

DEVELOPMENT OF CO₂ INJECTION METHOD “COSMOS” FOR CO₂ OCEAN STORAGE

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Introduction

Ocean storage of CO₂ was proposed by Marchetti¹ as one of greenhouse gas control technologies, where CO₂ is captured from flue gas of fossil fuels and injected into deep seafloor below the depth of 3500m to be sequestered from the atmosphere as shown in Fig. 1. In the last decade of the twenties century, there was a great progress in study on the ocean storage. Aya and his colleagues² and Nishikawa and his colleagues^{3, 4} reported the stability of liquid CO₂ drops covered with CO₂ hydrate films under deep-sea conditions. Shindo and his colleagues^{5, 6} proposed a mechanism of formation of CO₂ hydrate at the interface between liquid CO₂ and water to simulate the effect of CO₂ hydrate films on CO₂ dissolution. Ohsumi and his colleagues⁷ simulated the dissolution of CO₂ stored on deep seafloor. Hirai and his colleagues^{8, 9} and Teng and Yamasaki^{10, 11} reported dissolution rate of CO₂ hydrate films in deep sea. Brewer and his colleagues^{12, 13} carried out small scale field experiments of liquid CO₂ releasing to observe the behavior of released CO₂ droplets and to measure pH change nearby CO₂. Tamburri and his colleagues¹⁴ reported the influence of CO₂ on deep-sea animals.

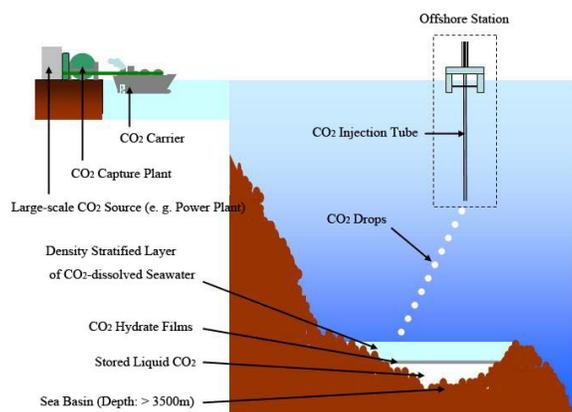


Fig. 1. Concept of CO₂ Ocean Storage

Then, Aya and his colleagues¹⁵ proposed a CO₂ sending method, COSMOS (CO₂ Sending Method for Ocean Storage) as a technology for the ocean storage. COSMOS is designed as a part of CO₂ Capture and Storage (CCS) system including capture, transportation and storage of CO₂. CO₂ is captured from flue gas of fossil fuels from large-scale CO₂ sources e.g. power plants and oil refineries. Then, captured CO₂ is to be liquefied and transported at the triple point of CO₂, where temperature is 216.6K and pressure is 0.52MPa. Liquid CO₂ is to be injected from an offshore station through an injection tube into water at 500m depth. Such cold CO₂ is heavier than ambient seawater even in the shallow water. If

a released CO₂ drop has a certain volume enough to keep its temperature at low, it reaches 2700m depth. Liquid CO₂ at the same temperature to ambient water has the same or higher density than the ambient water at 2700m depth or deeper waters. Once CO₂ drops reach the depth of 2700m, they naturally continue descending to deeper waters. Aya and his colleagues¹⁵ reported that if the diameter of a cold CO₂ drop released at 500m would be more than 1.0m, the drop could reach 2700m depth, that is, the control of released CO₂ drop size would be required to realize COSMOS. In this paper, the authors describe the outline of the COSMOS project of the National Maritime Research Institute (NMRI), Japan, focusing on the development of CO₂ injection method.

First Phase of COSMOS Project

The first phase of the COSMOS project was conducted in collaboration with University of Bergen, Norway and Monterey Bay Aquarium Research Institute (MBARI), USA from the fiscal year of 1999 to 2001 to examine the basis of COSMOS. Field experiments of small scale CO₂ releasing were carried out to demonstrate the concept of COSMOS.

Experimental

A schematic diagram of the CO₂ releasing unit for the field experiments is shown in Fig. 2. The CO₂ releasing unit as designed to be loaded and operated by a remotely operated vehicle (ROV). Prior to experiment, the CO₂ holder is filled with dry ice and locked by the lid with clutch mechanism. The power piston is held by prop oil. After melting of dry ice, the lid is unlocked and the ball valve is opened to move the prop oil to the oil collector. At the condition of 218K, 5MPa, liquid CO₂ is released by the power piston driven by compressed air from air chambers. The weight of the CO₂ releasing unit is 60kg. The inner volume of the CO₂ holder is 2 liters.

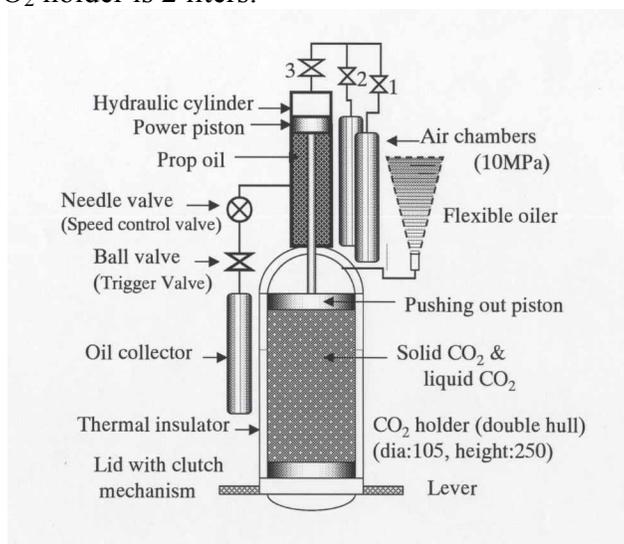


Fig. 2. Schematic Diagram of CO₂ Releasing Unit for Field Experiment

The first field experiment was carried out in Monterey Bay off California, USA in October 1999. The dive to the releasing depth of 450m took more than 30 minutes, which provided time enough to melt dry ice. Liquid CO₂ was released as a mass; however, it was immediately broken into small droplets of a few centimeters. This result suggested that the thermal insulation of the CO₂ holder was insufficient to

keep the temperature of CO₂ at low as 218K at 5MPa and the instability of drop surface led to the rapid break-up of the CO₂ drop.

Based on the above result, the CO₂ releasing unit was improved to have a thick thermal insulator including silica balloons and epoxy resin. A thermometer and a pressure gauge were installed to monitor the temperature and pressure in the CO₂ holder. In the second field experiment in October 2000, cold liquid CO₂ was successfully released at 500m depth. A descending CO₂ drop was followed by the ROV to observe its behavior. The drop surface was covered with a water-ice layer as shown in Fig.3, which prevented the drop from breaking up.



Fig. 3. CO₂ Drop Descending after Released at 500m Depth

Results and Discussion

The trajectory of the CO₂ drop released at 500m depth was shown in Fig. 4. The drop turned up after descending for 150 seconds because the density of CO₂ became lighter than ambient seawater by thermal expansion, which suggested CO₂ drops including enough amount of dry ice could continue descending.

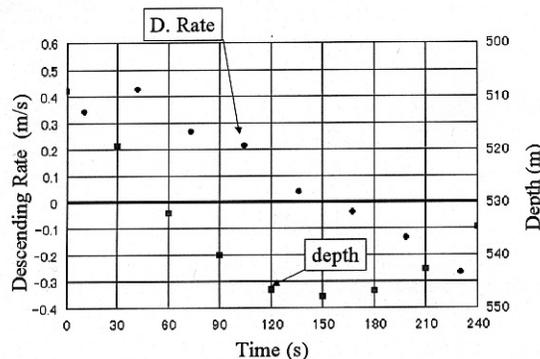


Fig. 4. Trajectory of CO₂ Drop Released in Field Experiment¹⁶

Then, Aya and his colleagues¹⁶ simulated the trajectory of CO₂ drop with diameter and fraction of dry ice in slurry drop, α , as parameters. The trajectory of a CO₂ drop released at 100m depth under the

condition of $\alpha = 0.5$ is shown in Fig. 5. A CO₂ drop with the initial diameter of 0.4m or larger can continue descending to deeper water beyond the critical depth, 2700m, while a drop with 0.38m or smaller diameter turns to ascend at shallower depths than 2700m after descending.

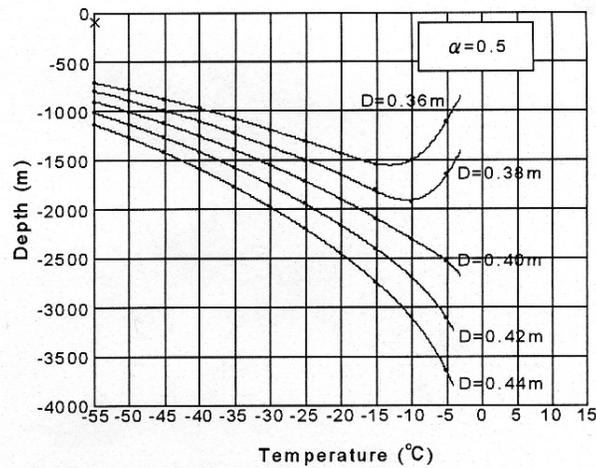


Fig. 5. Simulated Trajectories of CO₂ Slurry Drop¹⁶
(*D*: Initial Diameter, α : Fraction of Dry Ice in Slurry Drop)

Based on the results, COSMOS was improved, where a mixture of liquid CO₂ and dry ice, CO₂ slurry, is to be released because the latent heat of dry ice is expected to keep the temperature at low and form a thick ice layer around a slurry drop. Aya and his colleagues¹⁷ reported that the releasing depth is expected to be as shallow as 200m if the diameter of a released slurry drop was more than 40cm under the condition that the fraction of dry ice in the slurry was more than 0.5.

Second Phase of COSMOS Project

The second phase of the COSMOS project has been conducted in collaboration with IHI Marine United (IHI-MU) and the National Institute of Advanced Industrial Science and Technology (AIST), Japan since the fiscal year of 2005 to study the technical basis of the main elements for the improved COSMOS, that is, CO₂ releasing nozzle, CO₂ injection tube and offshore station. The characteristics of CO₂ slurry releasing has been investigated by lab experiments with a CO₂ slurry releasing unit.

Experimental

A schematic diagram of the CO₂ slurry releasing unit for lab experiments is shown in Fig. 6. The releasing unit consists of a slurry chamber, thermal insulator, piston, push rod, injection tube, and nozzle head. The inner volume of the slurry chamber is approximately 5 liters. The piston is driven by a hydraulic cylinder. A thermocouple and pressure gauge are installed to monitor the temperature and pressure in the slurry chamber. The injection tube and nozzle head are removable.

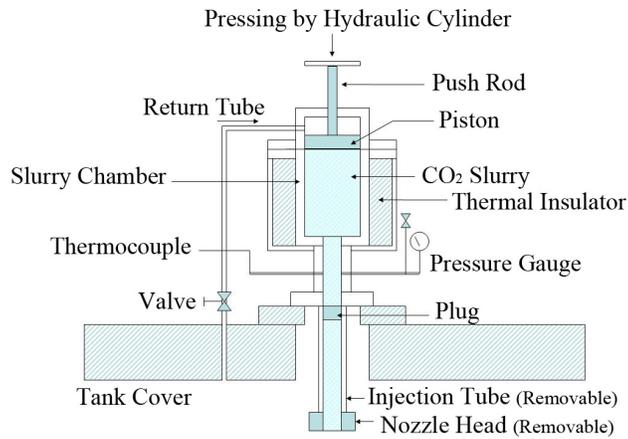


Fig. 6. Schematic Diagram of CO₂ Slurry Releasing Unit

As shown in Fig. 7, the CO₂ slurry releasing unit was mounted on a large high-pressure tank of NMRI to release CO₂ slurry drops in pressurized water in the tank. The tank has inner diameter of 1.1m and depth of 3.0m, and its maximum pressure for operational use with liquid CO₂ is 40MPa. Six monitoring cameras are vertically arranged in the tank. A thermocouple and a pH sensor are installed in the tank to measure temperature and pH.

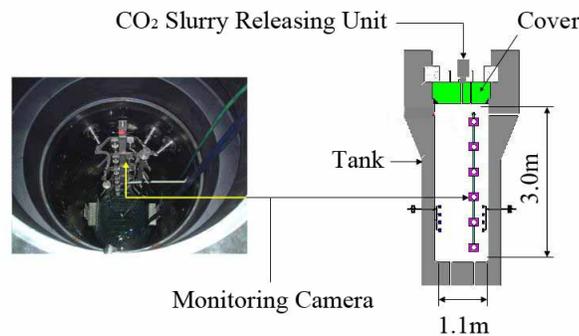


Fig. 7. Setting of CO₂ Slurry Releasing Unit on High-pressure Tank

In the experiment, the slurry chamber is filled with crushed dry ice. The return tube is filled with propylene glycol as antifreeze to prevent the piston from sticking. After sealed in the chamber, dry ice sublimates to increase the pressure in the chamber and to lower the temperature. At the triple point of CO₂, 216.6K and 0.52MPa, dry ice starts melting to provide CO₂ slurry. The valve is opened to enable the antifreeze move to the upper side of the piston and to equilibrate the pressure in the slurry chamber with that in the tank. Then, CO₂ slurry is injected by the piston driven by the hydraulic cylinder. Prior to the injection, the temperature and pressure in the tank were conditioned to 277K and 5MPa.

Results and Discussion

As shown in Fig. 8, CO₂ slurry was released in water at 5MPa as a mass and descended to the tank bottom. The slurry drops were covered with a water-ice layer. In the experiment, two types of nozzle head were used; one has a cylindrical hole with diameter of 60mm while another has a coned hole, the wider diameter of which is 120mm and narrower is 60mm, respectively. In both cases, at first, slurry drops with diameter almost the same to the nozzle hole were released. Then, tubular ice was gradually

formed on the nozzle heads because they were cooled by CO₂ slurry, which lead to that the tubular ice narrowed the flow of CO₂ slurry to form slurry drops with diameter smaller than that of the nozzle hole. This result suggests that the formation of tubular ice at the nozzle head should be suppressed to control the size of slurry drops. In addition, the ice on the cylindrical-hole nozzle covered wider area of the nozzle than that on the coned-hole nozzle, which implies the aspects of releasing nozzle could affect the size of slurry drops.

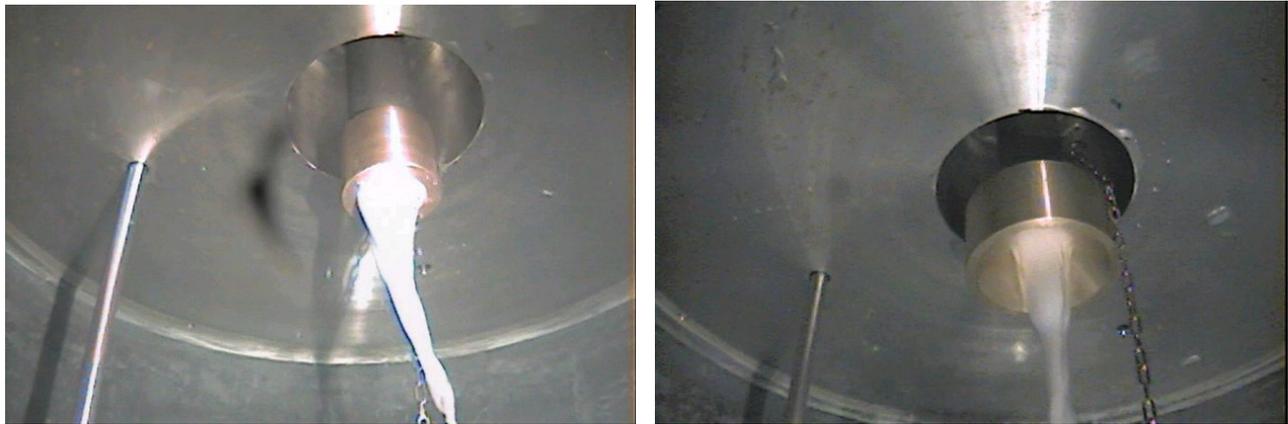


Fig. 8. Photos of Releasing of CO₂ Slurry
(Left: Cylindrical-hole Nozzle, Right: Coned-hole Nozzle)

The change in the temperature and pressure in the high-pressure tank due to the releasing of CO₂ slurry is shown in Fig. 9. The pressure was increased due to the releasing, which implies that melting of dry ice in slurry expanded the volume of the whole liquid CO₂ to increase the pressure. On the other hand, the temperature was decreased due to the releasing of slurry, which is expected to be due to the latent heat of dry ice in the slurry.

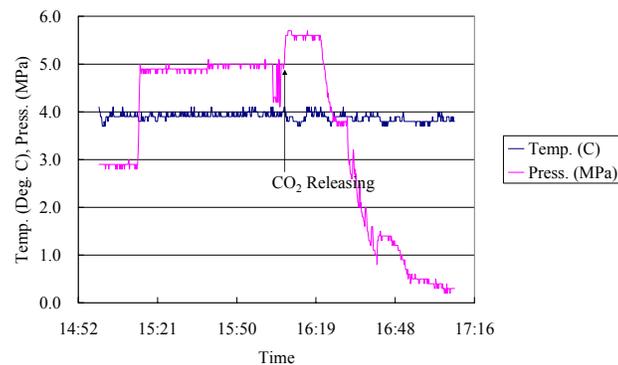


Fig. 9. Change in Temperature and Pressure in High-pressure Tank due to Releasing of CO₂ Slurry

The control of shape and size of CO₂ drops is important to send released CO₂ to the seafloor. As mentioned above, the formation of tubular ice on the releasing nozzle should be suppressed to control the shape and size of CO₂ drops. Then, it is expected that the releasing nozzle is covered with a sealant to prevent the formation of ice by contact of water with the nozzle cooled by CO₂ slurry. CO₂ drops are released to the ambient water after they are formed in the sealed nozzle to control the shape and size.

Summary

Ocean storage of CO₂ is one of greenhouse gas control technologies, where CO₂ is captured from flue gas of fossil fuels and stored on deep seafloor below the depth of 3500m to be sequestered from the atmosphere. The authors have worked for development and evaluation of a CO₂ sending method, COSMOS, where cold liquid CO₂ is released at 500m depth to descend to deep seafloor below 3500m depth. The outline of the COSMOS project for the development of CO₂ injection method is summarized as follows.

In the first phase of the COSMOS project, the concept of COSMOS was demonstrated by field experiments of small-scale CO₂ releasing, which were carried out at 500m depth in Monterey Bay off California, USA. Based on the results, COSMOS was improved, where a mixture of liquid CO₂ and dry ice, CO₂ slurry, is to be released because the latent heat of dry ice is expected to keep the temperature at low and form a thick ice layer around a slurry drop. The releasing depth is expected to be as shallow as 200m if the diameter of a released slurry drop was more than 40cm under the condition that the fraction of dry ice in the slurry was more than 0.5.

The second phase of the COSMOS project has been conducted to study technical basis of the main elements for the improved COSMOS. The characteristics of CO₂ slurry releasing has been investigated by lab experiments with a CO₂ slurry releasing unit. In the experiments, CO₂ slurry was released in water at 5MPa and descended to the tank bottom; however, tubular ice formed on the releasing nozzle narrowed the flow of CO₂ slurry to affect the size of slurry drops. The experimental result suggests that the formation of ice on the releasing nozzle should be suppressed to control the size and behavior of slurry drops. Then, it is expected that the releasing nozzle is covered with a sealant to prevent the formation of ice by contact of water with the nozzle cooled by CO₂ slurry.

Acknowledgement

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