

CARBONATION OF NATURAL ROCK AND STEEL SLAG USING SUPERCRITICAL CARBON DIOXIDE

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It is believed that the massive CO₂ released into the atmosphere has a serious consequence on the aggravation of green house effect. In order to solve this problem, the feasibility studies on the carbon dioxide disposal method based on combining carbon dioxide chemically with natural rock, such as wollastonite, and steel slag were performed in our laboratory. The process used a stirred batch reactor, in which supercritical carbon dioxide was absorbed into a rock slurry or a slag slurry to cause dissolution of CaO in the solid reactant and precipitation of calcium carbonate. The effects of operating variables – including reaction time, reaction pressure, particle size of solid reactant, and reaction temperature – on the conversion of solid reactants were investigated, and a reaction mechanism was proposed to explain these effects. The amount of CO₂ fixed in the solid phase was determined by means of thermogravimetric analysis. The particle size of solid reactant and the reaction temperature are the two important factors that determine the conversion of CaO containing in the solid reactants. The conversion of wollastonite is higher than that of steel slag; the highest conversion is 75% in 30 min for the former and 65% in 1h for the latter. Although the conversion of steel slag is lower, it is possible to use this industrial residue to replace the natural rocks for carbon dioxide disposal.

INTRODUCTION

It is believed that the release of massive carbon dioxide (CO_2) into the atmosphere by burning fossil fuels has aggravated the green house effect. To solve this problem, several techniques are being developed to reduce the amount of CO_2 released into the atmosphere, including physical storage, biological fixation, and chemical fixation. In our laboratory, the chemical fixation method has been adopted for the disposal of CO_2 [1]. The process used a magnetic-stirring reactor, in which supercritical CO_2 was absorbed into wollastonite (CaSiO_3) aqueous slurry to cause dissolution of the mineral and precipitation of calcium carbonate. At 413K and 8.6MPa, the conversion of wollastonite to CaCO_3 increased from 41% to 75% as the reaction time varied from 3h to 6h. They proposed a carbonation mechanism to explain the effects of operational variables, including particle size of rock, reaction temperature, reaction time, and solution composition. First, the water absorbs CO_2 and becomes acidic. Then the calcium contained in the wollastonite dissolves in the aqueous phase, which becomes more alkaline. Meanwhile the surface of wollastonite particles is coated by a SiO_2 -rich layer after dissolution of CaO. The SiO_2 layer sloughs off under pressure and agitation, allowing hydrogen ions to further attack the rocks. Finally, the aqueous solution becomes alkaline to precipitate CaCO_3 and to absorb CO_2 again. This cycle repeats until the calcium in the rocks is exhausted.

Although a high conversion of wollastonite carbonation can be obtained, the reaction time is too long to be practical. Since the attrition of SiO_2 layer is a key factor in the carbonation process, a reactor fitted with a impeller will be used for agitation to replace the magnetic stirring. It is hoped to achieve a high conversion in a shorter reaction time under vigorous agitation. Besides, the carbonation of steel slag (BOF slag) was also studied with an intension to replace the wollastonite with the industrial residues as a possible feedstock for mineral CO_2 sequestration.

I - EXPERIMENTAL

Figure 1 shows the set up for carbonation study. The main part of the system is a high-pressure reactor fitted with an impeller and a cooling tube. At the beginning of an experiment, the glassware containing 20 mL of 10 wt% wollastonite or slag slurry was placed in the reactor after the reactor temperature reached a setting level. The liquefied CO_2 , which came from a gas cylinder, was purged into the reactor to achieve a desired pressure. After the carbonation reaction proceeded for a certain period of time, the pressure was released slowly to atmospheric pressure and the temperature was lowered to room temperature in 20 min.

Finally the reacted sample was filtered and dried for TGA analysis.

The conversion of wollastonite or steel slag to CaCO_3 was based on the weight loss determined by TGA analysis. A typical TGA plot of reacted steel slag is shown in fig.2, in which ΔW_2 stands for the weight loss of sample due to the decomposition of CaCO_3 , yet the reason for the weight loss ΔW_1 is still not identified, probably due to decomposition of MgCO_3 . The TGA plot of reacted wollastonite is similar, but without ΔW_1 . The conversion was calculated using the following equation,

$$X(\%) = \frac{\Delta W / 44 \cdot 40}{W_R / M \cdot 40} \cdot 100 = \frac{\Delta W \cdot M}{44 \cdot W_R} \cdot 100 \quad (1)$$

Where 40 and 44 are the atomic weight of calcium and molecular weight of CO_2 ; X stands for the conversion, M stands for the weight of samples containing 1 gmole of calcium, and W_R stands for the weight of sample retained which is equal to the weight of the original sample.

II - RESULT AND DISCUSSION

Conversion of wollastonite

The conversion of wollastonite carbonation was investigated at different reaction temperatures and pressures under reaction time of 30 min, agitation rate of 500rpm and particle size between 90 and 125 μm . The results are shown in Fig.3. For the pressure varied from 19.74 atm to 78.95 atm, the conversion does not change much; however, the temperature effect is significant. The conversion is about 10% at 50°C and then increase sharply up to 75%

at 150°C, where it reaches the maximum. After that, the conversion drops a little bit to 65%.

Tai et al. [1] reported the conversion of wollastonite carbonation using a magnetic-stirring reactor and proposed a reaction mechanism, i.e., the attrition of the SiO_2 -rich layer occurred after the calcium in the rock dissolves into the solution allows further chemical attacks on the rocks. The reaction rate is much slower than the present study using an impeller-stirred reactor. For example, a 75% conversion in 6h as compared with 30min in this study. Apparently, the high agitation rate of impeller accelerates the attrition of the SiO_2 -layer coated on the surface of wollastonite particles. The experimental results reconfirm the attrition mechanism of wollastonite carbonation.

Effect of reaction time on slag conversion

Figure 4 shows the reaction time on the carbonation conversion of steel slag. When the reaction time varied from 1h to 3h, the conversion was almost the same, meaning that 1h was long enough for a conversion of 65%. The conversion did not increase with the reaction time after one hour was probably due to the blockage of pores by the CaCO_3 . Therefore SEM photos should be taken to examine the surface of slag before and after reaction.

Effect of reaction temperature on slag conversion

The reaction temperature was varied from 100 to 200°C to study its effect on the slag conversion. As shown in Fig. 5, a maximum conversion was found at 150°C, which was similar to the result of wollastonite as shown in Fig. 3. Tai et al [1] postulated the dissolution rate of wollastonite was probably the controlling step. When the temperature increased, the dissolution rate increased; however the solubility of CO_2 decreased leading to a higher pH, thus a low dissolution rate. The two opposite effects of temperature competed with each other and a maximum of conversion occurred. The same argument might be used in the case of slag carbonation.

CONCLUSION

A carbonation process for CO_2 sequestration is proven feasible by using natural rock (wollastonite) or Ca-rich industrial residue (steel slag) to react with supercritical CO_2 in a stirred tank reactor. Several operational variables were investigated, among which particle size of rock or slag and reaction temperature are the important factors that influence the conversion. Under specified conditions, the highest conversion is 75% in 30min for wollastonite, at 65% in 1h for slag. It is possible to use the industrial residue to replace the natural rocks for carbon dioxide disposal.

ACKNOWLEDGEMENT

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REFERENCE:

[1] Tai, C. Y., Chen, W. R. and Shih, S. M., *AIChE J.*, Vol. 52, **2006**, p. 292

FIGURE

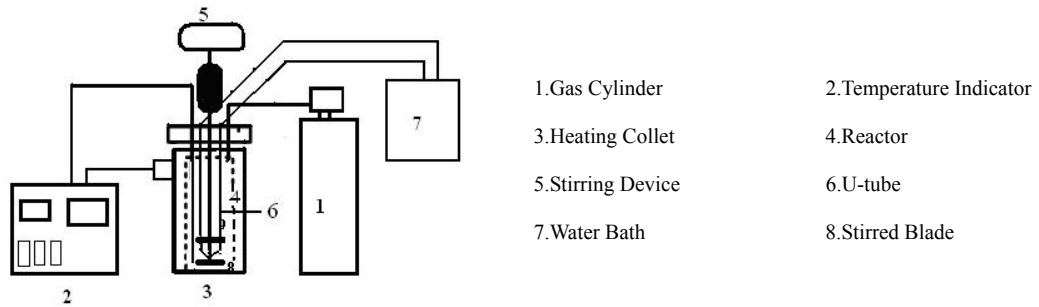


Figure 1 : Modified experimental set-up

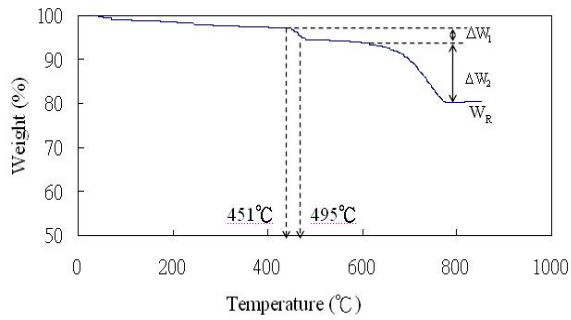


Figure 2 : TGA plot of reacted steel slag

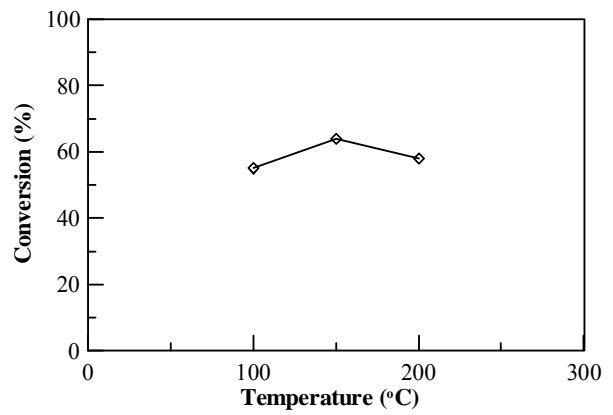


Figure 4 : Effect of reaction temperature on the carbonation conversion of steel slag
 t=1hr ; P=80bar ; 500rpm ; .
 steel slag sample d=63~90µm

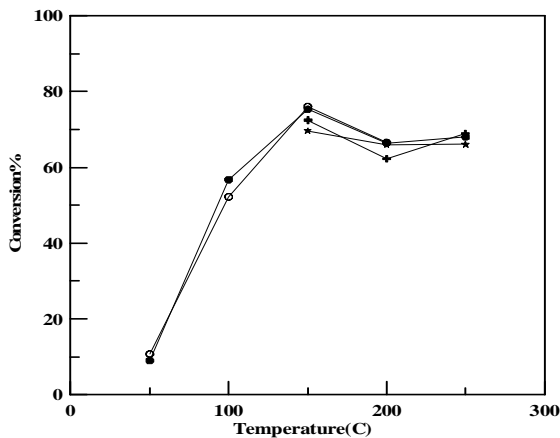


Figure 3 : Effect of reaction temperature on the carbonation conversion of wollastonite
 t=30(min) ; 500rpm ; Wollastonite sample
 125µm > d >90µm
 ○-P=19.74 atm ●-P=39.48 atm + -P=59.22
 atm □ -P=78.95 atm

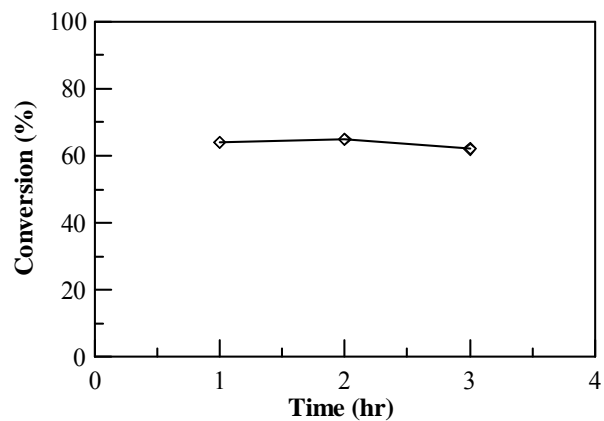


Figure 5 : Effect of reaction time on the carbonation conversion of steel slag
 T=150□ ; P=80bar ; 500rpm ; .
 steel slag sample d=63~90µm