

Disposal Options in View of Geochemical Cycle of Carbon

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1. Introduction

The use of fossil fuel like coal, oil and natural gases around world causes an increase of the carbon dioxide (CO₂) content in the atmosphere. Isolation of the anthropogenic carbon dioxide from the atmosphere could have some merits of moderating the enhanced greenhouse gas effect to avoid possible climatic changes.

As is the same in the case of the other waste disposal management, such as radioactive waste disposal, the engineering problems of transportation to the disposal site, it is generally agreed, can be managed with presently available techniques. There is much less agreement about the possible environmental effects of putting large quantities of CO₂ into the remote places from the human habitat. The fate of disposed CO₂ can be predictable by understanding of the geochemical cycle of carbon. Except in the case of solid-CO₂ terrestrial storage or the delayed release concept of anthropogenic CO₂ into the atmosphere (Seifritz, 1992), in which the natural geochemical processes of carbon cycling is not expected to be intervened, the disposed CO₂ would be involved in on-going carbon cycling processes on the Earth and at the same time mostly accelerate the reaction rate between CO₂ and medium materials accepting the CO₂.

This paper will address the examination of the isolation concepts using geological structures (oil and gas reservoir or aquifers) and the deep ocean as a sink of CO₂ in view of geochemical behavior of CO₂.

2. Liquid CO₂ behavior in the Earth's Conditions

To minimize transportation costs, the collected CO₂ is supposed to be compressed and liquefied. As a consequence, most disposal schemes assumed the liquid CO₂ injection through pipes into either the deep sea or geological structures. This means that the CO₂ is in a liquid phase exerting high pressures to the ambient in short-term basis and near source region of the disposal point.

An natural analog of the disposed CO₂ in geological reservoirs is found in the

commercial CO₂ producing wells, and Chivas *et al.* (1987) pointed out the possibility of violent explosions caused by the “cold” lethal gas outburst producing a maar on the surface of the Earth.

If a large amount of water coexists with the disposed CO₂, which is a more common condition encountered in the case of the subterranean injection of CO₂, the reactions between CO₂, water and host rock or aquifer solid will take place as Gunter *et al.* (1993) described. Since the final chemical form of the disposed CO₂ is either bicarbonate ion or carbonate minerals depending mainly on the mineralogy of the solid reactants, the pressure in the disposal site cavities or pores will gradually decrease in the course of the reactions. The safety assessment based on the worst case scenario might be surely more difficult than that being required in the high-level radioactive waste disposal, because larger volume of highly reactive exotic material is involved in the geological disposal of CO₂. Main concerns about siting the injection wells in densely populated areas is derived from the devastating release of CO₂ from Lake Nyos on 21 August 1986 resulted in the deaths of 1700 people (Le Guern and Sigvaldason, 1989, 1990).

The finding of the CO₂-rich fluid venting at Okinawa Trough sea floor (Sakai *et al.*, 1990) clearly shows the CO₂ hydrate formation in the deep ocean disposal of CO₂, while temperatures in the geological disposal does not fall within the domain of CO₂ hydrate stability (<ca. 10°C). It would really be a challenging job, if one could develop the technology that realize a huge amount of CO₂ concealed on the bottom of the ocean, in which the chemistry of CO₂ hydrate might play a major role.

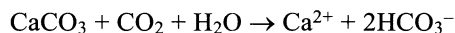
For the simple case of liquid CO₂ injection onto the ocean floor greater than 3000 m in depths making a “pool”, since the system is basically open, our examination could not be only limited on the chemical form of liquid CO₂, but should be extended to the solute CO₂ behavior (Ohsumi *et al.*, 1992). Ohsumi (1993) has pointed out that the enhancement of the carbonate dissolution at the injection region of the disposal site might be a promising concept to minimize the impacts on benthic organisms.

3. Enhancement of Carbon Stock as a Form of Bicarbonate Ion in Aqueous Phase

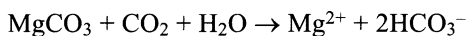
Reaction of the disposed CO₂ with silicate and carbonate minerals or dilution of CO₂ by a large amount of water gives bicarbonate ion in aqueous phase. This is a recurrence of a part of the ongoing geochemical cycle of carbon in geological timescales from early times of the history of the atmosphere of the Earth.

Limestone and evaporitic rocks, which now cover about 17% of the continents surface, are responsible for 63% of the river dissolved load to the ocean derived from weathering (Meybeck, 1988). Accordingly, in the carbonate-silicate long-term geochemical cycle modeling based on the classical Urey reaction (Bernier *et al.*, 1983), 68% of the global river input of bicarbonate ion (HCO₃⁻) to the ocean was attributed to the carbonate weathering-derived fraction. The

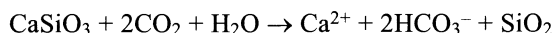
stoichiometry of the reactions



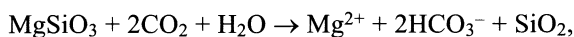
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shows that the half of the carbon in bicarbonate comes from the atmosphere. On the other hand, in the silicate weathering process shown by

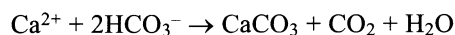


and



all the bicarbonate ion is derived from the atmosphere. Hence, 66% (100–68/2) of the river transport of inorganic carbon in the form of bicarbonate ion (0.4 GtonC/y) originates in atmospheric CO₂. If only this process were going on, the atmosphere would be depleted of CO₂ in less than 3000 years [(atmospheric CO₂ = 730 GtonC)/(CO₂ used annually on land by weathering = 0.27 GtonC C/y)]. There must be natural counter processes in balance with this CO₂ sink and the fate of the disposed CO₂ should be examined in the light of natural bicarbonate balance in aqueous system on the surface of the Earth.

Over very long timescales, the calcite precipitation reaction, mostly occurring in oceanic environments, as shown by



is responsible for the major mass balancing carbon flux into the atmosphere (Bernier *et al.*, 1983). In other words, the oceans cannot get rid of their entire inorganic carbon load, that due to continental weathering, using only the mechanism of calcium carbonate precipitation (Gaffin and Fujita, 1992). Calcium carbonate precipitation in ocean environments is accomplished by organisms that secrete the carbonate as hard parts. Thus, the rates of secretion must be controlled by ecological factors such as the availability of nutrients, and this along with widespread redissolution of carbonate on the seafloor may well lead to rate laws for oceanic carbonate that are rather complicated. This is why the ocean carbon cycling study should always be referred to in the assessment of the CO₂ disposal options.

Geological disposal concepts including CO₂-silicate direct reactions to precipitate carbonate minerals have nothing to do with this scenario; as shown in

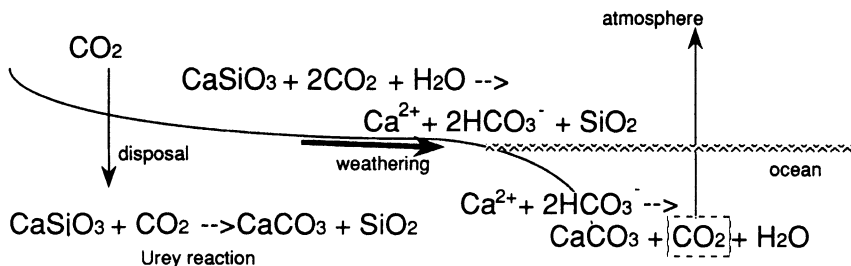
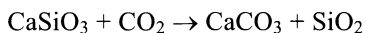
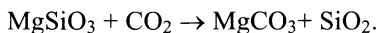


Fig. 1. Subterranean disposal of CO_2 causing the reaction with silicate minerals.

Fig. 1, it gives an short-circuit pathway of the Urey reaction,



and



In the more general idea of geological disposal options which includes in their scenario the processes of carbonate dissolution in reservoir and discharge or issuing of groundwater to the surface of the Earth resulting in enhancement of the riverine load of inorganic carbon (HCO_3^-) to the ocean, the final fate of disposed CO_2 is the same as in the case of direct ocean disposal of CO_2 . However, giving an additional detour route (timescales of hundreds to thousands years or more) before the enhancement of the oceanic inorganic stock of carbon is a merit of such geological disposal options.

4. Conclusions

If an appropriate siting, such as in the offshore aquifer, is feasible, the subterranean disposal options are the most promising in short-term basis, because its quite low probability of the accidental events and this along with coming about in remote places from the human habitable areas could be the key to the consensus in public. The final fate of the disposed CO_2 , however, remains an open question and there is a fertile field for geochemical research, in which some topics are common in the direct ocean disposal, in other words the understanding of carbon cycling in timescales from hundreds to thousands years is essential.

Before unavoidable damages to the deep benthic ecosystem in a limited area for a limited period should be carefully predicted, the deep ocean disposal of CO_2 could not be pondered on the basis of as equal risk perception as the conventional atmospheric disposal of CO_2 . The research along this line is required because it

is not certain that the emergency measures such as direct ocean disposal of CO₂ will not be needed in any part of the world.

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DISCUSSION

Question:

How do you suppose the CO₂ stock in the groundwater? For the global carbon cycle, what is the role of the stock of carbon dioxide.

Answer:

The groundwater residence time is just around one hundred or thousand years. The residence time or sequestration time is nearly equal to that of ocean disposal. If you put it into a deeper aquifer, e.g. two or three kilometer deep for the purpose of subterranean disposal, then we can expect CO₂ isolation from the atmosphere-hydrosphere system for ten thousand years or more.

Nakamura:

The presented evaluation of the time period of carbon dioxide for disposal

in the ocean is based on the present status of the earth environment. After one hundred years or more, the evaluation must be changed. The other value might be estimated after one hundred years. I want to put emphasis on the limitation of our knowledge; the carbon cycling at the present earth surface is the basis for evaluation shown here.

Ohsumi:

Carbon cycling on the surface of the Earth could be changed. That was the main issue just raised from the geophysicists a few decades ago. We are now conducting a really new geophysical experiments according to Roger Revelle. We have been or will be in some new system of carbon cycling.