



## HYDRATE FORMATION IN SEDIMENTS IN THE SUB-SEABED DISPOSAL OF CO<sub>2</sub>

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**Abstract**—Sub-seabed disposal is the safest disposal option for CO<sub>2</sub>. Water pressure and dilution into oceanic water prevent direct emission of CO<sub>2</sub> into the air. Sediments under the deep sea floor are usually cool because the deep oceanic water is very cool. CO<sub>2</sub> hydrate forms in the sediments in areas of the sea floor deeper than 300 m. The formation of CO<sub>2</sub> hydrate in sediment pores almost completely prevents the escape of CO<sub>2</sub>. Copyright © 1996 Elsevier Science Ltd.

### 1. AQUIFER DISPOSAL OF CO<sub>2</sub>

Natural gas (NG) and petroleum have been stored in underground reservoirs for millions of years. Depleted NG and oil reservoirs have left extensive porous reservoir rocks and trap structures that can contain gas and liquids safely. Impermeable cap rocks prevent the leakage of gas. Some NG deposits contain a large fraction of CO<sub>2</sub>. Thus it is possible to use underground depleted NG and oil reservoirs for long-term storage of CO<sub>2</sub>.<sup>1</sup>

A depleted NG reservoir will contain CO<sub>2</sub> up to the same pressure as the primary formation pressure of the NG before extraction. In NG fields, there exist natural caprocks that can confine gas at their primary pressures. Underground injection of CO<sub>2</sub> should be operated in such a way as to minimize a change of reservoir fluid pressure from the original pressure in order to avoid unnecessary changes of the geological environments such as fracturing of caprocks (Fig. 1).

The fluid pressure in underground aquifers is usually approximately equal to the hydrostatic pressure produced by a water column of nearly the same height as the reservoir depth (Fig. 1). However, the fluid pressures in confined aquifers and in NG and oil reservoirs are often higher than the normal hydrostatic pressure, but always lower than the lithostatic pressure, which is usually 2.0–2.7 times higher than the normal hydrostatic pressure. The critical point for CO<sub>2</sub> is at 31.1°C and 7.39 MPa. CO<sub>2</sub> is stored as a supercritical fluid in reservoirs deeper than about 800 m. Cooler reservoirs having a low geothermal gradient can store more CO<sub>2</sub> than warmer reservoirs having a high geothermal gradient (Fig. 1).

Tanaka et al<sup>2</sup> estimated that oil and gas reservoirs and aquifers in anticlinal structures in Japan have a storage capacity of 3.5 billion tonnes of CO<sub>2</sub>, mostly in the supercritical state, which is enough to accommodate about 7 years of CO<sub>2</sub> emissions from large fixed emission sources in Japan. However, most oil and gas reservoirs are not yet available because they have not yet been totally depleted.

The CO<sub>2</sub> can be stored in the dissolved state even in ordinary aquifers that do not have geological structures tight enough to trap gas and supercritical fluid. Gas is more soluble at higher pressures but less soluble at higher temperatures. The solubility of CO<sub>2</sub> in pure water is shown for the combined effects of temperature and pressure in Fig. 2. The contours indicate the soluble amount (kg) of CO<sub>2</sub> in a volume (m<sup>3</sup>) of CO<sub>2</sub> solution as a function of temperature and pressure based on experimental data.<sup>3,4</sup> The density of the CO<sub>2</sub>-solution was estimated using the model suggested by Ohsumi.<sup>5</sup> In Fig. 2, it is assumed that the fluid pressure is hydrostatic and the groundwater surface is equal to the ground surface.

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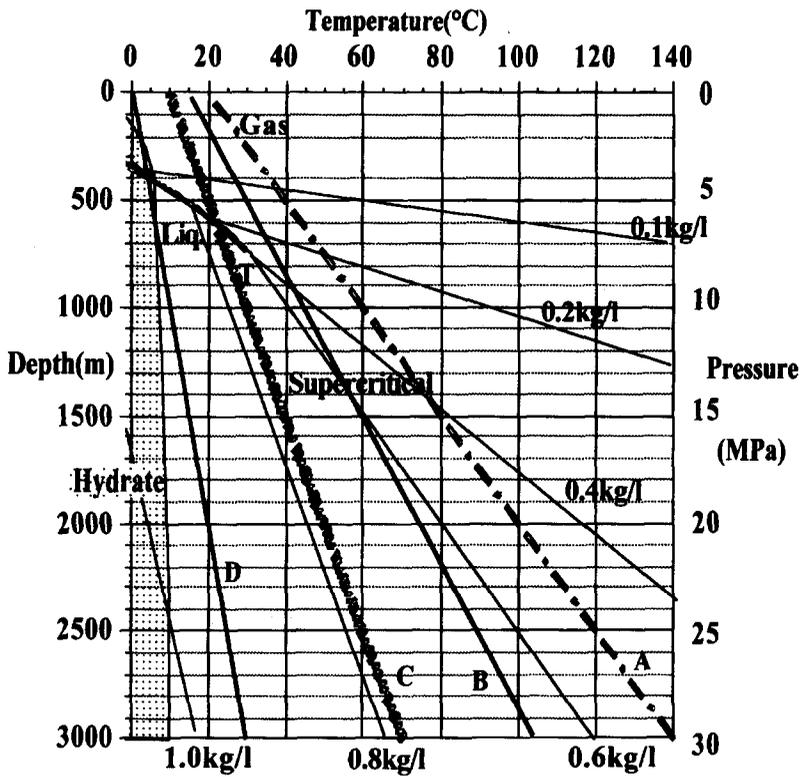


Fig. 1. Density (kg/l) of CO<sub>2</sub> at underground temperatures and hydrostatic pressures. The lines A, B, C and D indicate typical geothermal gradients. T denotes the critical point at 31.1°C, 7.39 MPa.

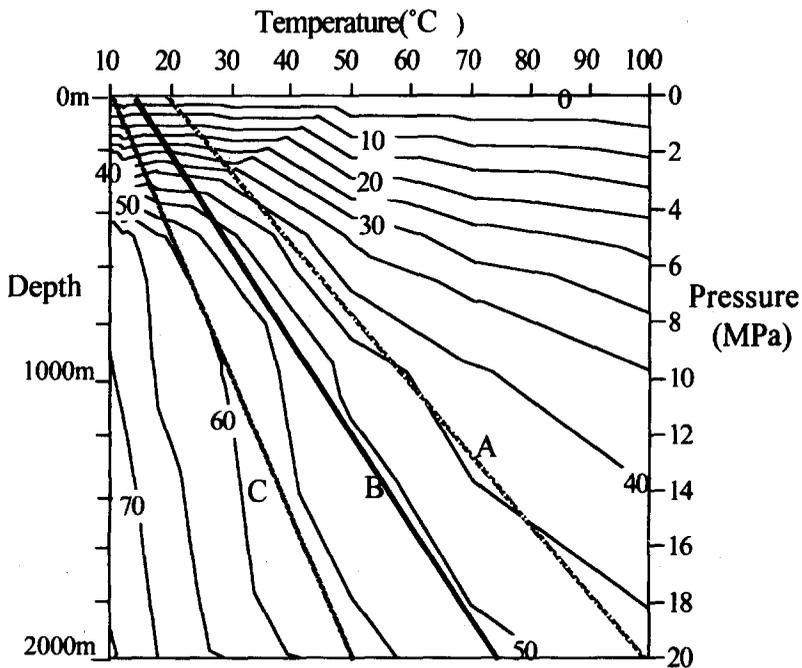


Fig. 2. Temperature–pressure profile for CO<sub>2</sub> solubility (kg/m<sup>3</sup>) in fresh water. Lines A, B and C denote geothermal gradients of 0.04 K/m, 0.03 K/m and 0.02 K/m, respectively.

Lines A, B, and C are simplified pressure–temperature profiles of sedimentary basins with geothermal gradients of 0.04 K/m (4°C/100 m), 0.03 K/m (3°C/100 m), and 0.02 K/m (2°C/100 m), respectively. The solubility of CO<sub>2</sub> in water is determined from Fig. 2 for the pressure–temperature conditions in cases A, B, and C (Fig. 3). It is evident that cool aquifers are able to contain more CO<sub>2</sub> than warm aquifers.

Tanaka et al<sup>2</sup> estimated that ordinary land aquifers in Japan can store 16 billion tons of CO<sub>2</sub> in the dissolved state in groundwater while offshore aquifers near the Japanese islands can accommodate 72 billion tons of CO<sub>2</sub>. Offshore aquifers have the highest potential for storage of CO<sub>2</sub> in and near Japan.

## 2. FORMATION OF CO<sub>2</sub> HYDRATE IN SUB-SEABED AQUIFERS

Subterranean disposal of CO<sub>2</sub> into sub-seabed aquifers is safer than disposal into land aquifers because the water pressure and dilution by oceanic water prevent direct emission of CO<sub>2</sub> into the air. Calcareous sediments on some areas of the sea floor interact with CO<sub>2</sub> converting it into the more soluble bicarbonate ion as follows:



The stable state of CO<sub>2</sub> hydrate has been mapped in a temperature–pressure diagram (Figs 1 and 4). The T–Q curve in Fig. 4 is the boiling curve of simple CO<sub>2</sub>. CO<sub>2</sub> hydrate is stable at lower temperatures and higher pressures than those indicated by the R–P–Q–S curve for the simple CO<sub>2</sub>–water system.<sup>6</sup>

The formation temperature of CO<sub>2</sub> hydrate is 2–3°C lower than the decomposition temperature, as indicated by the R–P–Q–S curve in Fig. 4. Also, formation of CO<sub>2</sub> hydrate requires a somewhat lower temperature in salt water than in pure water. The exact temperature and pressure for CO<sub>2</sub> hydrate formation in groundwater are not available. The dotted area in Fig. 4 suggests probable temperature–pressure conditions for CO<sub>2</sub> hydrate formation in aquifers.

The J–B–K curve in Fig. 4 is an example of a temperature profile in sea water (data were taken in the summer at 37.5°N, 134.5°E in the Japan Sea). The A–B line is a possible temperature profile for marine sedimentary basins, where B indicates the sea floor. As the temperature is below 5°C in many parts of the sea floor deeper than 300 m, CO<sub>2</sub> hydrate can be formed in many large areas in marine sediments just below the sea floor.

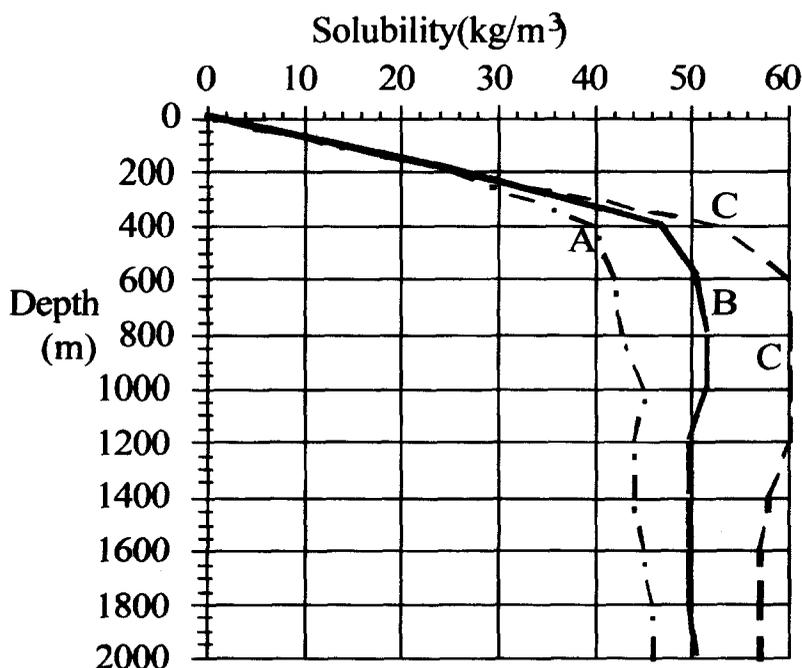


Fig. 3. Solubility profile in fresh aquifers. Curves A, B and C refer to the geothermal gradients of 0.04, 0.03 and 0.02 K/m, respectively.

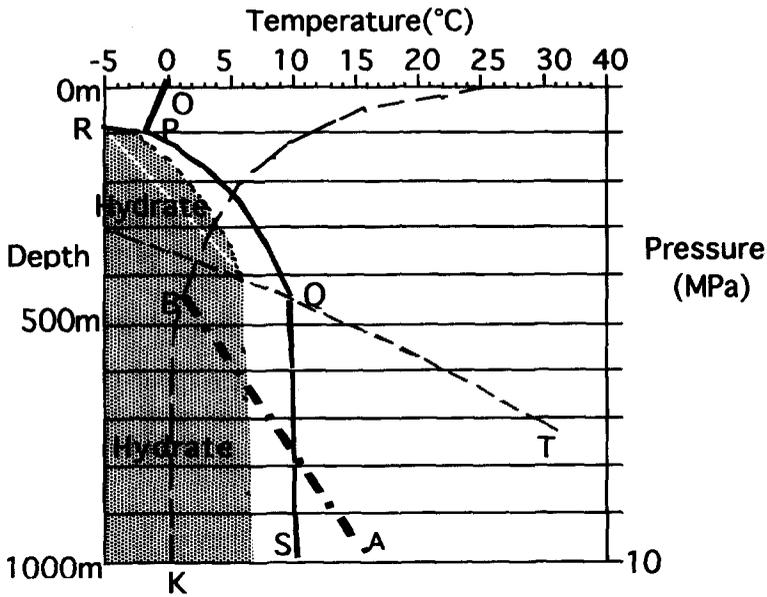


Fig. 4. Temperature–pressure range (dotted area) for  $\text{CO}_2$  hydrate formation in marine sedimentary basins. R–P–Q–S is the decomposition criterion of  $\text{CO}_2$  hydrate. J–B–K is a typical sea temperature profile. The line A–B indicates a temperature increase with depth in marine sediments where B is the sea floor. T denotes the critical point of  $\text{CO}_2$ .

Formation of  $\text{CO}_2$  hydrate in pores and gaps in rocks and sediments almost completely blocks the migration of fluid.  $\text{CO}_2$  that is injected into a deep reservoir migrates upward into cooler aquifers, saturates groundwater and eventually forms a  $\text{CO}_2$  hydrate cap at a depth of 200–400 m below the water surface in cool sedimentary basins (Fig. 5) at high latitudes, e.g. in countries such as Canada and Russia, and in large areas with cool marine sedimentary basins deeper than 300 m, e.g. in the Japan Sea, the northern Pacific Ocean, the northern Atlantic Ocean, the Arctic Ocean, and the Antarctic Ocean.

Once  $\text{CO}_2$  hydrate forms in aquifers,  $\text{CO}_2$ -hydrate plugs in gaps and pores in rocks are not easily decomposed because groundwater flows extremely slowly and is almost saturated with  $\text{CO}_2$  in narrow gaps around the  $\text{CO}_2$ -hydrate plugs.

Honjou and Sano<sup>7</sup> proposed  $\text{CO}_2$  storage in artificial caverns in Antarctic ice sheets. As simple  $\text{CO}_2$  evaporates above  $-78^\circ\text{C}$  and at atmospheric pressure,  $\text{CO}_2$  storage in open caverns is stable only in the polar regions which are not easily accessible. Because  $\text{CO}_2$  hydrate forms at elevated fluid pressure and temperature,  $\text{CO}_2$  storage below about 300 m water depth is stable in many easily accessible regions. Deep  $\text{CO}_2$  storage in aquifers is more resistible to climate change than  $\text{CO}_2$  storage in open caverns.

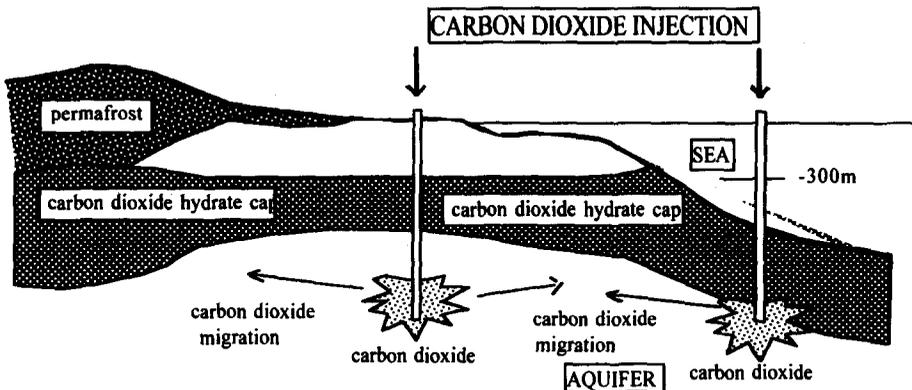


Fig. 5. Trapping of  $\text{CO}_2$  in sub-seabed aquifers and in cool aquifers.

### 3. CONCLUSIONS

Sub-seabed disposal of CO<sub>2</sub> is the safest disposal option. Water pressure and dilution by oceanic water prevent direct emission of CO<sub>2</sub> to the air. Formation temperatures lower than about 5°C and hydrostatic pressures greater than about 300 m of water are sufficient to form CO<sub>2</sub> hydrate in aquifers. CO<sub>2</sub> injected into deep reservoirs may migrate upward to aquifers and forms a CO<sub>2</sub>-hydrate cap in large areas of cool marine sedimentary basins deeper than 300 m. Formation of CO<sub>2</sub> hydrate in rock gaps almost completely prevents leakage of CO<sub>2</sub>. Although CO<sub>2</sub> is injected into some oil reservoirs for enhanced oil recovery (EOR), we have little knowledge concerning the behavior of underground CO<sub>2</sub>. Kinetic research is especially needed for CO<sub>2</sub>-hydrate plugging and its dissolution in rocks. Underground CO<sub>2</sub> in sub-seabed reservoirs is effectively contained by multiple barriers such as groundwater, impermeable caprocks, CO<sub>2</sub>-hydrate plugs, and sea water.

The complete isolation of huge amounts of CO<sub>2</sub> is possible in deep, cool marine sediments by the mechanism of CO<sub>2</sub> hydrate self trapping. Sub-seabed disposal in aquifers under the sea floor can be used to obtain CO<sub>2</sub>-emission-free fossil-fuel power generation.

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