ESTIMATION OF POTENTIAL OCEANIC REGIONS AND POSSIBLE CO₂ AMOUNTS FOR STORAGE USING SELF-SEALING OF CO₂ HYDRATE AROUND JAPAN

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Japan aims to reduce its greenhouse gas emissions by 80% by 2050 as a countermeasure against global warming. As part of its policy, by 2030, the Japanese government plans to put into action carbon dioxide (CO₂) capture and storage (CCS) initiatives. On the other hand, site surveys for deep saline aquifers (DSA) in Japan are underway. This paper shows the potential for CO₂ storage using self-sealing of CO₂ hydrate as a breakthrough to increase site options and the possible amounts of CO₂ to be stored around Japan. In particular, the potential oceanic regions and the possible CO₂ amounts are estimated.

Key Words: carbon dioxide, sub-seafloor, storage, temperature and pressure, CO₂ hydrate

1. INTRODUCTION

After the Paris agreement in 2015, Japan’s comprehensive countermeasure plan for tackling global warming¹ was approved by the Japanese Cabinet in 2016. Based on the plan, carbon capture and storage (CCS) will be taken into account until 2030².

The Japanese government is conducting demonstrations of carbon capture³,⁴, CO₂ storage in DSA⁵,⁶ and site surveys⁷. DSA is a primary method in Japan as well as in other countries. The potential regions and possible amounts for DSA have been estimated based on a volume calculation⁸,⁹.

Since multiple carbon capture options have been developed, other CO₂ storage methods in addition to DSA are necessary in order to increase site options.

CO₂ storage based on CO₂ hydrate has been introduced and potential oceanic regions for it were reported based on an artificial sealing layer using CO₂ hydrate in 2004¹⁰. However, the construction method of this artificial layer was not reported.

This paper presents potential oceanic regions for and possible amounts of CO₂ storage, focusing on self-sealing of CO₂ hydrate¹¹. Since publicly available ocean temperatures¹² are shallower than 2,000 m, this paper investigates ocean depths those are shallower than 2,000 m.

Here, gas hydrate takes the form of a cage-shaped three-dimensional lattice, such as a dodecahedron in which a gas molecule is trapped. The lattice is formed by water molecules with a hydrogen bond. It is a solid substance, similar to ice. If the molecule is CO₂, it is called CO₂ hydrate. If it is methane (CH₄), it is known as methane hydrate.

This report is arranged as follows: Section 2 shows the basic properties of CO₂ and CO₂ hydrate. Section 3 shows the seafloor temperature as the primary condition for CO₂ storage using CO₂ hydrate. Section 4 describes the geothermal gradients in the ocean as the secondary condition for the storage. Section 5 presents the estimated results in potential oceanic regions and possible CO₂ amounts using self-sealing of CO₂ hydrate, and Section 6 considers prospects.

2. BASIC PROPERTIES AND CO₂ UNDERGROUND STORAGE

This section describes the basic properties of CO₂ in order to facilitate an understanding of
CO₂ storage using CO₂ hydrate.

**Fig.1** shows the isothermal contours of CO₂ density in the relationship between pressure \( P \) and density \( \rho \). When focusing on the 10°C isothermal contour, the density changes from 0.135 kg/m³ to 0.862 kg/m³ at 4.5 MPa. This discontinuous change is a phase change from gas to liquid. CO₂ density becomes higher, when the temperature becomes lower and the pressure gets higher.

The densities of both fresh water and seawater with 35‰ salinity are calculated by the state equation for seawater EOS80\(^{13}\). These isothermal contours at 2°C are plotted in **Fig.1**. For example, the density of fresh water and seawater at 20 MPa is about 1,009.8 kg/m³ and about 1,038.2 kg/m³, respectively.

Since the CO₂ density is lower than that of the seawater as presented in **Fig.1**, a seal is needed to prevent leakage from a geological formation into the ocean, when storing CO₂ below the seafloor. The driving force for the leakage becomes smaller, when the CO₂ density becomes higher.

**Fig.2** shows the superposition of two kinds of schematic phase diagrams for CO₂\(^{14}\) and CO₂ hydrate\(^{15}\) in the relationship between temperature \( T \) and \( P \). In terms of the CO₂ phase diagram, the CO₂ phase is gas, liquid, solid or supercritical. These phases are distinguished by shades of gray.

The sublimation point plotted as a black square is the phase change of CO₂ from solid to gas at atmospheric pressure. At the triple point, three phases – namely gas, liquid and solid – exist at the same temperature and pressure. The critical point, where the density is that of liquid and the viscosity is that of gas, is at 31°C and 7.4 MPa. Red squares on the boundary between gas and liquid represent experimental data\(^{15}\).

The CO₂ hydrate stable zone in **Fig.2** is a region hatched by diagonal lines. The boundary passes through both \( Q_1 \) and \( Q_2 \), which are plotted as white circles. \( Q_1 \) is a quadruple point where four phases – CO₂ gas, CO₂ hydrate, water and ice – exist at the same temperature and pressure. \( Q_2 \) is also a quadruple point where four phases – CO₂ gas, CO₂ liquid, CO₂ hydrate and water – exist.

If both CO₂ and water are present, CO₂ can change phase into CO₂ hydrate in **Fig.2**. In other words, CO₂ fluid can change into a solid when accompanied by water. If this phase change from liquid to solid can work below the seafloor, there is also the possibility that it would work to seal pores in geological formations\(^{11}\).

**Fig.3** is a diagram representing CO₂ storage considering CO₂ hydrate generation below the seafloor. The thick black line schematically shows an example of the relationship between water depth and temperature in a case where the seafloor temperature is 5°C at a water depth of 1,000 m. It shows a case in which the geothermal gradient is 30°C/km.

The temperature and pressure of the region (1) are shown as a line segment (a) to (b) in **Fig.3**. The line segment (a) to (b) is within the CO₂ hydrate stable zone in **Fig.2**. The thickness of
the CO₂ hydrate stable region (1) is calculated to be 166 m by assuming the geothermal gradient is 30 °C/km.

The CO₂ in region (2) is liquid from the phase diagram in Fig.2, and the density of liquid CO₂ is lower than that of seawater as explained in Fig.1. However, if CO₂ hydrates were naturally generated in region (1) as a seal, it would be possible to store CO₂ in region (2). We assume that the sealing mechanism works for CO₂ storage in this paper and will call it CO₂ hydrate self-sealing from hereon.

3. ESTIMATION OF SEAFLOOR TEMPERATURE

In order to consider potential oceanic regions around Japan where CO₂ hydrate self-sealing could work, the seafloor temperature with a geothermal gradient is the primary concern. This section discusses seafloor temperature.

There is publicly available data on ocean temperature, and seafloor temperature can be estimated using ocean temperature data from near the seafloor. Another item of data is from the National Oceanic and Atmospheric Administration on isothermal contours in horizontal sections of ocean throughout the world. From those isothermal contours, it can be seen that the deeper the water, the lower the water temperature, and the deeper the water, the more constant the water temperature. Furthermore, it is necessary to evaluate the vertical distribution of temperature based on the measured data to estimate the seafloor temperature.

The ocean temperature has been measured by Argo floats in the Argo project. The Argo project is an international scientific project started in 2000 to observe oceans throughout the world using about 3,000 Argo floats. Argo floats are about 2 m long and weigh about 20 kg. They stay at 1,000 m, and periodically float and sink to measure vertical temperature and salinity profiles. The data from Argo floats are collected by satellites.

Fig.4 shows ocean areas divided into four – I to IV – taking into consideration the warm Kuroshio ocean current and isothermal contours in the northwestern Pacific Ocean. Ocean area I is a region in which the Kuroshio current is dominant in offshore Shikoku. Ocean area II is a region in which the warm Kuroshio current and the cold Oyashio current mix. Ocean area III is a region in which the Oyashio current is dominant, and ocean area IV is the Sea of Japan, where cold seawater of about 1 °C stays in the basin.

It should be noted that the area around the Tsushima Strait is not included in Fig.4 because the water depth is shallower than 200 m, and the Seto Inland Sea is excluded because it is less than 50 m deep. These bodies of water are too shallow to consider CO₂ hydrate self-sealing, because they are outside of the CO₂ hydrate stable zone in Fig.2.
Four representative tracks of the Argo floats are shown in Fig. 4. The start date, end date, node date and measurement interval are noted along each track. "ID" denotes the identification number for each Argo float. The measurement interval of the selected Argo floats in Fig. 4 is five days or ten days.

Fig. 5 shows the relationship between water depth and ocean temperature in ocean area I by an Argo float having an ID of 2903187. The ocean temperature is less than or equal to 5°C at the depth of 1,000 m, and about 2.5°C at the depth of 2,000 m. The temperature at depths greater than 1,400 m is almost constant.

The float flows free along the Kuroshio current as shown in Fig. 4. The Kuroshio is one of the world's major ocean currents. Ocean mixing is significant and affects deep-ocean temperatures as shown in Fig. 5.

Fig. 6 shows the relationship between water depth and ocean temperature in ocean area II. Temperatures at 1,000 m vary, but the variation is less than 5°C, and is less than 2.5°C at 2,000 m. The seawater temperature is colder than that in ocean area I. It tends to be lower at higher latitudes even at the same water depth.

Fig. 7 is in ocean area III. The temperature is about 3°C at a depth of 1,000 m, and about 2°C at 2,000 m. The variation in temperature distribution below depths of 1,000 m is less than 1°C.
Table 1 Measurement of the geothermal gradient below the seafloor.

| Well ID | D   | WD  | WL  | ST  | GG  |
|---------|-----|-----|-----|-----|-----|
| 438A    | 110 | 1,250 | 1,000 | 2.5 | 32  |
| 439     | 110 | 1,200 | 1,000 | 2.5 | 36  |
| 440B    | 40  | 4,300 | 700  | 2.5 | 24  |

*Fig.8* is in ocean area IV. The temperature is less than 1 °C in water below 500 m. The variation in temperature distribution is very small.

In addition, the temperatures below 1,000 m in ocean areas I, II and III correspond to the isothermal contours\(^{16}\). Also, the temperature below 500 m in ocean area IV corresponds to the isothermal contours\(^{19,16}\). Therefore, *Fig.5* to *Fig.8* represent the vertical temperature distribution in each respective ocean area.

The water depth affected by mixing induced by ocean currents is shallower than approximately 1,000 m in ocean areas I, II and III, and shallower than about 200 m in ocean area IV.

The isothermal contours indicate that the temperatures in deep-ocean areas that are less affected by mixing are constant from season to season\(^{19}\). Therefore, it is considered that the temperatures of the deep-sea areas correspond to the temperature of the seafloor.

The temperature in the Sea of Japan (*Fig.8*) is colder than that in the Pacific Ocean (*Fig.5*, *Fig.6*, *Fig.7*). The temperature below 400 m was relatively stable at about 1 °C.

*Table 1* shows a geothermal gradient in terms of three boreholes drilled offshore from the city of Hachinohe in northern Japan. The temperature from well head to well bottom is measured at the three boreholes, and the geothermal gradient is 32 °C/km, 36 °C/km and 24 °C/km, respectively.

The three boreholes are in the boundary area between the ocean areas II and III in *Fig.4*. The seafloor temperatures at a depth of 1,000 m range from 2.7 °C to 3.6 °C in *Fig.6*, and from 3.0 °C to 3.1 °C in *Fig.7*. It can be seen that the temperature at a depth of 1,000 m is almost the same as the seafloor temperature ST in *Table 1*.

4. GEOTHERMAL GRADIENT IN OCEANIC REGIONS

The geothermal gradient is important for estimating the thickness of the CO\(_2\) hydrate stable zone (1) in *Fig.3*. This section therefore considers the geothermal gradient in the ocean area.

The geothermal gradient on land areas has been summarized as a temperature gradient map\(^{20}\) and a map plotting the geothermal gradient at each site\(^{21}\). However, a summary of offshore geothermal gradients has not been found in literature surveys.

Thus, this section describes the state of the art in mapping geothermal gradients in the ocean. The first data are geothermal gradients measured using drilled wells\(^{22,23}\). The second data are estimated offshore geothermal gradients from measured heat flows\(^{24}\).

*Fig.9* shows the numbers of samples in a geothermal gradient range in a bar chart, using approximately 2,900 pieces of geothermal gradient data\(^{24}\). The interval of the range from 0 °C/km to 250 °C/km is every 5 °C/km; that from 250 °C/km to 500 °C/km is every 50 °C/km; and that from 500 °C/km to 5,000 °C/km is every 500 °C/km.

In the range from 0 °C/km to 250 °C/km, there would be two peaks, which are from 30 °C/km to 35 °C/km and from 105 °C/km to 110 °C/km. The average geothermal gradient on land areas is
about 30 °C/km\sup{20}. We assume that the average geothermal gradient offshore is 30 °C/km according to the measured data in Table 1.

However, there are geothermal gradients that are much larger than 30 °C/km in Fig.9\sup{24}. Offshore areas of the large geothermal gradient would be unsuitable for CO\textsubscript{2} storage, since large geothermal gradients are shown around active volcanos on land\sup{20}.

5. ESTIMATION OF POSSIBLE CO\textsubscript{2} AMOUNTS AND OCEANIC REGIONS FOR CO\textsubscript{2} STORAGE

To date, estimates for possible amounts of CO\textsubscript{2} storage using CO\textsubscript{2} hydrate self-sealing have not been considered. This section presents an estimation using the volume calculation in equation (1).

\[ M_{CO_2} = S_f \times A \times h \times \phi \times \rho \]  (1)

Table 2 summarizes the possible amounts of CO\textsubscript{2}. The possible amount of CO\textsubscript{2} storage \( M_{CO_2} \) in equation (1) is the product of storing ratio \( S_f \), potential oceanic region \( A \), average storing thickness \( h \), porosity \( \phi \) and CO\textsubscript{2} density \( \rho \). CO\textsubscript{2} density\sup{15} is used at 10 °C and 10 MPa as a constant value for simple calculation.

It is assumed that average \( S_f \) is 50%, average \( \phi \) is 50% and average \( h \) is 2 m. The thickness of the CO\textsubscript{2} hydrate layer in Fig.3 is set to 0 m, since there are no data at this step. It is also assumed that CO\textsubscript{2} is stored in unconsolidated sedimentary layers called a sea basin.

The potential oceanic region satisfies both the range of water depth and seafloor temperature in Table 2. Potential oceanic regions in the ocean areas from I to IV are shown in Fig.10 to Fig.13. Regarding the range of water depths, the maximum depth is 2,000 m, as the maximum depth of the Argo float in Section 3 is 2,000 m.

Potential oceanic region \( A \) in equation (1) is calculated using the geographic information system (GIS) considering both depth contours in the ocean area (M7000 series)\sup{25} and seafloor temperature in Section 3. M7000 series are the highest-density contour lines.

The inset figure in the lower-right of Fig.10 shows available regions of the M7000 series with its code numbers. This paper uses regions shaded in light red. Gray regions were not used, since the thickness of the marine sediment is too thin to store CO\textsubscript{2} due to the low sediment supply from inland rivers.

![Table 2](image)

Table 2: Subjects and results of possible amounts of CO\textsubscript{2} storage. The symbols of the parameters are based on the cited literature\sup{3}.

| Ocean area | Range of water depth | Seafloor temperature | Area of potential region | Storing ratio \( S_f \) | Storing thickness \( h \) | Porosity \( \phi \) | CO\textsubscript{2} density \( \rho \) | Possible CO\textsubscript{2} amount \( M_{CO_2} \) |
|------------|---------------------|----------------------|--------------------------|--------------------------|----------------------|----------------------|----------------------|----------------------------------|
| I          | 800 to 2,000 m      | ≤ 5 °C               | 130,853,561.072 m²       | 0.50                     | 2 m                  | 0.50                  | 0.90                  | 115,252,101,066 ton               |
| II         | 800 to 2,000 m      | ≤ 5 °C               | 43,020,271.347 m²       | 0.50                     | 2 m                  | 0.50                  | 0.90                  | 19,359,122,118 ton                |
| III        | 500 to 2,000 m      | ≤ 5 °C               | 37,378,254,460 m²       | 0.50                     | 2 m                  | 0.50                  | 0.90                  | 16,820,214,507 ton                |
| IV         | 500 to 2,000 m      | ≤ 5 °C               | 115,251,912,166 m²      | 0.50                     | 2 m                  | 0.50                  | 0.90                  | 51,986,360,472 ton                |

The total potential oceanic area using water depth contours is 326,506 km\textsuperscript{2} as shown in Table 2. This is about 86% of Japan’s land area of 380,000 km\textsuperscript{2}.

The total possible CO\textsubscript{2} amount is 146.9 billion tons, when it is assumed that the CO\textsubscript{2} storage ratio is 0.5, the pore ratio is 0.5, the effective layer thickness is 2 m and the CO\textsubscript{2} density is 0.9 ton/m\textsuperscript{3}. This possible CO\textsubscript{2} amount is almost the same as that for DSA\sup{9}.

A constant value for the CO\textsubscript{2} density was used in order to simplify the calculation. The CO\textsubscript{2} density changes in terms of both temperature and pressure are as shown in Fig.1.
only as far as 2,000 m. However, it is possible to consider depths greater than 2,000 m, as the seawater temperature decreases as the depth of the water increases.

6. CONSIDERATIONS

This section considers prospects for the long-term stability of CO₂ hydrate, the co-existence of CO₂ hydrate and methane hydrate, and available technologies for dealing with storage.

There are two reasons for the temperatures in the deep sea being cold and constant as shown in Fig.5 ~ Fig.8. The first is that cold seawater stays deep, since seawater increases in density as it becomes cooler. The second is that the mixing by ocean currents does not reach down to the deeper reaches of the sea. As a result, the environment in which CO₂ hydrate is stable as shown in Fig.2 and Fig.3 will remain as such for the long term.

Both CO₂ hydrate and methane hydrate can exist in the same ocean region, as their phase diagrams show. However, the boundary temperature of the phase diagram for CO₂ hydrate is colder than that of methane hydrate by a few degrees. This means that the depth from the seafloor where CO₂ hydrate exists is shallower than where methane hydrate exists by about 100 m, based on the average geothermal gradients.

Oils and gases have been exploited in offshore areas deeper than 3,000 m. CO₂ injection wells
have also been drilled into DSAs to depths of between 2,400 m and 2,800 m at the the Tomakomai pilot plant in Japan\(^5\). Pumps, pipes and related equipment could be used in offshore regions. Based on the preexisting technologies and their costs, it is necessary to consider better solutions.

7. CONCLUSION

This paper showed the potential of CO\(_2\) storage using CO\(_2\) hydrate self-sealing\(^{10}\) considering seafloor temperatures in Section 3 and depth contours\(^{25}\).

The estimated possible amount of CO\(_2\) storage based on volume calculation is about 146 billion tons. This amount is almost the same as that of DSAs estimated in Japan. Based on these results, CO\(_2\) storage using CO\(_2\) hydrate self-sealing could be considered as a second option.

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