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In situ experiments of cold CO_2 release in mid-depth

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Abstract

Carrier transported liquid CO_2 at -55 °C is denser than ambient seawater at mid-ocean depths. We have investigated whether this property effectively enables sinking of injected CO_2 from mid-depth to the ocean floor, >3500 m depth, where CO_2 is gravitationally stable as a lake on the dented sea floor. In order to obtain basic data for the realization of this idea, the National Maritime Research Institute, and the Monterey Bay Aquarium Research Institute, conducted three joint in situ experiments of CO_2 sending method for the ocean storage (COSMOS), to release cold CO_2 at the mid-ocean depths. The experiments were carried out in Monterey Bay from October 1999 to February 2002 using remotely operated vehicle (ROV) techniques to effect the controlled release and subsequent imaging. From the data obtained, it was clear that a cold CO_2 mass, released as a large unit, was apt to be broken up into small droplets by a Taylor type interface instability. Even for a unit of sufficient heat capacity for formation of a significant ice layer, break up into droplets due to liquid instabilities occurred in a short time. However, in experiments with a CO_2 slurry mass (a mixture of dry ice and liquid CO_2) of 8 cm size we observed that the released material could keep its shape and sink even further until the covering ice layer melted. The behavior of the CO_2 slurry mass strongly suggests that this technique offers the potential for effective transfer of released CO_2 from mid-depth to the ocean floor, and our experiments provide numerical constraints on the required design goals for this.

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1. Introduction

One advantage of the concept of storage of CO_2 on the ocean floor, at depths> 3500m where liquid CO_2 is gravitationally stable, is that the sequestration time with respect to atmospheric exposure is far longer than from injection at shallower depths. This depth, however, poses greater challenges of cost and technical difficulty than the dissolution of a rising plume, in which CO_2 is released between 2000 and several hundred meters depth as small droplets or bubbles. In order to get over this disadvantage, the authors [1] proposed the idea of CO_2 sending method for the ocean storage (COSMOS), utilizing the increased density of cold CO_2 as shipped by a CO_2 carrier, to achieve efficient transport to depth from a shallower injection point. Fig. 1 shows the original concept. Here the CO_2 is cooled down close to its triple point ($-56.6\ ^\circ$C) in order to reduce the tank pressure of a CO_2 carrier as much as possible. Such cold CO_2 is much denser than the ambient seawater at mid-depth (~500 m). Thus a cold CO_2 droplet released at mid-depth will sink until heat transfer from ambient seawater increases its buoyancy above the local value. A numerical analysis showed that if a cold CO_2 unit was larger than 1 m, it could sink to the ocean floor beyond 2750 m depth where, at thermal equilibrium, CO_2 has the same density as the seawater.

In order to explore this concept a team from the National Maritime Research Institute (NMRI), and the Monterey Bay Aquarium Research Institute (MBARI), conducted four joint in situ experiments in Monterey Bay, CA from October 1999 to February 2002. These experiments were specifically designed for testing of cold CO_2 release techniques developed under the COSMOS project. These field tests were supported by a continuing set of laboratory high-pressure tank experiments.

2. Joint in situ experiments

Table 1 summarizes the purposes and results of all four joint in situ ocean experiments. Experimental planning began in September 1997 during an informal visit to MBARI. Beginning

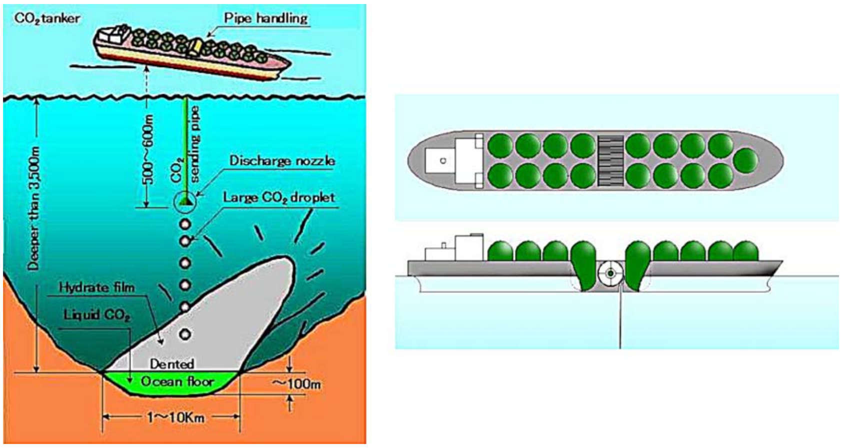


Fig. 1. Original concept of COSMOS proposed in 1998 at GHGT-4 [1].

Table 1
Summary of joint *in situ* experiments.

No.	Date	Purpose and result
1	1998.11.17–18	Initial testing of CO_2 release techniques at ambient temperature. The formation and dissolution for two types of CO_2 hydrates were observed. The pH change was large for disseminated snow-like hydrate, but small for flat hydrate membranes at the liquid interface.
2	1999.10.13	Functioning of the 1st CO_2 release nozzle was tested. CO_2 was warmed to ambient value due to insufficient thermal insulation; the CO_2 mass released was quickly broken up into small droplets by Taylor type interface instabilities (two dives).
3	2000.10.5–6	Cold CO_2 release was achieved for the first time. The movement of a CO_2 slurry (liquid + solid phases) mass of 8 cm diameter was precisely observed for 50 m of sinking. A thick ice layer covering the CO_2 prevented it from breaking up until melted by seawater (two dives).
4	2002.2.19–20	Cold CO_2 release was again achieved using a simpler (without a complicated pressure balancing system) nozzle. Similar sinking behavior of the CO_2 slurry mass was observed. The results suggest effective deep disposal from release CO_2 as slurry masses at 200 m depth (two dives).

in November 1998, field experiments were carried out once a year until February 2002. The experiments progressed from initial release of CO_2 at ambient temperature, to final release of a slurry (dry ice + liquid) as techniques improved. Our two institutes have now had a productive and cooperative relationship for 5 years. This has greatly facilitated rapid progress in ocean CO_2 sequestration research because NMRI has several high-pressure laboratory facilities for obtaining critical CO_2 (and hydrate) data, and MBARI has two ships and remotely operated vehicles (ROVs), indispensable for conducting in situ experiments [2].

2.1. First in situ experiment

The 1st in situ experiment was conducted on November 17–18, 1998. The purposes of this experiment were to examine the formation and dissolution process of CO_2 hydrate at relatively shallow depths (350–600m) in the real sea [2] and to observe the behavior of deep-sea animals such as Hagfish (*Eptatretus stouti*) to the CO_2 enriched seawater [3]. The first dive revealed that rapid release of CO_2 resulted in snow-like hydrate and slow release results in flat membrane-like hydrate on the interface between CO_2 and seawater. This behavior was anticipated from land-based experiments carried out at NMRI. The snow-like hydrate dissolved rather fast, which resulted in low pH around it. The flat hydrate membrane, however, dissolves very slowly, and the observed pH change was negligibly small.

2.2. Three CO_2 release nozzles for experiments

The purpose of the 2nd, 3rd and 4th in situ experiments was to acquire basic data for the development of the COSMOS concept. The data for cold CO_2 release techniques are of special importance since this is considered essential breakthrough technology. The important requirements for development of a cold CO_2 release nozzle for an in situ experiment are simplicity and effectiveness. The initiation of CO_2 release must be simple so that the ROV arm can effect the required manipulation. The thermal insulation must be sufficient to keep CO_2 cold for about 1 h during ROV transit to 500 m depth, and also sufficient to keep the mechanism for CO_2 release free from sea ice formation. The pressure in the chamber must be automatically balanced with the ambient pressure for smooth opening, and so on. Fig. 2 shows the three CO_2 release nozzles used for each in situ experiment.

2.3. *Second in situ experiment*

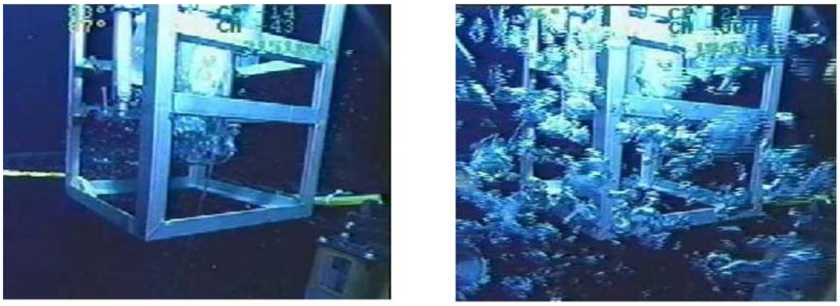
The 2nd in situ experiment, the 1st COSMOS field test, was conducted on October 13, 1999. The apparatus shown in the left-hand side of Fig. 2 was used. In this design, the thermal insulation was insufficient to keep the CO_2 temperature as low as required. During ROV transit to the release depth (around 500 m), CO_2 in the chamber was heated almost to the ambient seawater level before release. As shown in Fig. 3, the liquid CO_2, released as one mass as shown in Fig. 3(a), was quickly broken up into small droplets of a few centimeters size, and probably covered with hydrate film Fig. 3(b). Taylor type interface instabilities seemed to cause this rapid break-up. The numerical simulations [4] suggested that the heat capacity stored in a cold CO_2 mass of this size was large enough to grow a thick ice layer, which may prevent or greatly delay the break-up. A land-based experiment showed, however, that a large cold CO_2 droplet was apt to break-up due to the aforementioned instability before a thick ice layer covered the droplet.

2.4. *Third in situ experiment*

Considering the result of 2nd in situ experiment, the thermal insulation of the apparatus was greatly improved. The 3rd in situ experiment was conducted on October 5–6, 2000, in which a

1st nozzle 2nd nozzle 3rd nozzle

Fig. 2. Three CO_2 release nozzles used for 2nd, 3rd and 4th in situ experiments, respectively.



(a) Just released CO_2 mass

(b) A few seconds after release

Fig. 3. Heated CO_2 mass released into 450 m depth from the 1st nozzle.

CO_2 slurry mass (mixture of dry ice and liquid CO_2) instead of cold liquid CO_2 was successfully released at 500 m depth for the first time. In contrast to the liquid release mentioned above, the outer ice layer grew so fast that the CO_2 mass was initially prevented from breaking up. Fig. 4 shows an image of a CO_2 slurry mass of 8 cm diameter, covered with thick layer of ice, captured as it sank at 530 m depth. Supporting laboratory experiments at University of Bergen showed that rapidly formed sea ice has unusual properties including low heat conductivity [5], which should be taken into account in future modeling. Fig. 5 shows the trajectory of the CO_2 slurry mass released at 500 m depth. It shows that the CO_2 slurry mass reached 548 m depth, where it had then absorbed sufficient heat from the surrounding ocean that it slowed and began to ascend. When it reached 535 m depth during ascent, the ice layer melted and CO_2 mass broke up into small droplets in a similar way as the pure liquid release, after showing curious move-

Fig. 4. A CO_2 slurry mass sinking at around 0.3 m/s.

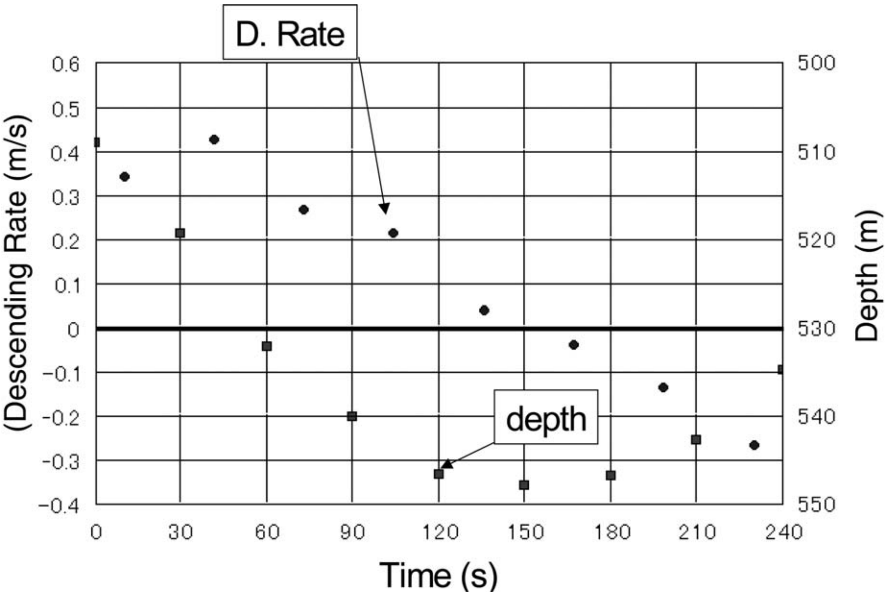


Fig. 5. Movement of a sinking slurry mass.

ments. This result suggests that the COSMOS slurry release of CO_2 is rather promising not only to realize deep disposal, but also to minimize the local pH change during dissolution.

2.5. Fourth in situ experiment

In order to confirm the promise of a CO_2 slurry release, the 4th in situ experiment was carried out on February 19–20, 2002. A very simplified release nozzle, without the sophisticated pressure balancing system, was tested. A slurry of CO_2/dry ice about 8 cm size was carefully released in two experiments at 500 m depth, and sinking and dynamic behavior similar to that observed in the 3rd experiment was observed.

3. Numerical simulation

3.1. Assumption of numerical simulation

It can well be anticipated that a larger slurry requires a longer time to be heated up and can sink to deeper depths. The maximum sinking velocity of 0.4 m/s in Fig. 5, however, is close to the allowable descending rate of the ROV we can use. This means that size of 8 or 10 cm of slurry mass is the maximum we can observe. Then we conducted a lot of numerical simulations to estimate the critical size of CO_2 slurry that can reach the ocean floor. The program [1] that had been used in the evaluation of original COSMOS was modified to deal with the CO_2 slurry. The assumptions adopted in the numerical simulations are:

1. The temperature of a CO_2 slurry is kept constant at the melting point while the dry ice remains.
2. The temperature at the outer surface of sea-ice layer covering a CO_2 slurry (or cold CO_2 droplet after the complete melt of dry ice) is equivalent to the freezing point of sea water (-1.91 °C).
3. The temperature of hydrate film appearing on the interface between the ice layer and slurry (or cold CO_2) is the same as the average temperature of CO_2 mass.
4. The Nusselt number [*Nu*] used in the heat transfer model between a slurry (or cold CO_2) and sea water is expressed by

   $$Nu = 2 + 0.34Re^{0.566}Pr^{1/3}, \tag{1}$$

   [6]

   where *Re* is Reynolds number and *Pr* is Prandtl number.
5. The dissolution of CO_2 droplet starts just after the disappearance of ice layer, and its rate is based on the diameter shrinking data of a CO_2 droplet covered with hydrate film [7]. (This assumption does not have much influence on the result because the ice layer melts completely at the very end of simulation.)
6. The buoyancy of ice and the density change following the melt of dry ice are considered in the calculation of motion. The resistance coefficient of a sphere, 0.2, is adopted.
7. The vertical temperature distribution at the North Pacific Ocean near Japan is applied.
8. Dry ice content, α, is treated as an important parameter.
9. The releasing depth is fixed at 100 m, which is shallower than 500 m in the original COSMOS.

3.2. *Results of numerical simulation*

After verifying that the above numerical model could correctly simulate the processes shown in Fig. 5, the sinking and ascending motions of larger CO_2 slurry masses, applicable to a real system, were examined using the same program. Fig. 6 shows the changes of depth, ice layer thickness, temperature and normalized mass after releasing into 100 m depth. The size of slurry

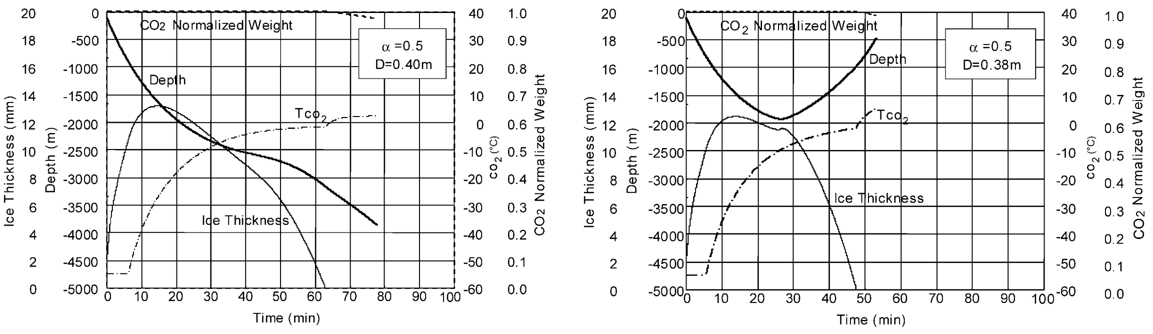


Fig. 6. Behavior of a CO_2 slurry mass released into 100 m depth.

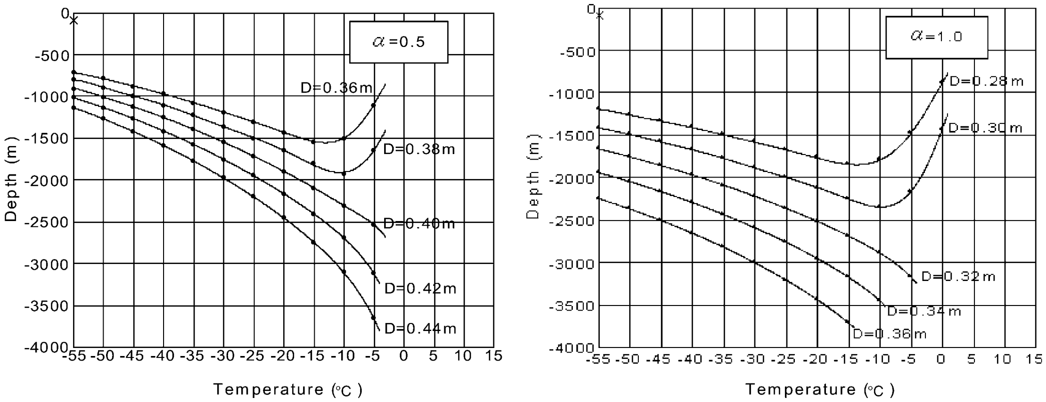


Fig. 7. Summary of CO_2 slurry movement.

mass in each sub-figure is 0.38 and 0.40 m, respectively, although the dry ice content α is 0.5 for both the sub-figures. In the case of 0.38 m, the slurry reaches 1900 m depth and u-turns, but in case of 0.40 m, it sinks to the ocean floor. This means the minimum size that can reach the storage site is between 0.38 and 0.40 m for $\alpha = 0.5$. The temperature is kept constant until dry ice completely melts and then starts to increase. The ice layer grows even after the dry ice melts and reaches over 12 and 13 cm for $D = 38$ and 40 cm, respectively. After that, the ice starts to melt. The dissolution of CO_2 does not occur and the normalized weight is unity until the ice layer covering the CO_2 mass completely melts. This means that the ice layer prevents not only the break-up of the CO_2 mass but also the dissolution of CO_2 into ambient seawater.

3.3. *Summary of numerical simulation*

Fig. 7 shows the summary of numerical simulations for dry ice content 0.5 and 1.0, in which the releasing point is shown by X. This figure supports the assumption that 100 m release is possible. Higher dry ice content requires a smaller critical size, of course, but too high dry ice content makes it difficult to release continuously. Then the result for $\alpha = 0.5$ will be examined. Slurries smaller than 38 cm sink from releasing depth of 100 m to 700 or 800 m with constant temperature, -55 °C, and then the temperature starts to increase but they continue to sink until reaching u-turn depths. However, slurries larger than 40 cm continue to sink to the ocean floor. Therefore, the critical size of CO_2 slurry mass is about 40 cm in case of dry ice content 0.5. On the other hand, the existing of u-turn depth for smaller slurries than the critical size means that the slurry release can be applied to the dissolution method as well as the storage method.

4. Proposal of improved technique

Based on the above-mentioned promise of release of a slurry mass of CO_2/dry ice, the authors propose an improved technique [8] as shown in Fig. 8. In the improved technique, CO_2 is transported as a slurry in order to keep the pressure of the CO_2 tanks as low as possible. The dry ice content (α) at release is adjusted by using the residual power of the main engine of the

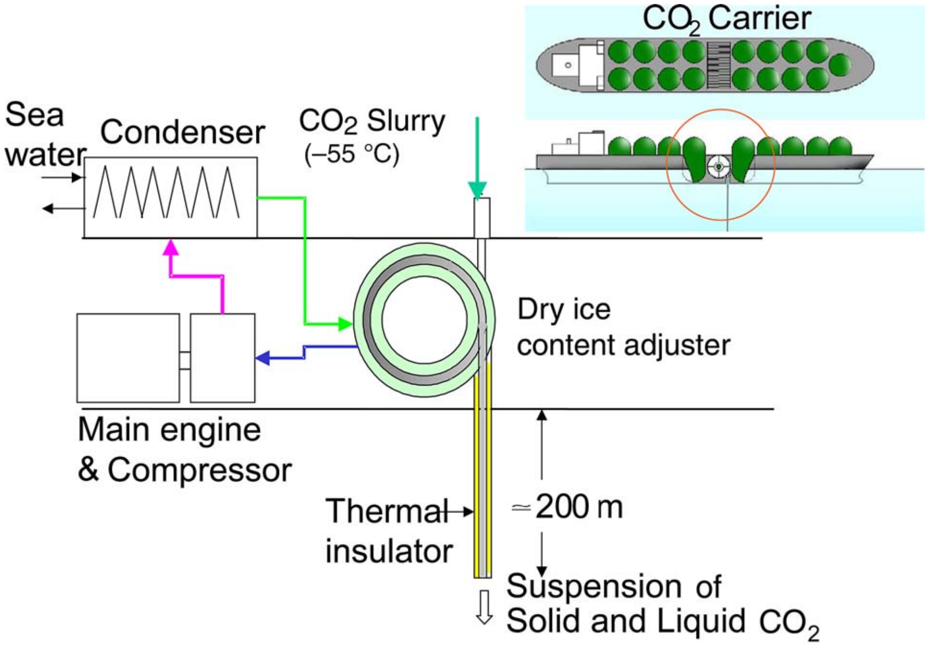


Fig. 8. Concept of improved COSMOS.

transport ship that is almost idle while releasing CO_2 at sea above the storage site. This improved technique, in which a release depth of 200 m is assumed for safety, has the following advantages:

1. CO_2 temperature can be kept constant at the triple point ($-56.6\ ^\circ C$) and the tank pressure of the carrier can be minimized (0.52 MPa) by transporting CO_2 in the slurry state.
2. The dry ice content, α, can be adjusted to the best value for ocean sequestration by using the residual power of the main engine during CO_2 release as shown in Fig. 8.
3. The minimum size of the CO_2 slurry to reach the ocean floor below 3500 m depth (0.40 m) is less than half of the original COSMOS design.
4. The discharge depth can be reduced to 200 m, which is shorter than the typical CO_2 carrier length, and this results in no complex pipe connections and manipulations at sea.
5. The u-turn depth can be selected arbitrarily by changing α and slurry size (nozzle diameter). And if a large CO_2 droplet breaks up around the u-turn depth due to the weakness of the ice layer covering it, as observed in the 3rd and 4th experiments, the dissolution of CO_2 starts at almost the deepest point. This means the improved COSMOS design can also be applied to the dissolution method, in which the full depth from ocean floor to the phase change depth (about 400 m) can be utilized for the dissolution process. In this way, the CO_2 concentration and pH change around a release site can be significantly reduced.
6. The proposed technique requires additional energy to make CO_2 slurry. This is a disadvantage of it. However, it is expected that the additional energy is not so much compared with that required at the CO_2 capturing process from flue gas.

5. Conclusions

The NMRI and MBARI team have conducted four joint in situ CO_2 release experiments in Monterey Bay from 1998 to 2002 in order to obtain basic data for the development of a cold CO_2 release nozzle, the breakthrough technology required to realize effective disposal of tanker transported liquid CO_2. Both land-based and in situ experiments suggested that simple cold liquid CO_2 release, the requirement of the original design, is theoretically possible but technically not easy, because of Taylor type interface instabilities causing liquid break-up. Two in situ experiments confirmed, however, that a slurry release technique was very promising to prevent the breaking up of CO_2 into small droplets. This is due to its large heat capacity, which enables a thick ice layer to grow rapidly, thus protecting against boundary instabilities. Based on these experimental results, an improved technique to release CO_2 as a slurry of liquid and solid phases is proposed. The improved technique has several advantages, such as reducing the size of the CO_2 nozzle diameter to less than one half of the original design. In addition, a shallower release depth of about 200 m is permitted, which eliminates difficult pipe connections and manipulations at sea, and application to the mid-water dissolution method by controlling the u-turn depth at which the released CO_2 will ascend.

The remaining subject is to confirm experimentally how the hydrodynamic instability of a CO_2 slurry mass larger than 40 cm can be suppressed by a rapidly formed ice layer.

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