B-56.1 Study on Evaluation of Deep Ocean Storage Method of Recovered Carbon Dioxide

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Abstract

The deep ocean CO_2 storage, in which liquid CO_2 is stored in a dented ocean floor deeper than 3500 m where liquid CO_2 is heavier than ambient seawater, is a promising measure to mitigate the global warming, because its sequestration term is expected longer than 2000 years, the vertical ocean circulation period. In order to get the necessary data for the evaluation of this method, the properties of CO_2 hydrate, dissolution and diffusion process of stored CO_2 and the biological influence of dissolved CO_2 were investigated through the land-based experiments, the numerical simulation and the *in situ* experiments.

On the properties of CO_2 hydrates, the hydrate membrane strength was measured by a modified Du-Nouy type surface tension meter, in fresh water, in saline water and in CO_2 rich water. As a result, it was found that the strength increases about 10 times just below the dissociation temperature and in CO_2-saturated water. And it was also found that the membrane deforms a lot under stress in sub-saturated water but it shows almost no deformation in saturated water. These unexpected phenomena are to be considered for the evaluation of CO_2 ocean sequestration. "Free water molecule model" proposed by the Aya et al. can well explain the above phenomena and made clear that the deformation is a kind of rebuilding process of hydrate membrane. Another experiment succeeded in simulating the overflow phenomenon discovered by Dr. Brewer et al. in their *in situ* experiment at Monterey Bay.

On the CO_2 dissolution and diffusion process, the numerical simulations for two and three dimensional systems around CO_2 storage site were conducted as a trust research to the Sojo University. The results show that the stratified layer formed above stored liquid CO_2 well suppresses the dissolution rate of CO_2 from the storage site and the pH lowering is only 0.2 above stratified layer, which implies the sequestration term longer than 2000 years can be expected

As another trust research, the Tokyo University of Fisheries conducted several *in situ* surveys in Suruga Trough and a deep seafloor depression south east of Haha Island, potential sites of CO_2 storage. The site in the latter location seems to be suitable from the scanty biomass. An investigation on the possibility of the endemic fauna, however, must be done from the point of conserving biodiversity. A preliminary study on the lowering effect of pH on a deep-sea Copepod (*Neocalanus cristatus*) was also conducted to show an equivalent tolerance range with oceanic zooplankton in shallow waters. Considering long-term effect of low pH and topographical character of the site, it is necessary to have intensive investigation around the site before considering storage experiments.

From the joint *in situ* experiment with the Monterey Bay Aquarium Research Institute, it was suggested that sea animals such as hagfish might be insensitive to the dissolved CO_2.

Key Words Carbon Dioxide, Deep Ocean Storage, Hydrate, Membrane Strength, Dissolution, Diffusion, Ecosystem, Storage Site, pH Dependence

1. Introduction

After the Third Conference of the Parties (COP 3) held in Kyoto December 1997, it became an emergent assignment for human being to establish effective measures to reduce CO_2 emission from the standpoint of greenhouse gas control. The ocean sequestration of CO_2, to be recovered from the concentrated sources such as a power plant or a regional energy center, is thought a direct and effective measure. For its realization, it is very important to establish the evaluation method and to develop the break through technology.

In this sub-subject, taking up CO_2 ocean storage method[1)], in which the limited ecological effect around storage site and the sequestration term longer than 2000 years corresponding to vertical ocean circulation are expected and once-stored CO_2 can be recovered if necessary, its realization and effectiveness as a measure to mitigate the global warming were studied.

Carrying out this sub-subject, indispensable data for the evaluation of CO_2 ocean storage, such as the strength of CO_2 hydrate membrane, the density of CO_2 rich seawater and the pH distribution around potential storage site are obtained. And from the **in situ** survey, the density and composition of biomass, the topographical features of potential ocean floor, tidal flow data, effects of low pH and dissolved CO_2 on the ecosystem, the necessary data to elucidate the impact on the ocean ecosystem, are expected to be got. Moreover, this research may stimulate the development of break through technology.

2. Research Objectives

The CO_2 ocean storage, which is suitable for huge amount of disposal and a long sequestration term as a measure to mitigate the global warming, has other advantages that the effected waters can be minimized and once-stored CO_2 can be recovered if necessary. Some disadvantages, however, are pointed out that the required depth is deeper than other sequestration methods and much affected by the hydrate properties not disclosed enough yet. Then hydrate related properties, such as mechanical strength of CO_2 hydrate membrane appearing on the interface between stored CO_2 and stratified CO_2 rich seawater and the density of CO_2 rich seawater, which are indispensable for the evaluation of CO_2 ocean storage, are measured by using existing high-pressure loops. And applying these data to the numerical simulation of dissolution and diffusion process, the distributions of CO_2 concentration and pH are to be obtained.

On the other hand, potential storage sites deeper than 3500 m are selected through checking the topographical maps of ocean floor, and the ecosystem around selected sites are surveyed by getting samples from ocean floor. And considering the pH distribution in the numerical simulation, the impact on the ecosystem is investigated by checking the low pH tolerance of **Neocalanus cristatus**, which inhibits in mid and deep waters of Sagami Bay.

Basing on the above results, the whole impact on the ocean environment around storage site is to be examined, and the merits and demerits of CO_2 ocean storage are compared with the suppression of the global warming.

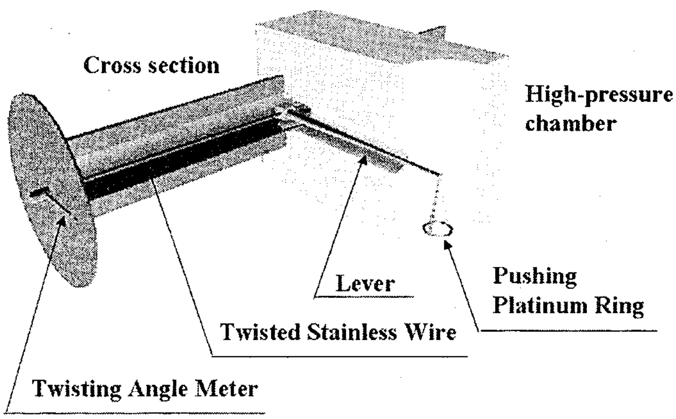

Fig. 1 Modified Du-Nouy type surface tension meter used to measure the membrane strength.

3. Research Method

By using the 40 MPa loop manufactured during FS subject in FY 1996-97, the mechanical strength of CO_2 hydrate membrane was measured for fresh water, saline water and CO_2 rich water [2]. Figure 1 shows the modified Du-Nouy type tension meter used in the strength measurement. The membrane strength, σ, was calculated by

$$\sigma = k(\theta - 2\Delta\theta)$$

where θ and $\Delta\theta$ are the twisted angle of stainless wire and the lowering angle of lever, respectively, k (=0.167 N/m) is the spring constant of measuring system determined by the material, length and diameter of wire, the length of lever. A servomotor twisted the wire at constant rotation velocity of 1.4 deg./sec. The concentration of salinity was adjusted to be 0.5 1.0 and 1.5 times of standard seawater by dissolving artificial salt, *Jamarin*, in softened water. The density of CO_2 rich water was directly measured by using the principle that the pressure of high-pressure loop sensitively decreases with small density increase of confined liquid.

The intermittent overflow phenomenon observed by Brewer et al. (MBARI) [3], which might have an adverse effect on the stored CO_2, was simulated by the 40 MPa loop used to membrane strength measurement. And the way to suppress the overflow phenomenon was surveyed [4].

As a trusted research to the Sojo University (former Kumamoto Institute of Technology), the diffusion process of dissolved CO_2 was numerically simulated for two and three dimensional depressions of ocean floor. Figure 2 shows the three dimensional depression analyzed in 2000. The related differential equations for continuity, momentum, concentration were numerically calculated. The data of CO_2 solubility with hydrate [5] and density increase of CO_2 rich water, which were obtained above land-based experiments, were applied in these analyses. The distributions of CO_2 concentration and pH in the depression and around it were estimated for about two years.

As another trusted research to the Tokyo University of Fisheries, two potential sites, Suruga Trough with depth of 3750 m (Site S) and a depression located at 100 km southeast of Haha Island (Site Og) were selected by checking the topographical maps of ocean floor. Research/Training Vessel Shinyo-Maru was used for sampling study for Sites S and Og. Each sampling gear was lowered during steaming at about 1 knot until the wire length reached 4700 m (maximum of winch capacity) and left 30 minutes before retrieval. The impact on the ecosystem was also investigated by checking the low pH tolerance of Copepod (*Neocalanus cristatus*). The pH was adjusted by reagent grade hydrochloric acid to and Copepods were kept unfed in dark at 3 ℃ before experiment as they usually distribute around 500 m in Sagami Bay.

As a joint experiment with the MBARI, the behavior of Hagfish to dissolved CO_2 was observed at the depth of 625 m see floor at Monterey Bay. For this *in situ* experiment, ROV Ventana and its mother ship Point Lobos were used.

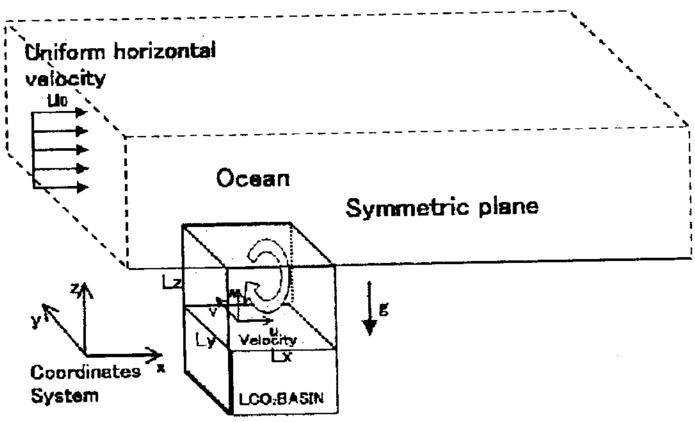

Fig. 2 Three dimensional depression applied to the CO_2 dissolution and diffusion analysis.

4. Results

4.1 Measurement of CO_2 hydrate properties

4.1.1 Strength of CO_2 hydrate membrane

The membrane strength of CO_2 hydrate formed on the interface between liquid CO_2 and three types of water (fresh water, saline water and CO_2 rich water), was measure by a Du-Nouy type tension meter fixed in the 40 MPa loop, and the flowing results were obtained:

(1) In fresh water and saline water, the strength is the order of 0.1 N/m for higher subcoolings than 4 K (Because the thickness was unknown, the strength was evaluated by 'N/m').

(2) Just below the dissociation temperatures, however, the strength has a sharp peak of 1 N/m (10 times than above value for high subcoolings) [1st strength abnormality]

(3) The temperature to appear 1st strength abnormality decreases with increase of salinity by the dissociation temperature decrease due to salinity.

(4) In CO_2 saturated water, the strength reaches more than 10 times of 0.1 N/m and almost no deformation appears like a brittle substance when stressed [2nd strength abnormality].

(5) Leaving from the saturated condition, the strength approaches fast to the level of 0.1N/m.

(5) The large elongation seen in sub-saturated water is the rebuilding of hydrate membrane.

(6) The 1st abnormality can qualitatively be explained by Yamane et al's model [6] in which the effect of energy fluctuations of each molecule on the dissociation and association probabilities is considered.

(7) The 2nd abnormality can qualitatively be explained by the "free water molecule model" proposed by Aya et al [5]. Here, the free water molecules are defined by water molecules that can dissolve the solute (CO_2) more.

Figures 3 [7] and 4 [6] show 1st and 2nd membrane strength abnormalities, respectively.

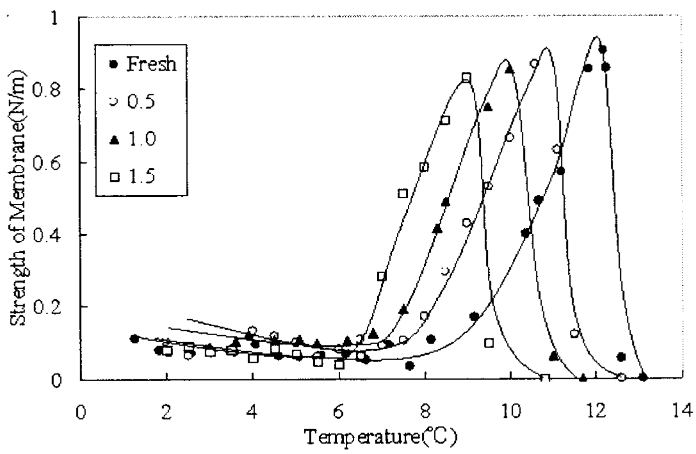

Fig.3 Strength of hydrate membrane in fresh and saline water.

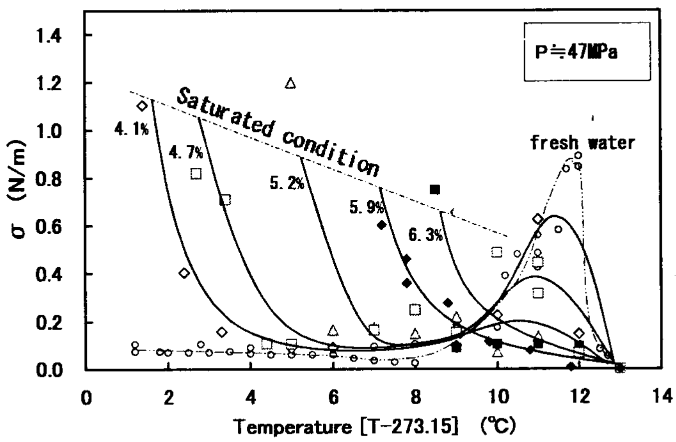

Fig.4 Strength of hydrate membrane in CO_2 rich water.

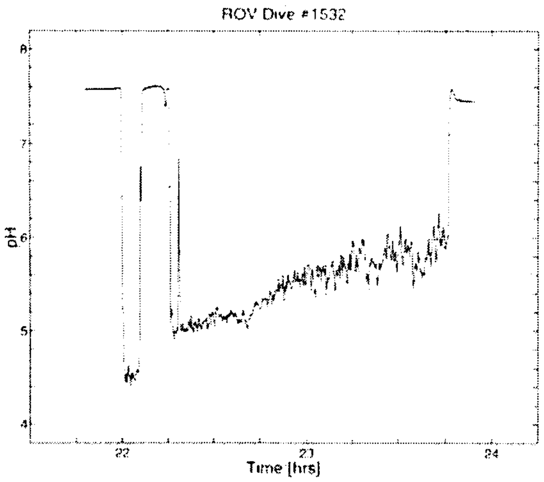

Fig.5 pH change in the beaker occupied with foam type hydrate.

4.1.2 Density increase of CO_2 dissolved water

From the absolute density measurement explained in section 3, the density increase of CO_2 rich water was to be 2.79 $kg/m^3/Wt\%$. This value is close to the value of 2.72 $kg/m^3/Wt\%$ measured by use of a vibration type densitometer [8].

4.1.3 *In situ* experiment to confirm land-based experiments

The joint *in situ* experiment with the MBARI, the flowing facts, which had been obtained by the land-based high-pressure experiment, were confirmed.

(1) The foam (snow) type hydrate forms very fast by discharging liquid CO_2 vigorously into an upside-down beaker put in the depth of 600 m. This type of CO_2 hydrate dissolves so fast that can reduce pH by 2. Figure 5 [9] shows the pH change in the beaker when foam type hydrate dissolves.

(2) The flat membrane type hydrate appears on the interface between liquid CO_2 and seawater when liquid CO_2 is discharged slowly. This hydrate dissolves so slowly that the pH decrease cannot be measured.

4.2 An innovative CO_2 sending system, COSMOS

A method to send cold CO_2 from shallow water to the depression on the ocean floor was proposed and its patent was approved in March 1999. This idea came from the fact that the cold CO_2 near the triple point (−56.6℃, 0.51 MPa) is heavier than the ambient seawater even rather shallow depth of 500 m. This system called as COSMOS (CO_2 Sending Method for Ocean Storage), however, requires an innovative release nozzle that can steadily release cold CO_2 droplets with a diameter larger than 1 m. Two joint *in situ* experiments with the MBARI were conducted at Monterey Bay to get the basic data for the development of above mentioned release nozzle. As a result, the technology to release cold CO_2 (−50℃) into the real sea was established. And the sinking process of a CO_2 slurry ball (mixture of dry ice and liquid CO_2) released into the depth of 500 m was observed for about 50 m. Figure 6 [10] shows a sinking CO_2 slurry ball covered with thin hydrate membrane and thick sea-ice. This successful observation gave a hint to modify the COSMOS, that is, new COSMOS, in which CO_2 is discharged as slurry balls into much shallower depth of 200 m, and the critical size is reduced to 40 cm, about 60 % smaller than the original COSMOS. Figure 7 [10] shows the concept of new COSMOS.

4.3 Intermittent overflow phenomenon

The intermittent overflow phenomenon of liquid CO_2 discovered by Brewer et al. in an *in situ* experiment was well simulated by the land-based experiment, and it was disclosed that water channels among CO_2 droplets covered with hydrate membrane played the pathways for

Fig.6 CO_2 slurry ball sinking in the real ocean.

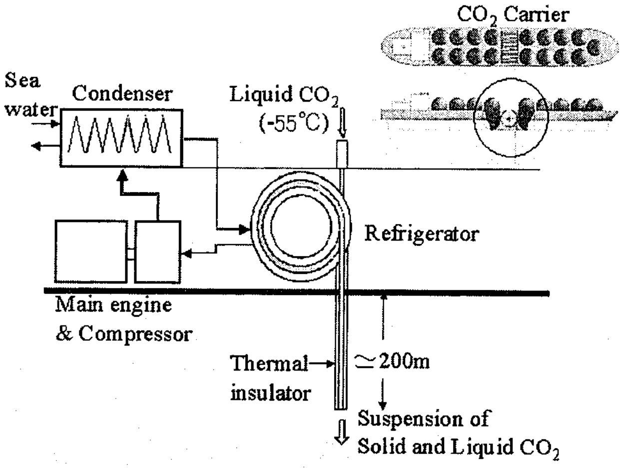

Fig.7 Concept of new COSMOS.

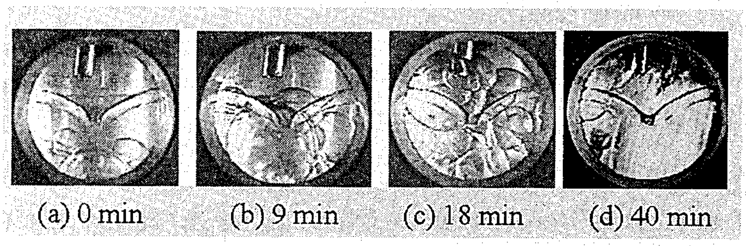

Fig.8 Simulation experiment of an overflow phenomenon observed by Brewer et al. in a sin situ experiment at Monterey Bay.

water molecules to be supplied to the hydration point at the bottom of a beaker and the needle type hydrate pushed up above droplets. Figure 8 [4)] shows the overflow phenomenon simulated by a high-pressure loop. On the other hand, when CO_2 was filled so slowly from the bottom of a beaker that CO_2 formed one mass without a channel, the overflow phenomenon was not observed for over 100 days.

4.4 CO_2 dissolution and diffusion process from a storage site

The numerical simulation of CO_2 dissolution and diffusion process for two and three dimensional storage sites were conducted. The most plausible results [11)] for three dimensional site (square pit type) are as follows:

(1) The velocity distribution and CO_2 flux in the depression above stored CO_2 reached almost steady condition after 1000 to 2500 hours.
(2) CO_2 concentration in the depression was higher by about 25% than two dimensional site (trench type).
(3) The peak CO_2 concentration in the site increases with increase of the background velocity, but it was below 0.1 Wt%.
(4) In the depression, pH decreases by 1 at certain points below 100 m height from storage level.
(5) There are some locations in the downstream of 10 km where pH decreases by 0.2.

Figure 9 shows how the CO_2 flux from top of stratified layer approaches to the saturated level. From this figure, the steady state CO_2 flux is to be 0.0004 mol/($m^2 \cdot h$)= 0.15kg/($m^2 \cdot yr$), which is correspondent to 0.15 mm height of liquid CO_2 dissolves a year. This result shows how the stratified layer formed above stored CO_2 suppresses the dissolution of CO_2 out of depression.

4.5 Biological effect

4.5.1 Sampling surveys in Suruga Trough (Site S) and south east of Haha Island (Site Og)

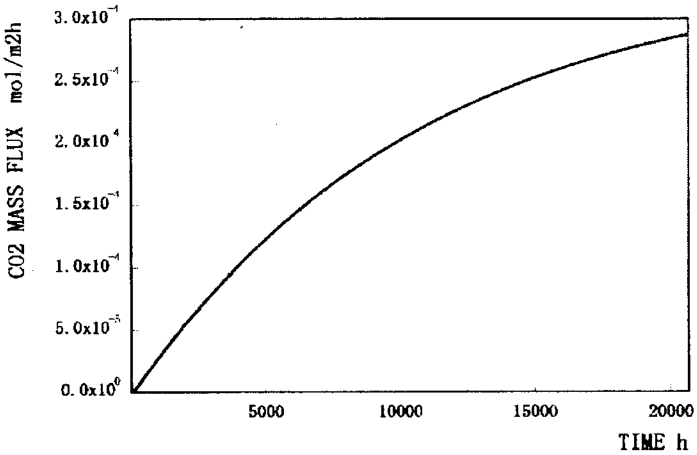

Fig.9 Upward CO_2 flux through the top of stratified layer.

The sampling surveys to above two sites, of which depth is deeper than 3500m, suitable for CO_2 storage, gave the flowing results:
(1) The topographies of both sites are similar, but Site S is abundant organic matter.
(2) Site Og is suitable for the CO_2 storage site because the benthic organisms are very scarce.
(3) The variety of species is high in Site Og, however.

4.5.2 Effect of low pH

Acute toxicity of lowered pH on Copepods (*Neocalanus cristatus*) was found below pH 6.2 as shown by Figure 10 [12)]. In the previous experiment, all of the Copepods (5 individuals) exposed pH 6.0 (initial) to 6.6 (96 hours) were survived. This result agrees well with Yamada and Ikeda's experiment [13)]. This suggests that acute toxicity does not appear at pH 6.5 in this species. The survival level of this species by CO_2, however, was pH 7.0 to 7.3. Since the pH level decreases to around 7.5 in deep water, the level causing acute toxicity by CO_2 for the species is very close to natural one. So the effects of high CO_2 concentration have also to be considered.

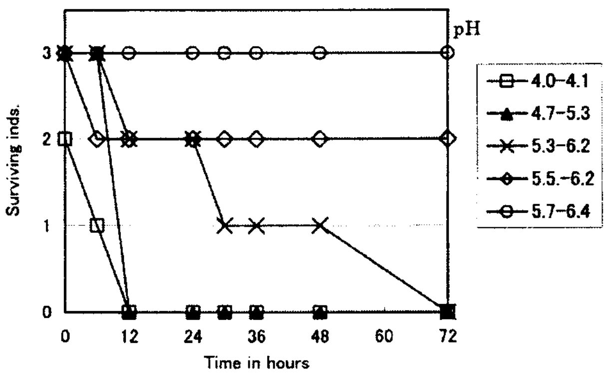

Fig.10 Effect of lowered pH on the survivals of *Neocalanus cristatus*.

4.5.3 Behavior of Hagfish inhaled high dissolved CO_2

In a joint *in situ* experiment with the MBARI, the behavior of deep animals (Black Hagfish and Sablefish) exposed to high CO_2 concentration was observed at the depth of 625 m. A Hagfish entered the upside-down beaker, in which foam type CO_2 hydrate was formed and pH was expected around 5, fell down to the seafloor and lay down for a few minutes. And then the Hagfish began to swim and entered the beaker again. It fell down and lay down on the

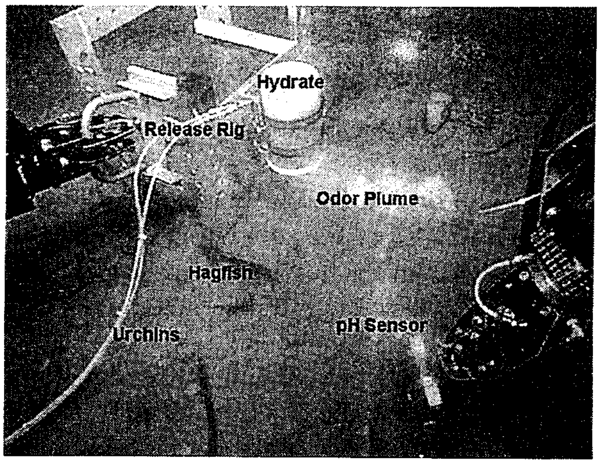

Fig.11 Hagfish swimming around the beaker from which the odor (bate) and CO_2 rich seawater flows out.

floor. The hagfish repeated entering and fainting. Figure 11 [14] shows the Hagfish swimming around the beaker filled with foam type hydrate.

This behavior may suggest that the deep animals such as hagfish are insensitive to dissolved CO_2.

5. Discussions

In order to evaluate the CO_2 ocean storage scenario, the various aspects on the CO_2 hydrate properties, the dissolution and diffusion process of CO_2, the influence on the ecosystem and an innovative CO_2 sending technology were studied, and a great progress, especially on the CO_2 hydrate, has been accomplished. Then the promise of this scenario has been proved, a lot of remained subjects, however, are still remained. At the final stage of evaluation procedures, a large scale **in situ** experiment is required to show its effectiveness and safety. Some small-scale experiments, such as joint experiments with the MBARI, have already conducted, but there exists a large gap between large-scale and small-scale experiments.

Before carrying out a large scale **in situ** experiment, at least the following issues unsettled in this study have to be elucidated.

5.1 Dual nature of CO_2 solubility

There are two solubilities in the hydrate forming region, that is, the solubility of CO_2 gas which can be extrapolated from the published data, and the solubility of CO_2 hydrate [15] of which data was obtained by the experiment during the FS subject. Even in the hydrate forming region, CO_2 droplet is usually not covered with hydrate membrane, but it is once covered with hydrate, other droplets around hydrated covered droplet are easily covered with hydrate. The difference between above two solubilities increases with decrease of temperature and reaches about three times at 2 Celsius, because the temperature dependence of those solubilities are opposite. This means that the dissolution rate of CO_2 droplet differs three times at most. Therefore the problem, when or in what condition(s) the solubility of CO_2 hydrate appears and how its solubility propagates in the real seawater, is one of the key issues for the evaluation of CO_2 ocean storage technology.

The high-pressure tank to be completed at the Natural Maritime Research Institute might be a strong tool to accomplish this subject.

5.2 Lunatic tidal wave of deep-water current

The current at a depression deeper than 3500 m is even characterized by the lunatic tidal wave. The diffusivity in the ocean is also dependent on the large-scale topography. Therefore, accurate data on tidal current, the diffusivity and so forth are necessary to estimate precisely the dissolution rate of CO_2 from the specified storage site.

5.3 Effect of pCO_2 and long-term effect

The effect of pCO_2 (dissolved CO_2) to the large variety of species has to be made clear not only for the acute fatal level but also for the long-term influence level.

5.4 Survey for potential Site(s)

One potential site (Og) was already selected in this study, but thorough investigation is necessary to choose the best site in the Pacific Ocean near our country.

5.5 An innovative technology and international collaboration

An innovative technology to send CO_2 with low cost to the depression on the ocean floor, such as new COSMOS, is also to be developed in parallel with other subjects related to evaluation of CO_2 ocean storage. The international collaborations are effective to achieve this type of development. For this purpose, the collaboration with the MBARI accumulated so far should be continued.

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