

DEVELOPMENT OF A CO₂ SEQUESTRATION MODULE BY INTEGRATING MINERAL ACTIVATION AND AQUEOUS CARBONATION

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OBJECTIVES

The overall objective of the proposed research program is to optimize the active carbonation process in order to design an integrated CO₂ sequestration module for Vision 21 plants. It is known that chemical surface activation helps to dissolve the magnesium from the serpentine minerals, and furthermore, the carbonation reaction can be conducted under ambient operating temperature and mild pressure conditions¹. The module consists basically of two integrated units for the activation and carbonation processes. In the activation unit, serpentine is mixed with sulfuric acid to activate the mineral. During the activation process, the magnesium is extracted from the serpentine mineral and forms a Mg²⁺ solution that will be sent to the carbonation reactor. As a consequence of the extraction process, a high-surface SiO₂ rich solid will be formed and precipitated. In the carbonation reactor, the CO₂ that has been separated from the flue gas of a power plant will be reacted with the Mg²⁺ solution to precipitate MgCO₃. During this process, the sulfuric acid will be regenerated and recycled to the activation reactor.

The proposed research program will firstly 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 SiO₂ solid. The extracted Mg²⁺ will then be reacted with CO₂ at various temperatures and pressures in a CSTR to optimize the variables (temperature, pressure, pH, and stirring speed) that predominantly affect the carbonation reactions. Computer experimental design tools will be used to identify the variables that predominantly affect the magnesium dissolution as well as the aqueous carbonation reactions. The activation and carbonation units will then be integrated into a CO₂ sequestration module. This will involve the integration of the two CSTR reactors (activation and carbonation) and their optimum operating conditions into a module. Finally, an economic assessment will be conducted to evaluate the economic viability of the proposed CO₂ sequestration module.

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 SiO₂ solid. Under Task 2 "Aqueous carbonation" the extracted Mg²⁺ will then be reacted with CO₂ 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 CO₂ 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 CO₂ sequestration module.

ACCOMPLISHMENTS TO DATE

Task 1 has been carried out through a chemical treatment with the reaction between serpentine and sulfuric acid. Two separate serpentine samples, -37 μ m and -4mm, were provided by the Department of Energy - Albany Research Center, from the Cedar Hills quarry in Pennsylvania. Experimentation has been divided into two sets with one set of experiments being conducted with the -37 μ m sample to determine the isolated effects of acid concentration, reaction time, reaction temperature and multi-stage leaching on magnesium removal. Additionally, a second set of tests have been carried out via a Taguchi statistical design of experiments, using the -4mm parent sample to assess the interactions between the experimental variables and to provide a maximum dissolution of magnesium. The -4mm sample was dry ground in a ball mill and sieved to the following size fractions, 300-150 μ m, 150-75 μ m, and 75-37 μ m and -37 μ m. An orthogonal array of three factors (i) sulfuric acid concentration; (ii) particle size; and (iii) reaction time were crossed with three predetermined levels to provide a balanced design with additional experiments on temperature variations carried out on several additional samples.

The magnitude of contribution and influence of the reaction variables within the dissolution stage were assessed through the reaction yields and the following analytical techniques, TGA, BET, and ICP-AES. The combined effects of acid concentration, reaction time, and particle size were studied using the Minitab® statistical software. This study has shown that sulfuric acid facilitated the dissolution of magnesium, made possible the removal of hydroxyl groups without an energy intensive heat treatment stage, and increased the surface area of the residual, silica rich solid. A baseline experiment, based on previous results, consisted of 2M sulfuric acid, a reaction time of 6 hours, 25°C, and -37µm serpentine particles. Increasing acid concentrations from the stoichiometric requirement to a molar excess, incrementally increased magnesium extraction. The effect of increasing the reaction time from 6 hours to 24 hours increased magnesium removal >40%. A 70% increase in magnesium removal resulted from a temperature increase from 25°C to 50°C. Several experiments were also conducted to evaluate the effectiveness of multi-stage leaching which yielded a 25% increase. The statistically designed experiments, with crossed factors and levels, showed significant interaction and contribution from the experimental factors, in decreasing order, acid concentration, particle size, and reaction time. The extraction of magnesium for its subsequent carbonation has been determined to be highly sensitive to these operating conditions and continues to be an area of focus.

Magnesium rich solutions from task 1 are being used as the feedstock for task 2, as the carbonation reactor has been completed and experimentation is currently underway. The primary or global variable for the carbonation reaction involves the careful determination and monitoring of the acidity of solution. It has been shown that an acidic solution is favorable for the removal of magnesium from serpentine, however in order to produce magnesite from the reaction between carbon dioxide and magnesium ions, a basic solution is required. Therefore our investigations within task 2 consist of the addition of sodium hydroxide or barium hydroxide. In addition to the alkaline addition, the effects of a buffer solution, stirring speed, reaction temperature, time, and pressure will be investigated. Carbonation efficiency will be assessed by increase in weight of the solid products and the percent stoichiometric conversion. A TGA and a LECO HCN will be utilized to determine the carbon dioxide content of the solid product and XRD will be used to ascertain the solid precipitates.

FUTURE WORK

Experimentation and analysis of the carbonation efficiency will continue with the evaluation of individual reaction variables. As the extent of influence of each carbonation variable is realized, a statistical experimental design will be implemented to better understand the interactions between the controlling variables. The sensitivity of carbonation research provides a range of external control in maximizing the carbonation efficiency. However the same sensitivity underscores complex chemical interactions. Therefore, further investigations will be conducted to better understand the kinetics and mechanisms associated with the leaching and carbonation of serpentine.

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 CO₂ 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 CO₂ Sequestration. (Phase I)

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REFERENCES

1. Kuchta, M. (2003). Mineral Carbonation: Activation of Serpentine Minerals for Enhanced CO₂ Sequestration. Energy and Geo-Environmental Engineering. University Park, Pennsylvania State University: 140.