

## Fixation of carbon dioxide with Wollastonite and its reaction products

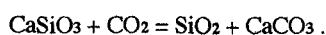
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**KEY WORDS:** Fixation of carbon dioxide/silica/calcium carbonate/wollastonite/

### ABSTRACT

The fixation of CO<sub>2</sub> with CaSiO<sub>3</sub> dispersed in water was carried out in the temperature range of 30 to 80°C. The microstructures of the reaction products were characterized with a SEM, TEM, and others. Reactions for the fixation were well expressed by an equation of interface reaction rather than by that of ion diffusion through a reaction layers. The activation energy of the reaction was 9.14 kcal/mol. The final reaction-products were SiO<sub>2</sub> and CaCO<sub>3</sub>, so that the net reaction was considered to be in the following,



The electron diffraction patterns of reaction products indicated that the SiO<sub>2</sub> obtained was amorphous and that the CaCO<sub>3</sub> obtained was in both calcite and aragonite.

### INTRODUCTION

Recent greenhouse effect mainly caused by CO<sub>2</sub> due to the activities of humankind is in an urgent problem to be solved. In this connection various methods to separate, to adsorb, and to fix CO<sub>2</sub> have been reported by many researchers. Among them the best method is considered to convert CO<sub>2</sub> to CaCO<sub>3</sub> or MgCO<sub>3</sub> by a chemical reaction of CO<sub>2</sub> with silicates

containing calcium or magnesium ions. From the view point, we have studied about the reaction of CO<sub>2</sub> with calcium silicates such as natural wollastonite(CaSiO<sub>3</sub>), the scraps of cement, asbestos, and others. In this paper, we intend to report experimental data about the microstructures of reaction products, CaCO<sub>3</sub> and SiO<sub>2</sub> and a mechanism in the reaction of CO<sub>2</sub> with CaSiO<sub>3</sub> dispersed in water.

### EXPERIMENTS

Natural CaSiO<sub>3</sub>, wollastonite, was used as a sample. It was crushed in a ball mill for 5 h in air. The resultant sample of 10g was placed in a glass vessel with 200 ml of distilled water. The glass vessel was set in a water bath controlled at a constant temperature. Then, CO<sub>2</sub> of the same temperature as that of the water bath was introduced for the reaction of CO<sub>2</sub> with CaSiO<sub>3</sub>. The reaction time was for 10, 20, 40, 80, and 160min. The reaction temperatures were at from 30 to 80°C. After an experiment, the specimen in the glass vessel was dried at 130°C for 10 h. The weight increase due to the production of CaCO<sub>3</sub> was measured. Reaction ratio,  $\alpha$ , was calculated by using  $W/3.79$ , in which the value of 3.79 was the weight increase when the CaSiO<sub>3</sub> of 10g reacted perfectly with CO<sub>2</sub> in the

reaction of  $\text{CaSiO}_3 + \text{CO}_2 = \text{CaCO}_3 + \text{SiO}_2$ , and  $W$  was the weight increase at reaction time  $t$ . The average value of 4 experimental data was used as a  $W$  value. The reaction products were observed with a scanning electron microscope (SEM) and a transmission electron microscope (TEM). The elemental analysis of them was carried out by energy dispersed X-ray analysis (EDX).

### RESULTS and DISCUSSION

$\text{CaSiO}_3$  used in this experiment was cylindrical in shape. The average size of the sample in width was about  $8 \mu\text{m}$  and the aspect ratio was about 50. If we assumed that the average diameter and length of the cylindrical  $\text{CaSiO}_3$  were  $r$  and  $l$ , and that the reaction layer at time  $t$  was  $x$ , the reaction ratio,  $\alpha$ , is expressed in the following equation,

$$\alpha = \{\pi r^2 l - \pi (r-x)^2 l\} / \pi r^2 l = 1 - (r-x)^2 / r^2 \quad (1).$$

For interface reaction, the growth rate of reaction layer,  $dx/dt$ , is proportional to the interfacial area, so the growth rate is expressed in the next equation,

$$dx/dt = 2k' \pi (r-x) l = K_s (r-x) \quad (2)$$

where  $K_s = 2\pi l k'$ . Integrating the equation (2) in considering the equation (1) and the boundary conditions that the reaction layer,  $x$ , is zero at  $t=0$ , the following equation can be obtained,

$$\ln(1-\alpha) = -2K_s t \quad (3).$$

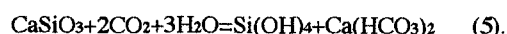
For a diffusion process, similarly the following equation can be obtained from the parabolic law,

$$\{1 - (1-\alpha)^{1/2}\}^2 = (K_d/r^2)t \quad (4),$$

where  $K_d$  is a rate constant. From the plots of equations (3) and (4),  $K_s$  and  $K_d$  can be obtained, respectively.

The relationship between reaction ratio,  $\alpha$ , and reaction time  $t$  indicated that the reaction ratio increased rapidly at initial stage, but after 10 min increased gradually. The reaction ratio was larger than 0.3 at  $80^\circ\text{C}$  for 160 min. This means that 10g of  $\text{CaSiO}_3$  can fix about 1g  $\text{CO}_2$ . The plots of equation (3) and (4) indicated that the data were well expressed in equation (3) rather than in equation (4). This would indicate that the reaction proceeded in an interface process. The activation energy obtained from the Arrhenius plots of reaction constants  $K_s$  obtained was 9.14 kcal/mol. The value is in common in liquid phase reaction.

The solubility data based on both thermodynamics and experiments indicated that high concentration of  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  ions<sup>3)</sup> at a condition of saturated  $\text{CO}_2$  was present in a solution during the experiment. So, at the condition,  $\text{Ca}^{2+}$  ions would react with  $\text{HCO}_3^-$  to form  $\text{Ca}(\text{HCO}_3)_2$ . It is expressed in the following equation,



Reaction products,  $\text{Si}(\text{OH})_4$  and  $\text{Ca}(\text{HCO}_3)_2$ , and residual raw material,  $\text{CaSiO}_3$ , existed in the solution in the glass vessel. The residual  $\text{CaSiO}_3$  could be separated from the solution by filtering  $\text{Si}(\text{OH})_4$  and  $\text{Ca}(\text{HCO}_3)_2$ , since they could pass through a filter paper because of their very small size in comparison with large  $\text{CaSiO}_3$ . The resultant solution contains  $\text{Si}(\text{OH})_4$  and  $\text{Ca}(\text{HCO}_3)_2$ . Into it the addition of ammonium solution decreased the solubility of  $\text{Ca}(\text{HCO}_3)_2$ . As a result,  $\text{CaCO}_3$  was precipitated from it. The precipitated  $\text{CaCO}_3$  was also separated from the solution by filtering  $\text{Si}(\text{OH})_4$ . Then a solution

containing only  $\text{Si}(\text{OH})_4$  was obtained. By vaporizing water from the solution containing  $\text{Si}(\text{OH})_4$ ,  $\text{SiO}_2$  could be obtained.

Figure 1 shows the SEM micrographs of  $\text{CaCO}_3$  particles obtained by the addition of ammonium. Clearly from the figure, there are two types of particles, one is angular particle with crystal habits, and the other is spherical. The SEM micrograph of spherical particles observed in high magnification indicated that the spherical particles were agglomerated with submicron particles as shown in Fig. 2. The X-ray diffraction pattern of the mixtures of both angular and spherically agglomerated particles indicated the diffraction peaks of both calcite and aragonite. Electron diffraction patterns indicated that angular particles with crystal habits were in calcite and the agglomerated ones were in aragonite.

The aragonite would rapidly precipitate from  $\text{Ca}(\text{HCO}_3)_2$  as  $\text{CaCO}_3$ , when the ammonia solution added to the solution containing  $\text{Ca}(\text{HCO}_3)_2$ . Its addition would introduce very high supersaturation of  $\text{Ca}(\text{HCO}_3)_2$  to the solution. This would make the nucleation and crystal growth of  $\text{CaCO}_3$  to take place everywhere in the solution. Then they would collide each other to coagulate just like the formation of spherulite. During the process, no  $\text{CO}_2$  generated, so the reaction by the addition of ammonium solution would take place in the following,



By filtering  $\text{CaCO}_3$  through a filter paper, a solution containing only  $\text{Si}(\text{OH})_4$  can be obtained.

By vaporizing water from the solution in an oven,  $\text{SiO}_2$  films could be obtained. In order to make

spherical  $\text{SiO}_2$  as shown in Fig.3, the addition of foreign ions with different valency is effective. The silica obtained by the addition of  $\text{Mg}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$  as nucleation agents was spherical. Its size was in  $68 \mu\text{m}$  and in  $75 \mu\text{m}$ , respectively. Electron diffraction patterns of both spherical and filmy silica indicated a halo, that is, they were amorphous.

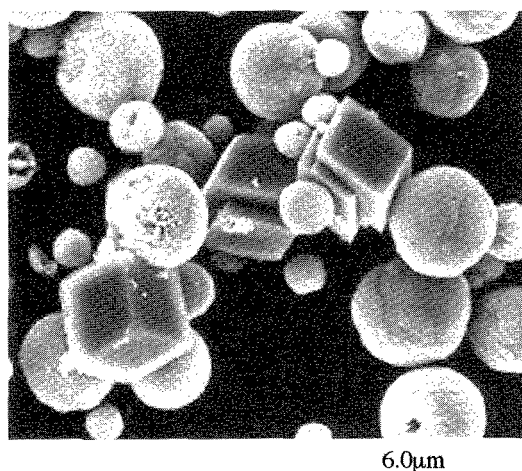


Fig.1 SEM micrograph of  $\text{CaCO}_3$  particles. There are two types of particles in which one is angular with crystal habits and the other is spherical.

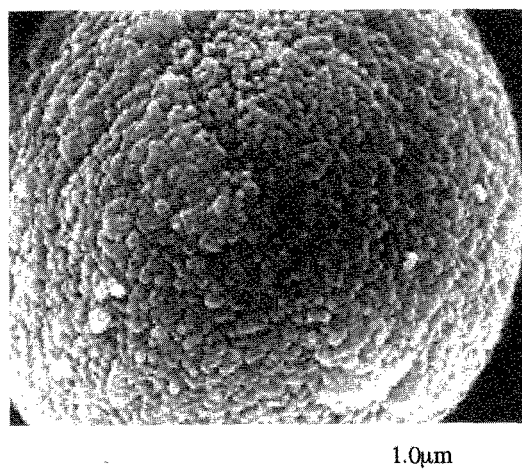
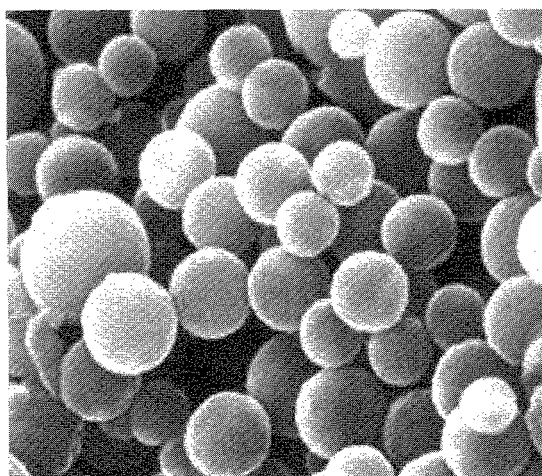


Fig.2 SEM micrograph of spherical particle indicates that the particle is agglomerated with submicron particles.

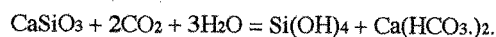


300nm

Fig.3 SEM micrograph of spherical silica. Such particles are obtained when additives such as  $Mg(OH)_2$  and  $Al(OH)_3$  were added in the solution with silicic acid and were dried.

### CONCLUSIONS

The reaction between  $CaSiO_3$  dispersed in water and  $CO_2$  was carried out in the temperature range of 30 to 80°C. As a result, it was found that  $CO_2$  could be effectively fixed by the following reaction,



The reaction was well expressed by an equation derived from the mechanism of interfacial reaction rather than the mechanism of diffusion of ions through a reaction layer. The rate determining step was speculated to be the interface reaction of  $Ca^{2+}$  ion on  $CaSiO_3$  with  $HCO_3^-$ . The activation energy of the reaction obtained were 9.14 kcal/mol. Reaction products were separated to  $CaCO_3$  and  $SiO_2$ . The  $CaCO_3$  particles

were divided into two types, one was calcite with crystal habits and the other was aragonite, which was spherical particle consisting of small particles about 0.1  $\mu m$ .  $SiO_2$  was obtained as films and spheres. In order to produce spherical particles of silica in high reproducibility, the addition of impurities such as  $Ca(OH)_2$  and  $Al(OH)_3$  was effective. Electron diffraction pattern indicated that both were amorphous.

### REFERENCES

- 1) R. A. Bermer, A. C. Lasaga, R. M. Garrels, *Am. J. Sci.*, **288**, 641(1983).
- 2) Takashi Okuma, *Kagaku*, **63**, 17(1993).
- 3) W. M. Latimer, *Oxidation Potential*, 2nd, **74**, 137(1956); N. Otaki, *Youeki no Kagaku*, Dainihonntosho, p.68(1978).
- 4) H. Hasegawa, *Gypsum & Lime*, No. 122, 33(1973).
- 5) J. Fukawa, Y. Moriyoshi, T. Ishigaki, T. Ikegami, and T. Urano, *Inorg. Mater.*, **4**, 205(1997).
- 6) J. E. Dutrizac, R. J. C. McDonald, and T. R. Ingraham, *Trans. AIME.*, **245**, 955(1969).
- 7) J. E. Dutrizac, R. J. C. McDonald, and T. R. Ingraham, *Met. Trans.*, **1**, 225(1970).
- 8) H. Y. Peter, C. K. Hansen, and M. E. Wadsworth, *ibid.*, **4**, 2137(1973).
- 9) E. Peter and F. Loewen, *ibid.*, **4**, 5(1973).
- 10) Y. Umezu, K. Tozawa, and K. Sasaki, *SENKENIHOU*, **29**, 794(1973).

(Received December 10, 1998; accepted April 14, 1999)