

# CARBONATION OF WOLLASTONITE USING SUPERCRITICAL CARBON DIOXIDE

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The feasibility of a CO<sub>2</sub> disposal method based on combining CO<sub>2</sub> chemically with silicate rocks was tested in this experiment. The process utilized a stirred batch reactor in which supercritical CO<sub>2</sub> was absorbed into a wollastonite (CaSiO<sub>3</sub>) slurry to cause the dissolution of mineral and then the precipitation of calcium carbonate. The amount of CO<sub>2</sub> fixed in the solid phase was determined by a thermogravimetric analysis. The effect of operating variables, including reaction temperature, mineral particle size, and CO<sub>2</sub> pressure on the conversion of wollastonite were investigated. A high conversion of 82% for the wollastonite of 40.5 μm mean size was achieved when the sample reacted at 80°C and 8.6 MPa for 6 h.

## INTRODUCTION

The fossil fuels, such as coal, oil and natural gas, are widely used in this century, so that a large amount of carbon dioxide is produced. It is believed that the massive CO<sub>2</sub> released into the atmosphere has a serious consequence on the aggravation of greenhouse effect. In order to solve this problem, a great effort has been devoted to the research area related to the reduction of carbon dioxide.

There are several feasible methods under developing, including physical storage, biological fixation and chemical fixation. Among them the chemical fixation seems potentially more effective than others at the present stage [1]. Actually, the weathering of alkaline rocks is thought to have played an important role in the reduction of atmospheric CO<sub>2</sub> on this planet. The CO<sub>2</sub> fixation by rock weathering has been investigated at atmospheric pressure; however, the conversion was very low [2,3]. O'Connor et al. [4] have been developing a carbonation process to convert the magnesium in olivine (Mg<sub>2</sub>SiO<sub>4</sub>) or serpentine [Mg<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>] into MgCO<sub>3</sub> using supercritical carbon dioxide as a reactant. The effects of operating variables, such as CO<sub>2</sub> pressure and reaction time, on the conversion of the silicate have been investigated, and a conversion of 78% was achieved in 30 minutes at 155 °C and 185 atm.

In a preliminary test of this experiment, different rocks were studied and then wollastonite with the highest conversion was selected for further study. The wollastonite rock, which is abundant on the earth, was suspended in water to react with CO<sub>2</sub> under supercritical conditions. The over-all reaction is given by the following equation,



The effects of several variables, including reaction temperature, mineral particle size, and CO<sub>2</sub> pressure, on the conversion of wollastonite were investigated. The conversion of wollastonite

was determined by a TGA analysis.

## EXPERIMENTAL SECTION

The wollastonite, a natural rock imported from mainland China, was obtained from the Feng-Deng ceramic company in Taiwan. The rock was pulverized and sieved into three different sizes, i.e., sample a (88-105  $\mu\text{m}$ ), sample b (53-63  $\mu\text{m}$ ), and sample c (37-44  $\mu\text{m}$ ), although the aspect ratio is higher than 5. These materials were used directly without any treatment. A schematic diagram of the apparatus used in this study is shown in Fig. 1. The reactor is a 275-mL stirred vessel with viewing windows. The temperature control of the reactor is achieved by circulating hot oil through a jacket around the reactor. A 220-mL glassware is placed in the reactor to contain reacting slurry. The working pressure of the reactor can go up to 21 MPa (3000 psig).

At the beginning of an experiment, a glassware containing 20-mL of 10wt% wollastonite slurry was placed in the reactor after the reactor temperature reached a setting level. Liquidified  $\text{CO}_2$ , which came from a gas cylinder, was pumped into the reactor to reach a desired pressure. Then we started to count the reaction time. After the slurry reacted for a certain period of time, the temperature was lowered to room temperature and the pressure was slowly released to atmospheric pressure. Then the reacted slurry was filtered and dried overnight at 105  $^\circ\text{C}$ . Finally, the dried solid was subject to the TGA analysis for weight loss at  $\text{CaCO}_3$  decomposition temperature, and the XRD analysis for crystal phase.

The conversion of wollastonite to  $\text{CaCO}_3$  was determined from the weight loss in a TGA analysis. A typical TGA plot of reacted wollastonite sample is shown in Fig. 2, in which  $\Delta W$  stands for the weight loss of sample in the temperature range between 600 and 900  $^\circ\text{C}$  caused by the decomposition of  $\text{CaCO}_3$ , and  $W_R$  stands for the weight retained at 900  $^\circ\text{C}$ . The conversion is calculated by the following equation,

$$X(\%) = \frac{\Delta W / 44 \times 40}{W_R / M \times 40} \times 100 = \frac{\Delta W \times M}{W_R \times 44} \times 100 \quad (2)$$

where 40 and 44 are the atomic weight of calcium and molecular weight of carbon dioxide respectively,  $X$  for the conversion and  $M$  for the weight of wollastonite which contains one g-mole calcium, i.e., 40 g calcium. The values of  $M$  are 128.16, 136.03 and 134.58 g/g-mol calcium determined by EDTA titration [5]. If the rock is of pure wollastonite,  $M$  is equal to 116.16 g/g-mol calcium.

## RESULTS AND DISCUSSION

### Preliminary test of rocks

In the preliminary test three different rocks were studied, including wollastonite [ $\text{CaSiO}_3$ ], albite [ $\text{NaAlSi}_3\text{O}_8$ ] and talc [ $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ ]. Both unreacted samples and samples reacted at 65  $^\circ\text{C}$  of albite and talc were subject to TGA analysis and the weight loss of the samples are negligible as shown in Fig. 3 for albite. It is clearly seen that carbonation did not take place, because there is almost no weight loss up to 900  $^\circ\text{C}$ . On the other hand, the weight loss of reacted wollastonite at 50  $^\circ\text{C}$  and 80  $^\circ\text{C}$  are significant, about 10% and 17% respectively as shown in Fig. 4. Therefore, reaction kinetics of wollastonite was further studied.

### **Effect of size on conversion**

Three different sizes of wollastonite were investigated in this study, i.e., 88-105  $\mu\text{m}$  (sample *a*), 53-63  $\mu\text{m}$  (sample *b*), and 37-44  $\mu\text{m}$  (sample *c*). The conversions of these samples at two reaction temperatures, 323K and 353K are shown in Fig. 5. The conversion of wollastonite increases with a decrease in particle size from sample *a* to sample *b*; however, there is no difference in conversion between the two smaller sizes. The first step of rock carbonation is believed to be the dissolution of rock into bulk solution and the sample of smaller size, which has higher surface area, should give a higher conversion. The results of sample *a* and sample *b* are consistent with the proposed mechanism; however, the results of the two smaller sizes are not. The particle size of the samples were then check with a laser light analyzer (Coulter 230). The mean sizes of the three samples were 147.6, 40.5, and 34.1  $\mu\text{m}$ . It is clear that the size of the two smaller samples are quite close, and thus give little difference in conversion.

### **Effect of temperature on conversion**

Figure 6 shows the effect of temperature on the conversion of wollastonite carbonation at  $P = 8.6 \text{ MPa}$  and  $t=6 \text{ h}$  for sample *a*. The conversion increases with increasing temperature in the temperature range between 323K (65 °C) and 413K (140 °C), changing from 30% to 75%. The result is as expected because the dissolution rate of silicate rock increases with temperature [6] and the reaction rate usually increases with temperature either.

### **Effect of pressure on conversion**

The pressure range investigated in this study was between 8.6 MPa and 13.9 MPa, while critical pressure of  $\text{CO}_2$  is 7.48 MPa. The reaction temperature and time were set at 413K and 6 h respectively. The pressure effect on the conversion of wollastonite carbonation is shown in Fig. 7, in which all the conversions are around 75%. Vorholz et al. [7] studied the equilibrium of  $\text{CO}_2\text{-H}_2\text{O}$  binary system and part of their results is shown in Table 1, which shows that the mole fraction of  $\text{CO}_2$  in water at 393.15K is rather independent of pressure in the range between 8 MPa and 15 MPa. It is reasonable to assume that the amount of  $\text{CO}_2$  dissolved in water at 413K is independent of pressure either and thus the pressure has no effect on the conversion.

## **CONCLUSION**

A carbon dioxide disposal method was proven feasible by using supercritical carbon dioxide to react with a wollastonite slurry. Several operating variables were investigated, among which particle size of rock and solution temperature are the most important variables that influence the conversion of wollastonite. The conversion increases with a decrease in particle size and an increase in temperature. Under the conditions of 80 °C and 8.6 MPa, the 40.5  $\mu\text{m}$  wollastonite reacted for 6 h has a conversion of 82%.

## **ACKNOWLEDGEMENT**

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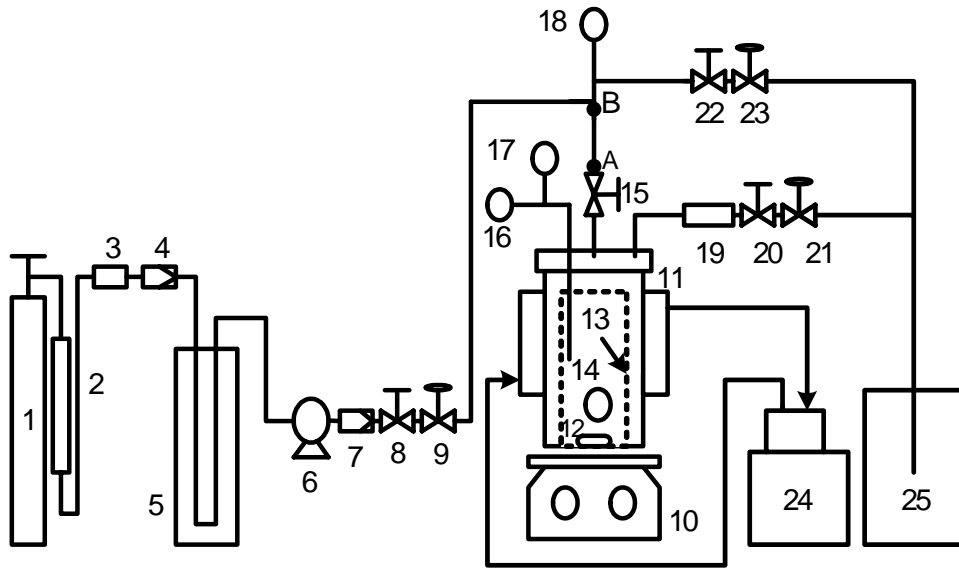
and Energy Commission of the Republic of China.

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**Table 1:** Mole fraction of CO<sub>2</sub> in aqueous and supercritical phase at 393.15K and various pressures. (from Vorholz et al., 2000)

Pressure (MPa)	$X_{CO_2}$	$Y_{CO_2}$
8.0	0.0136	0.9658
8.0	0.0105	0.9641
10.0	0.0121	0.9694
10.0	0.0126	0.9706
10.0	0.0113	0.9669
12.5	0.0132	0.9750
15.0	0.0142	0.9747



1.gas cylinder, 2.dry tube, 3.filter, 4.check valve, 5.condenser, 6.pump, 7.check valve, 8.ball valve, 9.micrometering valve, 10.stirrer plate, 11.reactior, 12.stir bar, 13.sample bottle, 14.eye glass, 15.ball valve, 16.temperature indicator, 17.pressure indicator, 18. pressure indicator, 19.filter, 20.ball valve, 21.micrometering valve, 22.ball valve, 23.micrometering valve, 24.oil bath, 25.sink

Figure 1: Experimental apparatus

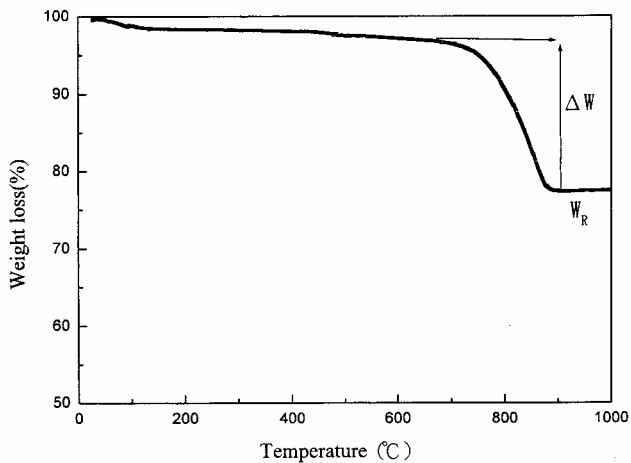


Figure 2:  
TGA plot of wollastonite reacted at P=8.6 MPa (1240 psig), T= 433K (160°C), and t = 6 h.

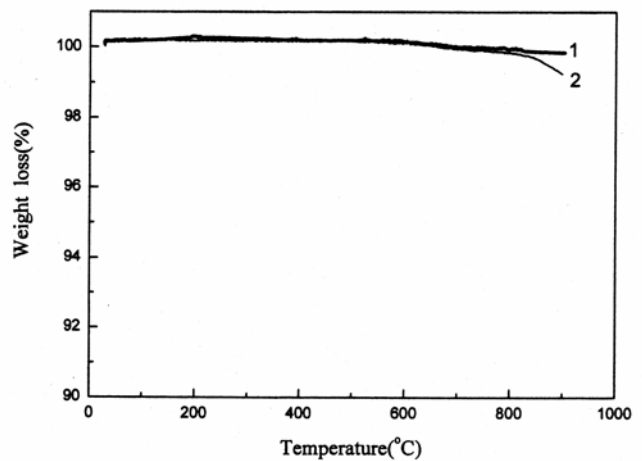


Figure 3:  
TGA plot of reacted and unreacted samples of albite. Heating rate at 10K/min in N<sub>2</sub>.  
Curve 1: unreacted,  
Curve 2: reacted at P=13.9MPa (2000 psig), T= 338K (65°C), t = 6 h

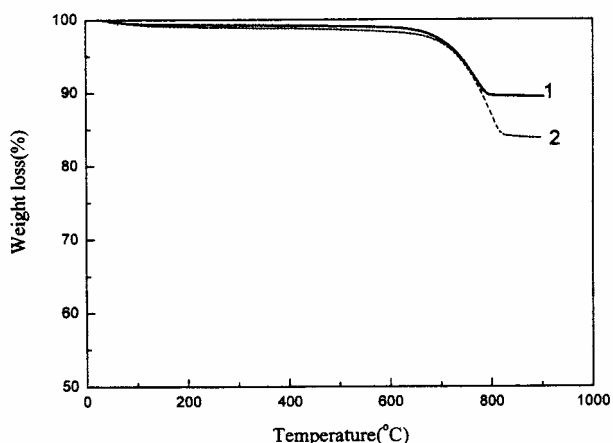


Figure 4:  
TGA plot of wollastonite reacted at different temperatures. Heating rate of 10K/min in N<sub>2</sub>. Reaction conditions: P = 8.6 MPa (psig), t = 6 h, and T = 50 °C for curve 1 and T = 80 °C for curve 2.

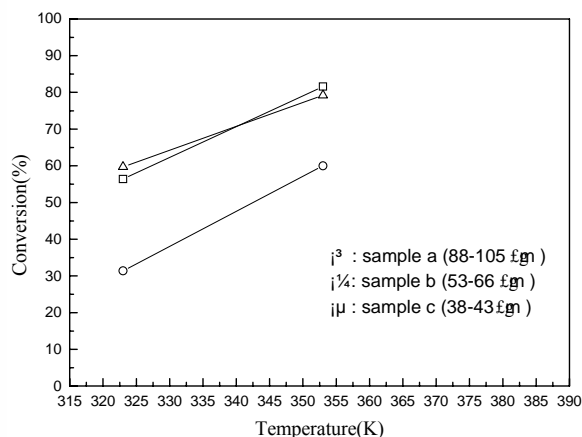


Figure 5:  
Conversion of wollastonite carbonation for various particle sizes at 323K and 353K. P = 8.6 MPa (1240 psig), t = 6 h.

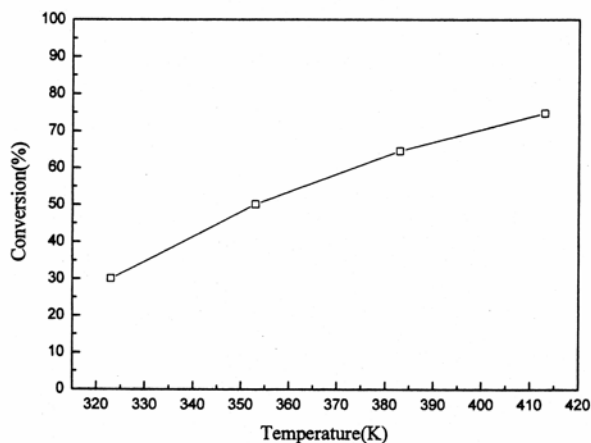


Figure 6:  
Effect of temperature on the carbonation conversion of wollastonite (sample *a*). Operating conditions: P = 8.6 MPa (1240 psig), t = 6 h.

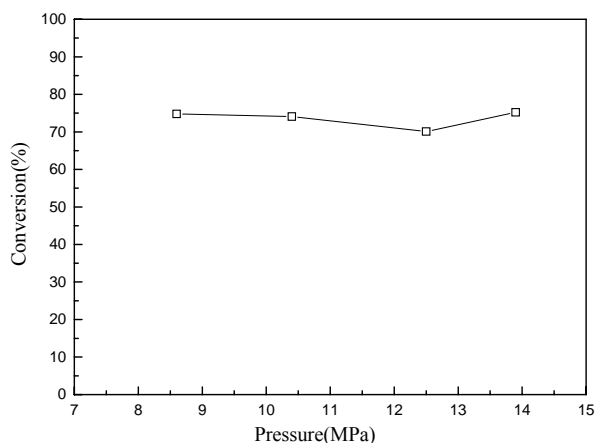


Figure 7:  
Effect of pressure on the carbonation conversion of wollastonite. T = 413K (140 °C), t = 6 h.