



SUBSURFACE BIOGEOCHEMICAL CARBON RECYCLING: CO₂-EGR WITH MICROBIAL METHANOGENESIS IN GEOCHEMICALLY SEALED AQUIFERS

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ABSTRACT

It is estimated that almost ten trillion cubic meters of methane are contained in sedimentary basins in Japan and under the seafloor around the Japanese Islands. Most of the natural gas resources, however, are hardly economically recoverable as the methane is adsorbed in coal seams, trapped in hydrate clathrate or dissolved in saline groundwater. Shallow subsurface accumulation of methane poses even a hidden threat of explosive global warming. Enhanced gas recovery by subsurface CO₂ injection (CO₂-EGR) is a practicable solution for the greenhouse gas control and for efficient use of unmineable energy resources.

Extremely light isotopic compositions of carbon in methane from many subsurface accumulations of natural gas suggest it was formed by methanogens. The subsurface lithoautotrophic microbes form methane again from disposed CO₂ without sunlight in anoxic aquifers. Re-extraction of subsurface methane, that has been converted from disposed CO₂ by methanogens, makes the carbon recycling complete.

Autogenous sealing by formation of CO₂-hydrate prevents the release of CO₂ in aquifers under sea floor deeper than 300m. In warm inland and shallow subsurface aquifers, leakage of CO₂ is prevented by carbon dioxide precipitation in a preset “ambush aquifer” with high pH and high calcium ion concentration. If necessary, lime water is injected into the “ambush aquifer” over the caprock of CO₂-reservoirs. Safe long containment of CO₂ and gas is important for methane fermentation in CO₂-reservoirs.

A subsurface ecosystem is similar to an archaic ecosystem that was adapted to anoxic CO₂-rich atmosphere under high pressure and temperature. Methanogenesis is active even in deep basaltic aquifers. Subsurface biogeochemical carbon recycling may realize greenhouse gas control with restoration of energy resources.

Key words: CO₂, Aquifer, Methane, Hydrate, Methanogen, Sealing, Recycling

CO₂-EGR

There is an enormous amount of methane in subsurface formations in the world. Most of the natural gas resources, however, are hardly economically recoverable as the methane is adsorbed in coal seams, trapped in hydrate clathrate or dissolved in saline groundwater. Shallow accumulation of methane is even a hidden threat of explosive global warming. The Geological Survey of Japan estimated that about 887 billion cubic meters of methane are dissolved in deep saline groundwater in aquifers in and around Japan and that almost 6 trillion cubic meters of methane are trapped as methane hydrate under the deep seabed around Japanese Islands. Yamaguchi and Yamazaki (1999) estimated that about 2.5 trillion cubic meters of methane are contained in aquifers in and around Japan. Recovery of subsurface natural gas constitutes a large new energy sources and eliminates future threat of inadvertent release of the greenhouse gas. Replacement of subsurface methane by anthropogenic CO₂ is a way of sequestering this anthropogenic greenhouse gas. Replacement of dissolved methane in groundwater by CO₂ can accommodate about 26 Gt of CO₂ in and around the Japanese Islands because CO₂ is some ten times soluble than methane in deep aquifers (Koide et al., 1993). Methane hydrate can absorb almost 12 Gt of CO₂ in and around the Japanese islands because the hydrate clathrate can absorb same volume of CO₂ as methane.

Coal seams can adsorb almost 10 Gt of CO₂ in and around the Japanese Islands because the coal can adsorb CO₂ twice as much as methane (Stevens et al., 1999). Enhanced gas recovery by subsurface CO₂ injection (CO₂-EGR) can sequester total 48 Gt of CO₂ in and around the Japanese Islands with the counter production of nearly ten trillion cubic meters of methane, while ordinary aquifers and depleted oil/gas fields can accommodate total 75 Gt of CO₂ in and around the Japanese Islands. CO₂-EGR is a prospective solution for the greenhouse gas control with efficient use of potential energy resources.

The extremely light isotopic compositions of carbon in methane contained in many subsurface accumulations of methane-rich natural gas around the world suggest that much of the gas was formed by methanogenic bacteria. Lithoautotrophic methanogens that belong to Archaea form methane from CO₂ and gain energy without sunlight in anoxic circumstances. A subsurface ecosystem is somewhat similar to an archaic ecosystem that is adapted to anoxic CO₂-rich atmosphere under high pressure and temperature. Methanogens are often blamed for greenhouse gas emission as they produce methane in digestive systems of cows and termites and in rice paddies. However, reapplication of CO₂-EGR for subsurface biogenic methane that is converted from disposed CO₂ makes the carbon recycling possible.

OCEANIC BASALT AS LIMITLESS CO₂ SINK AND HUGE UNUSED ENERGY SOURCE
 Takahashi et al. (2000) proposed geological sequestration of CO₂ in deep saline aquifers associated with oceanic and continental basaltic rocks. Layers of fractured basalt have significant porosity often as high as 10%-30%. CO₂ stored in the aquifers should react with the basalt host rocks over time to form solid (Ca, Mg)CO₃. Extensive layers of oceanic and continental basalt provide huge sink of CO₂.

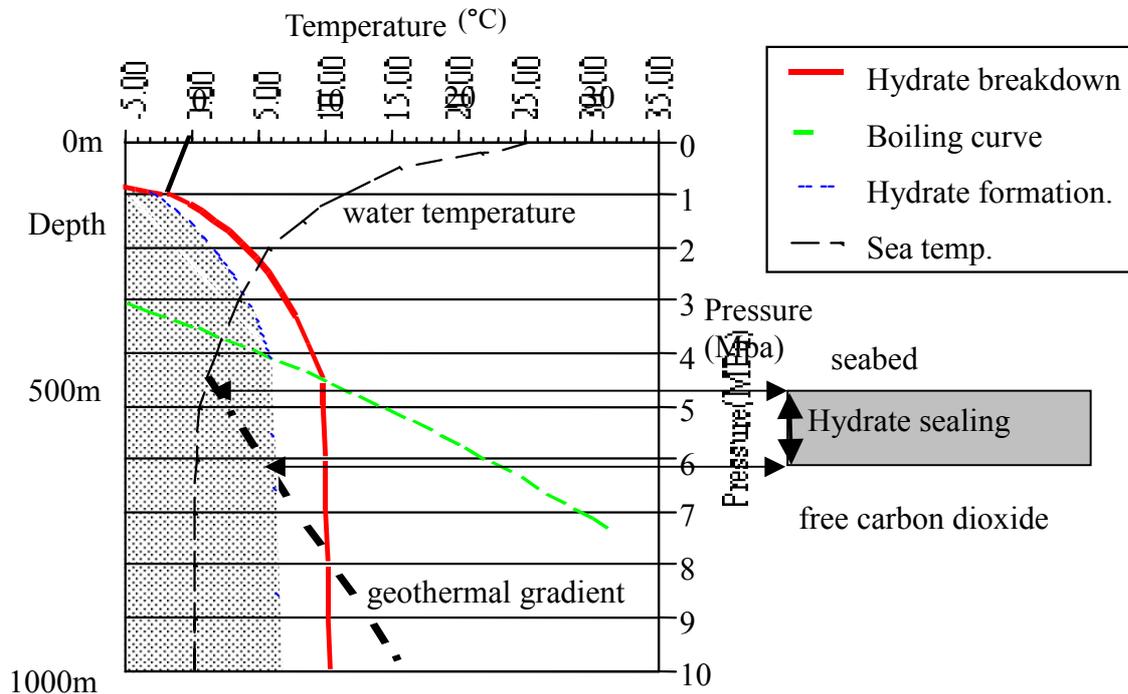


Fig.1 Autogenous sealing by hydrate formation in sub-seabed aquifers. Extremely cool water temperature and high geothermal gradient in the Japan Sea basin provides deep free CO₂ storage self-sealed in sub-seabed sediments.

Very cool deep-sea water keeps the sub-seabed shallow aquifers very cool. Hydrate clathrate is

stable at the high pressure and near zero Celsius temperature of shallow aquifers under deep seabed (Fig.1). However, hydrate clathrate is not stable in deep aquifers due to the higher temperatures imposed by the geothermal gradient. CO₂ injected into deep aquifers in oceanic basalt migrates freely at high temperature but forms hydrate clathrate when CO₂ escapes upward into cool sub-seabed aquifers. Oceanic basaltic layers provide leak-free CO₂ storage by autogenous hydrate sealing (Fig.2).

Bionic methanogenesis is active even in deep basaltic aquifers (Stevens and McKinley, 1995). Although deep aquifers in basaltic lava layers lack organic matter, methanogens can produce methane from CO₂ of inorganic origin and H₂ derived from reduction of thermal water by Fe(II) in basaltic glass. Artificial CO₂ injection into deep basaltic lava layers makes the aquifer environment similar to an archaic reducing environment where methanogens were dominant under high CO₂ pressure, high temperature and lack of organic matter (Fig.2). Hence, CO₂ stored in the deep basaltic aquifers can be reduced to methane by these organisms, so that artificial stimulation of natural deep biogeochemical carbon cycle by CO₂ injection may realize greenhouse gas control with restoration of energy resources. Basaltic layers forming oceanic crust have the potential to provide a virtually limitless CO₂ sink and a gigantic unused energy source.

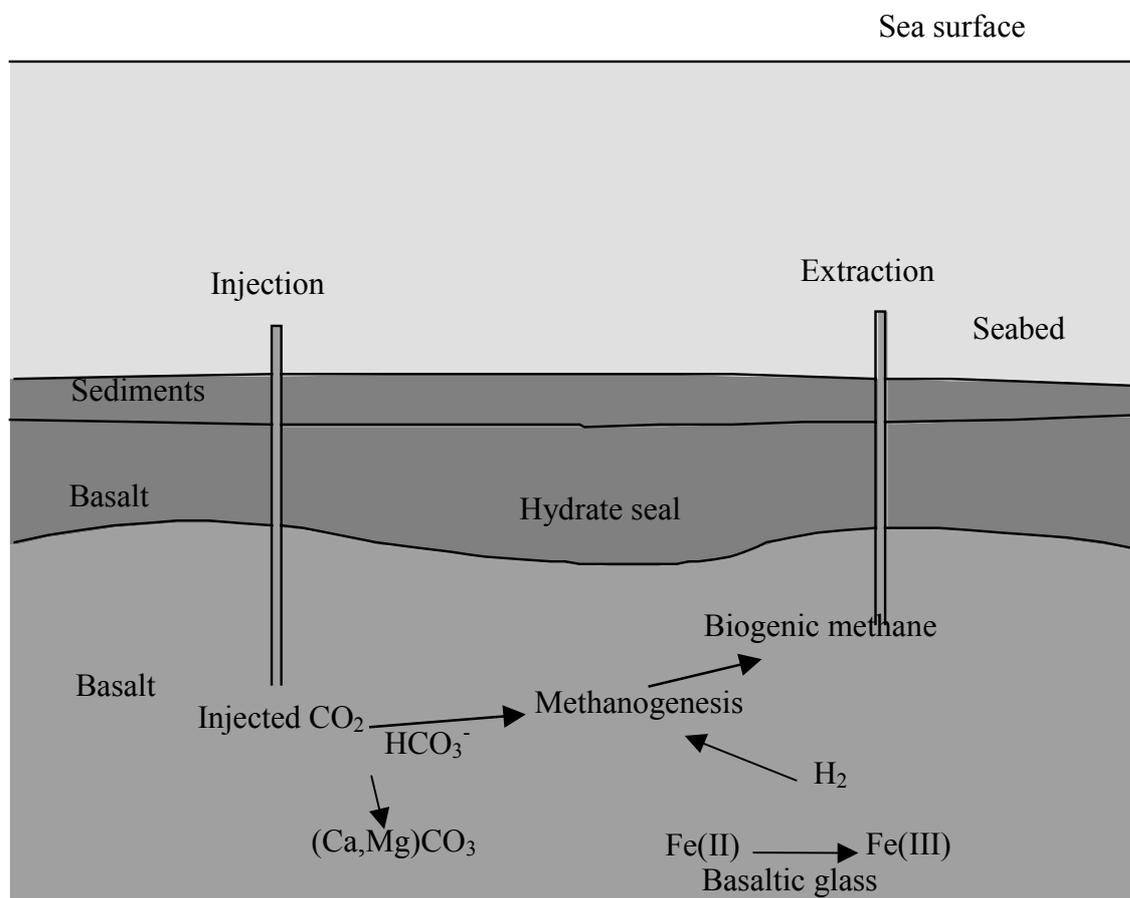


Fig.2 CO₂ sequestration and microbial methanogenesis in oceanic basaltic layers.

GEOCHEMICAL AUTOGENOUS SEALING IN “AMBUSH AQUIFER”

Gas-hydrate-filled layers are virtually perfect insulators of gas. Injection of CO₂ under permafrost and methane hydrate caps with counter extraction of trapped methane prevents acceleration of global warming, because injection of CO₂ strengthens the permafrost and methane hydrate caps

with CO₂ hydrate that is stable at higher temperature than ice at high pressure and than methane hydrate (Koide et al., 1997). CO₂ injection under gas-hydrate layers and under permafrost layers may realize the greenhouse gas mitigation and recovery of unused natural gas at the same time. CO₂ injection into deep aquifers forms CO₂ hydrate-filled layers under the water column beyond 300m under deep and cool sea floor. Autogenous sealing of CO₂ in deep and cool aquifers assures virtually complete and practically unlimited subsurface containment of CO₂. Autogenous sealing is very safe, because every crack in the seal will be automatically fill up even if earthquakes form gaps in cap rocks.

Autogenous sealing by hydration clogging is effective only under seafloor deeper than about 300m and at sub-permafrost inland regions. In Japan, the climate is too warm to form hydrate in inland aquifers or in shallow sub-seabed aquifers.

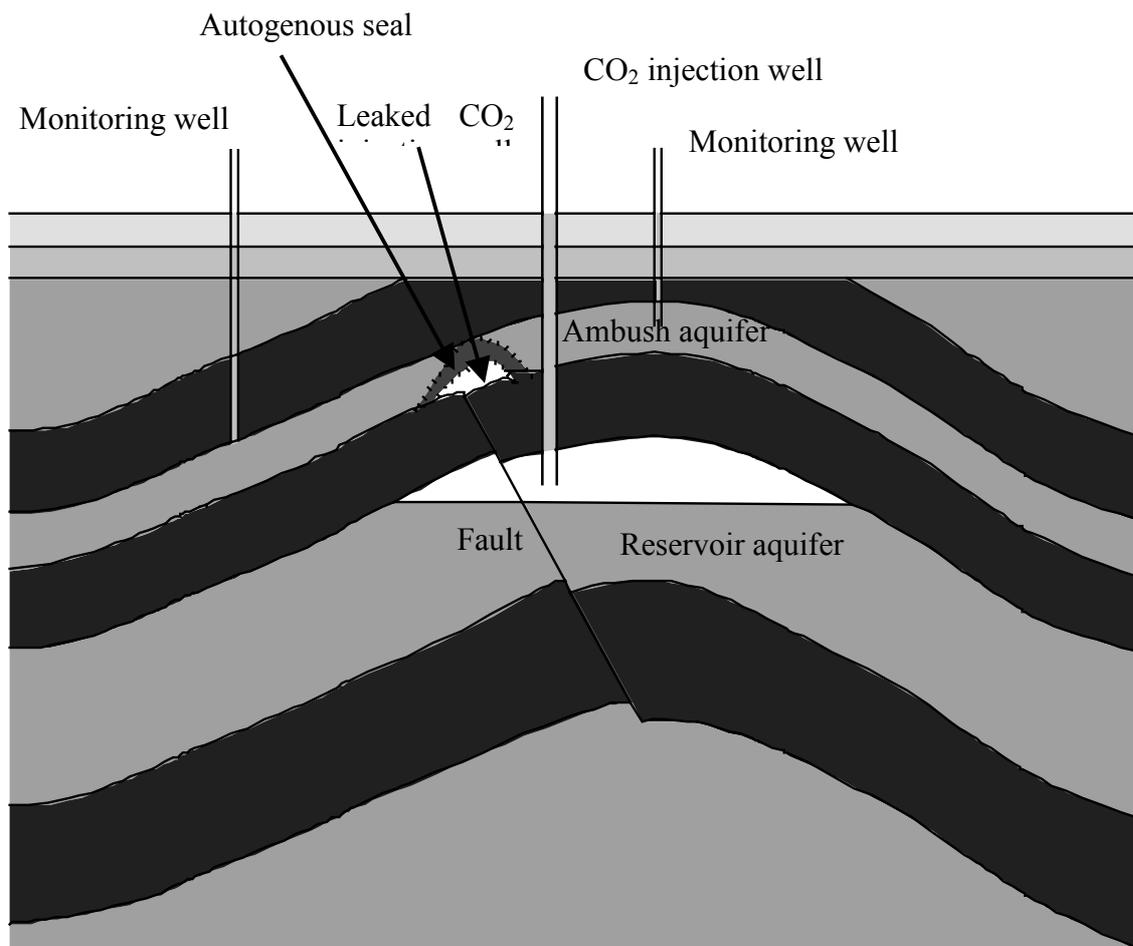


Fig.3 Autogenous sealing in an “ambush aquifer” prevents further leakage of CO₂.

In the geotectonically unstable Japanese Islands, geological formations are often inhomogeneous and/or densely faulted. However, it is very difficult to detect small gaps and to seal all gaps in deep caprocks. Usual grouting technologies are not effective for sealing of disseminated small gaps of caprocks because clogging ability of grouting materials prevents them to penetrate into disseminated small gaps.

The author proposes an “ambush aquifer” method to seal disseminated small gaps effectively. If CO₂ encounters alkaline groundwater rich in calcium ion, calcium carbonates precipitates and clogs pores and gaps in rocks. Autogenous sealing of CO₂ occurs in calcium-rich alkaline aquifers. If

gaps in caprocks or seepage of CO₂ are detected, calcium-rich alkaline “ambush aquifers” are formed by lime water injection into an overlying aquifer or into the gaps in the caprocks (Fig.3). Autogenous sealing in geochemically conditioned aquifers realizes safe storage of CO₂ in inland and shallow subseabed aquifers. Deep aquifers in sedimentary basins often contain methane-rich saline hot water formed by methanogens. Biogeochemical carbon recycling is also possible by CO₂ injection in methane-rich saline aquifers safely under a geochemically sealed aquifer.

CONCLUSION

Geological sequestration of CO₂ is a technically and economically feasible option for mitigation of greenhouse gas emissions. Autogenous sealing by hydrate formation and by geochemically conditioned “ambush aquifers” assures long-term containment and safety of CO₂ aquifer storage. Over many years of aquifer storage of CO₂, injected CO₂ may be converted into methane by methanogens. An important key for underground CO₂ recycling is the supply of hydrogen, a microbial energy source. This can come from microbial decomposition of organic matter, from geochemical water-rock interaction or from deep geothermal activities. Biogeochemical carbon cycle in basaltic layers forming oceanic crust provides a virtually limitless CO₂ sink and gigantic new energy source.

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