

Hitoshi Koide, Manabu Takahashi, Yuji Shindo, Yoshikazu Noguchi, Sumie Nakayama, Masaki Iijima, Kazuitsu Ito, Yoshiyuki Tazaki (1994.09) Subterranean disposal of carbon dioxide at cool formation temperature, Proc. CLEAN AIR'94, Canada, Session 6D p.63-72

**Subterranean disposal of  
carbon dioxide  
at cool formation temperatures**

by

Hitoshi KOIDE, Manabu TAKAHASHI  
Geological Survey of Japan  
1-1-3, Higashi, Tsukuba, Ibaraki, Japan

Yuji SHINDO

National Inst. of Materials and Chemical Research  
1-1, Higashi, Tsukuba, Ibaraki, Japan

Yoshikazu NOGUCHI, Sumie NAKAYAMA  
Electric Power Development Co.  
6-15-1, Ginza, Chuo-ku, Tokyo, Japan

Masaki IIJIMA, Kazuitsu ITO  
Mitsubishi Heavy Industries, Ltd.  
3-3-1, Minatomirai, Nishi-ku, Yokohama, Japan

Yoshiyuki TAZAKI  
Kanto Natural Gas Development Co.  
661, Mobara, Chiba, Japan

**ABSTRACT**

Cool and deep sedimentary basins can provide ideal reservoirs for disposal of carbon dioxide. Confined aquifers in depths of sedimentary basins, which cannot be used as source of drinking water due to the high salinity, can accommodate large amount of carbon dioxide under the high formation pressures.

The underground injection of carbon dioxide should be operated in the way to minimize the change of reservoir fluid pressure from the primary pressure which is usually almost equivalent to the hydrostatic pressure. Cooler reservoirs in low thermal gradient of sedimentary basins can host larger amounts of carbon dioxide than warmer aquifers. Cooler formation temperature than about 5°C under higher hydrostatic pressures than about three hundred meters of water column is enough to form CO<sub>2</sub> hydrate in aquifers. Formation of CO<sub>2</sub> hydrate in gaps of rocks virtually completely prevent leakage of carbon dioxide.

Subseabed disposal and subterranean disposal of carbon dioxide in cool districts are protective for environment and efficient for the mitigation of greenhouse gas emissions from fossil fuel power plants.

**KEYWORDS:** subterranean disposal, subseabed disposal, carbon dioxide, hydrate, sedimentary basin.

## **1. INTRODUCTION**

Huge volumes of CO<sub>2</sub> are emitted by burning of fossil fuels which have been extracted from underground deposits. The carbon dioxide is not so poisonous to animals and useful for plants. However, huge artificial emission of carbon dioxide is blamed as the main cause of global warming. The enormous volume of man-made CO<sub>2</sub> emission makes the development of effective mitigation technology extremely difficult.

About 60% of CO<sub>2</sub> emission in Japan are from fixed massive sources such as electric power plants, mills, etc. While the intensive efforts for development of CO<sub>2</sub> recovery technology from flue gas of power plants and mills, we should find suitable spaces for disposal of separated carbon dioxide. The ocean disposal of CO<sub>2</sub> is still troubled for the risk to marine environment.

The carbon contained in underground rocks is almost 100,000 times of atmospheric carbon. Fossil fuels contain a small fraction of underground carbon, but still reach about 5.5 times of atmospheric carbon (Berner and Lasaga, 1989) which is enough to cause the significant greenhouse effect. It seems a natural solution to return the carbon dioxide after burning of fossil fuels into underground rocks.

There exist many hot and cool springs of carbonated water. Some sorts of carbonated mineral water are people's favorite drink. Rock formations can prevent carbon dioxide from abrupt escape like the Lake Nyos event of 1986.

## **2. AQUIFER DISPOSAL OF CARBON DIOXIDE**

The natural gas and petroleum have been stored in underground reservoirs during some millions of years. The depleted natural gas or oil fields have porous and extensive reservoir rocks and trap structures that can contain gas and liquids safely. Impermeable cap rocks prevent the leakage of gas. Some of natural gas deposits contain a large fraction of carbon dioxide. It is possible to use underground depleted natural gas and oil reservoirs as storage of carbon dioxide.

Fluids in underground rocks are compressed at the hydrostatic pressure under the load of upward groundwater column. The hydrostatic pressure at the depth of  $x$  meters below the groundwater surface is normally nearly equal to the  $x/100$  MPa. The fluid pressure in confined aquifers is often somewhat higher than the normal hydrostatic pressure but always lower than the lithostatic pressure which is usually 2.5~2.7 times of the hydrostatic pressure.

A depleted natural gas reservoir is ready to contain carbon dioxide up to the same pressure as the primary formation pressure which was the pressure of natural gas before the extraction. In natural gas fields, there exist natural caprocks which can confine gas at their primary pressures. The underground injection of carbon dioxide should be operated in the way to minimize the change of reservoir fluid pressure from the primary pressure in order to avoid unnecessary change of geological environments such as fracturing of caprocks.

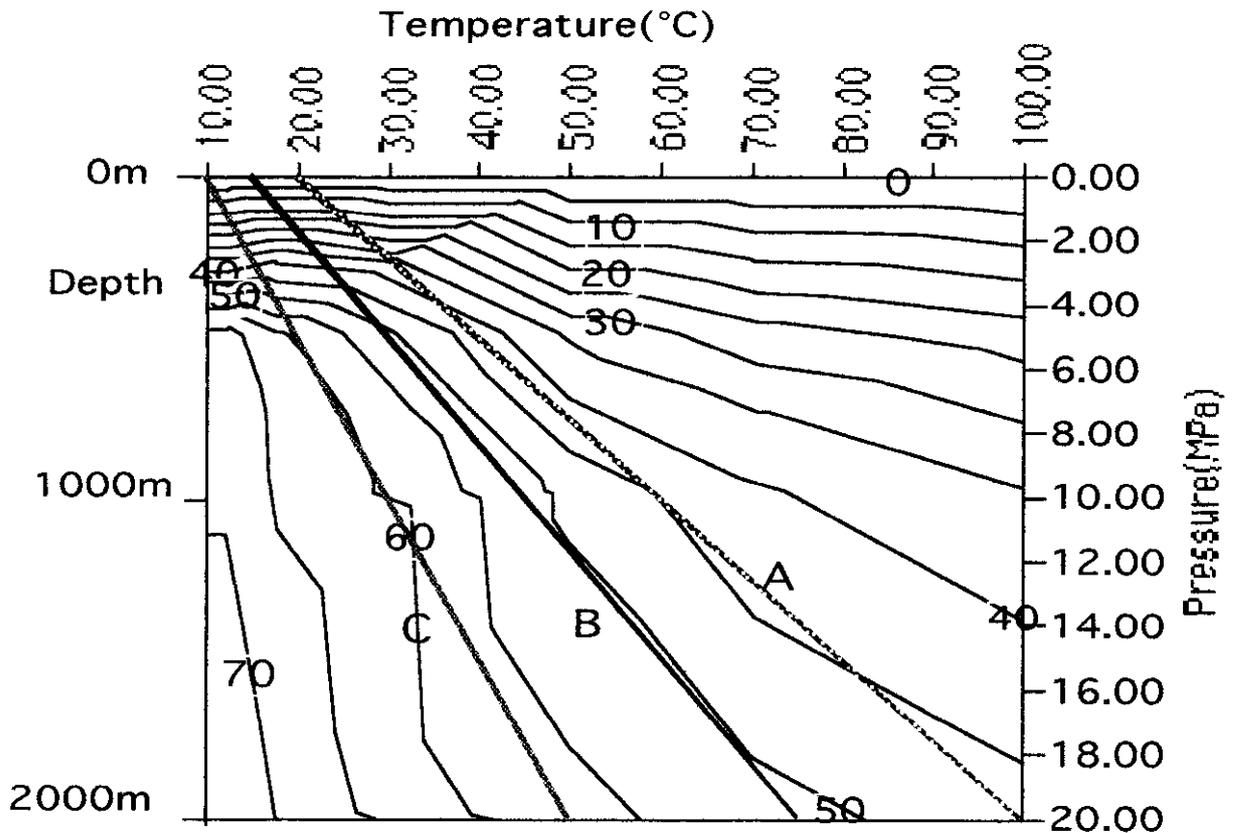


FIG.1 SOLUBILITY(kg/m<sup>3</sup>) OF CO<sub>2</sub> IN PURE WATER  
ON TEMPERATURE-PRESSURE PROFILE.

Lines A,B and C denote geothermal gradients:  
4°C/100m,3°C/100m and 2°C/100m, respectively.

Temperature also increases usually with depth. The rate of temperature increase to depth is usually 1°C/100m - 5°C/100m in many sedimentary basins. Gas is more soluble at higher pressures but less soluble at higher temperatures. Solubility of carbondioxide in pure water is mapped for combined effect of temperature and pressure in Fig.1. Contours indicate 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 after experimental data(Iijima et al,1993, Wiebe and Gaddy,1940). Density of CO<sub>2</sub>-solution was estimated by the theoretical method suggested by Ohsumi(1993). In Fig.1, it is assumed that the fluid pressure is hydrostatic and the groundwater surface is equal to the ground surface. Lines A,B and C are simplified groundwater pressure-temperature profiles of sedimentary basins with geothermal gradients 4°C/100m, 3°C/100m and 2°C/100m, respectively. Solubility profiles of CO<sub>2</sub> into water are figured from Fig.1 for the pressure -temperature conditions of cases A,B and C(Fig.2).

It is evident that cool aquifers can contain more carbon dioxide. On a low geothermal gradient case C, one cubic meters of solution can contain about 60 kg of CO<sub>2</sub> in deeper aquifer than 600m. If the porosity of reservoir rock is 20% and if only 20% of porosity is available for storage, one cubic meters of aquifer can accommodate about 2.4 kg of CO<sub>2</sub> in the case C. Saline aquifer can contain a little less CO<sub>2</sub>, as the solubility of CO<sub>2</sub> is lower in salt water than in pure water. Rough estimation suggests that one cubic meters of deep aquifer of effective porosity 20% may accommodate about 0.8~1.2 Nm<sup>3</sup> (volume at the atmospheric pressure and 20°C) of carbon dioxide which is dissolved in water.

As the circulation of groundwater is restricted in deep aquifers or aquifers which are trapped under impermeable layers, deep aquifers tend to contain old fossil water which is not suitable for drinking nor for agricultural use, mainly due to its high salinity. There are large volumes of useless aquifers in the depths of sedimentary basins in the world. Oil and gas exploration drilling rarely hits economically valuable deposits but often encounter useless aquifers which contain saline groundwater. Such groundwater often contains hydrocarbons such as methane. In some regions of Japan, they pump up fossil groundwater, and extract and use the dissolved methane and reinject water to prevent subsidence. Carbon dioxide is much more soluble in water than methane under same temperature and pressure. We can extract methane and dissolve more than 10 times carbon dioxide instead of methane into groundwater.

The CO<sub>2</sub> disposal capacity in useless aquifers can be roughly estimated by an areal method, one of techniques for calculation of oil reserves in unexplored regions (Koide et al.,1992). The estimation assumed that the suitable aquifers for CO<sub>2</sub> storage were to be found in the depths of 1% area of total sedimentary basins. This is very conservative assumption in view of repository siting conditions, applicable regulations and economic considerations. Effective thickness of reservoir is assumed to be 300m. Available pore volume is also assumed to be only 4% of reservoir volume. The solubility of CO<sub>2</sub> could be about 41 kg CO<sub>2</sub>/m<sup>3</sup>. Then, sedimentary basins may store 492,000 tons CO<sub>2</sub>/km<sup>2</sup>. The results of our brief estimation suggest that the CO<sub>2</sub>

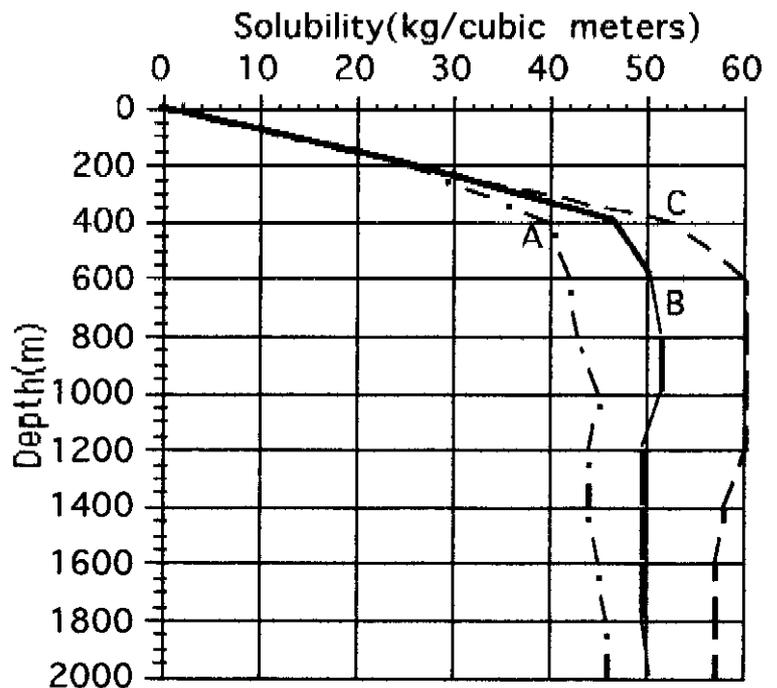


FIG.2 SOLUBILITY(kg/m<sup>3</sup>) PROFILE IN FRESH AQUIFERS. Curves A,B and C are the cases of geothermal gradients: 4, 3 and °C/100m, respectively.

storage capacity in sedimentary basins could reach well over 320 billion tons (=87gigaton-C) in the world (Koide et al.,1992).

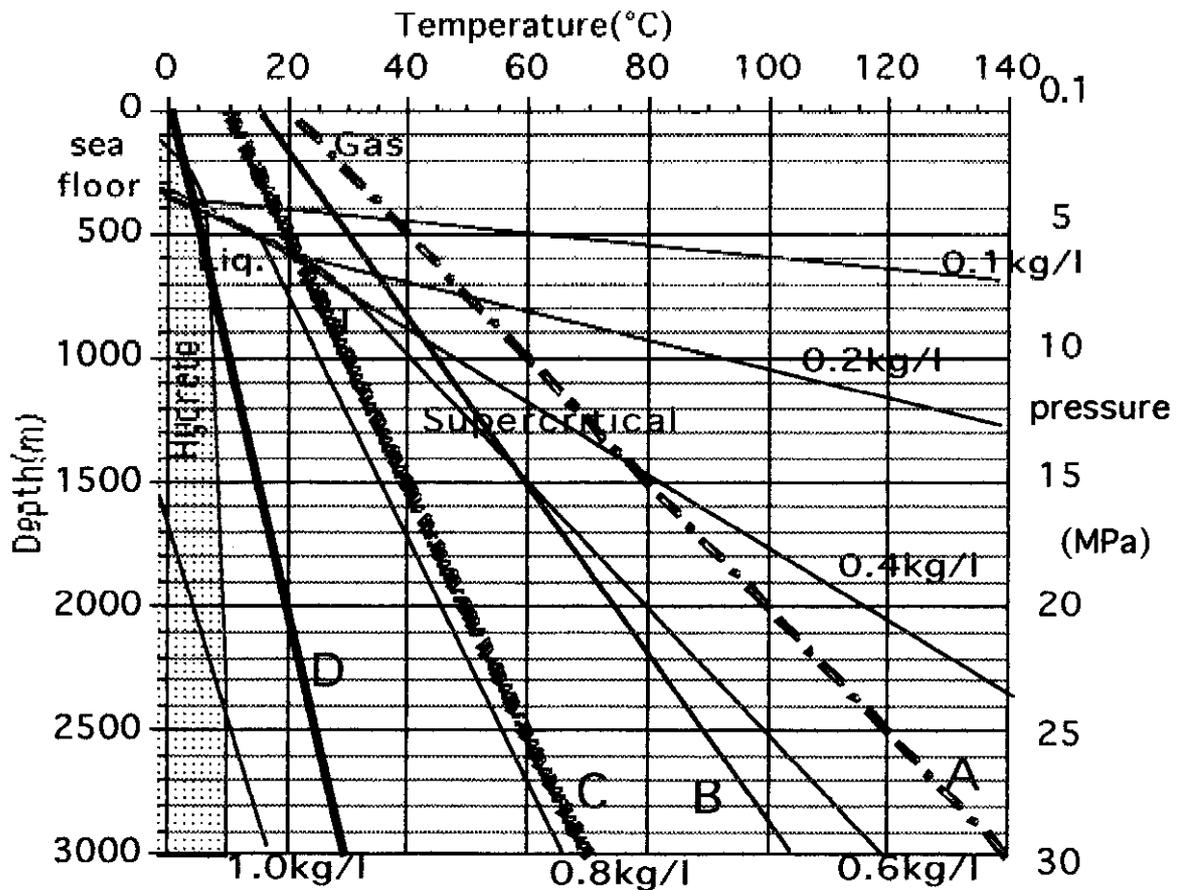


FIG.3 DENSITY OF CO<sub>2</sub> AT THE UNDERGROUND TEMPERATURE AND HYDROSTATIC PRESSURE. T denotes the critical point 31.1°C,7.39MPa.

More injection of CO<sub>2</sub> than soluble amount induces free carbon dioxide zone in underground aquifers. The critical point of carbon dioxide is at 31.1°C and 7.39MPa(Fig.3). Simple carbon dioxide is stored as a supercritical fluid in deeper reservoirs than about 800m. It is evident in density profiles(Fig.4 and Fig.3) that cooler

reservoirs of low thermal gradient can store more carbon dioxide than warmer reservoirs of high thermal gradient.

Underground reservoir can store about 10 times more carbon dioxide in the state of supercritical fluid than in the dissolved state in groundwater. If caprocks are tight and strong enough to contain the supercritical fluid, reservoir capacity becomes very large and operating costs are reduced. Three dimensional geological mapping of caprocks and careful leakage tests are necessary to store free carbon dioxide in subterranean reservoirs, while good caprocks are available in natural gas reservoirs.

### 3.SELF-TRAPPING OF CARBON DIOXIDE BY THE FORMATION OF CO<sub>2</sub>-HYDRATE

Stable condition of CO<sub>2</sub> hydrate is mapped in a temperature-pressure profile (Fig.5). The curve T-Q in Fig.5 is the boiling curve of simple carbon dioxide. CO<sub>2</sub> hydrate is stable on lower temperature and/or larger pressure than them indicated by the curve R-P-Q-S in simple CO<sub>2</sub>-water system (Saji, 1993, Chen, 1972). For formation of hydrate needs 2-3°C lower temperature than decomposition criteria of hydrate which is indicated by the curve R-P-Q-S in Fig.5 (Saji, 1993). Formation of hydrate needs somewhat lower temperature in salt water than in pure water. Exact criteria for formation of CO<sub>2</sub> hydrate in groundwater are not available. Dotted area in Fig.5 suggest probable temperature - pressure condition for formation of CO<sub>2</sub> hydrate in aquifer.

Formation of CO<sub>2</sub> hydrate is possible in sedimentary basins of very low geothermal gradient in very cool districts (geothermal gradient 1°C/100m, surface temperature 0°C on the case of line OE in Fig.5). The temperature is lower than 0°C at the bottom of permafrost zone. CO<sub>2</sub> hydrate is likely to be formed in aquifer beneath permafrost zone (A-B is permafrost zone in temperature profile A-B-D).

The curve J-B-K in Fig.6 is an example of temperature profile of sea water (data in summer, at 37.5°C, 134.5°C in the Japan Sea). The line B-A is a possible temperature profile of marine sedimentary basins, where B indicates sea floor. As the temperature is below 5°C in many parts of sea floor deeper than 300m, CO<sub>2</sub> hydrate can be formed in wide areas of marine sediments just below the sea floor.

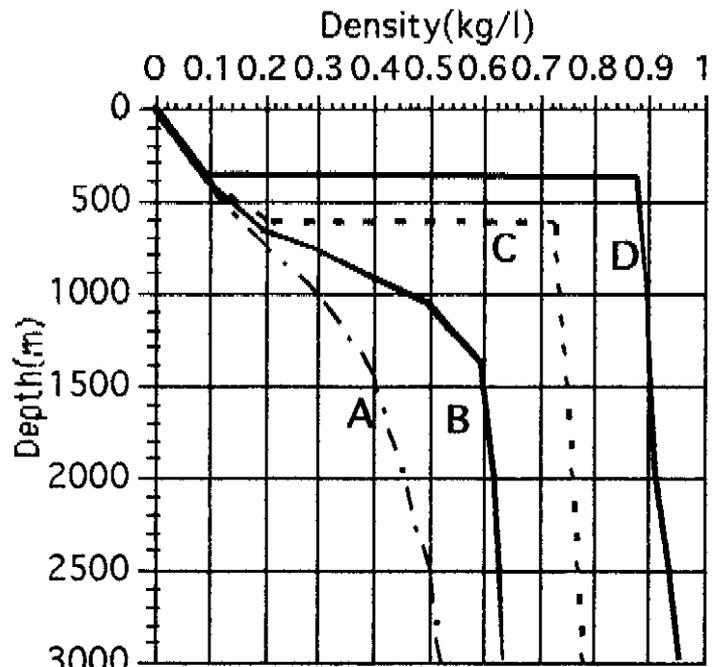


FIG.4 DENSITY PROFILE OF SIMPLE CO<sub>2</sub>

- A: geothermal gradient 4°C/100m, surface temperature 20°C,
- B: geothermal gradient 3°C/100m, surface temperature 15°C,
- C: geothermal gradient 2°C/100m, surface temperature 10°C,
- D: geothermal gradient 1°C/100m, surface temperature 0°C.

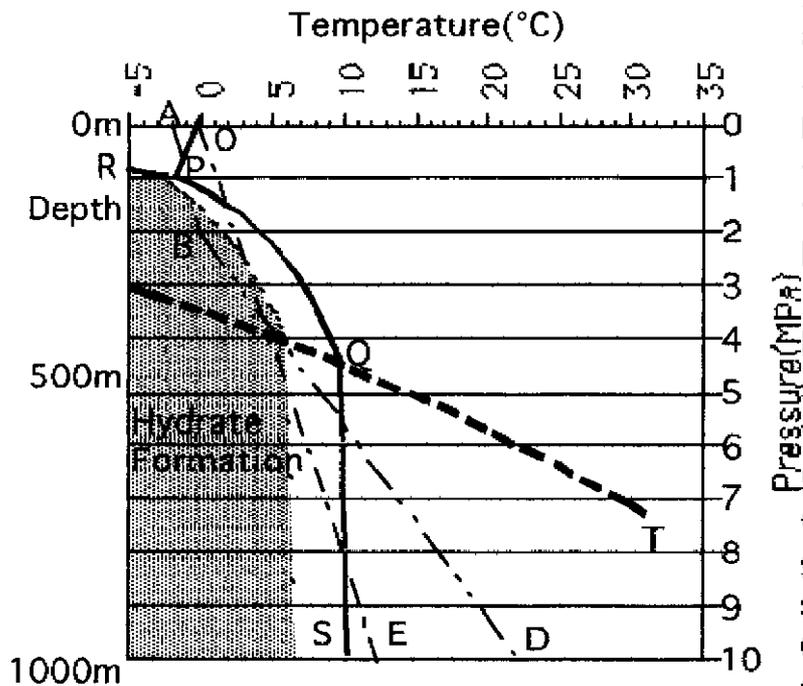
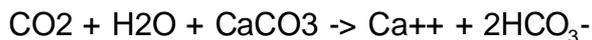


FIG.5 TEMPERATURE-PRESSURE RANGE(DOTTED AREA) FOR FORMATION OF CO<sub>2</sub> HYDRATE IN AQUIFER.

T is the critical point of CO<sub>2</sub>. The curve RPQS is the criteria for decomposition of CO<sub>2</sub> hydrate. OE is temperature profile of cool sedimentary basin of geothermal gradient 1°C/100m and surface temperature 0°C. ABD is temperature profile of permafrost zone.

Formation of CO<sub>2</sub> hydrate in pores and gaps in rocks and sediments virtually completely block the migration of fluid. Carbon dioxide which is injected in deep reservoir may migrate upward in aquifer and forms CO<sub>2</sub> hydrate cap at about the depth range of 200m-400m below the water surface in cool sedimentary basins in high latitudes in the countries such as Canada and Russia and in wide areas of cool marine sedimentary basins deeper than 300m(Fig.7).

Carbon dioxide in groundwater forms carbonic acid. Although the carbonic acid is weak acid, concentrated solution of carbon dioxide under high pressure is highly acidic. Acidic groundwater dissolve carbonate minerals to produce bicarbonate ions.



The carbonic acid attacks silicate minerals, too. Highly simplified chemical formula of silicate rock weathering may be written as follows(Berner and Lasaga,1989).

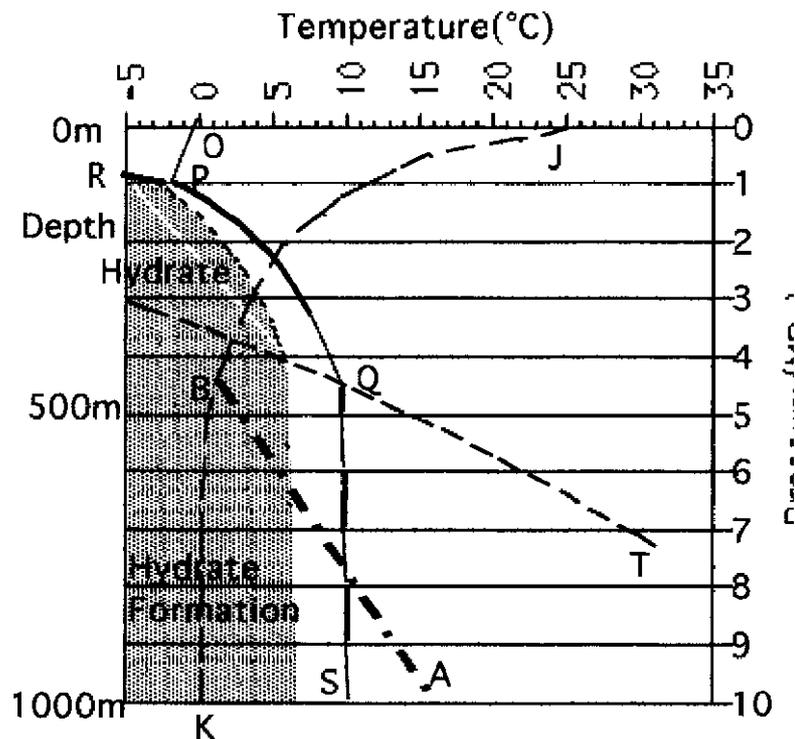
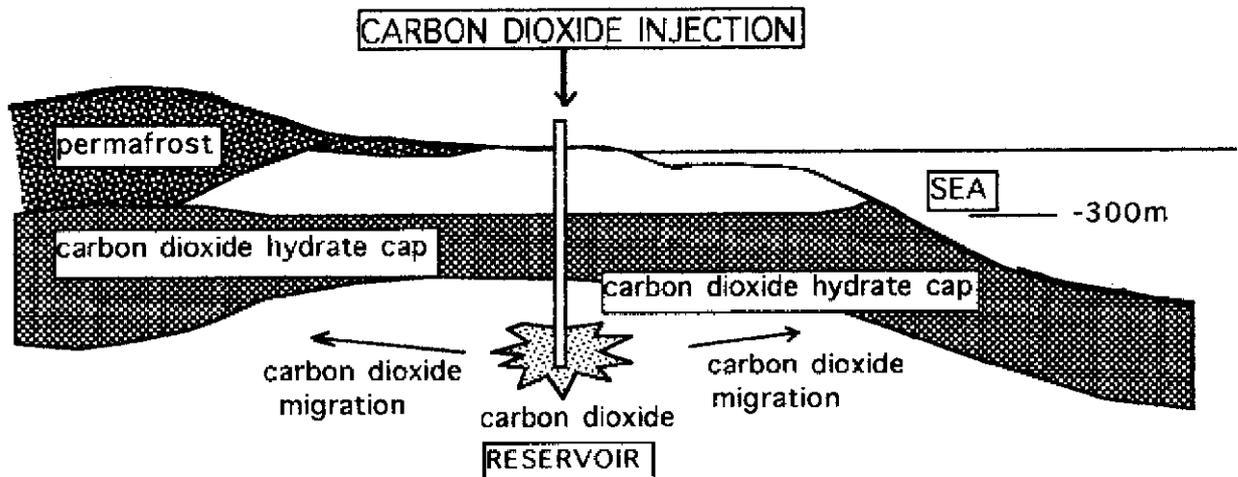


FIG.6 TEMPERATURE-PRESSURE RANGE (DOTTED AREA) FOR FORMATION OF CO<sub>2</sub> HYDRATE IN MARINE SEDIMENTARY BASIN.

The curve RPQS is the criteria for decomposition of CO<sub>2</sub> hydrate.

JBK is a typical temperature profile of sea. Line BA indicates temperature increase with depth in marine sediments where B is sea floor.



These processes of weathering of carbonate minerals and silicate minerals form bicarbonate ions to help containment of carbon dioxide and neutralize the groundwater.

Although mineralogy affects the chemical properties, groundwater is usually weak alkaline. When the solution of bicarbonate and calcium ions become alkaline, calcium carbonate would precipitate.



Precipitation of calcium carbonate may seal fractures to prevent further leakage of carbon dioxide. However, more study is necessary to clarify the behavior of carbon dioxide in various properties of groundwater and in various kinds of rocks.

#### 4. CONCLUSION

Saline aquifers provide suitable reservoirs for disposal of carbon dioxide, because saline water is useless as ordinary water resources, and because the groundwater flow in saline aquifer is extremely slow or restricted by impermeable layers. Useless aquifers of fossil water are found around oil and gas reservoirs and commonly in the depth of sedimentary basins. Small fractions of aquifers in terrestrial sedimentary basins in the world are enough to host about 320 gigaton of carbon dioxide.

The authors designed a prototype of CO<sub>2</sub> injection system into useless aquifers, while the carbon dioxide was separated from flue gas of fossil fuel power plant (Koide et al., 1992). The energy requirement for carbon dioxide injection into subterranean aquifers is about 73 kWh / ton-CO<sub>2</sub> and that the investment and operation costs for the system are about 3,000 yen/ton-CO<sub>2</sub>.

The CO<sub>2</sub>-emission-free electricity generation may become possible with the cost increase of about 30-60% (Koide et al., 1993).

The underground injection of carbon dioxide should be operated in the way to minimize the change of reservoir fluid pressure from the primary pressure which is usually almost equivalent to the hydrostatic pressure. Cooler reservoirs in low thermal gradient of sedimentary basins can host larger amounts of carbon dioxide than warmer aquifers. Cooler formation temperature than about 5°C under higher hydrostatic pressures than about three hundred meters of water column is enough to form CO<sub>2</sub> hydrate in aquifers. Formation of CO<sub>2</sub> hydrate in gaps of rocks virtually completely prevent leakage of carbon dioxide.

Carbon dioxide which is injected in deep reservoir may migrate upward in aquifer and forms CO<sub>2</sub> hydrate cap at about the depth range of 200m-400m below the water surface in cool sedimentary basins in high latitudes and in wide areas of cool marine sedimentary basins deeper than 300m. Precipitation of calcium carbonate, too, may seal fractures of rocks to prevent leakage of carbon dioxide.

Virtually complete isolation of huge amounts of CO<sub>2</sub> is possible in deep cool marine sediments and in cool sedimentary basins of high latitudes by CO<sub>2</sub> hydrate self trapping. Subseabed disposal and subterranean disposal in cool districts can realize CO<sub>2</sub> emission free fossil fuel power generation.

## REFERENCES

- Berner, R.A. and Lasaga, A.C. (1989) *Scientific American*, March:54-61.
- Chen, H.S. (1972) *USDOI, R & D Progress Report No.830*, 1-55.
- Iijima, M., Ito, K., Horizoe, H., Noguchi, Y., Tazaki, Y., Shindo, Y., Koide, H. (1993) *Kagaku Kogaku Ronbunshu*, 19:914-918.
- Koide, H., Tazaki, T., Noguchi, Y., Nakayama, S., Iijima, M., Ito, K. and Shindo, Y., (1992) *Energy Conversion and Management*, 33:619-626.
- Koide, H., Tazaki, T., Noguchi, Y., Iijima, M., Ito, K. and Shindo, Y. (1993) *Energy Conversion and Management*, 34:921-924.
- Ohsumi, T., Nakashiki, T., Shitashima, K. and Hiramata, K. (1992) *Energy Conversion and Management*, 33:685-690.
- Saji, A., Sakai, S., Noda, H., Tani, T., Kamata, H. and Kitamura, H. (1993) *Kagaku Kogaku Ronbunshu*, 19:745-751.
- Wiebe, R. and Gaddy, V.L. (1940) *J. Am. Chem. Soc.*, 62:815-817.