Influence of temperature and CO_2 concentration on the CO_2 absorption properties of lithium silicate pellets

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Carbon dioxide (CO_2) emissions, mostly resulting from fossil fuel combustion, are thought to cause climate change. Among the various technologies for reduction of these emissions, CO_2 separation is expected to have an immediate impact. In particular, it is more advantageous to separate CO_2 during the fuel reforming process than from the flue gas of the plant [1]. However, the CO_2 separation methods currently in practical use are not applicable to this process because of their poor heat tolerance. In order to solve this problem, a series of lithium-containing oxides for use as CO_2 absorbents at high temperatures [2] has been developed. Lithium zirconate (Li_2ZrO_3) was one of the oxides studied; it absorbs CO_2 at around 500 °C and emits CO_2 at temperatures above 750 °C [3–6]. Equation 1 represents its reversible reaction.

$$Li_2ZrO_3 + CO_2 \leftrightarrow ZrO_2 + Li_2CO_3 \qquad (1)$$

Recently, lithium silicate (Li_4SiO_4) has been developed for use as a new CO_2 absorbent at high temperatures [7]. Of the absorbents studied, it shows the most immediate CO_2 absorption and emission characteristics at high temperatures. The absorption rate of Li_4SiO_4 in a gas stream of 20 vol% CO_2 is equivalent to a CO_2 uptake of approximately 60 mg/min g-absorbent, which is more than 30 times faster than that of Li_2ZrO_3 [8, 9]. Equation 2 represents its reversible reaction.

$$Li_4SiO_4 + CO_2 \leftrightarrow Li_2SiO_3 + Li_2CO_3 \qquad (2)$$
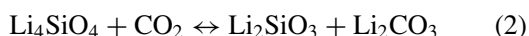
The studies and measurements described above were made for lithium silicate powder. Considering the practical use for large-scale CO_2 capture, a pellet-type absorbent is thought to be realistic. Therefore, a bench-scale CO_2 removal test was conducted to reveal the effectiveness of a reactor using a packed bed of lithium silicate pellets. At a gas flow condition of 20 vol% CO_2, the reactor achieved 100% CO_2 removal at 500 °C [10]. Investigation of more detailed absorption properties of this lithium silicate pellet is vital for designing practical apparatus for CO_2 capture at high temperatures. In this study, the influence of temperature on CO_2 absorption properties was investigated, which is an important operating condition of the apparatus. The relationship between CO_2 concentration and the absorption rate was also studied.

The lithium silicate samples used for these measurements were sphere-type pellets (LS-HE-905, average grain size: 5 mm, Toshiba Ceramics Co. Ltd., Japan). Fig. 1 shows a micrograph of the samples, which was observed by scanning electron microscope (SEM: JSM-5400LV, JEOL, Japan). The size of primary particles of the pellet was confirmed to be around 5 μm. They consist of lithium silicate, potassium carbonate, and lithium zirconate. Potassium carbonate was used as an additive to promote the absorption reaction of lithium silicate. Lithium zirconate is employed to suppress degradation of the absorption property during the absorption–emission cycle [11].

The weight increase of pellets due to CO_2 absorption was measured by using a thermogravimetric instrument (TG: TG-DTA2500, MAC Science Co. Ltd., Japan) in a controlled gas flowing environment. The initial weight of the pellet, placed in the instrument, was approximately 60 mg. N_2 gas and CO_2 gas balanced by air (CO_2/Air = 5, 10, 15 vol%) or 100% CO_2 gas was introduced from a gas cylinder, controlled by a gas flow meter and needle valve to keep the gas flow rate at 300 cc/min at atmospheric pressure. Prior to CO_2 absorption testing, samples were preconditioned and dried in flowing N_2 by elevating the sample to the absorption temperature (at 30 °C/min), which was selected in the range between 400 and 700 °C, and held for 20 min. Then, the flowing gas was changed to CO_2-containing gas. The weight increase due to CO_2 absorption was measured as a function of time at a constant temperature and constant concentration of CO_2 during 1 hr.

The CO_2 absorption capacity for the pellets was evaluated by heating a pellet at 5 °C/min in a gas flowing condition of 100% CO_2 until it showed a weight decrease due to CO_2 emission. It was 32.4 wt% and different from the capacity of pure Li_4SiO_4, which was

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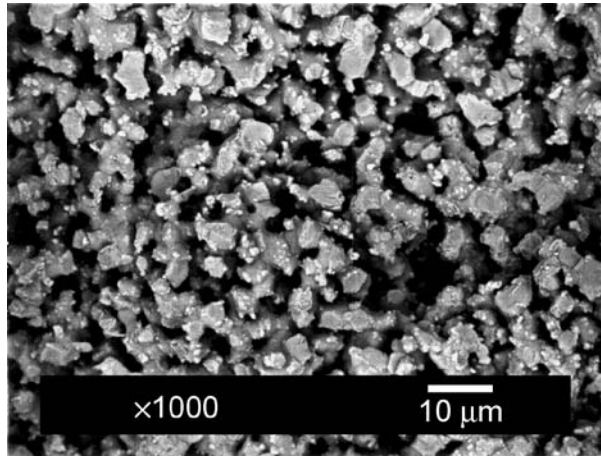
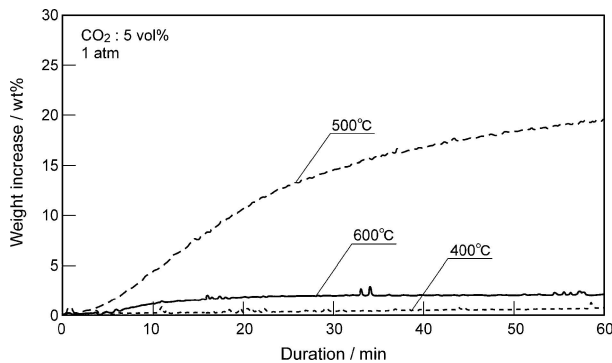*Figure 1*   SEM micrograph of the sphere-type lithium silicate pellet.

Figure 2   Weight increases of the Li_4SiO_4 pellet in 5 vol% CO_2.

Figure 3   Weight increases of the Li_4SiO_4 pellet in 10 vol% CO_2.
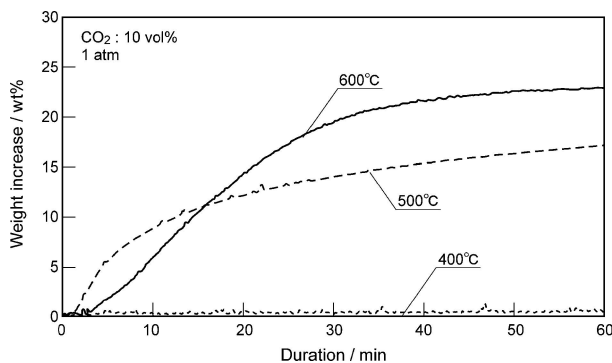

Figure 4   Weight increases of the Li_4SiO_4 pellet in 15 vol% CO_2.

calculated to be 36.7 wt% on the basis of Equation 2. This is thought to be due to some additives in the pellet. In this measurement, the emission temperature was similar to the temperature calculated on the basis of thermodynamic data [12], 720 °C.

In order to establish the influence of temperature on CO_2 absorption by Li_4SiO_4 pellets, detailed absorption properties of the pellets were investigated at 400, 500, and 600 °C. Considering practical applications, for example, in which CO_2 is removed from the gasification process of coal, the targeted CO_2 concentrations in this test were 10 and 15 vol%. In this case, the property in diluted CO_2, for example, 5 vol%, should also be acquired, because the concentration of flowing gas becomes lower along apparatus that contain packed pellet beds. Figs 2–4 illustrate the weight increases of the pellet due to CO_2 absorption for gas flow conditions of 5,
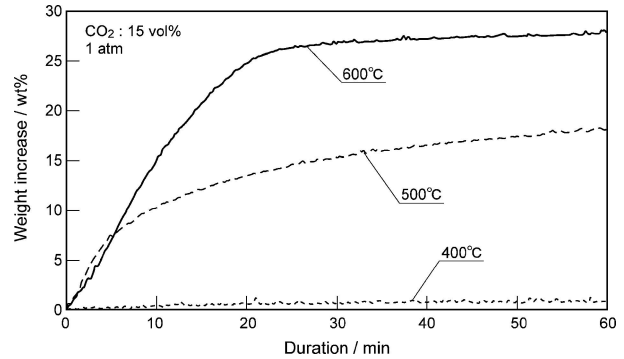
10, and 15 vol% CO_2, respectively. For all cases the amount of CO_2 absorption in 1 hr was lower than the capacity of the pellet. This is thought to be because of lower reactivity due to the diluted CO_2 atmosphere. From these figures, it was found that the absorption property changed drastically depending on the absorption temperature. At 400 °C, a very small amount of absorption was observed for every CO_2 concentration. The kinetics of this temperature seems too slow to show an obvious absorbing reaction. For 5 vol% CO_2, the amount of absorption in 60 min became larger with temperature increase from 400 to 500 °C; however, it became smaller with temperature increase from 500 to 600 °C. From the viewpoint of kinetics, absorption property should be higher with temperature increase. However, from the viewpoint of equilibrium, it should be lower since CO_2 absorption is an exothermic reaction and it is reported to decrease at the temperature close to emission temperature [13]. Therefore, drastic decrease of absorption property for 5 vol% CO_2 at 600 °C is ascribed to the influence of equilibrium. On the other hand, for 10 and 15 vol% CO_2, absorption property became larger with temperature increase and no decrease of it at 600 °C was observed. This is also ascribed to the influence of equilibrium, since the emission temperature on the equilibrium depends on CO_2 partial pressure and for 10 and 15 vol% CO_2, it is higher than that for 5 vol% CO_2.

It is obvious that temperature is one of the most significant conditions for the operation of practical apparatus. Therefore, an attempt was made to express the variation in the absorption property with temperature more clearly by evaluating the property over a wider temperature range from 400 to 700 °C with a smaller temperature interval for every 50 °C. The CO_2 concentration was fixed at 10 vol%, which is a typical value. Fig. 3 showed that the absorption temperature, where the largest amount of CO_2 absorption was obtained, changed depending on the duration. The weight increase in 15 min and that in 60 min from the start are illustrated in Fig. 5. The increase in 15 min showed the maximum value at 550 °C, whereas that in 60 min showed it at 600 °C. Furthermore, it was revealed that at temperatures higher than 600 °C, the value of the weight increase suddenly decreased and only a very small amount of absorption was observed. Consequently, it was confirmed that the temperature range that showed the highest value for the absorption
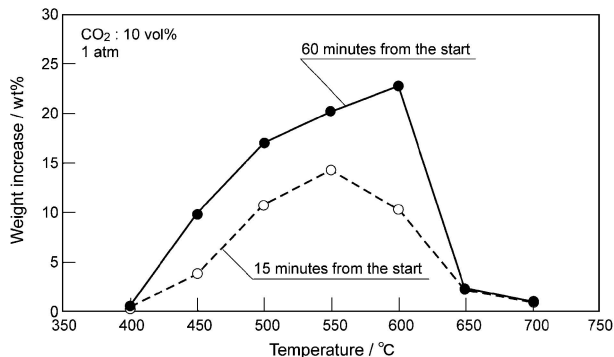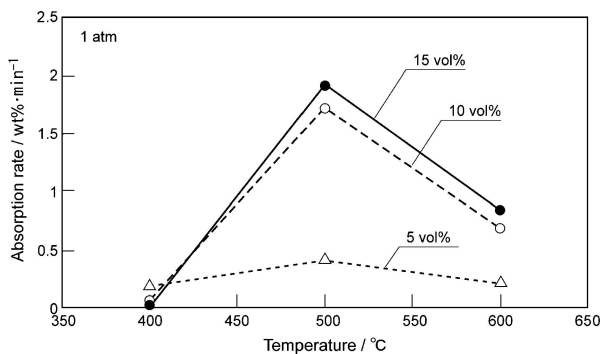
Figure 5 Weight increase in 10 vol% CO_2..

Figure 6 Influence of CO_2 concentration on absorption rate.

rate was limited. This result suggests that the absorption temperature should be controlled carefully in practical apparatus.

As the absorption proceeds, the absorption rate, i.e., the weight increase due to CO_2 absorption within a certain unit-time, is considered to be influenced by morphological change in the pellet due to formation of the products, which results in the difference in CO_2 diffusion [11]. In order to reveal the CO_2 absorption property of Li_4SiO_4 primary particles that form pellets, the initial absorption rate in 1 min from the start was investigated. As shown in Fig. 6, the absorption rate had a maximum value at around 500 °C for any CO_2 concentration. In addition, at 500 °C an obvious difference between the rate for 5 vol% CO_2 and that for 10 vol% CO_2 was observed, whereas little difference between the rate for 10 vol% CO_2 and that for 15 vol% CO_2 was observed. It is clear that the initial rate-determining step for higher CO_2 concentrations (from 10 to 15 vol%) and that for lower concentrations (around 5 vol%) were different. For higher concentrations of CO_2, the rate-determining step is considered to be the diffusion of Li_2O to the surface of the pellet, because the CO_2 concentration does not affect the absorption rate in this case [14]. However, for lower CO_2

concentrations, the rate-determining step is considered to be the surface reaction of Li_4SiO_4 with CO_2. This is a solid–gas reaction and the CO_2 concentration strongly affects the absorption rate.

From the results of this study, the following conclusions were reached.

1. The CO_2 absorption property of Li_4SiO_4 pellets is strongly affected by the absorption temperature.

2. For 10 vol% CO_2, the temperature between 550 and 600 °C showed the fastest CO_2 absorption. On the other hand, only a very small amount of CO_2 absorption was observed at temperatures higher than 600 °C.

3. The initial rate-determining step changed depending on the CO_2 concentration.

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