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**SUBSURFACE CO<sub>2</sub> DISPOSAL WITH ENHANCED GAS RECOVERY  
AND BIOGEOCHEMICAL CARBON RECYCLING**

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**ABSTRACT**

An enormous amount of methane has accumulated in the shallow subsurface in many part of the world. However, most of this natural gas resource is not economically recoverable at the present time as the methane is adsorbed in coal seams, trapped in methane hydrate (clathrate) or dissolved in saline groundwater. Shallow accumulations of methane pose the threat of potentially increasing the rate of global warming. Enhanced gas recovery by subsurface CO<sub>2</sub> injection (CO<sub>2</sub>-EGR) is potentially an option for greenhouse gas control combined with use of potential energy resources. CO<sub>2</sub> injection coupled with extraction of coal mine methane and coalbed methane may make emission-free closed circuit power plants possible. Coal seams in Japan and under the seabed around Japan could potentially adsorb about 10 Gtonne of CO<sub>2</sub> and in so doing displace 2.5 trillion cubic metres of coalbed methane. About 12 Gtonnes of CO<sub>2</sub> could potentially be sequestered in hydrate layers, displacing 6 trillion cubic metres of methane hydrate under the deep seabed around Japan. Similarly, about 26 Gtonne of CO<sub>2</sub> could potentially be sequestered in saline groundwater, displacing 6 trillion cubic metres of methane in sedimentary basins in Japan. Subsurface CO<sub>2</sub> injection, coupled with enhanced gas recovery (CO<sub>2</sub>-EGR) could potentially sequester a total of 48 Gtonne of CO<sub>2</sub> in and around the Japanese Islands, with the prospect of also having enhanced production of nearly ten trillion cubic metres of methane.

The extremely light isotopic compositions of carbon in methane suggest that methanogens formed

many of the subsurface accumulations of methane-rich natural gas in the world. Chemolithotrophic methanogens, form methane from CO<sub>2</sub>, thereby obtaining energy without sunlight under anoxic circumstances. Methanogens are often blamed for greenhouse gas emissions as they produce methane in organisms and in rice paddies for example. However, application of CO<sub>2</sub>-EGR for production of subsurface biogenic methane displaced by sequestration of CO<sub>2</sub> might result in enhanced carbon recycling. Present-day subsurface ecosystems are probably somewhat similar to ancient ecosystems adapted to exist in an anoxic CO<sub>2</sub>-rich atmosphere under high pressure and temperature. Biogenic methanogenesis is thought to occur even in deep basaltic aquifers offering the opportunity for deep subsurface biogeochemical carbon recycling utilising CO<sub>2</sub>-EGR to produce enhanced sequestration of greenhouse gases accompanied by the development of potential new energy resources.

Key words: CO<sub>2</sub> Aquifer, Methane, Coalbed Methane, Hydrate, methanogen, Sealing.

## **INTRODUCTION**

Japan started a new national R&D project on "Underground Storage of Carbon Dioxide" in the year 2000 (Kaya et al., 2000). The Research Institute of Innovative Technology for the Earth (RITE) is responsible for implementing this 5-year R&D program in co-operation with the Safety & Environmental Center for Petroleum Development (SEC) under contract from the New Energy and Industrial Technology Development Organization (NEDO) and under the supervision of the Ministry of International Trade and Industry (MITI). The main target of this program is to assure the long-term safety of underground storage of carbon dioxide through a small-scale in-situ injection test with some laboratory experiments. Social and economic aspects of the sequestration technology are also included in this study.

Although this R&D study is concerned with the simple CO<sub>2</sub> injection & storage concept mainly into offshore aquifers, some advanced concepts of CO<sub>2</sub> sequestration will also be studied in Japan. Japan is densely populated, industrialized and short of energy resources. Efficient use of underground energy resources is very important. The Japanese Islands are tectonically very active; they are located on the boundaries of four major plates: the Eurasian, Pacific Ocean, North American and Philippine Sea Plates. The long-term isolation of CO<sub>2</sub> may be feasible even in tectonically active formations. This paper deals with a proposal for the use of advanced technologies involving subsurface CO<sub>2</sub> injection with associated natural gas recovery followed by CO<sub>2</sub> sequestration and ultimately, formation of new hydrocarbon energy resources in the long term.

## COALBED METHANE AND OTHER SUBSURFACE METHANE

An enormous amount of methane exists in shallow subsurface formations around the world. However, most of the subsurface methane, which is dissolved in saline groundwater or trapped in hydrate clathrate is difficult, if not impossible to economically exploit. Shallow subsurface methane, which is about 20 times as powerful as a greenhouse gas as CO<sub>2</sub>, poses the hidden threat of greatly enhancing global warming. The Geological Survey of Japan estimated that about 887 billion cubic metres of methane are dissolved in deep saline groundwater in aquifers in and around Japan, and that almost 6 trillion cubic metres of methane are trapped as methane hydrate under the deep seabed around the Japanese Islands. Recovery of subsurface natural gas potentially constitutes a large new energy source and could minimise the future threat of inadvertent release of greenhouse gas. Replacement of subsurface methane by injection of anthropogenic CO<sub>2</sub> may be effective for sequestration of anthropogenic greenhouse gases and for mitigation of the threat of large scale natural greenhouse gas release. Replacement of dissolved methane in groundwater by CO<sub>2</sub> can sequester about 26 Gt of CO<sub>2</sub> in and around the Japanese Islands because CO<sub>2</sub> is some ten times more soluble than methane in deep aquifers (Koide et al., 1993). Methane hydrate can absorb almost 12 Gt of CO<sub>2</sub> in and around the Japanese Islands because the hydrate clathrate can absorb the same volume of CO<sub>2</sub> as methane.

Coal mine methane is not only dangerous to mine workers, but is also a significant source of greenhouse gas. Degasification of coal mines is very difficult, as methane is adsorbed in the micropores of coal seams. As CO<sub>2</sub> has a higher affinity of adsorption to coal than methane, injection of CO<sub>2</sub> into coal seams displaces the adsorbed methane. Coal seams offer a geological sink for CO<sub>2</sub> storage and a source of natural gas energy (Stevens et al., 1999). CO<sub>2</sub> sequestration into coal seams with recovery of coalbed methane can provide the opportunity to develop a CO<sub>2</sub> emission-free closed-circuit system of electric power generation (Fig. 1).

Only two underground coal mines are in operation in Japan, however numerous abandoned coal mines in Japan still contain significant amounts of coal and coal mine methane. Unminable coal seams also contain coalbed methane. Yamaguchi and Yamazaki (1999) estimated that about 2.5 trillion cubic metres of methane are contained in coal seams in and around Japan. Coal seams can adsorb almost 10 Gtonne of CO<sub>2</sub> in and around the Japanese Islands because the coal can adsorb twice as much CO<sub>2</sub> as methane (Stevens et al., 1999). Many coal fired power plants emit very large amounts of CO<sub>2</sub> into the atmosphere in the major coal field areas in Japan (Fig.2). Although mostly imported coal is burnt in the power plants in Japan, coal seams in Japan can sequester huge amounts

of CO<sub>2</sub> resulting in CO<sub>2</sub> emission-free coal-fired power plants. Counter extraction of coal mine methane and coalbed methane coupled with CO<sub>2</sub> injection may make emission-free closed circuit power plants possible.

## **STABILIZATION OF HYDRATE SEAL BY CO<sub>2</sub> INJECTION AND EXTRACTION OF SUBSURFACE METHANE**

Gas hydrate is formed in sediments just under the deep sea floor in areas of high pressure and low subseabed groundwater temperatures (Fig.3). Natural gas tends to accumulate under gas hydrate or permafrost layers, which act as highly effective seals of gas. It is possible that global warming may be accelerated by emission of trapped methane due to dissolution of permafrost or hydrate layers as a result of warming. Injection of CO<sub>2</sub> under the permafrost and methane hydrate caps, with counter extraction of trapped methane, may produce a CO<sub>2</sub> hydrate-filled layer under the permafrost layer and replace methane hydrate with CO<sub>2</sub> hydrate (Fig.4). As CO<sub>2</sub> hydrate is more stable at higher temperatures and pressures than ice and methane hydrate, the formation of CO<sub>2</sub> hydrate will potentially stabilise the hydrate seal even during global warming effects, and will prevent the escape of free gas and the disintegration of unconsolidated sediments. CO<sub>2</sub> injection under gas-hydrate and permafrost layers could potentially allow the production of natural gas, mitigate greenhouse gas emissions and stabilise frozen and hydrated ground at the same time.

Even more speculatively, Takahashi et al. (2000) have proposed geological sequestration of CO<sub>2</sub> in deep saline aquifers associated with oceanic and continental basaltic layers. Layers of fractured basalt have significant porosity often as high as 10% to 30%. CO<sub>2</sub> stored in the aquifers should react with the basalt host rocks over time to form solid (Ca, Mg)CO<sub>3</sub>. Extensive layers of oceanic and continental basalt could provide a huge sink for CO<sub>2</sub>. When CO<sub>2</sub> is injected into deep oceanic basalt. The CO<sub>2</sub> would migrate freely at high temperatures but form hydrate clathrate when it escapes upward into cool subseabed aquifers (Koide et al., 1997). If this model is correct, oceanic basaltic layers might provide a virtually limitless volume for long term CO<sub>2</sub> storage by autogenous hydrate sealing (Fig.5).

Biogenic methanogenesis is active even in deep basaltic aquifers (Stevens and McKinley, 1995), despite the fact that deep aquifers in basaltic lava layers lack organic matter. In deep basaltic aquifers, methanogens might produce methane from CO<sub>2</sub> of inorganic origin and H<sub>2</sub> derived from reduction of thermal water by Fe(II) in basaltic glass. CO<sub>2</sub> injection into deep basaltic lava layers would make the aquifer environment similar to an ancient reducing environment where methanogens were dominant

under conditions of high CO<sub>2</sub> pressure, high temperature and low concentrations of organic matter (Fig.5). CO<sub>2</sub> stored in deep basaltic aquifers would be reduced to methane by methanogens. Artificial stimulation of the natural deep biogeochemical carbon cycle by CO<sub>2</sub> injection may facilitate greenhouse gas control with the added benefit of renewal of energy resources (methane). If this were technically and economically feasible, in the future basaltic layers within oceanic crust may provide sites for virtually limitless CO<sub>2</sub> sequestration coupled with production of methane to provide an energy source for the future.

### **GEOCHEMICAL AUTOGENOUS SEALING IN AN “AMBUSH AQUIFER”**

As pointed out earlier, gas-hydrate-filled layers are excellent gas seals. CO<sub>2</sub> injection into aquifers in the deep ocean will form CO<sub>2</sub> hydrate-filled layers at sub-sea bottom depths greater than 300m, under the right pressure and temperature conditions. Autogenous sealing of CO<sub>2</sub> in deep cool aquifers (Fig.6) could provide long term subsurface containment of CO<sub>2</sub>. Autogenous sealing is likely to be effective because every crack of the caprock will be sealed even if earthquakes temporarily fracture the cap. However, autogenous sealing by “hydration clogging” is effective only where the seafloor is deeper than about 300m and at sub-permafrost levels in onshore regions. In Japan, the climate is too warm for hydrates to form in onshore aquifers or in shallow subseabed aquifers. In the geotectonically unstable Japanese Islands, geological formations are often inhomogeneous and/or densely faulted. It is also very difficult to detect open fractures in deep caprocks and usual grouting technologies are not effective for sealing small open fractures occurring within the caprock.

The authors therefore propose a model, termed an “ambush aquifer” in which it is possible to seal effectively disseminated small open fractures. If CO<sub>2</sub> encounters an alkaline groundwater rich in calcium ions, calcium carbonate precipitates and clogs pores and fissures in the rocks. Autogenous sealing of CO<sub>2</sub> occurs in calcium-rich alkaline aquifers. If fissures in the caprocks or seepage of CO<sub>2</sub> are encountered, calcium-rich alkaline “ambush aquifers” are formed by injection of carbonate-rich water into an overlying aquifer or into open fractures in the caprocks.

### **REPLACEMENT OF SUBSURFACE METHANE BY CO<sub>2</sub> LEADING TO BIOGEOCHEMICAL CARBON CYCLE**

The extremely light isotopic compositions of carbon in methane contained in many subsurface accumulations of methane-rich natural gas around the world suggest that methanogenic bacteria may have formed much of the methane. Lithoautotrophic methanogens belonging to the Archaea produce methane from CO<sub>2</sub> thereby gaining energy without the help of sunlight in an anoxic environment. A

subsurface ecosystem can be compared to an ancient ecosystem that is adapted to an anoxic CO<sub>2</sub>-rich atmosphere under high pressure and temperature. Methanogens are also of course, responsible for enhanced greenhouse gas emissions through methane generated in the digestive systems of cows and termites, and in rice paddies for example.

Autogenous sealing in geochemically conditioned aquifers could produce long-term safe storage of CO<sub>2</sub> in onshore and shallow offshore aquifers. Deep aquifers in sedimentary basins often contain methane-rich warm saline water. The methane results from the actions of methanogens in deep “fossil water” aquifers in the absence of sunlight in anoxic circumstances. It is likely that methanogens will also form methane from anthropogenic CO<sub>2</sub> sequestered for long periods in the subsurface. Re-application of CO<sub>2</sub>-EGR to subsurface biogenic methane converted from sequestered CO<sub>2</sub>, makes carbon recycling possible. Biogeochemical carbon recycling may also be possible through CO<sub>2</sub> injection into methane-rich saline aquifers under a geochemically sealed aquifer (Fig.7).

Underground formations in Japan and under the seabed around Japan contain approximately 2.5 million cubic metres of coalbed methane, 6 trillion cubic metres of methane related to gas hydrate and 0.9 trillion cubic metres of methane dissolved in saline groundwater. Coal seams in Japan and under the seabed around Japan must be able to adsorb about 10 Gtonne of CO<sub>2</sub>, replacing 2.5 trillion cubic metres of coalbed methane. About 12 Gtonnes of CO<sub>2</sub> might be trapped in hydrate layers, replacing 6 trillion cubic metres of methane hydrate under the deep seabed around Japan. About 26 Gtonne of CO<sub>2</sub> could potentially dissolve in saline groundwater thereby replacing 6 trillion cubic metres of methane in the sedimentary basins of Japan. Enhanced gas recovery by subsurface CO<sub>2</sub> injection (CO<sub>2</sub>-EGR) could potentially sequester a total of 48 Gtonne of CO<sub>2</sub> in and around the Japanese Islands, with the related production of a possible ten trillion cubic metres of methane (Table 1). Ordinary aquifers and depleted oil and gas fields could potentially sequester a total of 75 Gtonne of CO<sub>2</sub> in and around the Japanese Islands. Thus the total CO<sub>2</sub> sequestration capacity in and around Japan in ordinary aquifers, depleted oil and gas fields and by CO<sub>2</sub>-EGR could be as much as 113 Gtonne of CO<sub>2</sub>, while ordinary aquifers could potentially sequester about 3 Ttonne of CO<sub>2</sub>-EGR (Koide, 1999). CO<sub>2</sub>-EGR accompanied by efficient use of subsurface methane energy resources may be a potential solution for greenhouse gas control.

## CONCLUSIONS

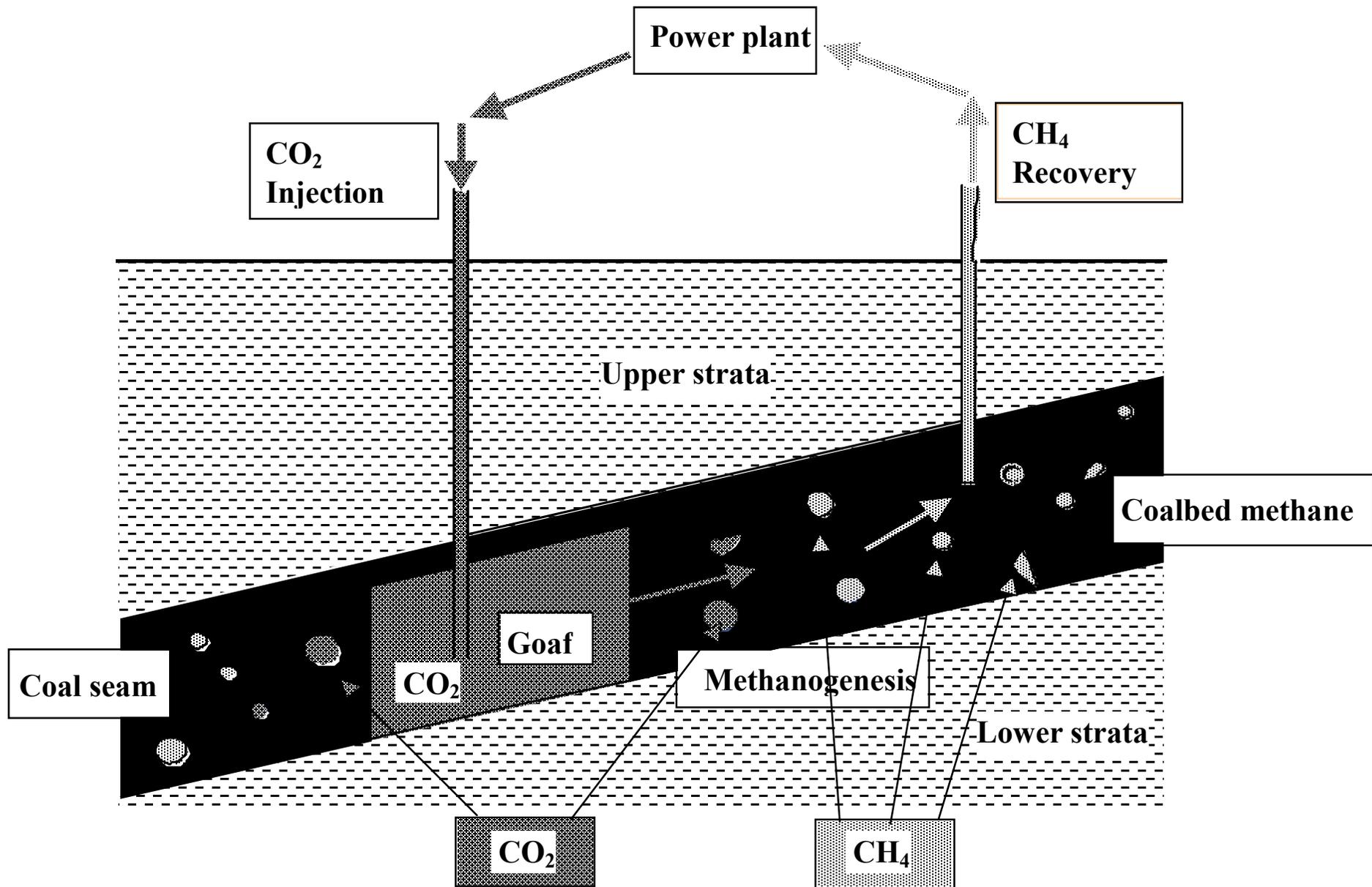
1. Geological sequestration of CO<sub>2</sub> is technologically and economically a possible option for mitigation of greenhouse gas emission.

2. CO<sub>2</sub> injection with coupled extraction of coal mine methane and coalbed methane could make CO<sub>2</sub> emission-free closed circuit power plants a possibility.
3. Coal seams in Japan and under the seabed around Japan could adsorb about 10 Gtonne of CO<sub>2</sub> displacing 2.5 trillion cubic metres of coalbed methane. Under the deep seabed around Japan about 12 Gtonne of CO<sub>2</sub> could be sequestered in hydrate layers, at the same time displacing 6 trillion cubic metres of methane hydrate. About 26 Gtonne of CO<sub>2</sub> could be sequestered in saline groundwater, displacing 6 trillion cubic metres of methane in Japanese sedimentary basins.
4. Enhanced gas recovery by subsurface CO<sub>2</sub> injection (CO<sub>2</sub>-EGR) has the potential to sequester a total of 48 Gtonne of CO<sub>2</sub> in and around the Japanese Islands with the coupled production of nearly ten trillion cubic metres of methane.
5. Autogenous sealing by hydrate formation and by geochemically conditioned so-called “ambush aquifers” may offer the opportunity for long-term safe containment of CO<sub>2</sub> in aquifers.
6. Long term aquifer storage of CO<sub>2</sub> could provide the opportunity for CO<sub>2</sub> to be converted into methane by methanogens. An important requirement for underground CO<sub>2</sub> recycling is hydrogen supply (the energy source). This could be derived from microbial decomposition of organic matter, from geochemical water-rock interaction and from deep geothermal activities. Perhaps in the future biogeochemical carbon cycle in basaltic layers in the oceanic crust could provide a virtually limitless CO<sub>2</sub> sink and a source of methane?

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*Fig.1 Closed circuit power plant with CO<sub>2</sub> injection and recovery of coalbed methane and coal mine methane.*

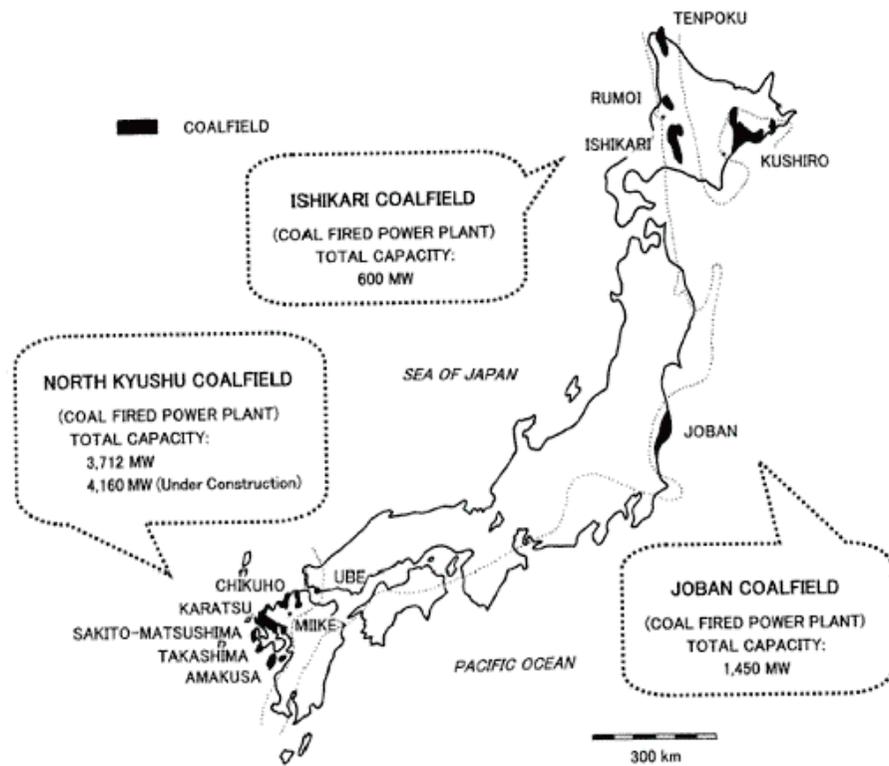
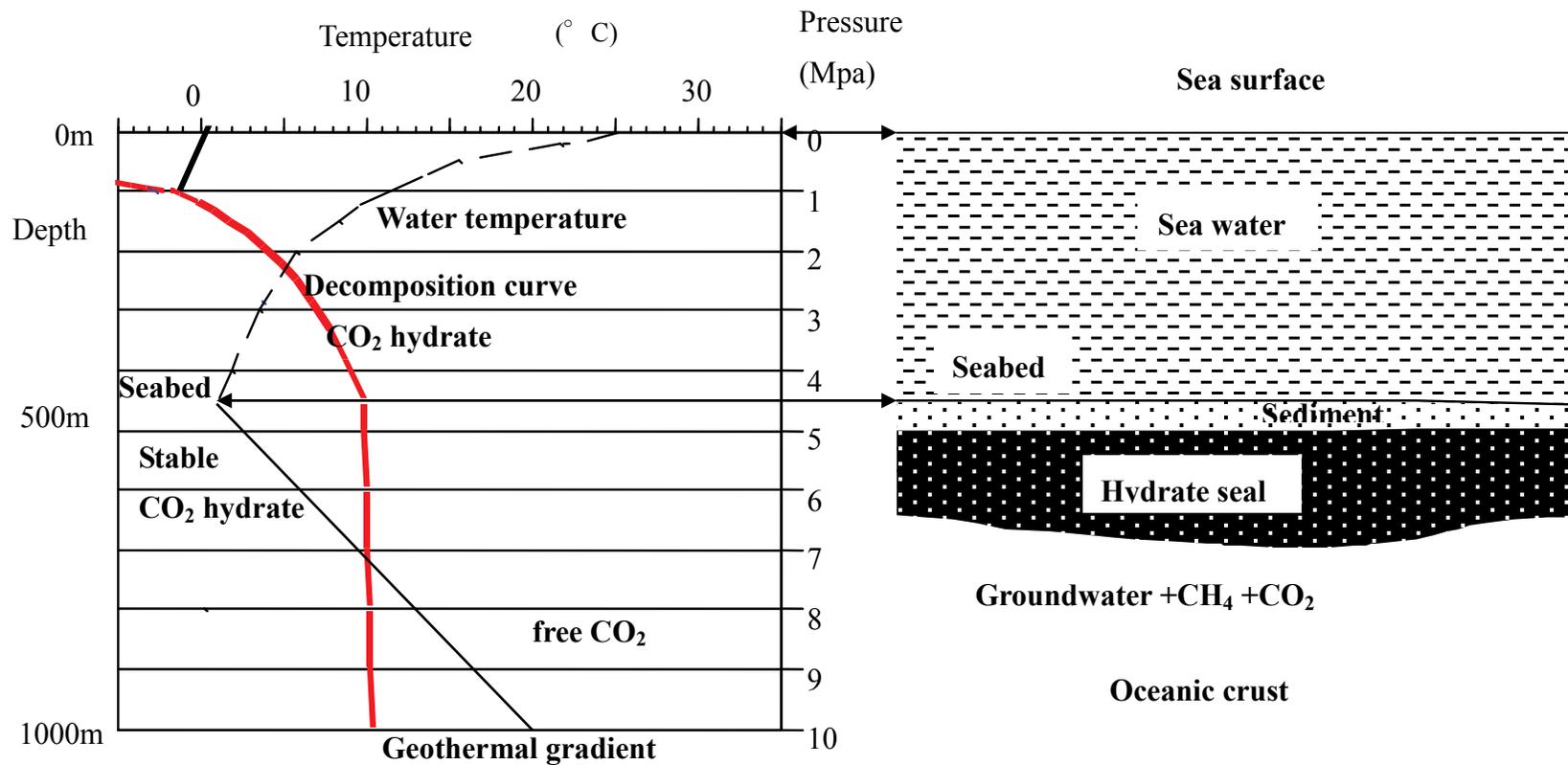
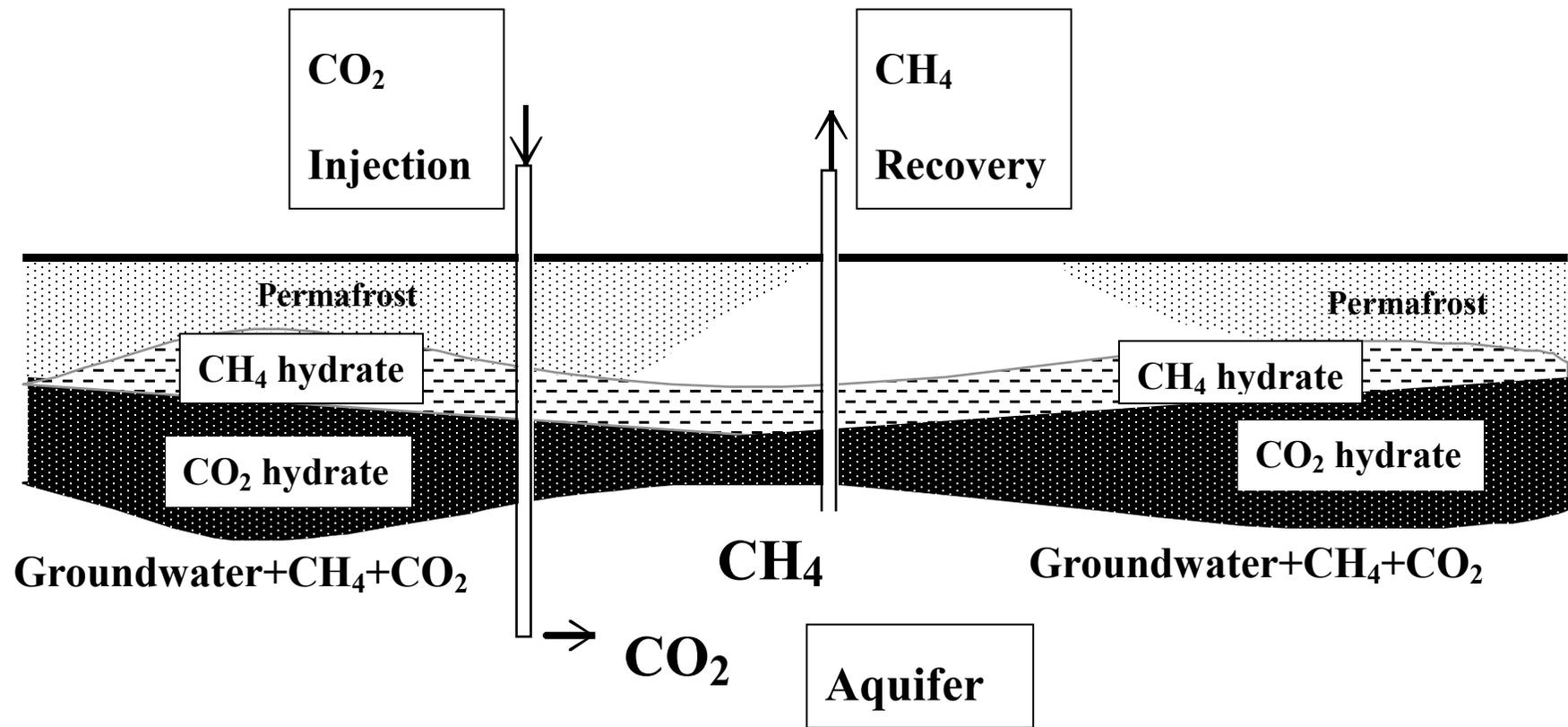


Fig.2 Capacity and CO<sub>2</sub> emission of coal-fired electric power plants in major coalfield areas in Japan

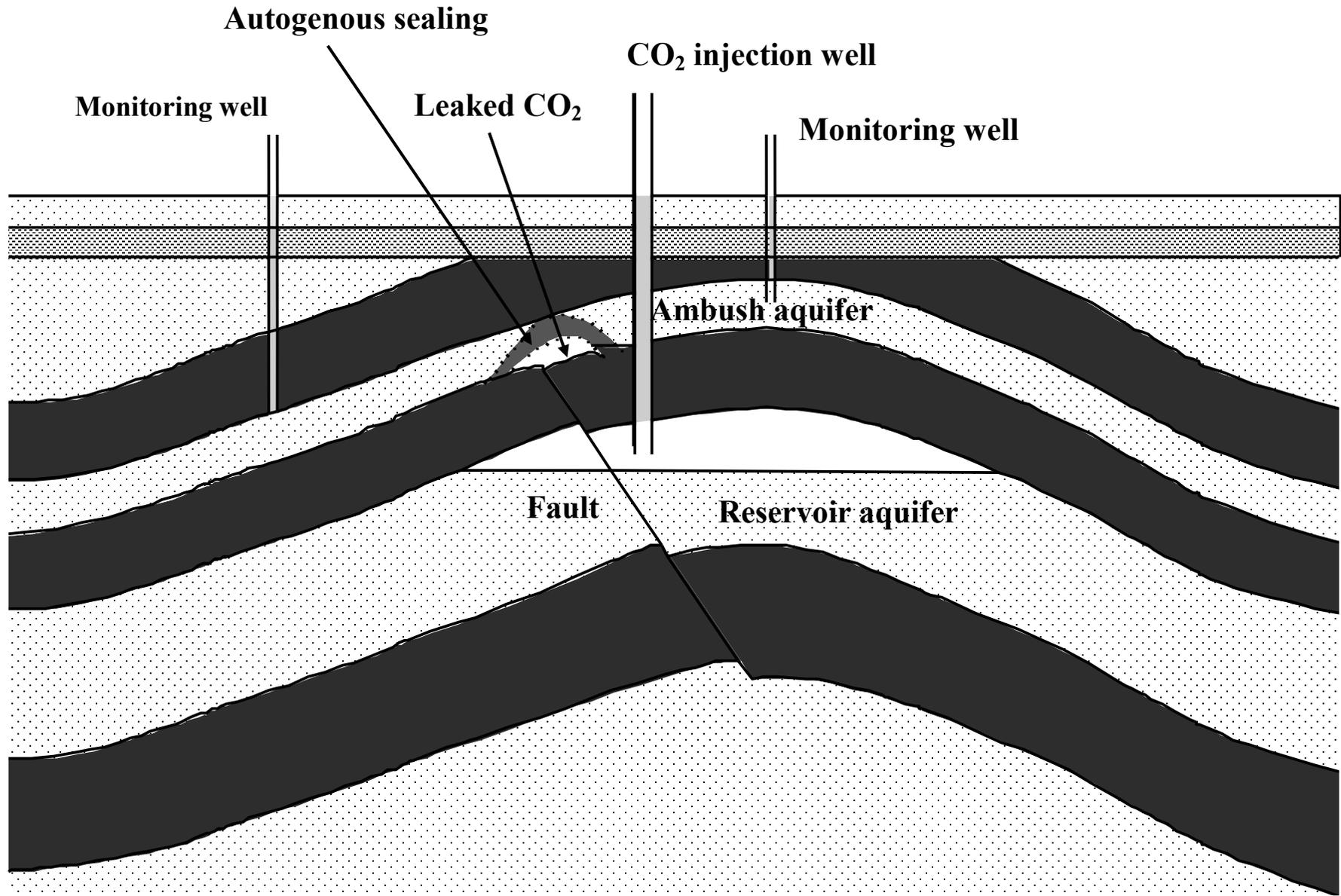


*Fig.3 Autogenous sealing by formation of CO<sub>2</sub> hydrate in subseabed aquifers. Cool water at deep ocean and high geothermal gradient in oceanic crust provides deep free CO<sub>2</sub> storage self-sealed in subseabed sediments.*

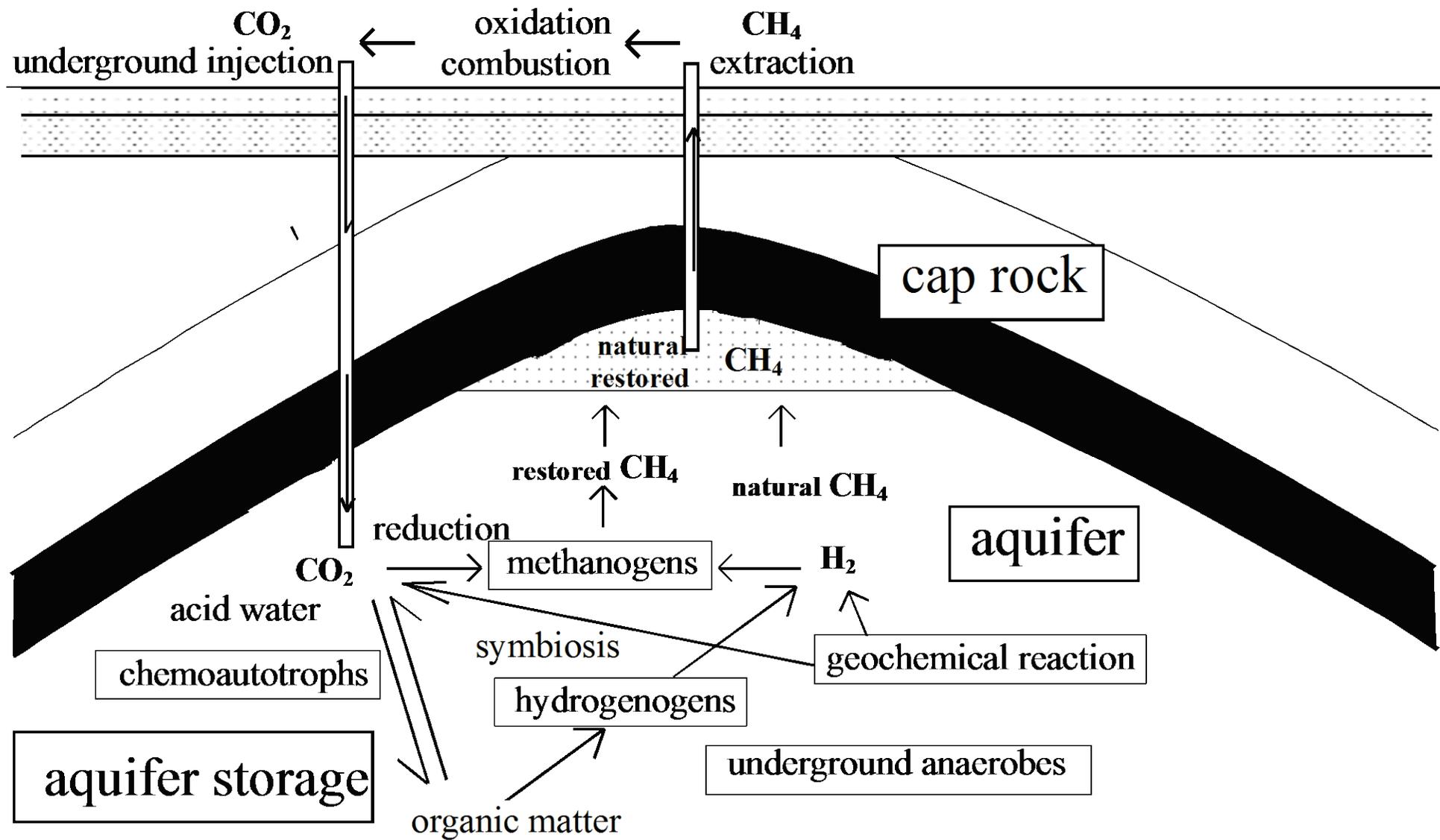


*Fig.4 CO<sub>2</sub> injection under permafrost and hydrate layers and counterextraction of methane stabilizes frozen sediments and prevents release of greenhouse gas by formation of CO<sub>2</sub> hydrate self-seal.*





*Fig.6 Autogenous sealing in an “ambush aquifer” prevents further leakage of CO<sub>2</sub>.*



*Fig.7 Microbial restoration of methane deposits in  $\text{CO}_2$  aquifer storage.*

***Table 1 Untapped methane resources and possible capacity of coupled CO<sub>2</sub> sequestration in Japan and under the seabed around Japan***

	<b>CH<sub>4</sub> possible reserve</b>	<b>possible capacity of CO<sub>2</sub> sequestration</b>
<b>Coalbed methane</b>	<b>2.5 Tm<sup>3</sup></b>	<b>10 Gtonne</b>
<b>Dissolved methane in saline groundwater</b>	<b>0.9 Tm<sup>3</sup></b>	<b>26 Gtonne</b>
<b>Methane hydrate</b>	<b>6 Tm<sup>3</sup></b>	<b>12 Gtonne</b>
<b>TOTAL</b>	<b>9.4 Tm<sup>3</sup></b>	<b>48 Gtonne</b>