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CO_2 capture system using lithium silicate for distributed power supply

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Abstract

Distributed power-supply systems have become more widespread recently. Recent distributed systems, such as fuel cells, offer high energy-use efficiency because they generate heat or hot water and electric power simultaneously. However, to avoid global warming, carbon dioxide (CO_2) from the exhaust gas has to be collected and separated, without emitting it to the atmosphere. We are investigating lithium silicate (Li_4SiO_4) (LS) because it has superior characteristics as a CO_2 absorber. Aiming at the construction of a CO_2 capture and separation system using LS, we are studying ways to process (capture and separate) the exhaust gas from distributed power-supply systems. We thought that the CO_2 capture and separate system we should design must process exhaust gases with 30% CO_2 concentration and 35 L/min flow rate and that it must capture and separate more than 50% of the CO_2 contained in the exhaust gases. However, as a result of a preliminary estimation, it became clear that the volume of the assumed CO_2 capture and separate system would be considerable. Therefore, we built a reduction model experimental setup with three reaction containers with three different aspect ratios. The results regarding container shape suggest that a long container would be advantageous..

Keywords: solid sorbent; lithium silicate; CO_2 capture; container shape; distributed power supply; exhaust gas

1. Introduction

Distributed power-supply systems are becoming more widespread recently. Recent distributed systems, such as the fuel cells, offer high energy-use efficiency because they generate heat or hot water, and electric power simultaneously. However, carbon dioxide (CO_2) emission control even for the distributed power sources will be required in order to reduce CO_2 emission and mitigate global warming in the near future. Carbon capture and separation (CCS) from the exhaust gas of distributed power sources

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is one of the key technologies and, various kinds of methods, such as physical adsorption, membrane separation, and chemical absorption, are expected to lead to CCS technology.

Meanwhile, in recent years, lithium composite oxides, such as Li_2ZrO_3, Li_4TiO_4, $LiFeO_2$ and Li_4SiO_4, which are the solid-state absorbents for chemical absorption, have been researched and developed. These materials can capture CO_2 from the exhaust gases from internal combustion engines and generators very effectively and regenerate repeatedly. Li_2ZrO_3 can be used at high temperatures, but it has problems in that it is heavy and costly because it uses expensive zirconia. Li_4TiO_4 is not suitable for repeated use by capture and separation because it is difficult to regenerate even at 1,000℃ (about 2-3% of absorbed CO_2). $LiFeO_2$ can absorbed at around 300-500℃, but the absorption capacity of lithium ferrite is limited to about 16% of its own weight. We selected lithium silicate (Li_4SiO_4) because of the following features. Lithium silicate (LS) can absorb CO_2 at around 500-600℃ and release it at 750 ℃ or higher and this temperature range is suitable for the CCS system of a distributed power source operated in the same temperature range, such as solid oxide fuel cells. Pure CO_2 can be obtained by swing operation of about 200℃. Moreover, LS has no less than 30% absorption capacity of its own weight. [1] -[9].

Aiming at the establishment of the CO_2 capture and separation system using LS, we are studying ways to process (capture and separate) the exhaust gas from distributed power-supply systems. In a reaction container of LS, the absorption reaction is activated as temperature rises, and the dissociative reaction of CO_2 finally occurs because equilibrium pressure is raised as temperature rises. When we compose a reactive container of the insulated filling layer, the reaction in the downstream part is strongly influenced by the reaction in the upstream part and the reactions will change in a container as time passes. Therefore, the influence of the cross-sectional diameter of the container and the aspect ratio in the direction of the flow on total CO_2 capture rate by the time-space integration is extremely large. However, such a research example is not so reported. In this research, we built an experimental setup in which the volume of the reaction container is 1/25 that of an actual reactor. We carried out reduction model experiments for absorption, regeneration, and re-absorption, aiming at obtaining the basic data for designing an actual CO_2 capture and separation system. In this report, we will describe our laboratory findings obtained for containers of different shape and discuss their implications.

2. Experimental method

2.1 Summary of experiments

The CCS we should design must be able to process exhaust gas with a 30% CO_2 concentration and 35 L/min flow rate. This is assumed to be the same condition as that of typical distributed power sources. Aiming at capturing and separating more than 50% of CO_2 in the exhaust, we made a rough estimate to decide the scale of the system. Here, the CO_2 recovery rate is defined by the ratio of the absorbed CO_2 to the total amount of CO_2 from the power source. As a result of a preliminary estimation, we found that the full-scale system of CCS requires about 11 L of packed bed reactor filled with LS and is too large to test directly. Then, using the result of a hydrodynamic calculation of the exhaust gas in the reaction container with a filling layer model and mass and heat balance calculation with chemical reaction, we built an experimental setup in which the volume of the reaction container is approximately 1/25 that of an actual reactor. This reduction model is convenient for setting the experimental conditions (temperature easily controlled with a small furnace, container size that is easy to handle, and so on). We carried out these reduction-model experiments to obtain basic data for designing an actual CO_2 capture and separation system.

2.2 Experimental setup

Figure 1 shows the experimental setup of this research. The container has a capacity of 440 mL and is filled with 190 g of LS. We sought to find a reaction container shape that would give the reaction conditions where the largest quantity of CO_2 is absorbed with high efficiency in the shortest time. Three types of containers packed with LS, each of which had a different aspect ratio between diameter and length, were prepared to obtain an optimized aspect ratio of the LS container and to evaluate the total CO_2 capture rate (Table 1).

Table 1. Dimensions of three reaction containers

Containers	Diameter × length (mm)	Volume (mL)
Long container	Φ69×117	437
Middle container	Φ108×48	439
Short container	Φ139×29	440

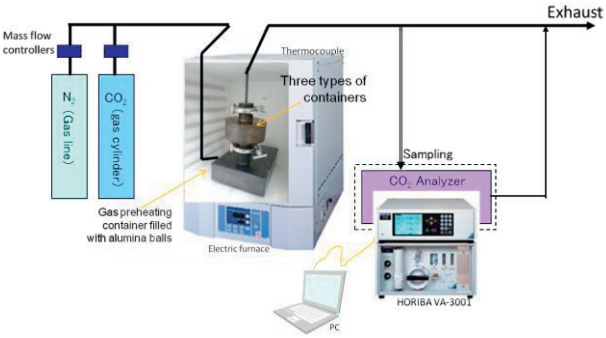
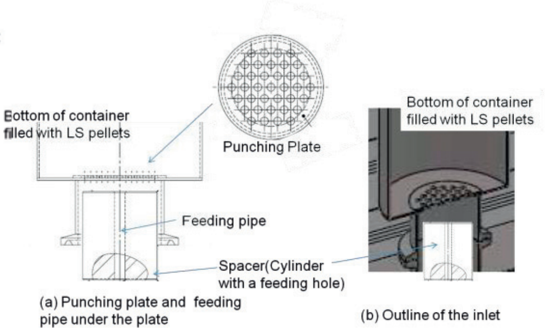


Fig. 1. Experimental setup.



(a) Punching plate and feeding pipe under the plate

(b) Outline of the inlet

Fig. 2. Gas inlet structure of the three containers.

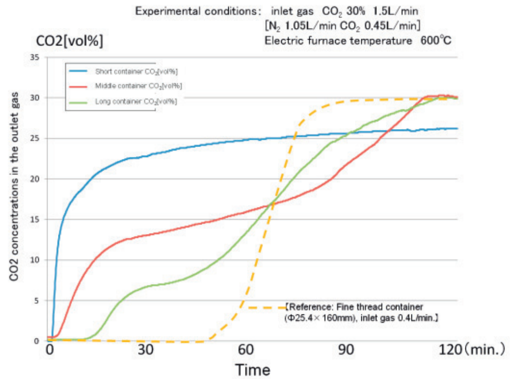
The three reaction containers were designed to make them exchangeable between inlet-and-outlet pipes in an electric furnace [between the gas preheating container and outlet pipe (the downstream)] and detachable. Figure 2 shows a cross-sectional view of the LS container. The simulated high-temperature exhaust gas (N_2-based supply gas) is supplied to the reactive container from the gas preheating container. A punching plate is welded to the bottom of the reactive container so that the pelletized LS (about Φ6.5 ×7 mm) would not fall, and the feeding pipe (air feeding pipe opening) is under the punching plate. The spaces between the punching plate [plate thickness 1.0mm; 37 holes (Φ3mm, 5-mm pitch, and 60-degree plover)] and the air feeding pipe opening are the Φ35×2.5mm. Gasket-less ferrules (NP ferrules) were welded to the containers and pipes so that the gas leakage would not occur by detaching the container. And we adopted a structure where the ferrules are united by clamping bands. One of the three types of containers (Table 1) and a gas preheating container (150×235×50mm), which was positioned at the lower position of the reaction container and filled with alumina balls to simulate high-temperature exhaust gas, were installed in a commercial electric furnace. The temperature (i.e, the reaction condition) was set by the heater of the furnace from outside the container (All heat sources were the heaters of the electric furnace). The simulated exhaust gas (N_2-based feeding gas) was heated to the same temperature as the exhaust gas from a distributed power-supply system. The feeding gas (simulated gas) was supplied to the reaction container and a small amount of sample gas was drawn from the outlet gas and the CO2 concentration in it was analyzed with an IR-CO_2 analyzer.

2.3 Absorption experiments

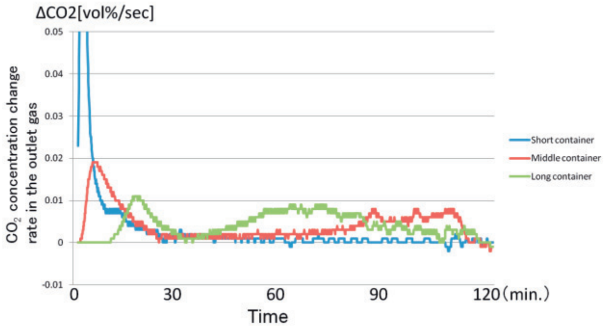
The conditions for the CO_2 absorption experiment were a 30% CO_2 feeding gas with a flow rate of 1.5L/min[CO_2 0.45 L/min、N_2 1.05 L/min] and furnace temperature of 600℃ while the three kinds of containers filled with LS were exchanged. At the beginning of the experiments, the feeding gas was started and then continued until the completion of absorption of CO_2 by the LS, about two hours. Before the experiment, N_2 gas flowed through the line while the temperature of the furnace was raised.

3. Experimental results and discussion

The three solid-line curves in Fig. 3(a), each show the change in CO_2 concentration in the outlet gas from the reaction container with time. These are the CO_2 concentrations observed in the outlet without absorption in the containers. Figure 3(b) shows the CO_2 concentration change rates in the outlet gas calculated from (a). This rate is related to the absorption velocity, that is, the CO_2 absorption change rate in the containers.



(a) CO_2 concentrations in the outlet with time.

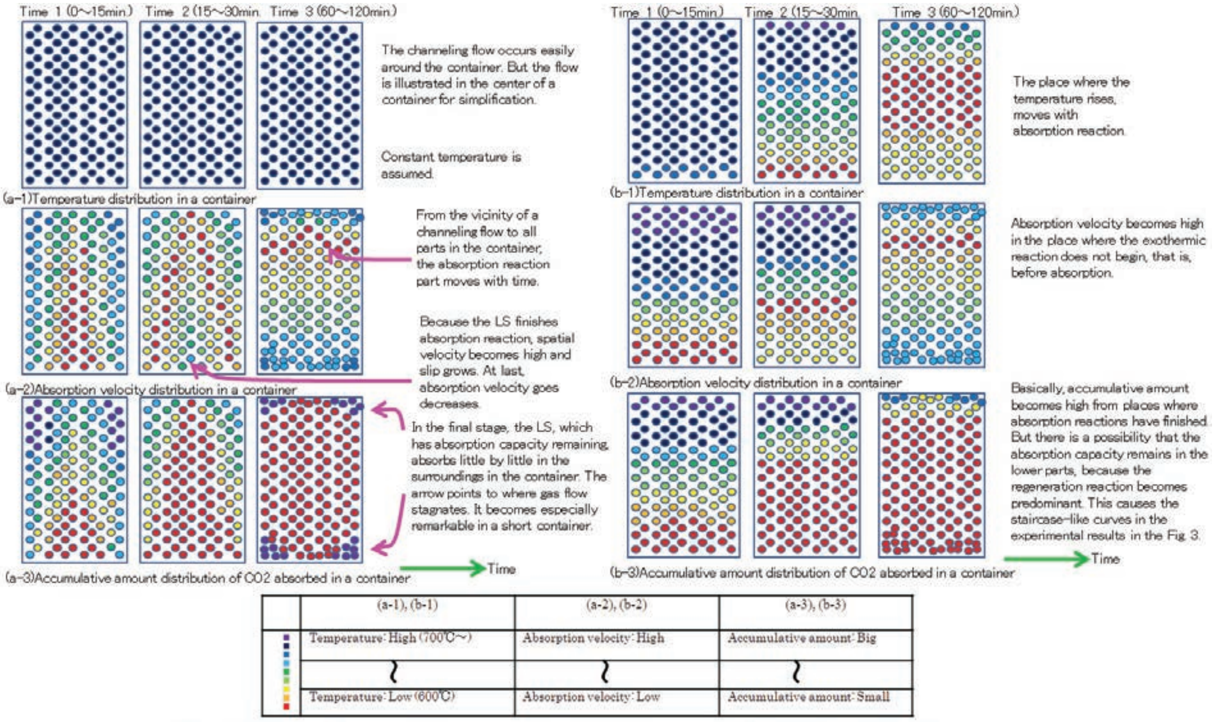


(b) CO_2 concentration change rate in the outlet gas with time.

Fig. 3. Results of absorption experiments.

First, from Fig. 3(a), one can see that the CO_2 concentration in the outlet gas increased to 20 to 25 % in the early stage of the experiment in the short container. In contrast, from the curve of the long container, it is understood that CO_2 is not seen in the outlet gas until about ten minutes after the start of the experiment. This is because the LS absorbed CO_2 well in the long container. From fifteen to thirty minutes after that, the CO_2 concentration rises. And after the CO_2 concentration curve becomes flat, the CO_2 concentration rises again from fifty minutes. These changes in Fig. 3(b) show that CO_2 absorption velocity in the long container slowed down once just after ten to thirty minutes and increased again after forty minutes. In contrast, the CO_2 concentration in the outlet gas increased to 20 to 25 % in the early stage of the experiment in the short container. It is thought there was no diffusion of CO_2 to the surrounding areas in the short container because, especially in a short container, feeding air is fed into the container at one point in the center at the bottom of the container. Therefore, in the early stage of the experiment, feeding gas makes a channeling flow (It doesn't become like the plug flow, and there is the lot of gas flowing around along stream lines where pressure loss is low. If the gas flows in the vicinity of container walls, pressure loss is low because the LS pellets are coarse.) at the early stage, and the CO_2 that is not absorbed by the LS goes out the outlet tube. The LS around the channeling flow absorbs CO_2 to full capacity early in the experiment. An intermediate response (of CO_2 concentration at the outlet) between that of the long container and short container is observed for the middle container.

There are two possible explanations for the staircase-like shape seen in the results for the middle and long containers as follows (see Figure 4).



The channeling flow occurs easily around the container. But the flow is illustrated in the center of a container for simplification.

Constant temperature is assumed.

From the vicinity of a channeling flow to all parts in the container, the absorption reaction part moves with time.

Because the LS finishes absorption reaction, spatial velocity becomes high and slip grows. At last, absorption velocity goes decreases.

In the final stage, the LS, which has absorption capacity remaining, absorbs little by little in the surroundings in the container. The arrow points to where gas flow stagnates. It becomes especially remarkable in a short container.

The place where the temperature rises, moves with absorption reaction.

Absorption velocity becomes high in the place where the exothermic reaction does not begin, that is, before absorption.

Basically, accumulative amount becomes high from places where absorption reactions have finished. But there is a possibility that the absorption capacity remains in the lower parts, because the regeneration reaction becomes predominant. This causes the staircase-like curves in the experimental results in the Fig 3.

	(a-1), (b-1)	(a-2), (b-2)	(a-3), (b-3)
	Temperature: High (700℃~)	Absorption velocity: High	Accumulative amount: Big
	≀	≀	≀
	Temperature: Low (600℃)	Absorption velocity: Low	Accumulative amount: Small

(a) First supposition **(b) Second supposition**

Fig. 4. Explanatory drawings for suppositions of fluid dynamics and chemical reactions in the containers.

The first assumes that the temperature inside the container (filling layer) is constant and the reaction is controlled by the supplied material (CO_2). In this case, the reason CO_2 is detected at the outlet of the container while the LS still has capacity for CO_2 absorption, would be a slip flow (CO_2 flows without making contact with the LS) in the container. Just after the beginning of feeding, the LS located around the stream line where the pressure loss lowers is reactive. (In Fig. 4(a), the stream line along the center axis in a reactive container is shown for simplification.) Next, the CO_2 concentration at the outlet of the container rises when the CO_2 reaches the outlet due to an increase of the amount of slip flows. In other words, the actual space velocity is increased by LS whose absorption reaction is completely finished. Then, the reactive part of the LS in the container spreads to the whole inside of the container. Finally, only the LS surrounding the inside of the container is reactive. Therefore, we think that CO_2 concentration curve rises like a stairs shown in Fig. 3. First, in the long container, CO_2 is not detected at the outlet so that LS absorbs the whole quantity of CO_2 that exists in the vicinity of the feeding inlet immediately after the beginning of the experiment. (The exhaust of 100% N_2 is observed.) However, after ten minutes, CO_2 starts to be detected at the outlet because the CO_2 not absorbed by the LS reaches the outlet of the container because of an increase in the amount of slip flow described above. After thirty minutes, the CO_2 spreads into all parts of the container and all of the LS contribute to the absorption reaction. Therefore, the CO_2 concentration curve becomes flat. Then, after forty-five minutes, the CO_2 absorption capacity of all the LS decreases and the CO_2 concentration at the outlet begins to rise, and absorption is finally completed and the process ends. Next, in the middle container, after five minutes, CO_2 starts to be detected at the outlet because the CO_2 not absorbed by the LS reaches the outlet of the container because of an increase in the amount of slip flow described above. After fifteen minutes, the CO_2 spreads into all parts of the container and all of the LS contribute to the absorption reaction; that is, absorption becomes predominant and part of the CO_2 concentration curve becomes flat. However, after eighty minutes, the absorption capacity of all of the LS in the container decreases and the CO_2 concentration at the outlet begins to rise, and absorption is finally completed and the process ends. In the short container, CO_2 reaches the outlet of the container just after the beginning of the experiment. Much of the feeding gases (N_2, CO_2) would flow in the vicinity of the center axis of the container. In the container, the spreading of the CO_2 continues and the LS pellets continue to absorb it, and the CO_2 concentration at the outlet continues to rise gradually. Within two hours of the experiment start, the LS still has absorption capacity for CO_2 in the surroundings of the container, and we speculate that two hours are required to reach a 30% CO_2 concentration at the outlet.

On the other hand, CO_2 absorption of the LS is an exothermic reaction. Therefore, while the LS is in an absorption reaction, the temperature of the LS pellets rises rapidly by more than 100℃[10]. The principal reason CO_2 is detected at the outlet of the container while the LS still has absorption capacity is that the regeneration reaction is predominant rather than the absorption reaction because of the temperature increase from this exothermal reaction. In this case, our speculation is as follows. In this absorption experiment, the LS temperature was set to 600℃. However, because of the exothermal reaction of the LS absorption of CO_2, the temperature of the LS pellets increases to about 700℃ and exceeds the temperature range where absorption speed is high (enters the temperature range where regeneration speed is high). Therefore, the CO_2 concentration at the outlet rises rapidly, showing the staircase-like curve, because many of the LS pellets enter a state where it is difficult to absorb CO_2. First, in the long container, just after the beginning of the experiment, the LS around the gas inlet is in a state (temperature range) where it absorbs all of the CO_2, and CO_2 is not detected at the outlet. (The exhaust of 100% N_2 is observed.) However, after ten minutes, CO_2 begins to be detected at the outlet because, due to the heat generated by absorbing CO_2, the temperature of LS increases and exceeds the temperature range where absorption speed is high (enters the state where it regenerates CO_2). After thirty minutes, the CO_2 concentration curve becomes flat because all of the LS contribute to the absorption reaction. Then, after forty-five minutes, the temperature of the whole container increases and exceeds the range of effective absorption. Lastly, the CO_2 concentration at the outlet begins to rise, and absorption is finally completed and the process ends. In the middle container, after five minutes, CO_2 is detected at the outlet because the temperature of the LS pellets around the channeling flow increases. After that, CO_2 spreads into the middle container and many of the LS pellets are in the range of the high-absorption reaction. Then absorption becomes predominant and the flat part of the curve appears. However, after eighty minutes, the temperature of the whole container increases and exceeds the range of effective absorption. And CO_2 concentration at the outlet begins to rise, and the absorption is finally completed and the process ends. In the short container, CO_2 reaches the outlet of the container just after the beginning of the experiment. Much of the feeding gases (N_2, CO_2) flows in the vicinity of the center axis of the container. The LS around the axis, just after the beginning of the process, generates heat by absorbing CO_2. After that, the temperature decreases a little and the LS reaches the equilibrium state in absorbing and regenerating (temperature is constant) promptly. In the container, the spreading of the CO_2 continues and the LS pellets continue to absorb CO_2, and the CO_2 concentration at the outlet continues to rise gradually. Within two hours, the state where the LS have absorption capacity of CO_2 in the surroundings of the container continues, and it is speculated that two hours are required to reach the 30% CO_2 concentration at the outlet.

For reference, the experimental result for a container (one-inch-pipe container of 160-mm length) longer than the long container described in Table 1, is shown by the yellow dotted line in Fig. 3. In this case, we think that the feeding gas would reach the outlet (from the inlet) with making contact with the surface of the LS pellets. The absorption reaction starts from the LS pellets in the vicinity of the entrance to the pellets in the downstream and proceeds sequentially. And after sixty minutes, the LS's absorption capacity is finally lost because the LS finish all the absorption in the container. CO_2 is then detected at the outlet and its concentration increases rapidly. It is guessed that the outlet CO_2 concentration rises momentarily (to vertical) if it is assumed that the absorption reaction of the LS happens instantaneously, and there is no slipping style flow at all. Here, the reason the CO_2 concentration rises from 0% to 30% with the delay for about 10-20 minutes is that it takes time for the LS to absorb CO_2 (takes time for chemical reaction). And judging from this result (the yellow dotted line in Fig. 3), the phenomenon－absorption rate control according to the temperature rise by the exothermal reaction in the second above-mentioned scenario －easily explains the rising part of the CO_2 concentration at the outlet shown in Fig. 3. However, it doesn't easily explain the flat part of the CO_2 concentration at the outlet in Fig. 3 even if the path of feeding gas from the inlet to outlet becomes long by its turning and crowding into the surroundings of the container. In contrast, the phenomenon－absorption rate control according to the slip flow of the first above-mentioned scenario－explains easily the flat part of the CO_2 concentration at the outlet in Fig. 3. However, it doesn't easily explain the rising part of the CO_2 concentration at the outlet even if the path of feeding gas from the inlet to the outlet becomes long by its turning and crowding into the surroundings of the container. Further theoretical and experimental examinations to measure the temperature distribution, flow velocity distribution, and the flow quantity distribution in a reaction container are necessary in the future in order to understand the details of the absorption reaction behavior in the containers [10]. However, the occurrence of both slipping flow and the temperature increase due to the exothermal reaction are certain. The effect of both occurred at the same time, and the resulting stairs-shaped graph of the CO_2 concentration at the outlet is related to the container shape, especially for the long container.

Regarding the problem of which reaction container shape to adopt, we show the CO_2 capture ratio calculated from the Fig. 3 in Fig. 5. Here, the CO_2 capture ratio is defined as a rejection ratio calculated from the temporal integration of the CO_2 in outlet gas divided by all of the fed CO_2. From Fig. 5, the smaller the temperature swing which causes the exelgy loss, the smaller the energy penalty. Therefore, a long container is advantageous, because it can be used for a longer

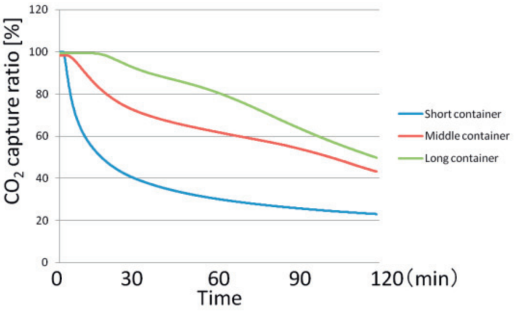


Fig. 5. CO_2 capture ratio derived from the results of Fig. 3.

period of time in the case that containers are exchanged
at the capture ratio of 50%.

4. Further research

In order to capture and separate CO_2 from the exhaust gas of a distributed power-supply system while it is in operation, it is indispensable to be able to use (capture and separate) the absorbent LS repeatedly. Therefore, understanding the characteristics of the LS and extracting the problems become the first steps, which require repeating many experiments with LS used to capture and separate CO_2. It is expected that it is necessary to use the LS repeatedly under calm capture and separation conditions. In that case, the necessary amount of LS increases compared with the amount CO_2 to be processed. In addition, to raise the collected CO_2 concentration from the capture system, there is a demand for securing the definite value of the CO_2 collection from the exhaust gas. In this case, conditions for using LS would become severe.

Moreover, there are various problems related to how to connect a distributed power source to the CCS and the CCS to an underground isolation system. Especially, we think that an effective way to reduce CO_2 emission would be to use the redundant (rejection) heat from solid oxide fuel cells (SOFC) operated at high temperature (above 750℃). But this is not easy because we must step into the design stage of the distributed power-supply system structures.

5. Conclusion

A reduction-model experimental setup that assumed distributed power-supply-exhaust processing was built and used for CO_2 absorption, regeneration, and re-absorption experiments. In this paper, we showed the results for and discussed the behavior of the absorption reaction in three reactive containers. The stairs-shaped graph of CO_2 concentration at the outlet was obtained because the slipping flow and the temperature increase by exothermal reaction would occur at the same time. The results and discussion suggest that it would be suitable to use a long container rather than a short one. Our investigations will continue, aiming at the achievement of setups that capture and separate CO_2 from the exhaust from distributed power-supply systems.

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