

GHGT-11

Geochemical clogging in fracture and porous rock for CO₂ mineral trapping

SeungYoul Yoo^{a*}, Yoshitada Mito^a, Akira Ueda^b, Toshifumi Matsuoka^a

^aGraduate School of Engineering, Kyoto University, Kyotodaigaku-Katsura, Nishikyo-ku, Kyoto 615-8540, Japan

^bGraduate School Division of Science and Engineering, University of Toyama, Gofuku 3190, Toyama 930-8555, Japan

Abstract

Geochemical trapping is regarded as one of the promising geologic sequestration of carbon dioxide (CO₂). Also carbonate mineralization takes advantage of permeability reduction to seal formations with decreasing CO₂ leakage risk and increasing storage safety. As precipitation rates tend to be faster and the solubility product shows lower value at higher temperature, the calcite- and kaolinite- rich rock produced through CO₂-water-rock interaction is expected to form the scale in geothermal reservoirs. Ca²⁺ released from rocks could be removed as carbonate minerals (CaCO₃) during CO₂ sequestration into aquifer rocks. However, when, where, and how much calcite deposits at the reservoir. For this reason, flow experiments and numerical calculation of advection-reaction model have been done to predict where and when the mineral deposits and permeability changes.

The experimental and numerical results provided that fluid velocity change between fracture and porous media have more than one-order discrepancy at isothermal condition. When the fluid velocity in fracture exceeds the critical velocity, surface erosion allows re-entrainment. Critical velocity in porous media is likely to be larger than that in fracture because internal erosion might interrupt the migration of deposit by re-settlement in pore spaces.

© 2013 The Authors. Published by Elsevier Ltd.
Selection and/or peer-review under responsibility of GHGT

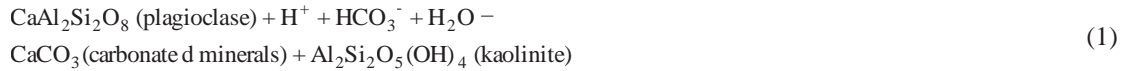
Keywords: Clogging; Carbonate; Mineralization; Fracture; Porous media; Precipitation; Erosion; Critical velocity

1. Introduction

Mineral deposition in the rock mass can bring significant changes in permeability and porosity. In fracture systems, individual fractures often provide dominant pathways for fluid flow, and relatively small changes in fracture aperture can significantly influence transport properties. Mineral-filled fractures and faults are commonly found in pathways for fluid flow with water-rock interaction. (e.g. hydrothermal reservoirs). Carbonated water-rock interaction is applied to Carbon Capture and Sequestration (CCS)

* Corresponding author. Tel./ fax: +81-75-383-3206.
E-mail address: civilyoo@gmail.com / s_ryu@earth.kumst.kyoto-u.ac.jp

technology because geochemical trapping takes advantage of permeability reduction to seal formations with a decreasing risk of CO₂ leakage while increasing CO₂ capture safety. The high temperature formation fluid seems to be favorable for immediate mineralization to overcome the slow geochemical reactions and contribute to the storage safety as shown in Fig. 1(a). CO₂-saturated groundwater has reacted with Ca-rich rocks and formed carbonated minerals and kaolinite as:



This chemical reaction moves towards the right side at higher temperature owing to the decrease of calcite solubility with increasing temperature [1]. In field experiments, dissolved CO₂ was injected into a high temperature borehole (OGC-2, 210°C) at the Ogachi geothermal site, Japan, where the hydraulic fracturing had been applied for the enhanced geothermal system (EGS) to induce a lot of fracture in the reservoir [2]. After sampling of formation fluid, the change of aqueous chemical evolution and groundwater level provided undisputed evidence that mineral precipitation occurred [3]. In order to reproduce CO₂ mineral trapping in laboratory scale, high pressure and high temperature flow experiments were performed using the SUS chamber packed with rock cuttings under almost the same hydrothermal condition [4].

Most laboratory-scale experiments for filtration of deposited particles are mainly implemented in porous media for convenience because there is little information about permeability change by geochemical reaction in fracture system. The fracture model has been experimentally verified for CaCO₃ precipitation in carbonated rocks to determine the influences of fluid velocity and saturation states [5]. A new experimental apparatus was designed to directly measure changes in fracture aperture in analog fractures subjected to the combined influence of a reactive fluid and an applied normal stress [6]. In spite of their contribution, the precipitation process of carbonates in fracture openings with a continuous fluid flow is still a challenging area. Therefore, two kinds of flow tests in fractured and porous media (Fig.1 (b)) can be comparable in flow rate changes while adjusting the differential total head (Δh). The carbonated hot spring fluid at Matsushiro, Japan is considered suitable for depositing carbonate minerals rapidly.

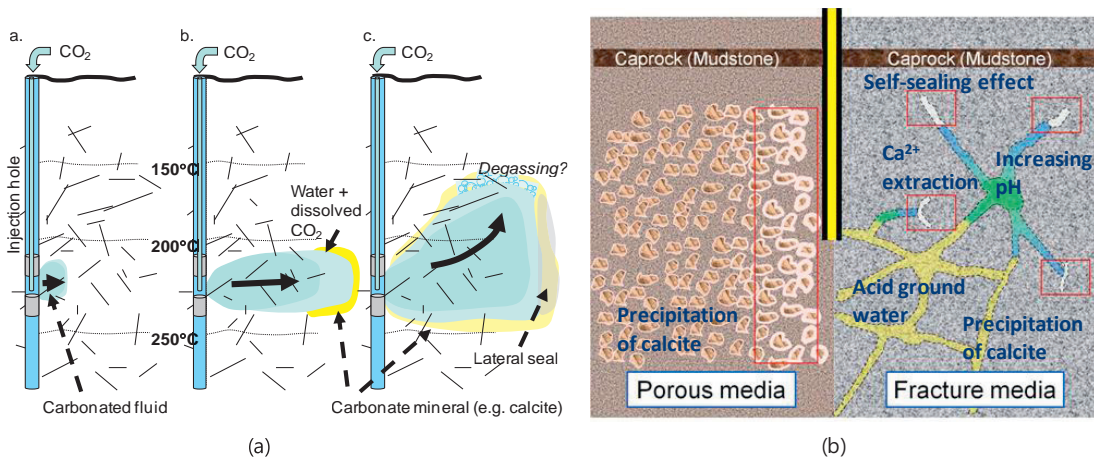


Fig. 1. Concept of CO₂ mineral trapping (a) at geothermal fields and (b) in the fractured and porous rocks.

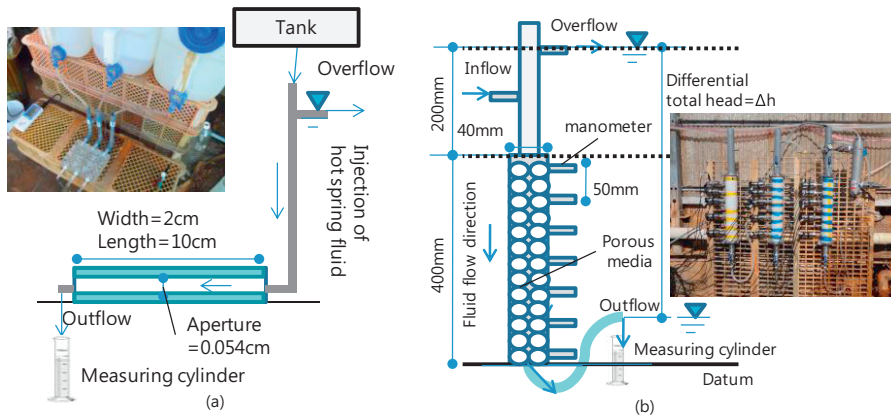


Fig. 2. Experimental setup using (a) fracture apparatus and (b) column apparatus.

2. Experimental setup

Fluid flow experiments in laboratory scale were targeted in hot spring area where is abundant in carbonated minerals under the relatively moderate temperature environment at the range of from 40 °C to 50 °C. Matsushiro hot spring fluid (Na-Cl-HCO₃ type) is especially rich in Ca (– 850 mg/L) and HCO₃ (– 1800 mg/L). After fluid sampling at the well for geological survey, the saturation index (S.I.) values with respect to calcite and aragonite were calculated as 1.09 and 0.96 from saturation index:

$$\text{S.I.} = \log(\text{I.A.P.} / \text{K}_{\text{sp}}) \quad (2)$$

where I.A.P. and K_{sp} are ion activity products and solubility products of carbonates, respectively. This neutral pH fluid is supersaturated with carbonates (S.I. > 0) enough to clog up the pipe with the carbonated scale which precipitation rate showed about 60mm per a year. Discharge flow rates can be observed at the constant Δh between the inlet and outlet through fracture and porous type- apparatuses.

2.1. Experimental methods for fractured rocks

Matsushiro hot spring fluid was injected into fracture media shown in Fig. 2(a) for about a day. Fracture apparatus made of acrylic was designed as an “open” fracture which means the planar surfaces remain parallel and thus are not in contact at any point. The width and length of fracture apparatus is designed to be 10cm and 2cm respectively. The initial value of hydraulic aperture was 0.54 mm. A side of the channel was covered with a transparent acrylic plate in order to observe the change in precipitation of carbonates in the flow path during experiments. Discharge flow rates can be controlled with the differential total head (Δh) by allowing overflow around the inlet part. Flow rate divided by Δh is proportional to the cube of hydraulic aperture (b). Initial solution saturation states with respect to calcite and aragonite were calculated from average measured pH ($= 6.6 \pm 0.1$) and temperature ($T = 41.1 \pm 3^\circ\text{C}$). The differential total head (Δh) should be calibrated by calculation of the head loss due to friction (h_f) as shown in Darcy-Weisbach equation that implies the head loss is independent with roughness of the pipe:

$$\Delta h = h_f = \psi \frac{L}{D_h} \frac{u^2}{2g} \quad (3)$$

where h_f is the head loss due to friction (m), L is the length of flow path (m), D_h is the hydraulic diameter, which is commonly used for fluid flow in non-circular tubes and channels, u is the average velocity of the fluid flow, equal to the volumetric flow rate per unit cross-sectional wetted area (m/s), g is

the local acceleration due to gravity (m/s^2), and ψ is the dimensionless coefficient called the Darcy friction factor. The law for flow in fractures can be generalized in terms of the Reynolds number ($Re = \rho uD/\mu$) where ρ and μ is density and viscosity of the fluid, respectively and ψ is the friction factor. We demonstrated the validity of the cubic law as long as the fluid flow was laminar ($Re_c = 370\sim 1310$; $Re < 2300$) with the various differential total head ($\Delta h = 10\text{ cm}, 15\text{ cm}, 20\text{ cm}$). If the flow is steady and isothermal, the flux per unit differential total head can be developed from Darcy's law and may be written in simplified form as:

$$\frac{Q}{\Delta h} = \left(\frac{C}{f}\right)b^3 \tag{4}$$

where b is an aperture of fracture and f is a roughness factor that $f = 1.0$ accounts for deviations from the ideal condition. According to some flow experiments, f equals to $0.83 (< 1.0)$ which is related in the smooth acrylic plates. A constant (C) in the case of straight flow with the channel width, w is given by:

$$C = \left(\frac{w}{L}\right)\left(\frac{\rho g}{12\mu}\right) \tag{5}$$

Results of the least squares fit for the experimental data are given in Fig. 3. The cubic law is valid for these fracture flow conditions because the value of n is 3. The critical velocity derived from the balance between driving force and shearing force is combined with ψ from Hagen-Poiseuille equation as below:

$$u_c = \sqrt{\frac{\tau_0}{\rho}} = u\sqrt{\frac{\psi}{8}} \tag{6}$$

2.2. Experimental methods for porous rocks

The same neutral pH hot spring fluid was injected into the column at $49\text{ }^\circ\text{C}$ for 43 hours. The equipment setup is designed to change the differential total head (Δh), which was kept at 42cm , by adjusting points between overflow and discharge as shown in Fig. 2(b). The SUS column consists of a cylindrical chamber with the inside diameter of 4.3 cm and the height of 40 cm . Seven manometers at intervals of 5 cm were installed on the side of columns to indicate the pressure head by the difference in fluid levels at each location. In order to measure the pressure automatically, fluid pressures at each point of $5\text{ cm}, 10\text{ cm}, 15\text{ cm}, 25\text{ cm},$ and 35 cm were measured with digital pressure sensors (Keyence, GP-M010). The column is packed with glass beads which are 2 mm average in diameter and 2.50 g/cm^3 density. The initial porosity of this packed column was 0.39 which was determined by the volume of water in pore and the volume of the column.

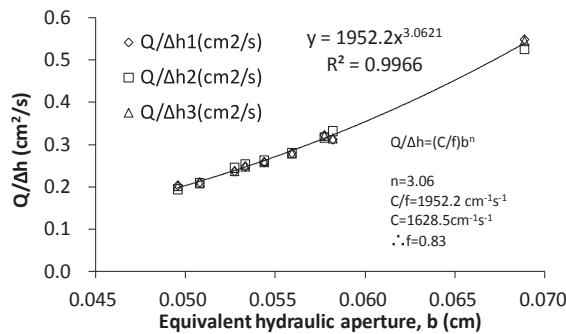


Fig. 3. The validation of cubic law with fracture apparatuses.

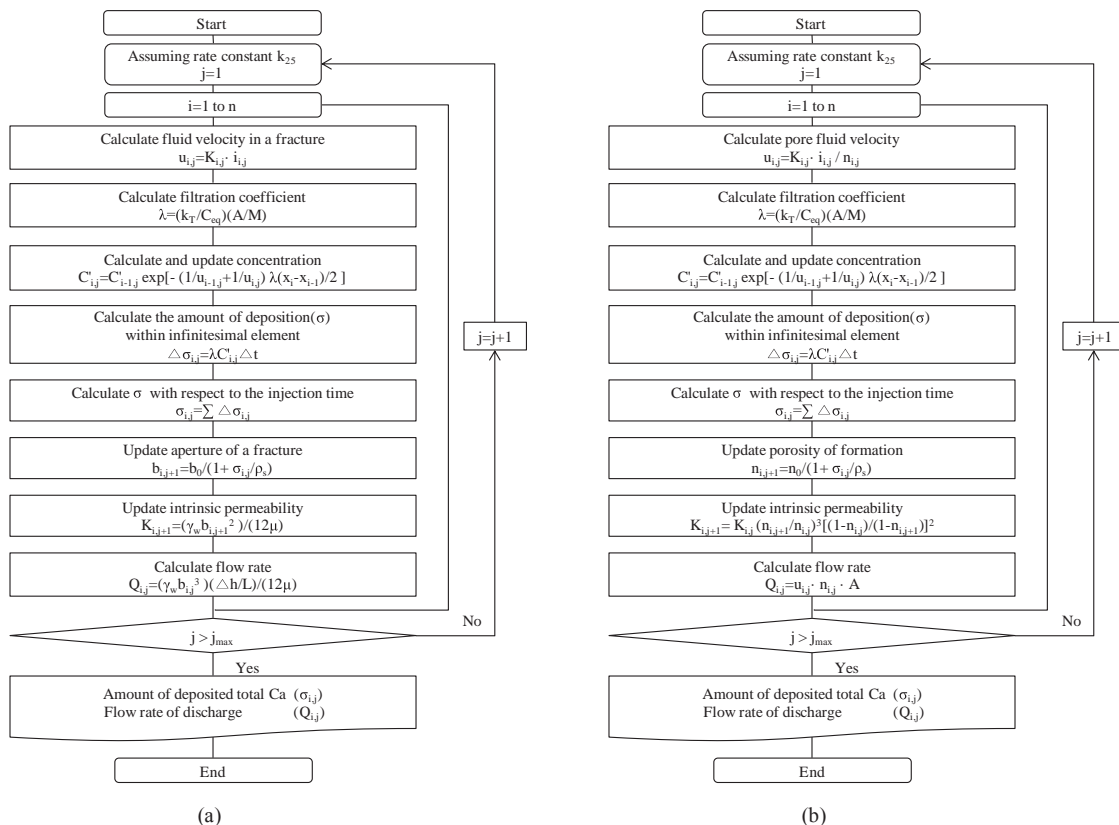


Fig. 4. Procedure for numerical calculation in the geochemical clogging model for (a) fractured rocks and (b) porous rocks.

Table 1. The concentration of chemical compositions for the neutral (pH = 6.6 ± 0.1) fluid sampling at Matsushiro (Unit: mg/L).

Na	K	Ca	Mg	Cl	SO ₄	SiO ₂	Sr	Fe	Mn	HCO ₃
4300	450	850	280	8600	210	170	14	11	1.3	1600

3. Geochemical clogging model

3.1. Advection-reaction equation

Step-wise numerical calculation developed for the geochemical clogging model takes in account various properties given by experimental conditions. Calcite deposits are represented as two-component system of Ca²⁺ and CO₃²⁻ as shown in:



The rate of calcite precipitation is regulated by both changes in Ca²⁺ and CO₃²⁻ concentration in the fluid. Bicarbonate is a major species in neutral solutions. The equilibrium conditions in Eq. (2), which also thermodynamically represents the real reaction, were calculated. For this reason, the precipitation rate is replaced as a one-component fluid with Ca²⁺ for convenience. When the concentration of Ca is less than that of CO₃ in the case of Matsushiro (Table 1), the amount of deposited Ca might be overestimated.

In this calculation, the conservation of mass for one-dimensional transport with calcite deposition in porous media is modeled by an advection-reaction formulation:

$$\frac{\partial C}{\partial t} = -u \frac{\partial C}{\partial x} - k_T \left(\frac{A}{M} \right) \left(\frac{C - C_{eq}}{C_{eq}} \right) \quad (8)$$

where C is the Ca^{2+} concentration in flowing water (g/cm^3), C_{eq} is the equilibrium Ca^{2+} concentration in water (g/cm^3), which is temperature dependent, t is time (s), u is the fluid velocity (cm/s), x is distance (cm), A/M is the specific reactive surface area (A) per kg of H_2O (M), and k_T ($\text{mol cm}^{-2} \text{s}^{-1}$) is the rate constant of the chemical reaction at T , which is a function of temperature by the Arrhenius equation:

$$k_T = k_{25} \exp \left[\frac{-E_a}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] \quad (9)$$

where E_a is the activation energy, R is the gas constant, T is the absolute temperature, and k_{25} is the rate constant at 298.15 K.

In the case of steady state flow when concentrations of Ca^{2+} and CO_3^{2-} are constant, the general solution of Eq. (8) can be described by Eq. (10) when the concentration at the inlet ($x = 0$) equals the influent concentration (C_i'):

$$C' = C_i' \exp \left[- \left(\frac{k_T A}{C_{eq} M} \right) \left(\frac{x}{u} \right) \right] \quad (10)$$

where $C' (= C - C_{eq})$ is the supersaturated concentration if S.I. > 0 and λ is the filtration coefficient as $(k_T / C_{eq}) \cdot (A / M)$.

3.2. Calculation procedure

Step-wise numerical calculation was programmed by a spread-sheet for the geochemical clogging model. This model takes into account various properties given by the experimental conditions and it is able to evaluate the amount of Ca ($\sigma_{i,j}$) and flow rates ($Q_{i,j}$). These properties can be assumed to be constant within a small discretized grid for computational purposes in each step following the procedure for the fractured (Fig. 4(a)) and porous types (Fig. 4(b)). The subscripts i and j represent the space grid index and the time index, respectively. The fluid velocity ($u_{i,j}$) in the fractured and porous rock can be expressed as:

$$u_{i,j} = K_{i,j} \cdot i_{i,j} \quad (11)$$

$$u_{i,j} = K_{i,j} \cdot i_{i,j} / n_{i,j} \quad (12)$$

where $i_{i,j}$ is the hydraulic gradient, $K_{i,j}$ and $n_{i,j}$ are the intrinsic permeability and the porosity of the porous media. This precipitation process has been described in the first-order rate law as:

$$\frac{\partial \sigma_{i,j}}{\partial t} = \lambda C'_{i,j} \quad (13)$$

Then, the total amount of deposited Ca is expressed as the cumulative amount of deposits in:

$$\sigma_{i,j} = \sum_{j=1}^j \Delta \sigma_{i,j} = \sum_{j=1}^j \lambda C'_{i,j} \Delta t \quad (14)$$

In fracture media model, the aperture at location i and time step $j+1$ may be expressed when filling up a crack with deposited Ca:

$$b_{i,j+1} = \frac{b_0}{1 + \sigma_{i,j} / \rho_s} \quad (15)$$

where b_0 means the initial aperture before injecting hot spring fluid. In porous media model, this deposited Ca changes the porosity. The porosity at position i and time step $j+1$ is updated when assuming $n_{i,j}$ is approximately equal to $n_{i,j+1}$:

$$n_{i,j+1} = \frac{n_0}{1 + \sigma_{i,j} / \rho_s} \tag{16}$$

where n_0 is the initial porosity and ρ_s is the density of Ca. Finally, the calculated flow rates in fractured and porous media can be matched to the observed data as:

$$Q_{i,j} = u_{i,j} \cdot n_{i,j} \cdot A \tag{17}$$

$$Q_{i,j} = \frac{(\gamma_w b_{i,j}^3)}{12\mu} \cdot \frac{\Delta h}{L} \tag{18}$$

where A is the cross-sectional area of the column packed with porous media.

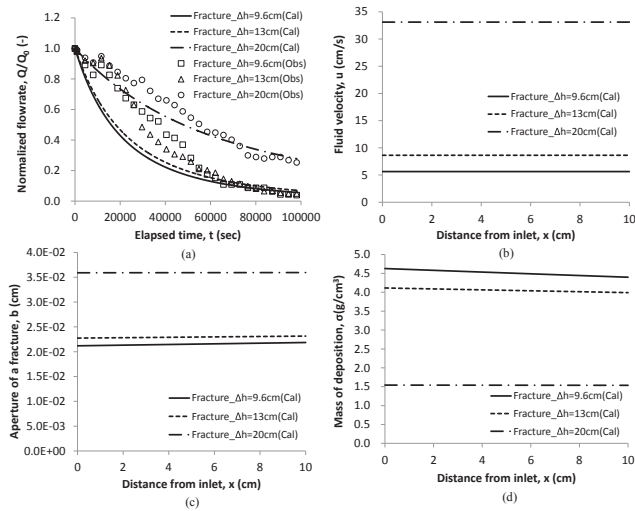


Fig. 5. Calculation results for fractured case. (a) Flow rate, (b) Fluid velocity, (c) Aperture of a fracture, and (d) Mass of deposition

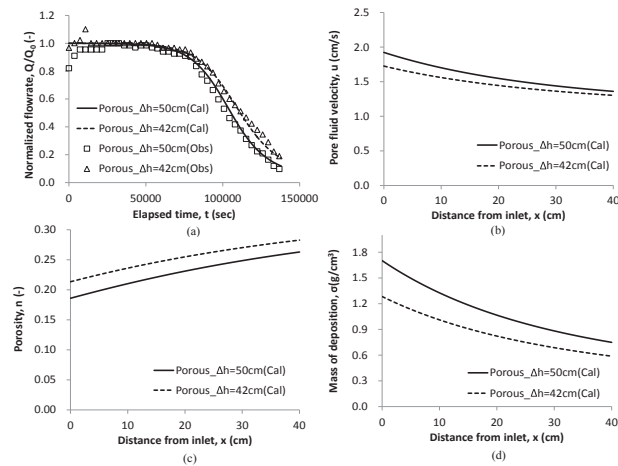


Fig. 6. Calculation results for porous case. (a) Flow rate, (b) Pore fluid velocity, (c) porosity, and (d) Mass of deposition.

4. Results and discussions

Permeability reduction with the deposition occurred because of high Ca and HCO_3 concentration. In order to evaluate the various flow properties between porous and fracture formation, calculated flow rates based on the proposed geochemical clogging model were compared with the experimentally observed data. For the fractured case, the decreased ratio of flow rate showed almost the same trend in spite of the different Δh at 9cm and 13cm (Fig. 6). The critical velocity corresponding to the onset of particle erosion was calculated from Eq. (6) to be 5.0, 5.8, 7.3 cm/s at a constant head drop of 9 cm, 13 cm and 20 cm. Deposited carbonates may be allowed to detach from the rock surface above a head drop of 9 cm because fluid velocity in fracture is larger than the critical velocity (= 5.0 cm/s) (Fig. 5(b)). In contrast, flow test in porous rocks were conducted in two cases of the differential total heads as 42cm and 50cm. The fluid velocity is not much higher than that of fracture and not sensitive with the change of Δh . Although the internal erosion test cannot be implemented, the observed flow rates showed that the re-entrainment has an insignificant effect on the reactive transportation of carbonates.

5. Conclusions

Fluid velocity with respect to the flow distance is distributed quite uniformly in the fracture case, however, in the porous case the pore fluid velocity with distance decreases exponentially. Since, fluid velocity is proportional to the differential total head and permeability of media, the magnitude of fluid velocity in the fracture case (5~35 cm/s) is much higher than that in the porous case (1.5~2.0 cm/s), even though the differential head of fracture (9.6~20 cm) is less than that of porous media (42~50 cm) (Fig. 5 and Fig. 6). Advection-reaction phenomena present the possibility that not only deposition, but also erosion in rock surfaces, may occur. These results agreed with the experimental results by Reddi et al. [7] that the critical velocities from internal erosion tests (corresponding to the porous media case) are several orders of magnitude greater than those in the case of surface erosion tests (corresponding to the fractured media case). It is recommended that fluid velocity should be kept less than critical velocity, especially in fractured rocks, for successful mineral trapping.

References

- [1] Chiba, H., 1991. Attainment of solution and gas equilibrium in Japanese geothermal systems. *Geochem. J.* 25, 335-355.
- [2] Kaieda, H., Ito, H., Kiho, K., Suzuki, K., Suenaga, H., Shin, K., 2005. Review of the Ogachi HDR Project in Japan. *Proceedings of World Geothermal Congress.* 1601.
- [3] Ueda, A., Kato, K., Ohsumi, T., Yajima, T., Ito, H., Kaieda, H., Metcalf, R., Takase, H., 2005. Experimental studies of CO_2 -rock interaction at elevated temperatures under hydrothermal conditions. *Geochem. J.* 39, 417-425.
- [4] Yoo, S.Y., Kuroda, Y., Mito, Y., Matsuoka, T., Nakagawa, M., Ozawa, A., Sugiyama, K., Ueda, A., 2012. A geochemical clogging model with carbonate precipitation rates under hydrothermal conditions. *Appl. Geochem.*, in press.
- [5] Lee, Y.J., Morse, J.W., 1999. Calcite precipitation in synthetic veins: implications for the time and fluid volume necessary for vein filling. *Chem. Geol.* 156, 151-170.
- [6] Detwiler, R.L., 2008. Experimental observations of deformation caused by mineral dissolution in variable-aperture fractures. *J. Geophys. Res.* 113, B08202.
- [7] Reddi, L.N., Xiao, M., Hajra, M.G., Lee, I.M., 2000. Permeability reduction of soil filters due to physical clogging. *J. Geotech. Geoenviron. Engrg., ASCE*, 126, 3, 236–246.