



## SELF-TRAPPING MECHANISMS OF CARBON DIOXIDE IN THE AQUIFER DISPOSAL

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**Abstract** - Sealing of pores and gaps in sedimentary layers by formation of CO<sub>2</sub> hydrate makes artificial caprocks which can prevent the leakage of carbon dioxide from deeper reservoirs of disposed CO<sub>2</sub>. Perfect isolation of CO<sub>2</sub> is possible in cool sedimentary basins under nearly permafrost conditions and in deep and cool submarine sediments.

Complete mitigation of greenhouse gas emission from fossil fuel power plants can be realized by deep subseabed disposal and subterranean disposal of carbon dioxide in cool districts.

### 1. DISPOSAL OF CO<sub>2</sub> IN NATURAL TRAP

The natural gas and petroleum have been stored in underground reservoirs during 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 can 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 to 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  $x/100$  MPa. The fluid pressure in confined aquifers is often somewhat higher than the normal hydrostatic pressure but lower than the lithostatic pressure which is usually about two 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 at least. 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 that might cause fracturing of caprocks.

Temperature also usually increases with depth. The rate of temperature increase with depth (geothermal gradient) is usually 1°C/100m - 5°C/100m in sedimentary basins. Gas is more soluble at higher pressures but less soluble at higher temperatures. The critical point of carbon dioxide is at 31.1°C and 7.39MPa. Simple carbon dioxide is stored as a supercritical fluid in deeper reservoirs than

about 800m. It is evident that cooler reservoirs of low geothermal gradient can store more carbon dioxide than warmer reservoirs of high geothermal gradient(Fig.1).

2. DISPOSAL OF CO<sub>2</sub> IN AQUIFER

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.

Although the tightness of caprocks for gas has not been proven for aquifers, the existence of fossil water is the evidence of confinement or extremely slow migration of groundwater in deep aquifers. Salinity of groundwater indicates the degree of isolation from fresh water. Highly saline aquifers are well confined or connected only to ocean. CO<sub>2</sub> dissolved in water is possibly isolated in saline aquifers during thousands of years.

Fossil 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 waste 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 weight of carbon dioxide instead of methane into groundwater<sup>1</sup>.

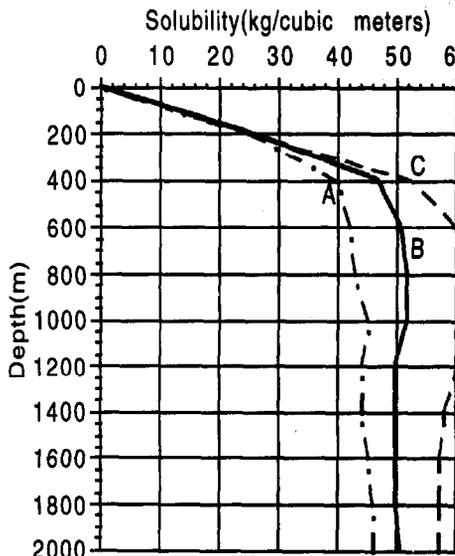


FIG.2 SOLUBILITY(kg/m<sup>3</sup>) OF CO<sub>2</sub> IN FRESH AQUIFERS.  
 A: geothermal gradient 4°C/100m, surface temperature 20°C,  
 B:geothermal gradient 3°C/100m, surface temperature 15°C,  
 C:geothermal gradient 2°C/100m, surface temperature 10°C..

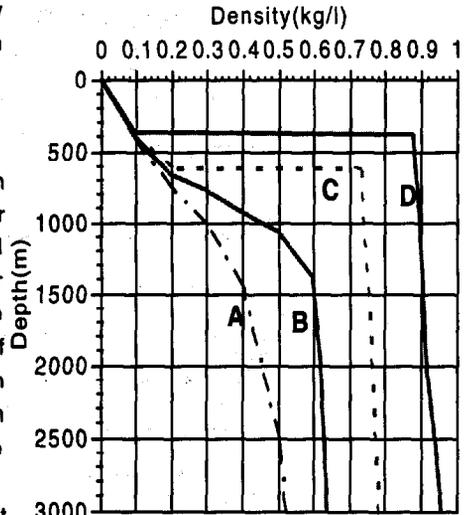


FIG.1 DENSITY OF UNDERGROUND SIMPLE CO<sub>2</sub>  
 A: geothermal gradient 4°C/100m, surface temperature 20°C,  
 B:geothermal gradient 3°C/100m, surface temperature 15°C,  
 C:geothermal gradient 2°C/100m, surface temperature 10°C,  
 D:geothermal gradient 1°C/100m, surface temperature 0°C.

Solubility of carbon dioxide in pure water at depth is estimated for several possible cases of geothermal gradients(Fig.2). It is again 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 somewhat lower in salt water than in pure water<sup>2</sup>. 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 at 20°C) of carbon dioxide which is dissolved in water.

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

Stable condition of CO<sub>2</sub> hydrate is shown in a temperature-pressure diagram (Fig.3)<sup>2,3</sup>. The curve T-Q in the Fig.3 is the boiling curve of simple carbon dioxide. CO<sub>2</sub> hydrate is stable on lower temperature and/or larger

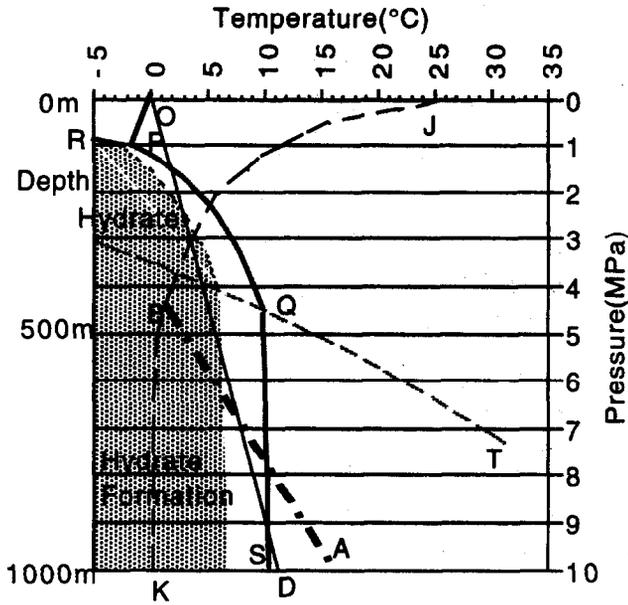


FIG.3 TEMPERATURE-PRESSURE RANGE (DOTTED AREA) WHERE FORMATION

OF CO<sub>2</sub> HYDRATE SEEMS POSSIBLE IN SEDIMENTS.

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

The line OD is a simplified possible temperature change with depth

in very cool sedimentary basins of high latitudes.

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

pressure than them indicated by the curve R-P-Q-S in CO<sub>2</sub>-water system<sup>3,4</sup>. 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 the Fig.3<sup>2</sup>. 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 saline groundwater are not available. Dotted area in Fig.3 suggests probable temperature -pressure condition for formation of CO<sub>2</sub> hydrate in aquifer.

Formation of CO<sub>2</sub> hydrate is possible in very cool sedimentary basins of low geothermal gradient with freezing surface temperatures (represented by line O-D in Fig.3). The temperature is lower than 0°C at the bottom of permafrost zone. CO<sub>2</sub> hydrate is likely to form in aquifer beneath permafrost zone.

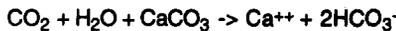
The curve J-B-K in Fig.3 is an example of temperature profile of sea water (data in summer, at 37.5°N, 134.5°E in the Japan Sea). The line B-A is a possible temperature - pressure change in marine sedimentary basins, where B indicates sea floor. As the temperature is below

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.

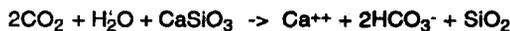
Formation of CO<sub>2</sub> hydrate in pores and gaps in rocks and sediments virtually completely block the migration of fluid. Carbon dioxide which is injected in deep reservoir may migrate upward in upper aquifer but forms CO<sub>2</sub> hydrate cap at about the depth range of 200m-400m below the water surface in cool sedimentary basins in high latitudes and in wide areas of cool marine sedimentary basins deeper than two or three hundred meters (Fig.4).

#### 4. CHEMICAL TRAP

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 dissolves 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<sup>5</sup>.



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 weakly 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. Precipitation of carbonates makes artificial caprocks to isolate carbon dioxide dissolved in groundwater. However, more detailed study for water-rock interaction is necessary to clarify the behavior of carbon dioxide in various properties of groundwater and in various kinds of rocks.

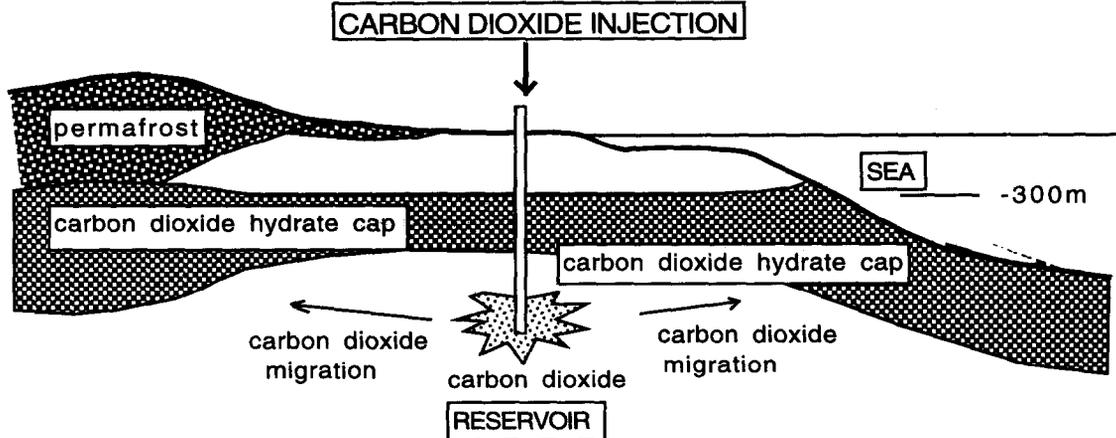


FIG.4 CO<sub>2</sub>-HYDRATE TRAPPING OF CO<sub>2</sub> IN DEEP AND COOL AQUIFER.

### 5.CONCLUSION

The underground injection<sup>1</sup> 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 a few 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 two or three hundred meters. Precipitation of calcium carbonate, too, may seal fractures of rocks to prevent leakage of carbon dioxide.

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.

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.

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