effective in the leaching of magnesium for its subsequent carbonation. The baseline experiment was performed at 6 hours and room temperature with a particle size of <37 μm and a 2 M sulfuric acid concentration. This experiment yielded 7125 ppm of Mg<sup>2+</sup>. Although the effects of time are too slight to appear within shorter time periods, a 24 hour reaction was

shown to provide a 46 % improvement in the extraction of  $Mg^{2+}$ . The effects of increased reaction temperature from 25°C to 50°C provided a 70% improvement on dissolution. Additionally, multi-stage leaching provided little gain in  $Mg^{2+}$  extraction whether it was a 2 stage acid leaching or 2 stages of acid leaching with 1 stage of base leaching in between. Although research efforts into the dissolution of serpentine will continue to optimize the reaction variables for the dissolution stage, the ability to carbonate these magnesium ions is central to mineral carbonation.

In contrast to the dissolution process where extreme conditions are favored, the carbonation reaction requires a more careful balance of reaction variables. Magnesite, although stable under ambient conditions, is vulnerable to dissolution in an acidic environment. Initial investigations revealed that a partial pressure of 650 psi resulted in too acidic of conditions for the formation of magnesium carbonates, regardless of the addition of a base. Further experimentation showed that the bicarbonate ion concentration remains two orders of magnitude too low without the addition of a buffer such as sodium bicarbonate, even at lower partial pressures. In addition, experimentation was also able to show that it is sodium bicarbonate responsible for the formation of carbonates.

## **FUTURE WORK**

The magnesium ion presents a unique challenge with respect to reaction products and reaction kinetics. Magnesite, although the thermodynamically favored magnesium carbonate, does not predominate under wide-ranging carbonation conditions due to kinetically favored metastable products such as nesquehonite, hydromagnesite, and lansfordite. Accordingly, future research will assess the minimum carbonation conditions required for the formation of the magnesium carbonates.

## **PAPERS PUBLISHED**

M.M. Maroto-Valer, D.J. Fauth, M.E. Kuchta, Y. Zhang, and M. Andresen (Submitted). Activation of Magnesium Rich Minerals as Carbonation Feedstock Materials for CO<sub>2</sub> Sequestration. (Phase I)

## **PATENT APPLICATIONS**

M.M. Maroto-Valer, D.J. Fauth, M.E. Kuchta, Y. Zhang, and M. Andresen (Submitted). Activation of Magnesium Rich Minerals as Carbonation Feedstock Materials for CO<sub>2</sub> Sequestration. (Phase I)

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2. Alexander, G., Maroto-Valer, M., Gafarova-Aksoy, P., Schobert, H.H., 2005. Development of a CO<sub>2</sub> Sequestration Module by Integrating Mineral Activation and Aqueous Carbonation. University Coal Research/Historically Black Colleges and Universities & Other Minority Institutions Contractors Review Meeting