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GEOLOGICAL SEQUESTRATION AND MICROBIOLOGICAL RECYCLING OF CO_2 IN AQUIFERS

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ABSTRACT

The world aquifers are estimated to have total storage capacity larger than three trillion tons of carbon dioxide. Systematic drilling survey for oil exploration suggests that the annual 70 million tons carbon dioxide injection is possible longer than 22 years in aquifers with anticlinal geological structures in and around Japan. The annual 70 million tons carbon dioxide injection separated from flue gas of fossil-fueled power plants into aquifers may reduce Japan's artificial carbon dioxide emission as much as 6% with annual cost of 420 billion yens that match 1,200 yens/c-ton carbon tax.

Extraction of methane dissolved in fossil groundwater squeezed out by the carbon dioxide injection makes possible to utilize low grade of natural gas resources. Hydrate-filled layers are formed under deep sea floor due to high pressure and cool temperature. Free natural gas tends to accumulate under gas-hydrate-filled layers and under permafrost layers, because the layers are perfect insulators of gas. Carbon dioxide injection is expected to stabilize gas-hydrate-filled layers and permafrost caps, because the carbon dioxide hydrate is stable at wider pressure-temperature range than methane hydrate and ice.

Carbon dioxide injection under gas-hydrate-filled layers or under permafrost layers may realize the greenhouse gas mitigation and recovery of unused natural gas. Autogenous sealing of carbon dioxide in deep and cool aquifers assures virtually complete and practically unlimited subsurface containment of carbon dioxide.

Chemoautotrophs fix carbon dioxide in deep aquifers even in the absence of sunlight. Thermophilic methanogens can convert the carbon dioxide into methane in anoxic and hot aquifers. Biogenic restoration of subsurface hydrocarbon deposits may be possible in CO_2-injected aquifers probably after tens or hundreds of years. Microbiological recycling of carbon dioxide in aquifers is an attractive possibility for energy-short countries such as Japan. Important key for underground CO_2 recycling is hydrogen supply, that is, energy sources from microbial decomposition of organic matter, from geochemical water-rock interaction and from deep geothermal activities. Wide diversity of underground microorganisms needs extensive search for favorable species and ecosystem.

EFFECTIVENESS OF GEOLOGICAL SEQUESTRATION OF CO_2 AS A MITIGATION OPTION

Japan emitted about 1.2 billion tons of CO_2 artificially in 1995, that is, already 8% larger than 1990 level. In the Third Session of the Conference of the Parties to the United Nations Framework Convention on Climate Change (COP-3) in Kyoto, 1997, Japan agreed to reduce greenhouse gas emission by 6% by the period 2008 to 2012 compared with 1990 level. It is very difficult for Japan to reduce the future greenhouse gas emission lower than 1990 level in spite of the best efforts for conservation of energy, development of new energy sources and the maximum boost in nuclear power generation. Then, only possible and quickly effective greenhouse gas mitigation option would be capture and storage of CO_2 from flue gas of fossil fueled power plants and factories to reduce greenhouse gas emission significantly below 1990 level.

Japan would be able to meet the COP3 target, if Japan takes immediately powerful action in geological sequestration of CO_2. It is assumed that 70 million tons of CO_2 would be captured in the early 21st century by chemical (amine) absorption method (90% efficiency) from flue gas of several new and powerful coal-fired power plants that would otherwise emit total 78 million tons of CO_2 in the air. As ocean sequestration of large amounts of CO_2 will be probably still unfavorable for protection of ocean environment, only feasible option that will be able to reduce CO_2 emission significantly, then, will be underground storage of CO_2 in unused aquifers.

Systematic fundamental drilling survey of geological structures for oil and gas exploration in and around Japan by Ministry of International Trade and Industry (MITI) - Japan National Oil Corporation found empty anticlinal structures that can store 1.5 billion tons of CO_2 (Tanaka et al., 1992), that is, enough capacity to accommodate 70 million tons of CO_2 annually longer than 22 years. Oil and natural gas reservoirs, too, can contain 2 billion tons of CO_2 (Tanaka et al., 1992). However, oil and natural gas reservoirs are available only when they become sufficiently depleted.

As energy, spent for capture, transport and underground injection, also causes emission of about 2 million tons of CO_2, net contribution of underground injection of CO_2 for reduction of CO_2 emission in the air is 68 million tons of CO_2

that is equivalent to 6% of artificial CO_2 emission of 1990 level in Japan. On the basis of preliminary cost estimation of Akai et al. (1993), geological sequestration would cost 424 billion yens for capture, transportation and underground injection of CO_2 to reduce 6% of artificial CO_2 emission of 1990 level. If this cost for geological sequestration of CO_2 is directly surcharged on the electric power generation cost of the CO_2-source fossil-fueled power plants, electricity charge would soar high. However, all users of fossil fuel energy should bear evenly expenses for geological sequestration of CO_2, because it contributes to reduce Japan's total artificial emission of greenhouse gas to meet COP3 target. If the expenses for geological sequestration of CO_2 were paid by carbon tax, carbon tax would be enough at a reasonable rate of 1,200 yen per 1 tons of carbon, that is, 0.13 yen per 1 kWh of electricity or 0.8 yen per 1 litter of gasoline.

Fossil fuels have been main energy source for human activities since the Industrial Revolution and would be the most important energy source in the world in the foreseeable future. Especially, coal has great potential as world's energy source but also is blamed as the worst CO_2 emitter. Koide et al. (1992) estimated that the storage capacity of saline aquifers is 320 billion tons-CO_2 in the world. However, this estimation is too much conservative as they assumed that CO_2 is dissolved at groundwater in 300m thick aquifers in only 1% area of world aquifers. It seems better to revise the storage capacity of world aquifers to 3 trillion tons-CO_2 at least. Zero emission fossil-fueled power plants with geological sequestration of CO_2 are feasible option for reduction of greenhouse gas emission. Positive sides of geological sequestration of CO_2 are discussed in the following sections.

AUTOGENOUS SEALING OF CO_2 IN AQUIFERS

Natural gas-hydrate-filled layers are often found under deep sea floor due to high pressure and cool temperature. Natural gas tends to accumulate under the gas-hydrate-filled layers and under permafrost layers, because the layers are virtually perfect insulators of gas. It is feared that global warming may be accelerated by emission of trapped methane due to dissolution of permafrost layers and hydrate layers by global warming. Injection of CO_2 under permafrost (Fig.1) and methane hydrate caps (Fig.2) with counter extraction of trapped methane prevent acceleration of global warming, because injection of CO_2 strengthen permafrost and methane hydrate caps with CO_2 hydrate that is stable at higher temperature than ice at high pressure and than methane hydrate (Koide et al., 1997a). CO_2 injection under methane hydrate layers and under permafrost layers may realize the greenhouse gas mitigation and recovery of unused natural gas at the same time.

CO_2 injection into deep aquifers may form CO_2 hydrate-filled layers under about 300m water column under deep and cool sea floor (Fig.2, Koide et al., 1997b). Autogenous sealing of CO_2 in deep and cool aquifers assures virtually complete and practically unlimited subsurface containment of CO_2. Autogenous sealing is very safe, because every crack shall be automatically filled even if earthquakes form gaps in cap rocks (Koide, 1997).

Intrusion grouting of calcium hydroxide solution is expected to induce similar sealing effects, because precipitation of calcium fills gaps in rocks when calcium hydroxide meets CO_2. Sealing of drill holes by calcium hydroxide is important to prevent leakage of CO_2.

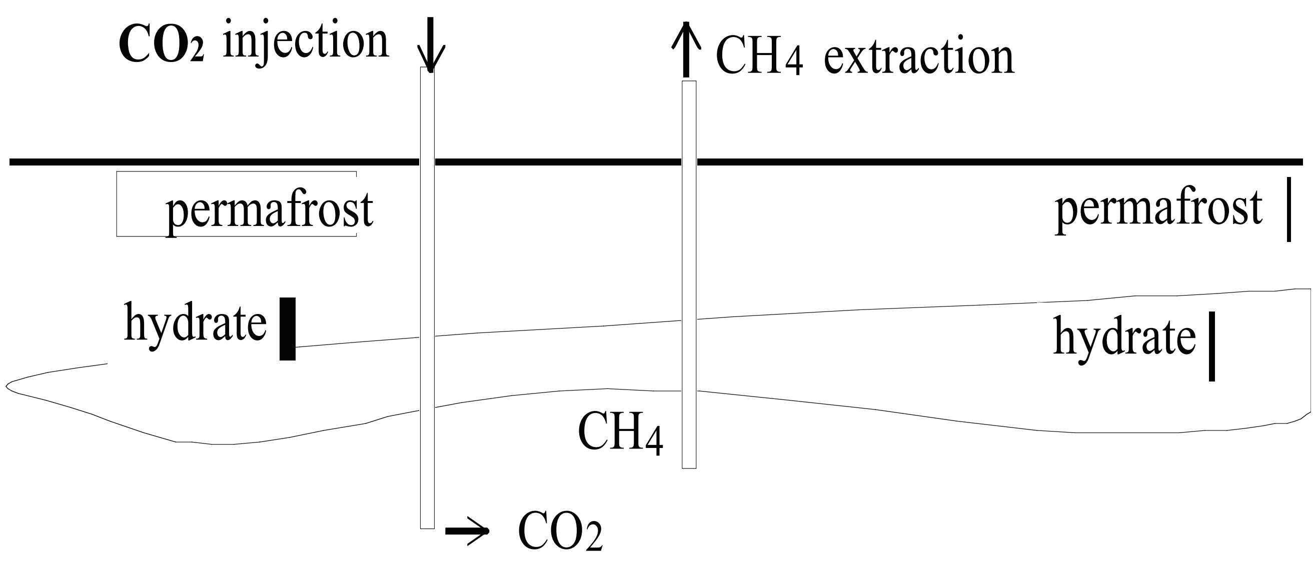

Fig.1 Injection of CO_2 under permafrost layer and extraction of methane.

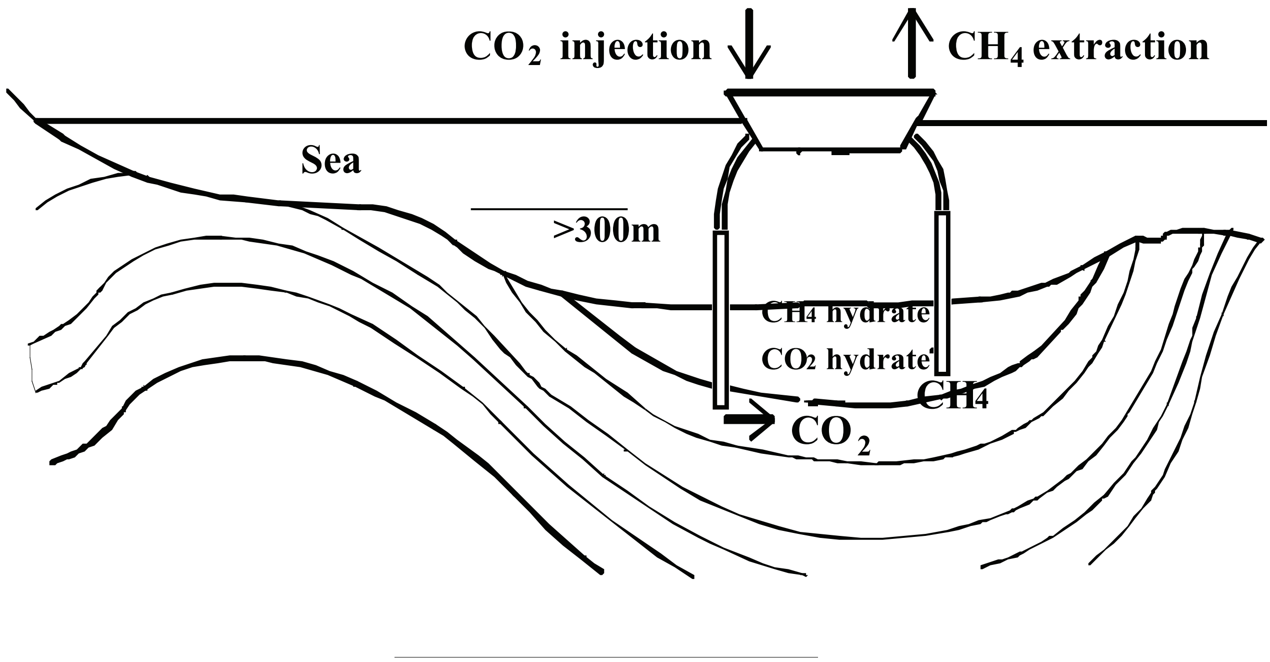

Fig.2 Injection of CO_2 under methane hydrate layer and extraction of methane.

UNDERGROUND MICROBIAL CO_2 FIXATION AND RESTORATION OF HYDROCARBON DEPOSITS

Saline fossil groundwater in sedimentary basins is often saturated with methane. Fossil groundwater is pumped up and natural gas dissolved in groundwater is separated and commercially used in a few sedimentary basins such as Kanto basin in Japan, although methane-dissolved groundwater is found in most of sedimentary basins. Dissolved natural gas deposits are not usually economically rich. Exploitation of natural gas deposits in Tokyo area has been prohibited generally, because pumping up of groundwater often caused subsidence. Underground injection of CO_2 can prevent subsidence owing to upholding of groundwater pressure in aquifers. Underground injection of CO_2 and counter extraction of groundwater realize recovery of methane dissolved in pumped up fossil groundwater to utilize low grade of natural gas resources while preventing subsidence (Koide et al., 1992).

Nakai(1960) made carbon isotope measurements on several dissolved natural gas deposits in Japan and found that carbon in CH_4 has isotopic values ranging from -65.5 to -74.8 per mil deviated from P.D.B. standard, while carbon in CO_2 has isotopic values from +2.0 to -12.2 per mil. He concluded that an isotopic equilibrium between CH_4 and coexisting methane indicates that bacterial processes formed these aquifers saturated with methane. Extremely light isotopic compositions of carbon in CH_4 suggest that methanogens formed some of dissolved methane deposits in Japan. Anaerobic chemoautotrophic methanogens belong to Archaea that are similar to early microorganisms that evolved in anoxic harsh environments on the primitive Earth. Methanogens have wide diversity. Many of them can survive in extreme environments such as high temperature, high pressure and high salinity. Most of methanogens form CH_4 from CO_2 and H_2 and gain energy.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

Thus, bacterial methanogenesis is made without help of sun light. Methanogens are blamed for greenhouse gas emission as they produce methane in bowels of cows and termites and in rice paddy, as they are abundant in such anoxic habitats. Anaerobic microorganisms are abundant and active even in deep aquifers. Accumulations of methane-rich natural gas of bacterial origin have been found in many sedimentary basins in the world (Rice and Claypool, 1981). Stevens and McKinley (1995) found that methanogens are active in aquifers deeper than 1000m in the Columbia River Basalt Group, U.S.A. Bacterially formed methane are formed even in the depth of 4,500m in the Po basin, Italy (Mattavelli et al., 1983).

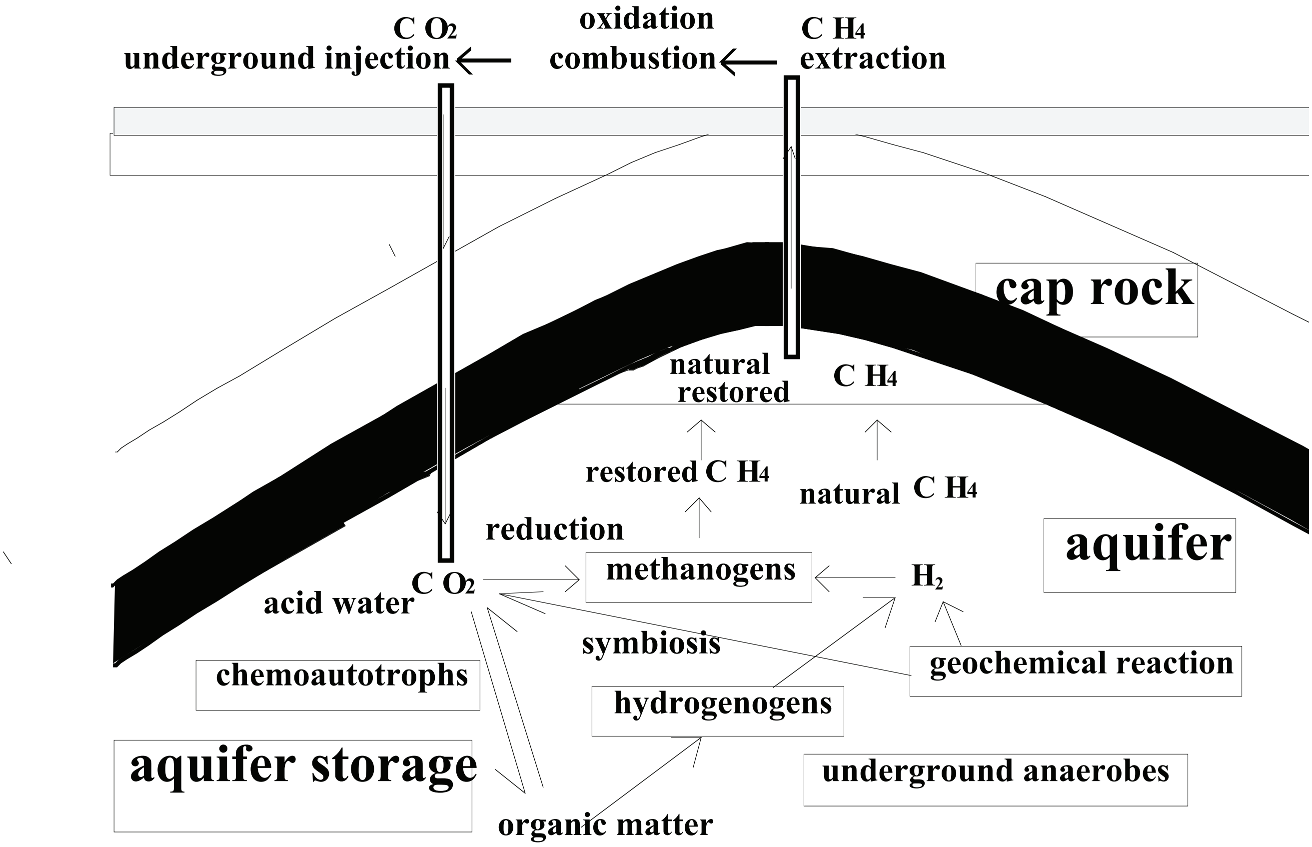

Fig.3 Geological sequestration of CO_2 and microbial restoration of methane deposit.

If CO_2 is injected into aquifers and dissolved in groundwater in which methanogens are active, methanogens reduce CO_2 into CH_4 as long as H_2 is available. Methane is less soluble in water and lighter than CO_2. Therefore, methane tends to be separated from water and migrate upward. If there exist no traps, methane is emitted finally into the air to accelerate global warming. Methane is much more efficient greenhouse gas than CO_2. However, if the aquifer has geological trapping structure, methane tends to accumulate at the top of reservoir under cap rock and may revive natural gas deposits (Fig.3). Chemotrophic methanogenesis is usually much slower than photosynthesis. However, appreciable amounts of biogenic methane probably form during tens or hundreds of years of CO_2 storage in aquifers at adequate conditions.

Deep aquifers are usually at high temperature, at high pressure and often at high salinity. Some kinds of methanogens, belonging to Archaea, are active at extreme conditions such as high pressure, high temperature and high salinity. As metabolism is faster at higher temperature, warm aquifers are favorable for fast methane production unless temperature is too high. Thermophilic methanogens such as *Methanobacterium thermoautotrophicum* and *Methanococcus jannaschii* are possibly suitable for fast brew of methane. Extensive search for favorable species is needed as methanogens have wide diversity.

Hydrogen H_2 supply into CO_2-dissolved groundwater is key to biogenic restoring of methane deposits, because hydrogen is energy source for methanogenesis. Stevens and McKinley (1995) pointed out that basalt - water reaction supplies hydrogen to induce active methanogenesis in deep basalt aquifers. Hydrogen is supplied by deep water-rock interaction in active geothermal regions. Anaerobic hydrogenogens produce H_2 from organic matter. Symbiosis of methanogens and hydrogenogens is favorable for active production of methane, as hydrogenogens are active when methanogens consume H_2 for methanogenesis. Adequate set of methanogens and hydrogenogens should be searched to form suitable ecosystem for methanogenesis in aquifers. As many sandy aquifers are not rich in organic matter, organic materials should be enhanced for active fermentation by alternate injection of CO_2 and organic fluid waste or solution of organic matter that is otherwise to emit CO_2 and/or CH_4 finally into the air. Elimination or reduction of sulfate is important as sulfate reducers prevent methanogenesis (Lovley and Chapelle, 1995). The coordinated ecosystem may efficiently rejuvenate methane deposits during CO_2 aquifer storage.

Chemoautotrophs fix CO_2 into organic matter without help of sun light. A mixotrophic bacterium, a kind of *Pseudomonas* which was separated from an oil spill at Sagara oil field, Japan, converts CO_2 into medium-chain alkane and alkene anaerobically in the presence of H_2 (Morikawa and Imanaka, 1993, Morikawa et al., 1998). This finding suggest possibility of bacterial oil production in addition to chemoautotrophic fixation of CO_2 during aquifer storage of CO_2 .

CONCLUSION

Geological sequestration of CO_2 is a technically and economically feasible option for mitigation of greenhouse gas emission. Autogenous sealing by hydrate formation and microbial fixation of CO_2 assure long-term containment and safety of CO_2 aquifer storage. During many years of aquifer storage of CO_2, injected CO_2 may be fixed into organic matter by chemoautotrophs and furthermore converted into methane by methanogens. Biogenetic restoration of subsurface hydrocarbon deposits is possible in CO_2-injected aquifers probably after tens or hundreds of years. Important key for underground CO_2 recycling is hydrogen supply, that is energy source, from microbial decomposition of organic matter, from geochemical water-rock interaction and from deep geothermal activities. Due to wide diversity of underground microorganisms and environments, extensive and careful search for favorable species and ecosystem is needed for microbiological fixation and recycling of CO_2.

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