Quantitative analysis of CO2 storage into limestone stratum

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Carbon dioxide (CO_2) storage in underground or underwater has been studied for decreasing CO_2 released from the burning of fossil fuels in order to mitigate recent global warming. Particularly, storage in underground is thought to be one of the most promising methods because the influence on ecosystem is comparatively small, and existing enhanced oil recovery (EOR) technique can be applied easily.

In many of underground storage technologies, injection of CO_2 to a limestone stratum is advantageous for carbon dioxide isolation. Dissolution of the $1m^3$ of the limestone results in isolation of 0.9tons of CO_2 by form of carbonate ion. Therefore, injection of CO_2 to limestone stratum decreases probability of CO_2 leakage to the atmosphere, or acidization of the underground water. However, lack of information on the quantitative evaluation of the reaction rate between limestone and CO_2 under high pressure condition as can be seen in underground storage hinders us to analyze how much limestone dissolves and how much CO_2will be captured.

In this study, we developed a device in which mixture of seawater and liquid CO_2 reacts with limestone in flow and high pressure condition for measurement CO_2-limestone reaction rate and identifying factors controlling it by changing parameters such as chemical composition and flow speed.

The device consists of metal container and flow lines which can bear up to 20MPa inside the device. Flow speed of seawater and liquid CO_2 can be adjusted in a range of 0-25ml/min and 0-50ml/min, respectively. Temperature and pressure inside the pressure container were monitored. The limestone sample used in this study is pure calcite with 2-4 mm particular sizes. Seawater flowing out of the reaction vessel was collected, and its pH and alkalinity were measured with an electrode (Horiba F-54) and a continuous flow-through type analyzer (Kimoto et al., 2001; Watanabe et al., 2004), respectively. Dissolution rate and carbonate system parameters of seawater before and after the reaction were calculated from pH and alkalinity.

The dissolution rates of the limestone in this study were 10-1000 times larger than the results in existing experiment (e.g., Keir, 1980) performed under atmospheric pressure. The dissolution rates decreased exponentially as the reaction proceeded. The pH and partial pressure of CO_2 changed from 4-5 and 1-2atm before the reaction to 5-6 and 0.8-1atm after the reaction, respectively; this indicates that the seawater was neutralized and CO_2 was dissociated by the dissolution into ions by the dissolution of limestone. The dissolution rate and hydrogen-ion concentration in seawater showed positive correlation, while concentration product of calcium and carbonate ions showed inverse correlation with the dissociation rate. This tendency agrees with a result of Chou et al. (1989) which performed under atmospheric pressure, qualitatively. In addition, dissolution rates become larger as flow speeds of the seawater and liquid CO_2 were larger.

The high dissolution rate in this study is though to be caused by protonation reaction ($CaCO_3 + H^+$ -) $Ca^{2+} + HCO_3^-$). As the dissolution proceeds, hydrogen-ion concentration decreases and precipitation of limestone might be enhanced from the increase of calcium and carbonate ions; thereby causing the dissolution rate to show down. Increased flow speed promotes rapid exchange between seawater on the surface of limestone and in bulk in high-flow condition, which might cause larger dissolution rate.

The result of this study gives important prediction of CO_2 storage into limestone stratum in the future. On the day of conference, we will present quantitative estimation of the dissolution of limestone and the amount of CO_2 storage in the case of hypothetical injection into a limestone stratum.