Mineral carbonation in peridotite rock for CO_2 sequestration and a method of leakage reduction of CO_2 in the rock

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PROFESSIONAL PAPER

In the recent years, the amounts of green house gases have dramatically increased. This situation led to changing in climate conditions. One of the effective ways to reduce these amounts in atmosphere is CO_2 capturing from huge spreading sources and injection it into geological formations. Peridotite is a type of rock that reacts with CO_2 at higher rate when compared to the other rocks. Since the reaction of CO_2 with peridotite is exothermic, the reaction can be self sustaining; therefore, it can reduce overall energy consumption and costs of CO_2 emission. There are several factors that have effects on the reaction, in this paper effects such as pressure, temperature, salinity, acidity, and stirring on the rate of reaction are discussed, and using horizontal wells and bilateral drilling in order to increase rate of reaction and increase the amount of storage are recommended.

Key words: CO_2 sequestration, CO_2 capturing, peridotite rock, CO_2 leakage, bilateral drilling

1. Introduction

The increasing concentration of CO_2 gas in the earth's atmosphere has being affecting the earth's climate and has resulted in global warming. Humans are daily contributing to this by burning billions of tons of fossil fuel that contribute to the in increasing of CO_2 in the atmosphere. In order to decrease global warming, it is necessary to decrease or to stabilize the amount of CO_2 in the atmosphere, and CO_2 sequestration is one of the solutions to help overcome this problem.

CO_2 sequestration in geological underground formation can be done via injection CO_2 to a saline formation, gas or oil field, or a coal steam. Among all ways, reaction of CO_2 with saline formation is promising way for CO_2 sequestration, because of large potential storage and favorable thermodynamics.

One of the problems of CO_2 sequestration is the different behaviors that each mineral formation exhibits when it comes in contact with CO_2, which is function of reaction conditions. Therefore, the rate of the reaction of the minerals with CO_2 is very slow, and it takes many years for reactions to be finish completely. Assuring that CO_2 trapped in a brine formation is thermodynamically favorable is one of the issues that many researchers are focusing their studying on.

Because of high rate of reaction of CO_2 with peridotite in comparison to other minerals, the rock appears to be a good candidate for CO_2 sequestration. Also the reaction of CO_2 with peridotite is exothermic and self sustaining. In this paper, the factors that have an effect on the solubility of CO_2 with peridotite, the leakage of CO_2 from peridotite rock, increasing the rate of reaction, and trapping more CO_2 in peridotite are considered. A few solutions are also recommended.

2. Literature Review

The amount of produced CO_2 gas from fossil fuel is almost 6 GtC per year (Freund and Ormerod, 1997), which tends to increase air pollution and increase the temperature in the atmosphere. One of the ways of CO_2 reduction in the atmosphere is to inject the CO_2 to deep geological formation (Holloway 1997); such as saline formations, gas and oil field or coal steam. Storing of gas CO_2 as a mineral carbonation first time was proposed by Seifritz in 1990. After that mineral carbonation was considered as geological prospective by Ouxsmm in 1992. In order to estimate the amount of CO_2 in minerals, some laboratory experiments were conducted (Pearce et al 1996, Rochette et al 1996).

Magnesium (Mg) and calcium (Ca) almost consist 2 percent of earth crust, which often are bounded with silicates (Brownlow 1979). Therefore, Ca/Mg Silicate can be found in many places within the earth's crust, especially in upper. A research group at the Albany Research Laboratory reported that the minerals that consist of Ca/Mg can be carbonated at high pressures and temperatures.

Irving and Wylie considered the factors that have an effect on the solubility of CO_2 in earth's mantle, which consists of an abundance of peridotite rock. Stabilities of many carbonates were investigated at high pressures and temperatures in order to simulate the behavior of CO_2 at the mantle condition (R.C Newton 1975, W.E Sharp 1975). Therefore, study has been shown that magnesium carbonate ($MgCO_3$) and enstatite ($MgSiO_3$) are stable over most of range of temperatures and pressures that are found in the upper mantle.

3. Carbonation Process in the Nature

Mineral carbonation can naturally happen at any time when the reaction of CO_2 in the atmosphere occurs with minerals on the earth's surface and results in the carbon-

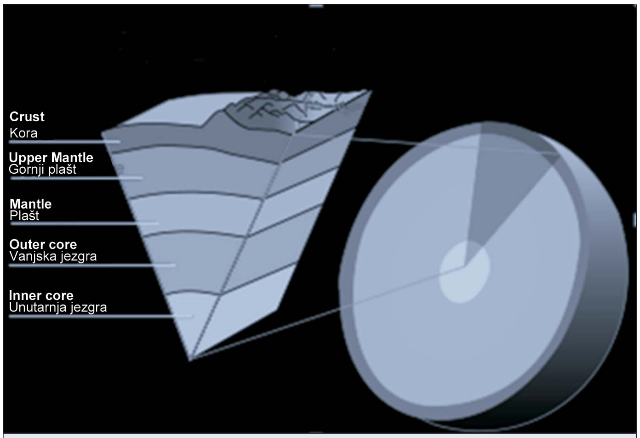

Fig. 1. Layers of the earth
Sl. 1. Slojevi zemlje

ation of the cations such as Mg, Ca, Fe, etc. This process is called the weathering process. This process occurs spontaneously, but the rate of reaction is very slow, and it takes several years for the minerals to be carbonated naturally.

4. Carbonation for CO_2 Sequestration

Mineral carbonation is one of the ways for trapping CO_2 underground. Mineral carbonations have some advantages such as

- Stable thermodynamically
- Benign environmentally
- No production wastes.
- Large potential sequestration capacity
- Reduction of overall energy consumption, because of exothermic process

In this paper, the peridotite rock that has a good capacity for CO_2 sequestration is studied, and the factors that have an effect on reaction rate of it are considered.

5. Peridotite Rock

Peridotite is medium grained indigenous rock that is the dominant rock in the upper part of the earth's mantle (Figure 1). Peridotite often consists of olivine and pyroxene that are rich in magnesium and calcium. Below, the chemical reaction of CO_2 with olivine and pyroxene is considered.

6. Olivine Rock

Olivine rock often consists of magnesium, oxygen and silicon. Olivine is the most abundant mineral in the earth's mantle until a depth of 700 km. The composition is usually combination of SiO_4^{2-} and Mg^{2+}. At the beginning, silicon bonds with 4 oxygen molecules and forms a pyramid structure so that the charges of cations and anions are balanced, and Mg^{2+} occupies the empty space between the SiO_4 (Figure 2). The reaction of olivine with CO_2 can be accomplished by the following reaction:

$$MgSiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2$$

As can be seen from the above equation, the direct reaction of olivine and CO_2 can produce magnesium carbonate and SiO_2, of which $MgCO_3$ is relatively more stable than Mg_2SiO_4. In the presence of water, undoubtedly the rate of forming a solid carbonation increases. CO_2 can react with olivine in the presence of water according to the below reaction:

$$Mg_2SiO_4 + CO_2 + 2H_2O \rightarrow Mg_3Si_2O_5(OH)_4 + MgCO_3$$

From above reaction, magnesium carbonate and serpentine form, of which serpentine is one of the silicates that is more stable than olivine because of its lower free energy.

The reaction of olivine in the carbonic acid system cannot be done in one step, it reacts in 3 steps:

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H_2CO_3 \rightarrow H+ + HCO_3^-$$

$$Mg_2SiO_4 + 4\,H^+ \rightarrow 3Mg^{2+} + SiO_2 + 2\,H_2O$$

$$Mg^{2+} + HCO_3^{--} \rightarrow MgCO_3 + H^+$$

When CO_2 and H_2O react, H_2CO_3 is produced. According to the first chemical reaction, H_2CO_3 can chemically have equilibrium with H^+ and HCO_3^-. After that olivine reacts with H^+, and the Mg cation is released into the solution. Then the cation can have a reaction with bicarbonate, finally solid carbonate forms and then precipitates.

7. Pyroxene

Pyroxene is one of the groups in an inosilicate mineral, which is abundantly found out in peridotite. The general chemical formula for pyroxene is AB $(Si)_2O_6$, in which A can be one of the ions such as magnesium, calcium, iron, and etc, and B can be one of the ions like magnesium,

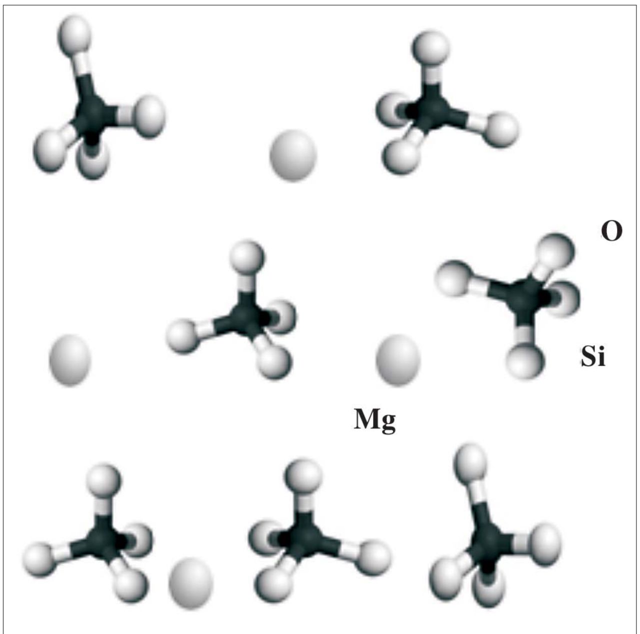

Fig. 2. Structure of olivine
Sl. 2. Struktura olivina

aluminum, etc. Most commonly, pyroxene can often be found out as Ca (Mg) $(SiO_3)_2$.

The reaction of pyroxene with CO_2 can be accomplished according to the below reaction:

Pyroxene + CO_2 → Dolomite + Quartz

$Ca/Mg\ (SiO_3)_2 + 2\ CO_2 \rightarrow Ca/Mg\ (CaCO_3)_2 + 2\ SiO_2$

When in underground conditions, CO_2 reacts in the presence of water. As can be seen from the below equation, calcium carbonate is formed and precipitates out as solid carbonate.

$CaMgSi_2O_6 + CO_2 + H_2O \rightarrow Ca_2Mg_5Si_8O_{22}\ (OH)_2 + CaCO_3 + SiO_2$

According to free energy, enthalpy, and entropy, the reaction of peridotite for CO_2 sequestration is suitable thermodynamically.

There are a lot of factors that have an effect on the reaction of CO_2 and peridotite. Below, the effects of pressure, temperature, acidity, salinity, stirring and contact surface area of reaction on the rate of reaction for CO_2 are considered.

8. Pressure

Pressure is one of the most important factors that affect the solubility CO_2 and peridotite. Increasing the pressure is expected to improve the generation of the carbonation (Dahine et al 2000). Increased pressure causes to CO_2 to go into solution and consequently, increases the solubility of the CO_2 in an aqueous solution, but also increases the rate of reaction with peridotite. Although increased pressure improves the solubility of CO_2, the risk of leaking the CO_2 out of the formation increases, therefore, the optimum pressure should be used.

As can be seen from chemical reaction (1), CO_2 reacts with H_2O and produces H_2CO_3. H_2CO_3 in the solution can reach equilibrium with H^+ and HCO_3^-. Increasing the pressure can cause the concentration of HCO_3^- in the solution to increase and consequently, more peridotite can react with bicarbonate.

9. Temperature

The effect of temperature on the solubility of peridotite and CO_2 is complicated. Trapping CO_2 in peridotite in presence of water can exhibit a dual behavior. Increasing the temperature results in the reduction of the CO_2 solubility in an aqueous system, because it can increase the kinetic energy of the CO_2. Increasing the temperature causes an increase in the molecular motion, and to break the intermolecular bonds and consequently, the CO_2 will escape from the solution. On the other hand, increasing temperature can improve the solubility of CO_2 with peridotite. These effects result in an optimum temperature of 185 °C (p_{CO2} =152 bar) and 155 → °C (p_{CO2} = 116 bar) for olivine (Gerdemann et al 2002, O'Connor et al 2005). In order to find the highest solubility of peridotite in an aqueous solution, optimum conditions should be investigated.

10. Acidity

Acids and complex agents can be beneficial in CO_2 sequestration in saline formation. For increasing reactivity of the formation, some acids such as HCl, H_2S, acetic acid, oxatic acid, etc can be used.

Although acids can increase rate of reaction CO_2 with peridotite, high reduction of pH can complicate the behavior of carbonation and precipitation. High reduction of pH causes the solubility of the peridotite to increase and more cations will be released from the formation, but this reduces the concentration of bicarbonate in the solution. The solution with weak alkaline $7 < pH < 11$ has a better carbonation result (Dahlin et al 2000). As can be seen from the figure 3 with the reduction of pH from 9 to 3, the concentration of bicarbonate reduces rapidly.

To solve this problem, it is recommended first to reduce the pH by adding the acid to the solution so that more cations are released from peridotite, then the solution pH is increased so that carbonation of the cations and precipitation of them is accomplished at a higher rate.

11. Salinity

Mineral reactions usually happen in the presence of an aqueous saline solution, and the salinity of the solution can have an important role in increasing the solubility of an aqueous system and minerals. The rate of reaction is increased when a salt solution is used instead of distilled water (O Conner et al 2000, Dahin 2000). Salinity of the solution can increase the ionic strength and cations such as Mg, Ca, and Fe can easily be separated from peridotite rocks.

Injection of CO_2 into the peridotite rock formations that consist of $MgCl_2$, NaCl, $CaCl_2$, etc causes some of the formation's cations to react with bicarbonate in the solution, and the rest of the cations react with chloride anion (Cl^-) from the salts. Presence of $NaHCO_3$ in the solution

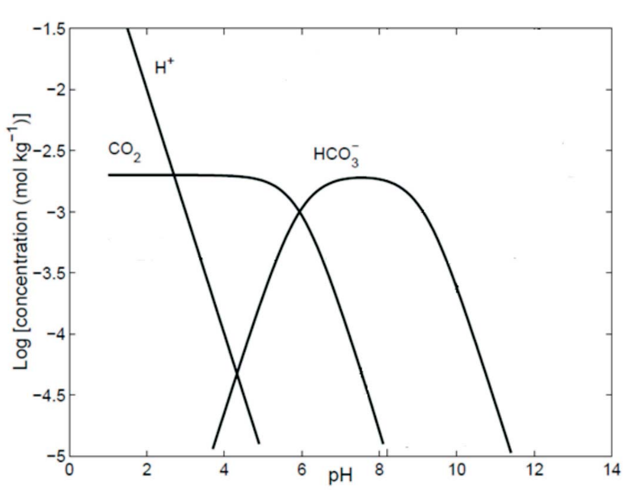

Fig. 3. The effect of PH on concentration of bicarbonate (HCO_3^-)

Sl. 3. Učinak pH na koncentraciju bikarbonata (HCO_3^-)

results in increasing bicarbonates in the aqueous system, and consequently the solubility of the peridotite increases.

12. Stirring Effect

Another factor that increases the rate of the peridotite reaction is the stirring effect. Instead of continuous injection of CO_2 into to the formation, injection can be done in an alternating fashion. In other words; first CO_2 is injected into the formation, and then injection is stopped for a period in order to allow time for the formation to react with the CO_2. Then the injection is started like before, and then this alternating injection method can be repeated until the storage is completely filled. During the initial injection cycle when performing the alternating process, the CO_2 floods the formation conventionally, but with the repeated injection of the CO_2 turbulence is created in the solution and contact with the formation is enhanced. This results in more gas permeating into the rock pours, and the surface reaction of the CO_2 with peridotite to increase.

13. Leakage problem of CO_2 and Solution for it

One of the most important problems of CO_2 sequestration is leakage of the gas from the formation to the earth's surface. The leaking off of CO_2 tends to kill a lot of aquatic life in the oceans.

Since injection of CO_2 by vertical wells causes some of the CO_2 that is injected to disperse into other formations, the use of horizontal wells is strongly recommended. The use of horizontal wells has several advantages such as

- Controlling the distribution of CO_2 in the formation
- Increasing the reaction surface area of the CO_2
- Increasing the storage capacity

In order to increase the trapping of CO_2 in the formation, bilateral drilling can be used (Figure 4). With this technology, two horizontal wells are drilled parallel to one vertical well, which one of them is drilled in upper formation that includes the peridotite, and lower well is drilled in the formation that is under the peridotite. For better distribution of the CO_2 horizontally into peridotite, hydraulic fracturing techniques can be used in upper well.

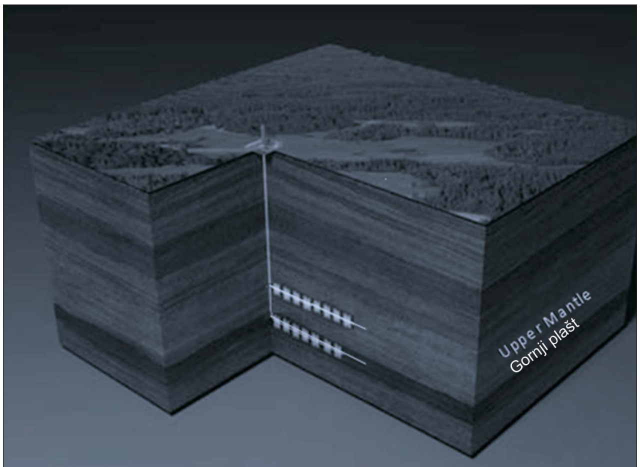

Fig. 4. Bilateral drilling in perdotite and lower layer
Sl. 4. Usmjereno bušenje u peridotitu i donjem sloju

Since the reaction of CO_2 with peridotite is done at higher rate in comparison to other rocks, the production of carbonates takes place at higher rates. Since carbonations are solid and are denser than other minerals in the aqueous system, they precipitate in the rock pores and reduce the permeability of the peridotite. Producing carbonation is associated with the increasing volume in the rock, and large stresses can create some fractures in some parts of the rock. Since they created new fractures that are not connected together, this can increase the storage of CO_2 and can reduce the risk of leakage in the formation. The reduced permeability in the upper rock causes it to behave as impermeable rock for lower formation, and prevents the escaping of the gas from lower formation. Injection to the lower horizontal well can be done once the presence of the solid carbonate in upper formation is assured. This technology not only increases the trapping of CO_2 in peridotite, but also it leaves a lot of CO_2 in lower formation trapped for a long period of time.

14. Problems for CO_2 Sequestration in Peridotite Rock

Although injection of CO_2 into peridotite has several advantages when compared to other minerals, it has some disadvantages such as most of peridotite is formed in upper mantle of earth, and drilling long distances has a high cost associated with it. Also monitoring of the CO_2 for leakage in upper mantle is very difficult and requires advanced technology.

Injection of CO_2 into the peridotite needs to make use of advanced technologies to provide for the required pressure and temperature for increasing rate of reaction. Also, some of salts, complex agents, and acids are very expensive and can increase the cost of CO_2 sequestration.

15. Conclusion and Recommendation

The structure of peridotite, which often consists of olivine and pyroxene, was considered and the reactions of peridotite with CO_2, in the presence of H_2O and without H_2O, were investigated.

Some factors that have an effect on the rate of the reaction between peridotite and CO_2, such as pressure, temperature salinity, acidity, and stirring on the rate of reaction were investigated.

In order to store more CO_2, increase the rate of reaction, and decrease the risk of leakage, the use of either bilateral wells or horizontal wells are recommended.

References

1. Akinfiev, N., McGovern,J., and Yantovski, E. (2010). Zero Emission Power Generation with CO_2 Reducion by Fayalite. International Journal of Thermodynamics, Vol 8, No 3.
2. Huijgen, W. J. J. (2007). Carbon Dioxide Sequestration by Mineral Carbonation, PhD thesis.
3. Huijgen, W. J. J., Comans R.N.J. (2003-2004). Carbon Dioxide Sequestration by Mineral Carbonation. Literature Review.
4. Kelemen, P., and Matter, J. (2000). In situ Mineral Carbonation in Peridotite for CO2 Capture and Storage. Lamont Doherty Earth Observatory, Columbia University.
5. Morimoto, N. (1998), Nomenclature of Pyroxenes. American Mineralogist, Volume 73, pages 1123-1133.
6. Newton, R. C., Sharp, W.E. (1975). Stability of Forsterite + CO_2 and it's bearing on the Role of CO_2 in the Mantle. Earth and Planetary Science Letters, 26(1975) 239-244.
7. O'Corner, W.K., Dahlin, D.C., Nilson, D.N., Rush, G.E., Gerdemann, S.J., Walters, R.P., and Turner, R.C. (2001). Aqueous Mineral Carbonation Studies Using Olivine and Sepertine, Albany Research Center.
8. Wei, X. (2003). Technological Evaluation of Mineral Sequestration of CO_2 by Carbonation. Ms. Thesis.

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