



Basalt Reactivity with CO₂ and H₂O: Implications for Carbon Sequestration
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Abstract

Climate change causes widespread concern and carbon capture and storage is considered as the most effective method to ameliorate the situation. Basalt rocks, a sort of geological storage sites, have a good capacity, injectivity and confinement. This review indicates the interior formations of basalts and explained the injected CO₂ distribution in the basalts. The conditions of basalt rocks can be thought as a function of depth from the ground surface and this is important for real project injection. Physical and chemical properties of basalts are key factors to be considered in the study of CO₂ storage process. Kinetics of CO₂ and basalt's dissolution as well as precipitation are explained. As a two-phase flow system, studying capillary pressure and saturation of CO₂-brine system in basalts is also important in the study of storage processes.

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INTRODUCTION

In the modern world, the major power source is fossil fuels and this supply society with life quality. Emissions of CO₂ from fossil fuels into the atmosphere can lead to the problem of climate change. Over the past century, the CO₂ level in atmosphere has been increased from 280ppm to 400 ppm, resulting in global temperature increasing by 0.8°C (Leung *et al.*, 2014). In comparison with other methods such as renewable energy, carbon capture and storage (CCS) is considered as the most effective method to solve the problem of global warming, and geological formations are attractive places for storing CO₂ after being captured.

Many researchers (Suekane *et al.*, 2008; Leung *et al.*, 2014; Mathias *et al.*, 2014; Lemieux, 2011) have discussed the mechanisms of those geological storage formations such as oil and gas reservoirs, unmineable coal bed and saline aquifers. Besides, they also show specific methods for injection and storage in global commercial scale (current and planned projects). Bachu and Bennion (2009) explained three characteristics of geological storage; capacity, injectivity and confinement, all of which appear on above geological formations. Some mafic rocks, such as basalt rocks have much divalent cations e.g. Fe²⁺

and Mg²⁺. They also have a huge potential for CO₂ storage because of their storage capacity and rocks' permeability (McGrail *et al.*, 2006). Many researchers have discovered the possibility of using CO₂-water solution to dissolve basalt powder. However, as basalt rocks are widely covering continent and sea floor with large formations and great thickness; reaction mechanisms in CO₂ are also important to study the storage processes.

For effective and safe storage, CO₂ must be injected as supercritical form which is higher than 304K and 7.4 MPa (Lu *et al.*, 2011; Prasad *et al.*, 2012; Gislason *et al.*, 2010a; Matter *et al.*, 2007; Gysi and Stefánsson, 2011; Wolff-Boenisch *et al.*, 2011; Goldberg *et al.*, 2008). CO₂ can be dissolve and react with basalt rocks at interior formations for long term. The reaction between CO₂ and basalt rock is very complex and their dissolution rate as well as basalt rocks' metal cations are necessary for safe CO₂ storage (McGrail *et al.*, 2006; Rosenbauer *et al.*, 2012; Goldberg *et al.*, 2008; Prasad *et al.*, 2012; Gislason *et al.*, 2010a; Matter *et al.*, 2007; Wolff-Boenisch *et al.*, 2011; Gysian and Stefansson, 2011).

Basalt interior formations for CO₂ distribution and storage

Basalt rocks have a huge capacity for storing CO₂. This is not only because of their widely distribution but also because of their structure and composition. Figure 1 shows a schematic diagram of a major structure of a lava flow in Columbia River Basalt Group. It can be found that the interior of basalt is connected and have permeability for fluid flowing. Figure 2 further shows interior pores and connectivity of basalts.

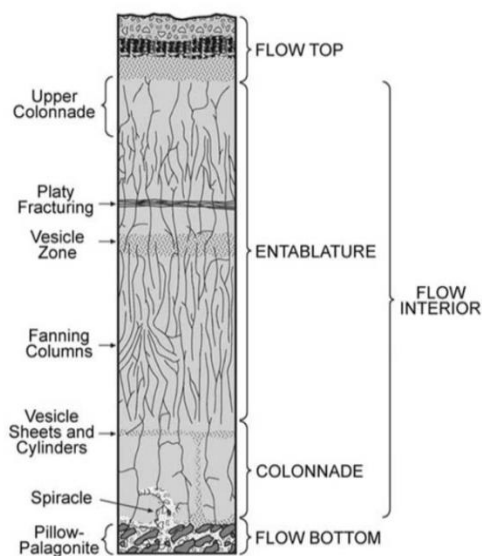


Figure 1: A major structure of lava flows in Columbia River Basalt Group (McGrail *et al.*, 2006).

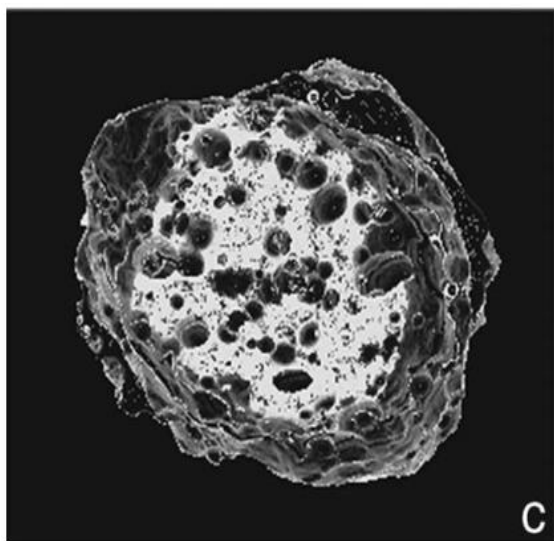


Figure 2: Lava flow top X-ray micro-tomographic imageGroup (McGrail *et al.*, 2006)

The flow top of lava flows is porous and permeable and this formation is considered viable for CO₂ storage because of their high internal connectivity as well as high reactive composition. The dense basalt rocks which are of low permeable have effective seals to prevent the leakages of CO₂ from the storage reservoirs (McGrail *et al.*, 2006). Because of the structure of lava flows interior; groundwater which is overlying basalt rocks can permeate in the lava flows and reach the basalt aquifers whose bottom is impermeable sediments. From those descriptions, it can be assumed that supercritical CO₂ can be injected through a pipeline into basalt aquifers, and then dissolved in the water and react with basalt rocks. Basalt formations can be influenced by different conditions such as temperature, pressure and flows. After reaching flow top formations, CO₂ solution can move through connected porous and react with dissolved divalent cations such as Fe²⁺ and Mg²⁺. McGrail *et al.*, (2006) explained that CO₂ injection at the depth of 1000m, the temperature of the CO₂ could be controlled at 40°C as shown in figure 3. Similarly, Gysi and Stefansson (2011) carried out experiments at 40°C to study CO₂ sequestration in basalt rocks, including key reactions and chemical mass transfer in CO₂-water-rock interactions. The red line in the figure 3 shows that the temperature data is fitted for an exponential equation (1) (McGrail *et al.*, 2006).

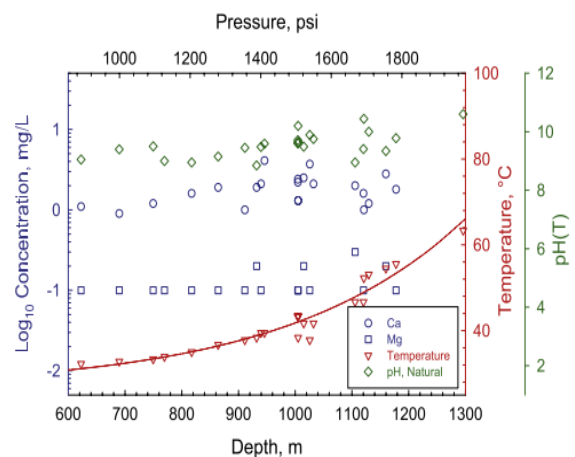


Figure 3: Columbia River basalt groundwater composition and temperature variation with depth (McGrail *et al.*, 2006)

$$T = T_0 + a \times e^{bd}, \text{ where } T_0 = 26.5 \pm 3.1 \text{ } ^\circ\text{C}, a = 0.63 \pm 0.5 \text{ } ^\circ\text{C}, b = 0.0032 \pm 0.0006 \text{ m}^{-1} \quad (1)$$

In contrary from those researchers, Rosenbauer *et al.*, (2012) set up a series of experiments at 50-200 °C, and found that at 100 °C, CO₂ had a highest reaction rate with basalt sample powder.

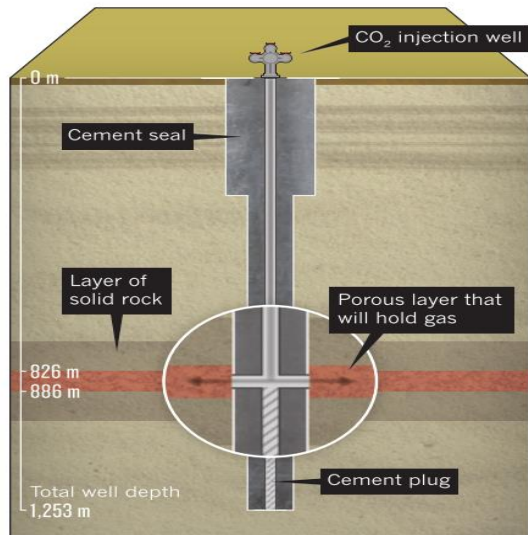


Figure 4: A sketch for injecting carbon dioxide into porous basalt layers (Tollefson, 2013)

Apart from injecting CO₂ into saline aquifers, the above figure 4 shows a pilot project for CO₂ storage in porous basalt formations at depth between 826m to 886m. As usual, supercritical CO₂ is injected through a pipeline which is sealed by cement. This project used the basalts formation porous properties and composition to store CO₂ for long term. Notably, this type of project can predict the conditions suitable for CO₂ storage in basalt rocks. Basalt rocks which are overlying sea floors are also considered having high potential for storing CO₂. Under sea basalt rocks, pores are filled with sea water and the rocks are feasible formations for the storage (Goldberg *et al.*, 2008).

Using basalt rocks to store CO₂ mainly have three mechanisms which are structural trapping, hydrodynamic trapping and mineral trapping (Akintunde *et al.*, 2013). Supercritical CO₂, which has lower viscosity than water, is a kind of Newtonian fluid. On the macroscopic level, fluid flow in porous structure is predicted by Darcy's law (equation 2), which is valid in laminar flow. However, this law is not quite accurate because it ignores ionic phenomena and pores shape as well as size. Besides, fluid in rocks can also have capillary movement through pores, whose diameter mostly less than 1 mm because of capillary tension.

$v = k * i / \mu$, where, k is permeability coefficient, i is the potential head gradient, μ is fluid viscosity

Reactions during CO₂ storage in basalt rocks

Basalt rocks storage ability is not only determined by interior connectivity but also their chemical composition. Different picrite's composition which was found from different references shows difference existing in the same sort of rocks and, specific estimation of geological formations needs to be done for any storage project.

The permeability of rocks such as basalts is determined by their porosities. Usually permeability and porosity have a log relationship performing increasing porosity leads to permeability increase. According to Jarrard and Schaar (1991), porosity can be estimated by sample's electrical conductivity which is a function of temperature and fluid salinity.

CO₂ storage capacity and rate are determined by these main factors; CO₂ dissolved rate, cations dissolved rate and reaction rate (Gysi and Stefansson, 2011; Rosenbauer *et al.*, 2012; Prasad *et al.*, 2012; Matter *et al.*, 2007; McGrail *et al.*, 2006). It can be found that different researches on geological storage have differences about the reaction between CO₂ and basalt rocks. Further, it can be agreed that different basalt rocks need to use different formulas for estimation (Gysi and Stefansson, 2011; Rosenbauer *et al.*, 2012; Prasad *et al.*, 2012; Matter *et al.*, 2007; McGrail *et al.*, 2006).

Mass transport in basalt formation

Estimating the rate of formation of carbonate mineral needs three basic details: dissolved CO₂ concentration, basalt cations (such as Mg²⁺ and Ca²⁺) releasing rate and those cations concentration required to precipitate carbonates (McGrail *et al.*, 2006). According to McGrail *et al.* (2006), the dissolved CO₂ concentration, a function of time and reservoir space, need to be estimated by reservoir simulation and, basalt cations releasing rate is a function of pH, temperature and basalt rocks surface area. For the last basic detail, geochemical modeling can be used. Gislason *et al.* (2010) stated that CO₂ mineral sequestration rate is limited by the slowest rate of basalts dissolution and releasing rate. In addition, Gislason and Oelkers (2003) carried out a series of experiments for basaltic glasses dissolution and concluded with an equation for their dissolution rate at 6-300 °C and pH at 1-11. However, Haug *et al.* (2011) indicated a special condition for olivine

carbonation at 11.5MPa and 185°C, carbonation process is controlled by magnesite precipitation instead of the rate of rocks dissolution. Ignoring special temperature condition, the normalized release rate of basalts data can fit well for equation (3) (McGrail *et al.*, 2006). This rate gives the mass dissolved per area per day and for basalt rocks, surface area as well as pores area should also be considered, as shown in equations (4), (5) and (6) (McGrail *et al.*, 2006).

$$r_d = k_0 10^{\eta[\text{pH}]} \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

where r_d is the normalized release rate; k_0 is the intrinsic rate constant; η is the coefficient of pH power law; E_a is the active energy; R is the gas constant and T is for temperature.

$$S_r = \frac{A_p}{V_p} = 6 \times \exp\left[-\left(x_0 + \frac{5b^2}{2}\right)\right] \quad (3)$$

where S_r is the specific surface area; A_p is the total surface area of pores; V_p is the volume of each pore; x_0 is the mean pores diameter and b is the distribution shape parameter.

$$A_p = n \int_0^\infty \pi x^2 P_p(x) dx \quad (4)$$

where; x is the pore diameter; $P_p(x)$ is pore size distribution.

$$V_p = \frac{4}{3} \pi \left(\frac{x}{2}\right)^3 = \frac{1}{6} \pi x^3 \quad (5)$$

Considering the effect of pH, Ca concentration can be used to estimate Calcite precipitation induction time (t_p) (McGrail *et al.*, 2006).

$$t_p = \frac{(C_s - C_0)(10^{\eta\text{pH}_f - 10^{\eta\text{pH}_0}}) 10^{-\eta(\text{pH}_f + \text{pH}_0)} V_p}{f_{Ca} k_0 \eta (\text{pH}_f - \text{pH}_0) \exp\left(\frac{-E_a}{RT}\right) A_p} \quad (6)$$

where $\frac{V_p}{A_p}$ can be replaced by $\frac{1}{S_r}$; C_s is the equilibrium concentration of Ca associated to Calcite; C_0 is the initial Ca concentration; the subscript f represents the condition of equilibrium; f_{Ca} is the mass fraction of Ca in a sample.

According to McGrail *et al.* (2006), the rate of dispersion of dissolved CO_2 may have more impact than cations releasing rate; and the Damkohler number (Da) for the CO_2 -water-basalt system can show the one that controls the precipitation rate. Da is a ratio of chemical rate of the mass transport as

shown in equation (7) (McGrail *et al.*, 2006). It shows that dispersion of CO_2 convection will be faster than carbonate precipitation in addition to a low permeability system.

$$Da = \frac{S_r f_{Ca} r_d}{\frac{\beta(\rho_s - \rho_0)gK}{\nu l} C_s} \quad (7)$$

where β is the porous system coefficient which can be approximately equal to 0.5; ρ is the liquid density in pores; g is the gravitational acceleration constant; K is the permeability of the porous medium; ν is the liquid's viscosity, l is the length of the sample which can be regarded as a cube and C_s is the concentration of the dissolved CO_2 .

P^c – S relationship

CO_2 sequestration in basalt rocks can be considered as a sort of two-phase system. Researchers have done some researches relevant to supercritical CO_2 -brine system by studying the relationship among capillary pressure (P^c), saturation (S) and permeability (K). According to Abidoye *et al.* (2014) and Khudaida and Das (2014), supercritical CO_2 -brine system can be influenced by fluid's viscosity, two fluids' density ratio and the media's heterogeneity. Studying the P^c - S relationship of the geological sequestration system can use a basic equation (8) which is built according to mass conservation, momentum conservation and constitutive equations (Abidoye *et al.*, 2014).

$$\phi \frac{\partial S_i}{\partial t} + \nabla V_i = 0 \quad (8)$$

where ϕ is the porosity; i represents the phases; v is phase velocity which follows Darcy's law as shown in equation (8).

According to Abidoye *et al.* (2014), geological temperature and pressure can influence the supercritical CO_2 -brine system; as that increasing pressure can result in decreasing CO_2 -brine interfacial tension. Similarly, decreasing temperature can result in decreasing capillary pressure and thus more CO_2 can be dissolved. One reason is because decreasing temperature can also decrease CO_2 -brine interfacial tension (Abidoye *et al.*, 2014). Most experiments studying P^c - S relationship of the geological sequestration system measure pressure drop across the domain to get capillary pressure and outflow brine to get saturation. Some new researches indicate that dynamic effect should be included to study capillary pressure and saturation relationships (Das and Mirzaei, 2012; Das *et al.*, 2007).

CONCLUSION

CO₂ storage in basalt rocks relies on the interior connectivity and composition of their formations. Due to the porous nature of the basalt rocks with its cations contents, supercritical CO₂ can be injected directly into porous basalt rocks. Though the interior part of basalt rocks appears to have low permeability, it is feasible for groundwater as well as CO₂ solution to flow through the porous media of the rock. Deep sea basalt formations storage injection site is similar to basalt aquifers while deeper geological formations are also feasible. Different basalt rocks have a similar composition but existing small differences in specific content percentage and, that can influence the reaction estimation. Though, it is feasible for supercritical CO₂ to flow in basalt rocks, however, their specific flow, reaction or storage rate still required to be estimated for different basalts conditions. Different researchers focus on looking for best reaction conditions among CO₂-brine-basalt, as they regarded mineral trapping as the most important mechanism. Some researchers mentioned other CO₂ storage mechanism like solubility and displacement but there is few modeling and simulation for the system. Like most geological storage sites, basalt rocks have a good capacity and injectivity, thus studying CO₂-brine system is very important and this has been well developed in saline aquifers study. Most recent experimental studies on CO₂ sequestration in basalts used artificial rock samples which are made with basalt particles. Kinetics of the reaction between CO₂-brine and basalts as well as system capillary pressure with saturation can also be carried out using a real basalt samples under a simulation of an actual project condition.

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