Absorption of Carbon Dioxide at High Temperature with Molten Alkali Carbonate Using Bubble Column Reactor

Yugo KANAI1, Koichi TERASAKA2, Satoko FUJIOKA2 and Kenichiro FUKUNAGA3

1Department of Chemical Engineering, Fukuoka University, 8-19-1 Nanakuma, Jonan-ku, Fukuoka-shi, Fukuoka 814-0180, Japan
2Department of Applied Chemistry, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama-shi, Kanagawa 223-8522, Japan
3School of Science for Open and Environmental Systems, Graduate School of Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama-shi, Kanagawa 223-8522, Japan

Keywords: CO2 Absorption, Molten Salt, Molten Alkali Carbonate, Bubble Column, High Temperature

The purpose of this study is to examine the possibility of establishing a novel CO2 absorption process with molten alkali carbonate using a bubble column reactor. In our previous study, a hot CO2 recovery process using Li4SiO4 suspended in molten Li2CO3–K2CO3 was developed. In the process, molten alkali carbonate itself showed great potential for CO2 absorption at high temperature. If a hot CO2 absorption process were established using only molten alkali carbonate, it could make the system simpler and the operating temperature range could be extended without the limitation of reaction temperature of solid absorbent. In the study, molten Li2CO3, Na2CO3, K2CO3 and its eutectic mixture were selected as CO2 absorbent. A bubble column was chosen as the device for gas absorption at high temperature. First, the CO2 absorption performance of each single molten alkali carbonate was investigated. The result showed that the molten Li2CO3 had a great ability to absorb CO2 at high temperature. Li2O was thought to be produced by decomposition of Li2CO3 during the melting and purging process and a reaction of CO2 with Li2O occurred during the absorption process. Further, the CO2 absorption performance of the bubble column was investigated and the experimental results showed that the mass transfer of CO2 into molten Li2CO3 was the rate-controlling step. The operational conditions of the bubble column were optimized. The superficial gas velocity was an important operational parameter that affected both the CO2 absorption rate and total amount of CO2 finally absorbed in the bubble column. The operating temperature also greatly affected the amount of absorbed CO2.

Introduction

In order to prevent greenhouse gas (GHG) emissions, CO2 capture and storage (CCS) has been considered an important technology (Abanades et al., 2015). Furthermore, CO2 capture and utilization (CCU) have attracted attention. CCU is a recycling process where CO2 is considered as an essential carbon feedstock and the captured CO2 can be used for the production of value-added products. Two major technical approaches have been proposed in order to put CCU into practice. One approach is CO2 capture and conversion via electrolysis in molten salt (Wu et al., 2017). With the aid of eutectic salts electrolyte, CO2 can be captured and subsequently converted into solid carbon (Yin et al., 2013) and valuable chemicals of carbon nanomaterials (Ren et al., 2015). The other approach is high temperature and high efficiency CO2 capture using solid absorbents. Lithium-containing oxides such as Li2O (Mosqueda et al., 2006) and Li4SiO4 (Kato et al., 2005) were found to be high performance CO2 absorbents at high temperature. Some researchers confirmed that the CO2 absorption performance of those lithium oxides was enhanced in molten carbonate liquid phase. Deng et al. (2016) reported that the absorption performance of Li2O-containing Li–Na–K ternary molten carbonate was larger than that of solid Li2O. Kanai et al. (2012) also developed a high temperature CO2 capture process by suspending Li4SiO4 in Li–K binary molten carbonate. The captured high temperature CO2 is an ideal C1 feedstock that can be applied in synthesizing carbonaceous products.

In the process of developing a high temperature CO2 capture process using Li4SiO4 slurry, the authors found that molten alkali carbonate itself had a great potential for CO2 absorption at high temperature (Kanai et al., 2013). A eutectic mixture of Li2CO3–K2CO3 absorbed CO2 100 times more than other molten salt at high temperature. If a hot CO2 absorption process were established using only molten alkali carbonate, it could make the system simpler. Operation in a two-phase system is easier than a three-phase system when considering practical operation. Further, the operating temperature range would be extended. In a three-phase system, the operating temperature is restricted by the reaction...
temperature of solid absorbents. For example, Li$_2$SiO$_4$ reacts with CO$_2$ at 720°C, and thus the operating temperature of Li$_2$SiO$_4$ slurry is set at the limit to this temperature. On the other hand, the operating temperature of molten carbonates can be set freely above their melting point. Further, the melting point can be controlled by eutectic salt effects, mixing with other carbonate and varying the composition of eutectic mixture. Molten carbonate is stable relative to water and produces very little heat of reaction therewith. Further, molten carbonate can physically absorb SOX gas. Thus, it can overcome these impurity problems. However, when considering the application to CCS or CCU, it is desirable to apply to pre-combustion capture to obtain pure CO$_2$ gas.

In this study, the possibility of establishing a novel CO$_2$ absorption process using molten alkali carbonate was examined. Li$_2$CO$_3$, Na$_2$CO$_3$, K$_2$CO$_3$ and its eutectic mixture were selected as candidates for CO$_2$ absorbent at high temperature. From the viewpoint of chemical engineering, the configuration of the gas absorption device is also important. A bubble column was chosen as the device for gas absorption. Bubble columns are superior in heat and mass transfer, compactness, low maintenance and operating cost. Therefore, they are suitable for the high temperature operation using molten carbonates. The industrial design of reactor was carefully proposed taking into consideration the huge pressure drop. First, the CO$_2$ absorption performances of single molten Li$_2$CO$_3$, Na$_2$CO$_3$, K$_2$CO$_3$ and its eutectic mixture were selected as candidates for CO$_2$ absorbent at high temperature. From the viewpoint of chemical engineering, the configuration of the gas absorption device is also important. A bubble column was chosen as the device for gas absorption. Bubble columns are superior in heat and mass transfer, compactness, low maintenance and operating cost. Therefore, they are suitable for the high temperature operation using molten carbonates. The industrial design of reactor was carefully proposed taking into consideration the huge pressure drop. First, the CO$_2$ absorption performances of single molten Li$_2$CO$_3$, Na$_2$CO$_3$, K$_2$CO$_3$ and its eutectic mixture were investigated. Although many studies have been carried out concerning Li–K binary molten carbonate and Li–K–Na ternary molten carbonates, the CO$_2$ absorption performances of each single molten alkali carbonate have not yet been studied. Further, the understanding of the contribution of each component in the eutectic mixture is also important.

Second, the possibility of establishing a CO$_2$ absorption process using molten Li$_2$CO$_3$ was examined since Li$_2$CO$_3$ showed a unique CO$_2$ absorption performance among these alkali carbonates. To begin with, the overall CO$_2$ absorption process in a bubble column and rate-controlling step in the absorption process were examined. The estimation of the rate-controlling step is essential for scale-up of the device. Then, the effects of two important parameters in the bubble column, superficial velocity and temperature, on the amount of absorbed CO$_2$ were studied to optimize the operation of the bubble column. Finally, it was confirmed whether the regeneration of the absorbent was possible by a simple stripping operation. For an industrial application, the regeneration of the absorbent and cycling stability of the process is important for continuous operation.

Li–K binary molten carbonate and Li–K–Na ternary molten carbonates have recently received much attention as liquid phase with remarkable physical and chemical properties. Many studies have been carried out concerning the physical properties (Corradini et al., 2016), stability (Kaplan et al., 2011), and electrochemical behavior (Ijije et al., 2014a). The chemical interactions between CO$_2$ and molten alkali carbonates (Ijije et al., 2014b) and CO$_2$ solubility in equilibrium (Claes et al., 1996, 1999) were studied eagerly. However, there are few studies examining the possibility of establishing a CO$_2$ absorption process in a practical gas absorption device and considering scale up for industrial application. The results obtained in this study could provide further insight about the CO$_2$ absorption performance of molten alkali carbonate in practical gas absorption device.

1. Materials and Methods

1.1 Preparation of carbonate

Li$_2$CO$_3$ (99.0% purity, Wako Pure Chemical Industries, Ltd.), Na$_2$CO$_3$ (99.5% purity, Wako Pure Chemical Industries, Ltd.), K$_2$CO$_3$ (99.5% purity, Wako Pure Chemical Industries, Ltd.) and its eutectic mixture were used for CO$_2$ absorbent in the bubble column. A predetermined amount of carbonate was measured using an electronic balance.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Molten Carbonate</th>
<th>Composition [mol%]</th>
<th>Height of liquid [cm]</th>
<th>Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ absorption in single molten carbonate</td>
<td>Li$_2$CO$_3$, Na$_2$CO$_3$, K$_2$CO$_3$</td>
<td>100</td>
<td>10</td>
<td>950</td>
</tr>
<tr>
<td>CO$_2$ absorption in eutectic mixture</td>
<td>Li$_2$CO$_3$–Na$_2$CO$_3$, Li$_2$CO$_3$–K$_2$CO$_3$</td>
<td>(24, 48, 74, 87), (19, 38, 50, 70, 84, 90)</td>
<td>10</td>
<td>950</td>
</tr>
<tr>
<td>CO$_2$ absorption process using Li$_2$CO$_3$</td>
<td>Li$_2$CO$_3$</td>
<td>100</td>
<td>10</td>
<td>750, 800, 850, 900, 950</td>
</tr>
</tbody>
</table>

Fig. 1 Schematic of setup of bubble column reactor
The loaded amount of carbonate was determined to make the height of the liquid even in bubble column, i.e., it was decided to equal the volume of molten carbonates after melting. The height of liquid in the bubble column was fixed at 10 cm (e.g., it corresponds to 145 g of Li$_2$CO$_3$ at 950°C). The carbonates were prepared in a dry oven at 100°C for a day. Table 1 shows a summary of the experimental conditions of molten carbonates used in the study.

### 1.2 Setup of bubble column

Figure 1 shows the schematic of setup of the bubble column reactor. The red arrows show the gas flow. CO$_2$ and N$_2$ gas were fed from cylinders. The flow rates of feed gases were controlled by mass flow controllers (Model-3660, Kofloc Co., Ltd.). Ball valves were located behind the mass flow controller so as to switch instantly the gaseous species. A pre-heater was put in front of the bubble column in order to heat the feed gas up to the absorption temperature. It was a stainless cylindrical vessel filled with Raschig rings. The vessel was heated using a circular electric furnace (ARF-50KC, Asahi Rika Seisakusho Co., Ltd.) and the temperature of the furnace was controlled via thermal regulators (AMF-2P, Asahi Rika Seisakusho Co., Ltd.). The pre-heated gas was blown into the bubble column through a single nozzle made of SUS-316 L with an inner diameter of 0.54 cm. The bubble column reactor was prepared from stainless steel SUS-316 L. The inner diameter and the height of the bubble column were 3.1 cm and 40 cm, respectively. The bubble column was heated using a circular electric furnace (ARF-50KC, Asahi Rika Seisakusho Co., Ltd.) and the temperature of the furnace was controlled via thermal regulators (AMF-2P, Asahi Rika Seisakusho Co., Ltd.). The temperature in the bubble column was measured via a type-K thermocouple (SCHS-0, Nikkato Co., Ltd.). The outlet for exhausted gas was located in the canopy of the column. The flow rate of the exhausted gas was measured by a mass flow meter (Model-3810S, Kofloc Co., Ltd.). The CO$_2$ concentration in the exhausted gas was measured by an infrared CO$_2$ detector (GMT221, Vaisala Co., Ltd.). The temperature in the bubble column, the mass flow rate and the CO$_2$ concentration in exhausted gas were recorded simultaneously by a data logger (NR2000, Keyence Corp.).

### 1.3 CO$_2$ absorption measurement

Figure 2 shows the scheme of the experimental procedure. First, a specified amount of carbonate was loaded into the bubble column, and then the bubble column was set into the electric furnace. The temperature of the furnace rose to a specified operating temperature with a heating rate of 15°C/min. The temperature was fixed at the same temperature during the purging, absorption and stripping process. Only during experiment were the purging and stripping temperature varied to study the effect of temperature on regeneration of absorbent. The carbonate was heated in an air atmosphere until the carbonate melted completely. After the confirmation of the melting, the canopy of the bubble column was tightened and the nozzle was inserted into the molten carbonate. All gas paths were connected and 100 mol% N$_2$ gas was fed to the bubble column. The N$_2$ gas was used for purging all CO$_2$ gas absorbed during the melting process and to make a CO$_2$ free condition in the bubble column. The feed of N$_2$ gas continued until the CO$_2$ concentration in the exhaust gas became zero. The temperature of molten carbonates was confirmed by the thermocouple and after the temperature was stabilized, the CO$_2$ absorption measurement was carried out. The CO$_2$ concentration in feed gas was set at 20 mol%. The superficial gas velocity in the bubble column, $U_G$, was fixed at $U_G = 0.662$ cm/s unless stated otherwise. The CO$_2$ absorption was continued until the absorption finished completely. The CO$_2$ absorption rate $r$ mg/min was calculated from the CO$_2$ mass balance between the feed and exhaust gases. The total amount of absorbed CO$_2$ per unit mass of molten carbonate $q$ mg CO$_2$/g molten carbonate was calculated by the integral of the CO$_2$ absorption rate over absorption time. Stripping of absorbed CO$_2$ gas was carried out by 100 mol% N$_2$ gas for 100 min. The amount of stripped CO$_2$ gas was also measured to confirm whether it equaled the amount of absorbed CO$_2$ gas. A second CO$_2$ absorption measurement was performed as necessary.

### 2. Results and Discussion

#### 2.1 Investigation of CO$_2$ absorption performance of molten alkali carbonate in bubble column

CO$_2$ absorption performances of a single molten Li$_2$CO$_3$, Na$_2$CO$_3$ and K$_2$CO$_3$ in the bubble column were investigated and then, CO$_2$ absorption in eutectic mixtures of Li$_2$CO$_3$–
Na₂CO₃ and Li₂CO₃–K₂CO₃ were studied varying the composition of mixture.

### 2.1.1 CO₂ absorption in single molten alkali carbonate

First, the CO₂ absorption performances of molten Li₂CO₃, Na₂CO₃, and K₂CO₃ were studied. Table 2 shows a summary of the melting point of each carbonate. The operation temperature was fixed at 950°C for stable operation in the liquid phase. The amount of CO₂ absorbed per unit mass of molten carbonate, \( q \), was investigated.

Figure 3 shows the result of \( q \) in each single molten alkali carbonate. The result shows that molten Li₂CO₃ has a great capacity to absorb CO₂ gas at high temperature. The amount of CO₂ absorbed in Li₂CO₃ was about 50 times more than the other two carbonates. It was reported that CO₂ solubility in Na₂CO₃–K₂CO₃ (58:42 mol%) at 800°C was 3.24 mg/g (Claes et al., 1996) and in Li₂CO₃–K₂CO₃ (38:62 mol%) at 863°C was 5.45 mg/g (Kanai et al., 2013). The results of \( q \) in Na₂CO₃ and K₂CO₃ at 950°C were values close to those solubility studies. On the other hand, the result of \( q \) in Li₂CO₃ showed the outstanding value. The value was on the same order as the amount of CO₂ absorbed by solid lithium-containing oxides absorbent, e.g., 367 mg/g by Li₄SiO₄.

In order to profoundly understand this unique result obtained in Li₂CO₃ molten carbonate, time-series data of CO₂ absorption rate \( r \) and temperature \( T \) in the bubble column were examined. Figures 4–6 show the variation of \( r \) and \( T \) in each single molten carbonate. The single molten Li₂CO₃ showed a unique result in both variations of \( r \) and \( T \). Considering the variation of \( r \), the CO₂ absorption in Na₂CO₃ and K₂CO₃ ended in 5 min. On the other hand, the CO₂ absorption in Li₂CO₃ continued for 200 min. Considering the variation of \( T \), the temperatures of molten Na₂CO₃ and K₂CO₃ remained constant during CO₂ absorption. In contrast, the temperature of molten Li₂CO₃ increased immediately with a start of CO₂ absorption. Further, the variation of \( T \) corresponded to the variation of \( r \), i.e., the temperature remained high as long as the CO₂ absorption rate took a large value and the temperature started to decrease at the same time with decreasing the CO₂ absorption rate. These results suggested that a simple physical absorption of CO₂ occurred.
in molten Na\textsubscript{2}CO\textsubscript{3} and K\textsubscript{2}CO\textsubscript{3}. On the other hand, it suggested that a chemical absorption accompanying exothermic reaction occurred in molten Li\textsubscript{2}CO\textsubscript{3}.

The Li\textsubscript{2}CO\textsubscript{3} melts into molten carbonates at around 720°C. Further, it was well known that molten Li\textsubscript{2}CO\textsubscript{3} decomposes into Li\textsubscript{2}O and CO\textsubscript{2} according to the following equation.

\[ \text{Li}_2\text{CO}_3 \rightarrow \text{Li}_2\text{O} + \text{CO}_2 \] (1)

The decomposition of molten Li\textsubscript{2}CO\textsubscript{3} strongly depends on the pressure of CO\textsubscript{2} above the melt. Yamauchi et al. (2006) reported that in 100 mol% CO\textsubscript{2} atmospheres, the decomposition of molten Li\textsubscript{2}CO\textsubscript{3} was not observed up to 1000°C. However, in synthetic air, the decomposition started from the melting point at 710°C and completed at 820°C. Kaplan et al. (2010) also reported that complete decomposition of molten Li\textsubscript{2}CO\textsubscript{3} occurred at temperatures lower than 900°C in continuous air flow, which removes CO\textsubscript{2} as it is produced. The large values of an equilibrium dissociation pressure, P\textsubscript{CO2}, of molten Li\textsubscript{2}CO\textsubscript{3} have been reported by several researchers, e.g., 6.7×10\textsuperscript{4} Pa at 843°C (Janz and Lorenz, 1964).

In this experiment, Li\textsubscript{2}CO\textsubscript{3} was heated at 950°C in exposure to air. Further, the subsequent purging process was carried out in a less than 100 mol% N\textsubscript{2} atmosphere. Therefore, it was considered that Li\textsubscript{2}O was produced during this melting and purging process. Figure 7 shows the phase diagram of Li\textsubscript{2}CO\textsubscript{3}–Li\textsubscript{2}O (Bazhenov et al., 2010). It shows the ratio of Li\textsubscript{2}O dissolved in the melts at different temperatures. The solubility at 950°C is 28 mol%. Therefore, upon heating, Li\textsubscript{2}CO\textsubscript{3} is converted into a solution of Li\textsubscript{2}O. Subsequently, the solid Li\textsubscript{2}O particles accumulate in the melt.

During CO\textsubscript{2} absorption measurement, the produced Li\textsubscript{2}O in molten Li\textsubscript{2}CO\textsubscript{3} reacted with CO\textsubscript{2} as the reverse reaction of Eq. (1).

\[ \text{Li}_2\text{O} + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 \] (2)

This reaction is known as an exothermic reaction. Therefore, the observed temperature increase in molten Li\textsubscript{2}CO\textsubscript{3} was thought to be caused by the heat production from the reaction of Li\textsubscript{2}O with CO\textsubscript{2}.

As compared with molten Li\textsubscript{2}CO\textsubscript{3}, the decomposition of molten Na\textsubscript{2}CO\textsubscript{3} and K\textsubscript{2}CO\textsubscript{3} hardly occurs. Janz and Lorenz (1964) reported that P\textsubscript{CO2} of Na\textsubscript{2}CO\textsubscript{3} was 2.0×10\textsuperscript{3} Pa at 885°C. Spedding and Mills (1965) reported that P\textsubscript{CO2} of Na\textsubscript{2}CO\textsubscript{3} was 1.2×10\textsuperscript{3} Pa at 950°C. These values were about a hundredth lower than P\textsubscript{CO2} of Li\textsubscript{2}CO\textsubscript{3}. Thus, the decomposition of carbonate did not occur in Na\textsubscript{2}CO\textsubscript{3} and K\textsubscript{2}CO\textsubscript{3} and CO\textsubscript{2} was absorbed in the molten carbonates by a simple physical absorption.

2.1.2 CO\textsubscript{2} absorption in eutectic mixture Second, CO\textsubscript{2} absorption performances in eutectic mixtures of Li\textsubscript{2}CO\textsubscript{3}–Na\textsubscript{2}CO\textsubscript{3} and Li\textsubscript{2}CO\textsubscript{3}–K\textsubscript{2}CO\textsubscript{3} were studied varying the composition of mixture. The operation temperature was fixed at 950°C. The amount of CO\textsubscript{2} absorbed per unit mass of molten carbonate \( q \) and a variation of temperature \( T \) in the bubble column were investigated.

Figure 8 shows the result of the amount of CO\textsubscript{2} absorbed, \( q \), for each composition of eutectic mixture. The \( q \) increased exponentially with increasing the composition of Li\textsubscript{2}CO\textsubscript{3}. In particular, \( q \) increased sharply from where it was beyond 75 mol% in the composition of Li\textsubscript{2}CO\textsubscript{3}.

Figure 9 shows the variation of \( T \) in the Li\textsubscript{2}CO\textsubscript{3}–Na\textsubscript{2}CO\textsubscript{3}
eutectic mixture during CO₂ absorption. The end of each line represents the end of CO₂ absorption time. The result shows that the temperature of eutectic mixture increased during CO₂ absorption. The more the composition of Li₂CO₃ increased, the more the temperature rose. On the other hand, in the composition under 25 mol%, a rise in temperature hardly occurred. Further, the more the composition of Li₂CO₃ increased, the longer CO₂ absorption continued.

The results suggested that the decomposition of Li₂CO₃ occurred also in eutectic mixture during the melting and purging process. Li₂O produced by the decomposition increased with increasing the composition of Li₂CO₃ in the eutectic mixture. The q was considered to increase with increasing the Li₂O in the eutectic mixture. Looking from another perspective, the decomposition of Li₂CO₃ was thought to be reduced by mixing with other carbonates. Figure 10 shows the equilibrium dissociation pressure, P_{CO₂}, of each molten carbonate reported in a previous study (Janz and Lorenz, 1964; Spedding and Mills, 1965). They reported that the P_{CO₂} decreased largely by mixing Li₂CO₃ with Na₂CO₃ and K₂CO₃. This knowledge about dissociation pressure also suggested that decomposition of Li₂CO₃ reduced by mixing with other carbonates. By mixing with another carbonate, the melting temperature of Li₂CO₃ decreased by the eutectic salt effect and made possible to operate the bubble column at lower temperature than the melting point. On the other hand, it was found that the amount of absorbed CO₂ decreased by mixing with another carbonate.

Comparing the CO₂ absorption performance between Li₂CO₃–Na₂CO₃ and Li₂CO₃–K₂CO₃, there was no difference between two eutectic mixtures at the condition where the composition of Li₂CO₃ was high. It was supposed that chemical absorption of CO₂ by Li₂O produced by the decomposition of Li₂CO₃ was dominant in the overall absorption at this condition. Therefore, differences between Na₂CO₃ and K₂CO₃ did not appear. On the other hand, at the condition where the composition of Li₂CO₃ was low, the Li₂CO₃–Na₂CO₃ eutectic mixture absorbed more CO₂ than Li₂CO₃–K₂CO₃ eutectic mixture. As shown in Figure 2, Na₂CO₃ molten carbonate physically absorbed more CO₂ than K₂CO₃ molten carbonate. This difference of performance in physical absorption leads to the difference of the result in eutectic mixture.

2.2 Examination of the possibility of establishing CO₂ absorption process using Li₂CO₃ Molten Li₂CO₃ showed a unique CO₂ absorption performance due to its decomposition characteristic. Using the characteristic, a continuous CO₂ absorptions process is able to be realized. Thus, the possibility of establishing a CO₂ absorption process using Li₂CO₃ was examined. Figure 11 shows the presumed scheme of phase change of Li₂CO₃. It is not entirely a two-phase system initially designed since solid Li₂O is produced in molten Li₂CO₃ in the process. However, it is a simple system using only Li₂CO₃ and the continuous operation is possible to control a CO₂ concentration above the melt temperature.

Figure 12 shows an industrial design for a bubble column reactor. The inside of this air lift bubble column reactor is divided into reaction and decomposition chambers by a partition. When considering the application to the CCS or CCU, pure CO₂ gas should be captured. Thus, it is desirable to carry out the decomposition process by the temperature control using waste heat. Some researchers (Yamauchi et al., 2006; Kaplan et al., 2010) reported that the decomposition of Li₂CO₃ occurs even in 100 mol% CO₂ atmospheres by increasing the temperature. The melts circulate between two chambers by the density difference without mechanical power and continuous CO₂ capture is feasible in a single column. The bubble column is suitable taking the high corrosiveness of molten salt into consideration. On the other hand, at the commercial scale, the huge pressure drop will become a problem. Therefore, it is necessary to carefully choose the industrial design of the reactor. The proposed air lift reactor excelsences superior in operational cost and recovery efficiency. It enables downsizing of the bubble column.

First, the overall CO₂ absorption process in the bubble column and rate-controlling step in the absorption process were examined. Second, the effects of operational conditions on the amount of absorbed CO₂ in the bubble column were studied. The effects of two important operational parameters in the bubble column, superficial velocity and temperature, were considered. Finally, it was confirmed whether the regeneration of the absorbent was possible by simple stripping operation. The repeatability of CO₂ absorption performance in the second cycle after the regeneration of absorbent was investigated.

2.2.1 Examination of overall CO₂ absorption process and rate-controlling step First, the overall CO₂ absorption process in the bubble column and rate-controlling step in the absorption process were examined. Figure 13 shows the scheme of the overall absorption process. The overall CO₂ absorption process consists of two steps, i.e., mass transfer of CO₂ into molten Li₂CO₃ and chemical reaction of CO₂.
with Li₂O particle. In the mass transfer step, the CO₂ dissolves from a bubble into molten Li₂CO₃ and transfers to the surface of Li₂O particle. In the chemical reaction step, the CO₂ reacts with Li₂O at the reactive interface of the particles. Some circumstances of the process suggest that mass transfer is the rate-controlling step: The reaction is carried out at high temperature where reaction occurs at a high reaction rate and the reaction of Li₂O with CO₂ is a first order reaction (Mosqueda et al., 2006). In order to confirm the rate-controlling step of the process, the CO₂ absorption measurement was carried out varying the superficial gas velocity \( U_G \) in the bubble column. Figure 14 shows the effects of \( U_G \) on overall CO₂ absorption rate \( r \). The \( r \) increased with increasing \( U_G \). The result shows that the reaction was accelerated by agitation in the column. The experimental result also indicates that mass transfer is the rate-controlling step. Here, the fact should be noted that some part of Li₂O is dissolved into molten Li₂CO₃ as shown in Figure 2. The dissolved Li₂O is dissociated into lithium cation (Li⁺) and oxide anion (O²⁻) in the melt, then CO₂ is absorbed by O²⁻ to form carbonate ion (CO₃²⁻). The CO₂ absorption occurs at the gas–liquid interface. Thus, mass transfer is also the rate-controlling step in this pathway.

The CO₂ mass transfer rate \( N \) from the bubble phase to liquid phase of molten Li₂CO₃ is expressed as the following equation. Here, \( k_L \) is the liquid film mass transfer coefficient, \( C_g \) is CO₂ concentration at the gas-liquid interface and \( C_L \) is CO₂ concentration in the liquid phase.
\[ N = k_L(C_i - C_L) \]  

(3)

It is considered that sufficient reactive interfaces of Li₂O particle are ensured. Fresh CO₂ gas is constantly supplied into the bubble column. Thus, it is presumed that the reaction of Li₂O with CO₂ is a first-order irreversible reaction governed by the concentration \( C_i \). The CO₂ chemical reaction rate \( v \) is expressed as the following equation.

\[ v = kC_L \]  

(4)

In the experimental set-up, the values of \( C_i \) and \( k \) are determined by trial and error to satisfy the following equation.

\[ \frac{dC_L}{dt} = N - v = k(C_i - C_L) - kC_L \]  

(5)

The values of \( C_i \) and \( k \) are determined by CO₂ physical absorption experiments into pure Li₂CO₃.

At the steady state, the value of \( N \) equals \( v \). Thus, the overall absorption rate is expressed as the following equation.

\[ N = v = \frac{C_i}{(1/k_L) + (1/k)} \]  

(6)

As the mass transfer is the rate-controlling step, the CO₂ absorption rate is finally given as the following equation.

\[ v = kC_i \]  

(7)

2.2.2 Effects of operational conditions on amount of absorbed CO₂ in bubble column

Second, the effects of operational conditions on the amount of absorbed CO₂ in the bubble column were studied. The CO₂ absorption performance is determined by not only the theoretical CO₂ absorption mechanism, but also the characteristics of the gas absorption device. The superficial velocity and temperature are important operational parameters of bubble columns and greatly affect the characteristic of device. Thus, their effects were investigated.

Figure 15 shows the effect of superficial gas velocity \( U_G \) on the amount of absorbed CO₂ \( q \). The results show that the \( q \) increased with increasing the \( U_G \). The CO₂ absorption rate \( r \) increased with increasing the \( U_G \) as shown in Figure 12. Moreover, the result shows that the total amount of CO₂ finally absorbed in the bubble column was also increased with increasing the \( U_G \). The \( q \) is thought to be determined by the amount of Li₂O reacting with CO₂ during the absorption process. Further, the amount of produced Li₂O is determined by the operational conditions in the melting and purging process. It increases the amount of produced Li₂O and \( q \) increases as a result. The result shows that \( q \) increased greatly by increasing \( U_G \). The effect of increasing \( q \) was mainly due to the increase of the amount of produced Li₂O since the ratio of unreacted Li₂O is considered to be a few %, at most. In our process using Li₂CO₃ in the bubble column, it was found that the superficial velocity was a very important parameter in two aspects. It increased the overall CO₂ absorption rate described in Eq. (7). In addition, it also increased the total amount of CO₂ finally absorbed in the bubble column.

Figure 16 shows the effect of operating temperature \( T \) on the amount of absorbed CO₂ \( q \). The results show that the \( q \) increased with increasing the \( T \). The \( q \) increased remarkably over 900°C. If the overall Li₂CO₃ loaded in the bubble column decomposed into Li₂O and all Li₂O reacted with CO₂, the stoichiometric value of \( q \) would be 596 mg CO₂ per 1 g molten carbonate. Therefore, the result shows that 34% of Li₂CO₃ decomposed into Li₂O at 950°C. On the other hand, at less than 900°C, only several percent of Li₂CO₃ decomposed. Kaplan et al. (2010) carried out thermodynamic analysis for 10 mg of Li₂CO₃ and it was found that complete decomposition of 10 mg of Li₂CO₃ occurred at the tempera-
use of the process, the absorption temperature is determined by the temperature of CO₂ containing flue gas. In the process using Li₂CO₃, it was able to increase the CO₂ absorption performance by varying the stripping temperature with fixing the absorption temperature on the target temperature.

**Conclusion**

The present study examined the possibility of establishing a novel CO₂ absorption process with molten alkali carbonate using a bubble column reactor. A series of CO₂ absorption measurements showed that molten Li₂CO₃ had great potential for CO₂ absorption at high temperature. The CO₂ absorption performance of eutectic mixture also increased exponentially with increasing the ratio of Li₂CO₃ in composition. The CO₂ absorption of molten Li₂CO₃ resulted from the production of Li₂O by decomposition of Li₂CO₃ during the melting and purging process. The produced Li₂O reacted with CO₂ during the absorption process. Utilizing the characteristic of molten Li₂CO₃, the possibility of establishing a CO₂ absorption process using molten Li₂CO₃ was examined. First, the overall CO₂ absorption process in a bubble column was investigated and the experimental results showed that mass transfer of CO₂ into molten Li₂CO₃ was a rate-controlling step. Second, the effects of operational conditions were studied and it was found that the superficial gas velocity was an important operational parameter that affected both the CO₂ absorption rate and total amount of CO₂ finally absorbed in the bubble column. The superficial gas velocity was supposed as influencing the decomposition of Li₂CO₃ during the purging process and flow pattern in the bubble column during absorption process. The operating temperature also greatly affected the amount of CO₂ absorbed since the decomposition characteristic depended on the temperature. Regeneration of absorbent was possible by a simple stripping process and CO₂ absorption performance was maintained after regeneration.

**Nomenclature**

\[
\begin{align*}
C_l & = \text{CO}_2 \text{ concentration in liquid phase} \quad [\text{mg/m}^3] \\
C_i & = \text{CO}_2 \text{ concentration at gas-liquid interface} \quad [\text{mg/m}^3] \\
k & = \text{reaction rate constant} \quad [\text{m/min}] \\
k_l & = \text{liquid film mass transfer coefficient} \quad [\text{m/min}] \\
N & = \text{mass transfer rate} \quad [\text{mg/m}^2\cdot\text{min}] \\
P_{CO_2} & = \text{equilibrium dissociation pressure} \quad [\text{Pa}] \\
q & = \text{amount of absorbed CO}_2 \text{ per unit mass of molten carbonate} \quad [\text{mg/g}] \\
r & = \text{CO}_2 \text{ absorption rate} \quad [\text{mg/min}] \\
T & = \text{temperature} \quad [\text{°C}] \\
t & = \text{arbitrary time} \quad [\text{min}] \\
U_G & = \text{superficial gas velocity} \quad [\text{cm/s}] \\
\nu & = \text{chemical reaction rate} \quad [\text{mg/m}^2\cdot\text{min}] 
\end{align*}
\]

**Literature Cited**


