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MATERIALS AND INTERFACES

Feasibility of CO₂ Fixation via Artificial Rock Weathering

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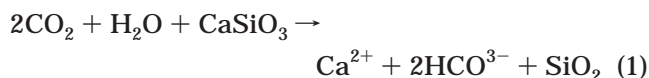
Artificial rock weathering can potentially fix a large amount of CO₂ generated from industrial and other sources with a slight expense of mechanical energy. From technological, economic, and environmental perspectives, artificial rock weathering is a preferential method to dispose carbon dioxide. Carbonate and hydrogen carbonate ions are formed spontaneously when carbon dioxide is dissolved in an aqueous solution owing to the negative Gibbs free energy. The calcium silicate component of wollastonite reacts with carbonate ions and becomes calcium carbonate and silicate. Such a reaction is economically feasible because this transformation does not require energy infusion. The products are naturally stable and can be discharged safely without pollution. Experimental results indicated that, in an aqueous solution, 1 ton of wollastonite could fix nearly 140 kg of carbon dioxide. No carbonation was observed when using talc under our experimental conditions. The study indicates that the reaction rate of artificial rock weathering may still be too slow for commercialization. Therefore, successful commercialization hinges on accelerating rock weathering reaction without increasing operational cost and increasing the efficiency of rock utilization.

Introduction

The human production of carbon dioxide has begun to change the climate; thereby, necessary steps must be taken to prevent further change. Many strategies have been proposed to remedy carbon dioxide, including chemical transformation and photocatalytic reduction of CO₂ to valuable products, such as methanol or methane.¹ The chemical fixation of carbon dioxide is one of effective and feasible means to reduce the concentration of CO₂ generated from industrial and other sources in atmosphere. However, the Gibbs free energy of carbon dioxide is at low grade from a thermodynamics perspective. Any transformation of carbon dioxide requires energy infusion. Low-cost energy resources and carbon dioxide-free processes are essential to convert carbon dioxide to valuable products. Thus, upgrading carbon dioxide may not be economically practicable.

The downgrade of carbon dioxide via carbonation is another feasible route. The carbonation can be naturally carried through rock weathering. Rock weathering, a naturally spontaneous reaction, requires no energy infusion. The weathering process can be viewed as an acid–base reaction where an acid, H₂CO₃, is neutralized by a solid base such as rock.² The rock weathering of wollastonite comprises of several reactions, and can be summarized in two reactions. Equation 1 is silicate weathering in which 2 mol of CO₂ become hydrogen carbonate ion. Equation 2 is the formation of calcium carbonate in which 1 mol of CO₂ is released. The overall reaction is that in which 1 mol of CO₂ is fixed in calcium carbonate as shown in eq 3.³ A similar carbonation of talc may also occur as shown in eq 4.⁴

Silicate weathering



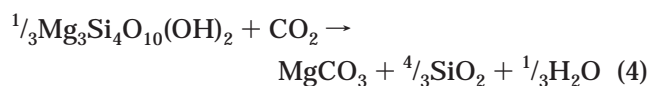
Carbonate formation



Overall reaction of wollastonite



Overall reaction of talc



Geological estimates have indicated that the atmospheric concentration of carbon dioxide 100 million years ago was 20–30 times higher than the current level. At least half the amount of carbon dioxide was fixed by rock weathering, resulting in the current concentration of carbon dioxide, i.e., 300–400 ppm, in the atmosphere.³ The total amount of carbon dioxide generated by human activity has doubled the concentration of carbon dioxide in the atmosphere since the industrial revolution. Currently, there is a net increase of 3 billion metric tons of carbon dioxide in the atmosphere annually.⁵ However, such an amount of carbon dioxide only engages a minute fraction of the geochemical carbon cycle because most of the carbon is stored in the form of calcium carbonate on earth. Even if all of the existing and reserved fossil fuels were to be burned, the amount of carbon dioxide released would only be

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Table 1. Compositions of Rocks

	wollastonite (wt %)	talc (wt %)
SiO ₂	50.48	55.98
Al ₂ O ₃	1.14	0.3
Fe ₂ O ₃	0.17	0.01
CaO	43.69	0.01
MgO	0.78	34.69
K ₂ O	0.14	0.03
Na ₂ O	0.09	0.42
TiO ₂	0.01	
Ig. loss	0.06	2.47

less than 0.007% of the total carbon mass on earth.³ Therefore, storing CO₂ generated from industrial and other sources via rock weathering would only consume a very small amount of rock in the earth. Moreover, the disposal of products, calcium carbonate and silicate, would only negligibly impact the environment since they are natural materials.

Igneous rocks are essentially free of carbonate, thus making them ideal for CO₂ fixation. While Ca- and Mg-bearing minerals are available in abundant quantities, only certain rocks can most likely be processed economically. Wollastonite and talc, which naturally contain abundant Ca and Mg, respectively, are promising candidates to investigate their ability to fix CO₂ in an aqueous solution.

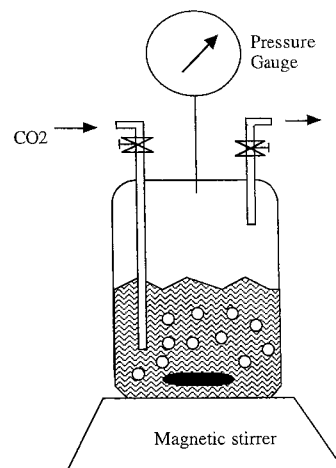
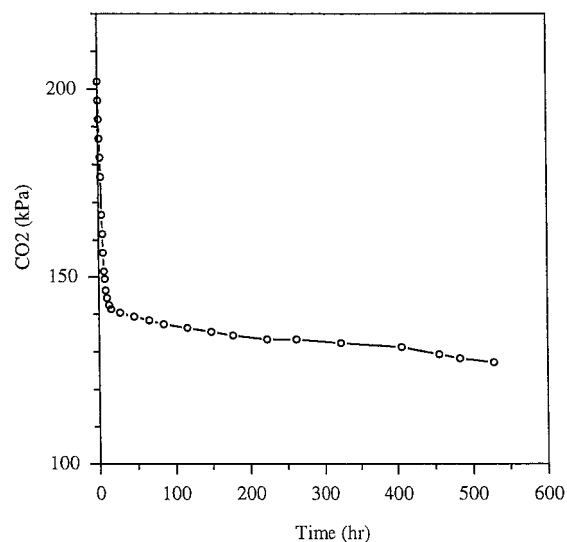
CO₂ has been reduced to its current level over a span of millions of years. As expected, a major difficulty in artificial rock weathering is the reaction rate. Therefore, the task is to accelerate these natural reactions. Mild conditions, such as ambient temperature or pressure, are preferable because the deposition of CO₂ is not for profit. Thus, expensive equipment or complex processes would be unacceptable in commercialization. This feasibility study presents a novel method using rock weathering to store carbon dioxide in an aqueous solution without adding reagents.

Experimental Section

Wollastonite and talc were obtained from the Feng-Deng Ceramic Co. (Taiwan). They are natural rocks (imported from China) pulverized to powder with very wide size distribution. The median sizes of wollastonite and talc are ~440 and ~310 μm, respectively. These samples were used directly without pretreatment. Table 1 lists the compositions of wollastonite and talc as provided by the supplier.

The experiments were performed at room temperature and low pressure so that no special equipment was required. Carbon dioxide was fixed in an 0.5 L aqueous solution using a 2-L bottle as shown in Figure 1. Wollastonite or talc was dispersed in distilled water in the bottle with a magnetic stirrer. The saturated CaO solution is near 0.13 g/100 mL of water. The loading of wollastonite was intended to make a saturated Ca²⁺ solution, assuming the maximum dissolution of 43.69 wt % CaO in wollastonite. Therefore, the excess loading of wollastonite was 2 g in 0.5 L of distilled water, i.e., 4 mg/mL, and the same loading was applied to talc. The air in the bottle was purged by carbon dioxide several times, then CO₂ pressure was increased to 202 kPa by adjusting a back-pressure regulator. Next, the CO₂ pressure variation was monitored by a pressure gauge. The absorption was performed from several hours to 22 days.

The solid content of solution after CO₂ absorption was collected by centrifuging, then dried at 120 °C and

**Figure 1.** Schematic of CO₂ absorption system.**Figure 2.** CO₂ absorption by wollastonite in aqueous solution.

weighed. The amount of CO₂ fixed in solid content was verified and measured by thermogravimetry (TGA) and differential thermal analysis (DTA).

Results and Discussion

Rock weathering occurs naturally on the earth as long as water, rocks, and carbon dioxide are available.² An obstacle to artificial rock weathering may be the dissolution of calcium silicate.⁶ Therefore, in this study, a powdered form of rock was used to accelerate the dissolution. The effective compositions of carbonation are CaO or MgO. Therefore, the rock containing the most CaO or MgO is the best candidate. Table 1 lists two kinds of rocks used herein. Both rocks contain more than 50 wt % of SiO₂. Wollastonite contains nearly 44 wt % of CaO and talc contains nearly 35 wt % MgO. Notably, the composition was measured by elemental analysis and was not necessarily the free form of CaO or MgO. These rocks are widely available and appropriate for investigating the CO₂ fixation via carbonation.

Figure 2 indicates that the CO₂ pressure decreases in a wollastonite aqueous solution in 22 days. The CO₂ pressure initially declined rapidly in the first 5 h indicating the dissolution of CO₂ and the formation of carbonate/hydrogen carbonate ions in an aqueous solution. The subsequent gradual decrease of CO₂ pressure might be due to a minor leak of a valve or might be

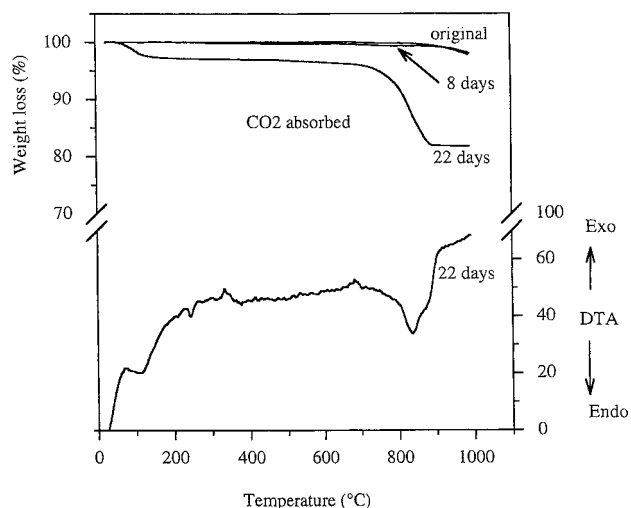


Figure 3. TGA and DTA of original and CO₂ absorbed wollastonite.

attributed to the carbonation of calcium ion from wollastonite. This step involves the dissolution of wollastonite and is much slower than CO₂ dissolution. The CO₂ pressure only influences the concentration of carbonate/hydrogen carbonate ions in aqueous solution. Therefore, the variation of CO₂ pressure is only a minor factor of the carbonation rate because the rate-limiting step is the dissolution of wollastonite.

Figure 3 depicts the TGA/DTA analysis of solid content after CO₂ absorption using wollastonite. As shown in Figure 3, original wollastonite and 8 days of CO₂ absorption do not contain a volatile component up to 1000 °C. For 22 days of CO₂ absorption, a significant weight loss in the range 800–900 °C was due to the release of CO₂. An endothermic reaction also supported the decomposition reaction of CaCO₃. The reaction of wollastonite + CO₂ = calcite (CaCO₃) + quartz (SiO₂) most likely occurs under a much milder condition.^{7,8} The weight loss is ~14 wt % due to CO₂ releasing. Theoretically, a nearly 25 wt % loss due to CO₂ is expected if 44 wt % of CaO of wollastonite can be fully utilized. The carbonation rate could be so slow that it is not yet complete within 22 days. The dissolution of wollastonite and the carbonation in aqueous solution are thus the rate-determining steps. Another reason of slow rate may be a thin product layer, i.e., CaCO₃, that developed on the outer surface of wollastonite particle retarding further carbonation.

Figure 4 displays the TGA/DTA analysis of solid content after CO₂ absorption using talc in 22 days. The TGA curves of original and CO₂ absorbed talc are very similar. For CO₂ absorbed talc, an additional small amount of weight loss was in the temperature range 100–200 °C, suggesting the water release. The final weight loss above 700 °C could simply be the ignition loss of talc, which was also evidenced by an endothermic peak from DTA. Therefore, the carbonation could be not detected in talc, at least under our experimental condition in an aqueous solution. Possibly, the Mg²⁺ cannot be released from the talc in an aqueous solution under ambient condition; otherwise, the dissolution is too slow to be detected.

Conclusion

This study has demonstrated CO₂ fixation by artificial rock weathering. Experimental results indicate that CO₂

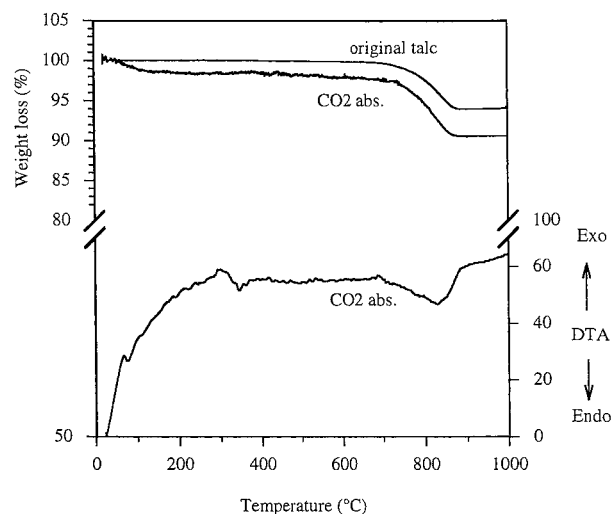


Figure 4. TGA and DTA of original and 22-day CO₂ absorbed talc.

can be stored in rocks, such as wollastonite. According to the TGA results (Figure 3), ~140 kg of CO₂ can be stored by 1 ton of wollastonite. The pulverization of rock, such as wollastonite, requires electricity that may generate CO₂ if fossil fuel is used. Kojima et al. estimated that 18.7 kg of CO₂ would be released when 1 ton of wollastonite was crushed from 200 mm to 75 μm.⁹ The fixation of CO₂ via artificial rock weathering may still have a large net CO₂ storage, even including other additional operations. Theoretically, nearly 345 kg of CO₂ can be stored per ton of wollastonite if the entire 44 wt % CaO is available for carbonation under most favorable conditions. Although the experiment results revealed that the amount of CO₂ deposition was less than anticipation, the potential storage of CO₂ still has a large capacity for improvement using wollastonite. Natural rock is abundantly available at a fairly reasonable price. The final products are environmentally friendly, since rock weathering has been producing them for several hundred million years.

The detailed mechanism of wollastonite carbonation may still be unclear. The kinetic rate is still too slow to keep up with the carbon dioxide produced by human activities. Although pure CO₂ was used in this study, the rate of artificial rock weathering will not be substantially held back even if we use flue gas which contains only a few percent CO₂. The major obstacle is the dissolution of wollastonite in water. The ion, Ca²⁺, must be released from the tetrahedral SiCaO₃ structure to perform carbonation. Until now, the most direct method to accelerate dissolution is to provide large surface, i.e., small particles. Other chemical treatments, such as acid or basic reagents, might be effective but will be fairly expensive considering the enormous amount of CO₂ storage. How to accelerate the reaction rate will be the key issue of commercialization.

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