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Technical Paper

Multi-physics numerical analyses for predicting the alterations in permeability and reactive transport behavior within single rock fractures depending on temperature, stress, and fluid pH conditions

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Abstract

The aim of the current study was to establish a validated numerical model for addressing the changes in permeability and reactive transport behavior within rock fractures based on the fluid pH under coupled thermal-hydraulic-mechanical-chemical (THMC) conditions. Firstly, a multi-physics reactive transport model was proposed, considering the geochemical reactions that depend on the temperature, stress, and fluid chemistry conditions (e.g., fluid pH and solute concentrations), as well as the changes in permeability in the rock fractures driven by these reactions, after which the correctness of the model implementation was verified by solving the 1D reactive transport problem as a fundamental benchmark. Secondly, the validity of the model against actual rock fractures was investigated by utilizing the model to replicate the measurements of the evolving permeability and the effluent element concentrations in single granite fractures obtained by means of two flow-through experiments using deionized water (pH ~ 6) and a NaOH aqueous solution (pH ~ 11) as permeants under stressed, temperature-elevated conditions. The model predictions efficiently followed the changes in fracture permeability over time measured by both experiments. Additionally, the observed difference in the changing rates, which may contribute to the difference in the fluid pH between the two experiments, was also captured exactly by the predictions. Moreover, in terms of the effluent element concentrations, among all the elements targeted for measurement, the concentrations of most elements were replicated by the model within one order of discrepancy. Overall, it can be concluded that the developed model should be valid for estimating the changes in permeability and reactive transport behavior within rock fractures induced by geochemical reactions which depend on the fluid pH under coupled THMC conditions.

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1. Introduction

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In order to evaluate the performance of a geological disposal facility of high-level radioactive waste (HLW), for the prevention of radionuclide migration, the fluid flow

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and mass transport behavior in the rock mass that works as a natural barrier must be examined over the long duration (Japan Nuclear Cycle Development Institute, 2000). The fluid flow and mass transport behavior within the rock mass may often be controlled by the permeability of the rock fractures. Thus, for the robust isolation of HLW, it is important to predict the changes in fracture permeability under the anticipated environment around the natural barrier. During the period of geological disposal, the rock mass containing the waste package may be subjected to high-temperature and high-confining stress conditions due to heat radiation from the waste package and earth pressure under the deep subsurface (Japan Nuclear Cycle Development Institute, 2000; Tsang, 2012). In addition, the pH of the pore water in the rock mass may be increased by the leaching of the cementitious materials included in the artificial barrier and shotcrete supporting the disposal cavity (i.e., the formation of an alkaline environment) (Japan Nuclear Cycle Development Institute, 1999a, 1999c). Under such a convolved environment, the occurrence of geochemical reactions may be induced between the minerals composing the rock and the pore water, such as the mineral dissolution at the contacting asperities (pressure dissolution) and the mineral dissolution/precipitation at the free surface (free-face dissolution/precipitation) within the rock fractures, which depend on the temperature, stress, and fluid pH (Lasaga, 1984; Polak et al., 2003, 2004; Yasuhara et al., 2004; Palandri and Kharaka, 2004). From past experimental works (Polak et al., 2003, 2004; Beeler and Hickman, 2004; Yasuhara et al., 2004, 2006, 2011; Kinoshita and Yasuhara, 2012; Robert et al., 2016), it has been confirmed that the geochemical reactions induced by the above-mentioned coupled conditions, namely, the coupled thermal-hydraulic-mechanical-chemi cal (THMC) conditions, will alter the permeability of the rock fractures over time. For example, Yasuhara et al. (2011) conducted long-term flow-through experiments on single granite fractures using deionized water under stressed and temperature-elevated conditions, and confirmed that the fracture permeability decreased by more than one order of magnitude within a few hundred hours, probably due to the time-dependent fracture compaction by the mineral dissolution at the contacting asperities within the fractures (i.e., pressure dissolution). Kinoshita and Yasuhara (2012) performed a series of flow-through experiments on single rock fractures in granite under various fluid pH, stress, and temperature conditions. Their experimental work showed that the amount of abrupt permeability degradation under alkaline conditions, mainly attributed to the influence of pressure dissolution accelerated by the elevation in temperature, was greater than that under neutral conditions.

On the other hand, several numerical models that can consider the changes in permeability in the rock fractures, induced by the geochemical reactions under coupled THMC conditions, have previously been proposed (Yasuhara and Elsworth, 2006; Taron et al., 2009;

Bernabe and Evans, 2014; McDermott et al., 2015; Bond et al., 2016, 2017; Ogata et al., 2018, 2020). Among the models, many of them (Yasuhara and Elsworth, 2006; Bond et al., 2016, 2017; Ogata et al., 2018) have tried to numerically reproduce the actual measurements obtained from laboratory experiments. For instance, Bond et al. (2016, 2017) utilized various coupled mathematical THMC models (0D \sim 2D), employing the homogenized and discretized treatments of the fracture aperture, to reproduce the results of flow-through experiments by using deionized water as the permeant with single rock fractures in granite and novaculite (Yasuhara et al., 2006, 2011). While some of the models used in their studies, which included the laws of geochemical reactions based on the stress, temperature, and fluid pH, were able to follow the measurements relatively well, the numerical results had to be adjusted by calibrating the fitting parameters in the wide range of 245 to 10^6 in the calculations of the geochemical reactions.

On the contrary, the reactive transport model with THMC coupling, presented by Ogata et al. (2018) and implemented in COMSOL MULTIPHYSICS (COMSOL, 2014), which is a multi-physics simulation software using FEM, was able to replicate the experimental data obtained from flow-through experiments (Yasuhara et al., 2011) by using single fractures of granite and mudstone without the need for calibrating the fitting parameters in as wide a range as that performed in Bond et al. (2016, 2017). In addition, Ogata et al. (2020) proposed a more advanced coupled thermal-hydraulic-mechanical damage-chemical (THMDC) model that can compute a series of rock permeability alteration processes from fracture generation to the subsequent sealing of the fracture aperture, due to the pressure dissolution in the natural barrier within a geological disposal facility of HLW, by combining the mechanical damage model and the reactive transport model (Ogata et al., 2018). In that work (Ogata et al., 2020), the calculation system linking COMSOL and the versatile geochemical code PHREEQC (Parkhurst and Appelo, 2013) was introduced to yield a solution to the reactive transport process with complex reactions for the multi-minerals (i.e., pressure dissolution and free-face dissolution/precipitation) to be more accurately and robustly based on the abundant thermo-dynamic databases and flexible geochemical solver installed in PHREEQC. Such computational frameworks, connecting COMSOL and PHREEQC, have been successfully built by other researchers (e.g., Wissmeier and Barry, 2011; Nardi et al., 2014); however, these frameworks are not designed to handle the pressure dissolution like the one by Ogata et al. (2020). Despite the authors having vigorously developed the coupled models in that way, the pH dependence on the geochemical reactions is not considered in their models (Ogata et al., 2020, 2018) at that stage. As a matter of fact, in terms of the fluid pH, the model validations/predictions in the previous studies, listed above (Yasuhara and Elsworth, 2006; Bond et al., 2016, 2017; Ogata et al., 2018, 2020), were conducted only under conditions where the flowing fluid within the rock fractures was almost neutral. Thus, at present, there are no validated numerical models for predicting the permeability evolution of rock fractures based on the fluid pH under coupled THMC conditions. Solving this issue would be significantly important to gaining a better understanding of the fluid flow and mass transport behavior within the rock mass in environments around geological disposal facilities of HLW where the fluid is expected to be alkaline.

The aim of the present study was to overcome the above-mentioned issue. In this study, an upgraded multiphysics reactive transport model was proposed by adding the consideration of the pH dependence on the scheme of the geochemical reactions (i.e., pressure dissolution and free-face dissolution/precipitation), and the changes in permeability in the rock fractures driven by these reactions, to our previous model (Ogata et al., 2018). Additionally, with reference to Ogata et al. (2020), the linking of COMSOL and PHREEQC was performed as a numerical implementation system for the model. Then, the proposed model was applied to reproduce flow-through experiments using single granite fractures under various fluid pH, stress, and temperature-elevated conditions (Kinoshita and Yasuhara, 2012), and validated by making comparisons with experimental measurements, such as the evolution in permeability and the element concentrations dissolved in effluent water. Meanwhile, this work complements a recent study by the authors (Ogata et al., 2021), whose aim was to simulate the evolution in permeability and the reactive transport behavior within actual rock fractures. In this recent study, the numerical simulations applied the uncertain assumption that the system of interest was under the spatiotemporally constant fluid pH and far-fromequilibrium conditions. These shortcomings were improved by applying the capability of determining the spatiotemporal distributions of the fluid pH and saturation indices for multi-minerals based on the geochemical computation in PHREEOC.

It is noted that attempting to present the first validated numerical model for the changes in permeability and reactive transport behavior within actual rock fractures influenced by the fluid pH values (e.g., alkaline pH) under coupled THMC conditions is the novelty of the current work.

2. Numerical model

2.1. Model description

The numerical model used in this work is based on the Finite Element Method (FEM) that is able to address the coupled THMC interactions, including the changes in permeability in the rock fractures over time driven by the geochemical reactions depending on the thermal, stress, and fluid pH conditions. This model was proposed by incorporating the dependence of the fluid pH on the progress rates of the kinetic geochemical reactions into our previous model (Ogata et al., 2018). In the experiments to be replicated by the numerical analysis in this work, the distributions of temperature and stress within the rock specimens are assumed homogeneous. Therefore, only the coupled process, which includes the fluid flow, reactive transport with geochemical reactions, and updating of the geometry over time within the rock fractures, are computed here. The governing equations that make up the proposed model are introduced in the following.

The field of fluid flow within the fractures of a saturated rock is described by the conservation of the water mass and by assuming the Darcian flow, as follows:

$$\frac{\partial(\rho_w \varphi)}{\partial t} + \nabla \cdot (\rho_w \boldsymbol{u}) = f_w \tag{1}$$

$$\boldsymbol{u} = -\frac{k}{\mu} \nabla p \tag{2}$$

$$k = \frac{b_h^2}{12} \tag{3}$$

where ρ_w [kg m⁻³] is the density of the fluid, φ [-] is the porosity, \boldsymbol{u} [m/s] is the fluid velocity vector, f_w [kg m⁻³ s⁻¹] is the source term for the flow, k [m²] is the permeability of the rock fractures, μ [Pa s] is the fluid dynamic viscosity, p [Pa] is the water pressure, and b_h [m] is the hydraulic aperture of the rock fractures.

The reactive transport behavior within the rock fractures is simulated by solving the basic advection-diffusion equation, which disregards the sorption process.

$$\frac{\partial(c_q \varphi)}{\partial t} + \boldsymbol{u} \cdot \nabla c_q = \nabla \cdot (\tau \varphi \boldsymbol{D} \nabla c_q) + r_q \tag{4}$$

where $c_q \text{ [mol m}^{-3}\text{]}$ is the concentration of solute q in the pore water, $D \text{ [m}^2 \text{ s]}$ is the dispersion tensor, τ [-] $(\tau = 1.0)$ is the coefficient related to tortuosity, and r_q [mol m⁻³ s⁻¹] is the source term for solute q supplied by the geochemical reactions. The dispersion tensor is expressed as (Scheidegger, 1961).

$$\boldsymbol{D} = D_b \boldsymbol{I} + \alpha_T |\boldsymbol{u}| \boldsymbol{I} + (\alpha_L - \alpha_T) \frac{\boldsymbol{u}^T \boldsymbol{u}}{|\boldsymbol{u}|}$$
(5)

where $D_b [\text{m}^2 \text{s}^{-1}]$ is the diffusion coefficient tensor, and α_L [m] and $\alpha_T [\text{m}]$ are the longitudinal and transversal dispersion coefficients, respectively. The diffusion coefficient is temperature-dependent and is represented by an Arrhenius-type equation (Revil, 1999).

$$D_b = D_b^0 \exp\left(-\frac{E_D}{RT}\right),\tag{6}$$

where D_b^0 [m² s⁻¹] and E_D [J mol⁻¹] are the pre-exponential factor and the activation energy of the diffusion of the solute, respectively, R [J mol⁻¹K⁻¹] is the gas constant, and T [K] is the system temperature. In this work, the target rock consists of multi-minerals. When the number of minerals contained in a targeted rock is *m*, the total source of the solute supplied by the geochemical reactions is computed by.

$$r_q = \sum_j^m v_{q,j} R_j \tag{7}$$

where v_q [-] is the stoichiometry coefficient of solute q in the pore water and R_j [mol m⁻³ s⁻¹] is the rate of the geochemical reactions for mineral j.

In this work, the mineral dissolution/precipitation at the free surface of the fractures (i.e., free-face dissolution/precipitation) and the mineral dissolution at the asperity contact of the fractures (i.e., pressure dissolution) are taken into account as geochemical reactions in the model. Thus, R_i is expressed by.

$$R_j = R_j^{FF} + R_j^{PS} \tag{8}$$

where R_j^{FF} [mol m⁻³ s⁻¹] and R_j^{PS} [mol m⁻³ s⁻¹] are the rates of the free-face dissolution/precipitation and pressure dissolution of mineral *j* within the rock fractures, respectively. As depicted in Fig. 1, when the micro fracture domain, composed of a pore space and contacting asperities, is set as the representative element (Yasuhara et al., 2004), the rate of the dissolution/precipitation of mineral *j* at the free surface of the fracture wall (free-face dissolution/precipitation), R_j^{FF} , can be given as described in Lasaga (1984) and Ogata et al. (2018), as follows:

$$R_j^{FF} = \frac{2\chi_j f_{r,j} k_{+,j}}{b} \left(1 - SI_j\right) \tag{9}$$

where $f_{r,j}[-]$ is the roughness factor of mineral j, $\chi_j[-]$ is the volumetric ratio of mineral j, $k_{+,j}$ [mol m⁻² s⁻¹] is the mineral dissolution rate constant, $SI_j(=Q_j/K_{eq,j})$ is the saturation index of mineral j, $Q_j[-]$ is the ionic activity product of



REV in fracture area

Fig. 1. Geometrical model that includes representative element within rock fracture domain proposed by Yasuhara et al., 2004 (illustrated in Ogata et al. (2020)). Tributary area A_t^I is the representative element composed of asperity contact area $R_c A_t^I$, and the pore space.

mineral j, $K_{eq,j}$ [-] is the equilibrium constant of mineral j, and b [m] is the mechanical aperture of the rock fractures. When SI < 1, free-face dissolution occurs; when SI > 1, free-face precipitation occurs (reprecipitation of the dissolved mineral in the pore water and the precipitation of other secondary minerals). As for the free-face precipitation, only secondary mineral precipitation is taken into account in the current work, while the reprecipitation of the dissolved mineral in the pore water is not considered, based on the observation of the precipitated materials on the fracture surface by post-experimental microscopy in the flow-through experiments using a granite fracture under hydrothermal conditions (Yasuhara et al., 2011).

The rate of mineral dissolution at the contacting asperities within the rock fracture namely, pressure dissolution, R_j^{PS} , can be formulated as the following equation based on the reference (Ogata et al., 2018):

$$R_j^{PS} = \frac{3\chi_j f_{r,j} V_{m,j} k_{+,j}}{RTb(1-R_c)} \left(\frac{\sigma_n}{R_c} - \sigma_c\right)$$
(10)

$$R_c = \frac{A_t^c}{A_t^l} \tag{11}$$

where R_c [-] is the contact area ratio of the fracture asperities, $V_{m,j}$ [m³/mol] is the molar volume of the solid of mineral *j*, σ_n [Pa] is the effective stress acting on the rock domain, equal to the confining pressure minus the pore water pressure, σ_c [Pa] is the critical stress, A_t^l [m²] is the total fracture cross-sectional area in the representative element, and A_t^c [m²] is the contact area within the fracture of the representative element.

The dissolution rate constants of the minerals, that are important parameters for computing the geochemical reactions, are expressed by the Arrhenius-type equation depending on the temperature and the fluid pH conditions, given as (Palandri and Kharaka, 2004).

$$k_{+,j} = k_{1,j} a_{H^+}{}^{n_{1,j}} + k_{2,j} + k_{3,j} a_{H^+}{}^{n_{3,j}}$$
(12)

$$k_{i,j} = k_{i,j}^{298.15K} \exp\left[\frac{-E_{i,j}}{R} \left(\frac{1}{T} - \frac{1}{298.15K}\right)\right]$$
(13)

where $k_{i,j}^{298.15K}$ (i = 1, 2, 3) [mol m⁻² s⁻¹] is the rate constant of mineral j at 298.15 K (25 °C) under acid, neutral, and base mechanisms, respectively, $E_{i, j}$ (i = 1, 2, 3) [J mol ⁻¹] is the activation energy of mineral j under acid, neutral, and base mechanisms, respectively, a_{H+} is the activity of H⁺, and n_1 and n_3 are the dimensionless catalysis constants for the acid and base mechanisms, respectively. The most important improvement done in this study to our previous model (Ogata et al., 2018) is incorporating Eq. (12) for describing the pH dependence on the rates of the geochemical reactions and the changes in the chemically induced permeability.

In the current work, the changes in fracture aperture with time are induced only by the geochemical reactions of the free-face dissolution and the secondary mineral precipitation and the pressure dissolution. Among the considered reactions, both precipitation on the fractures and pressure dissolution cause a decrease in the fracture aperture, while free-face dissolution brings about an increase in the fracture aperture. Thus, the fracture aperture at an arbitrary time t, b(t), is defined as.

$$b(t) = b_0 + \int_0^t \dot{b}^{FF} dt + \int_0^t \dot{b}^{PS} dt$$
(14)

where b_0 [m] is the initial fracture aperture, \dot{b}^{FF} [m s⁻¹] is the rate of change in the fracture aperture by the free-face dissolution/precipitation, and \dot{b}^{PS} [m s⁻¹] is the rate of change in the fracture aperture by the pressure dissolution. \dot{b}^{FF} and \dot{b}^{PS} are expressed by the following equations. \dot{b}^{FF} can be formulated with reference to the literature (Lasaga, 1984; Ogata et al., 2018). On the other hand, \dot{b}^{PS} can be defined based on the reference (Yasuhara et al., 2004).

$$\dot{b}^{FF} = \frac{\sum_{j}^{n} \dot{M}_{j}^{FF} \cdot V_{m,j}}{A_{i}^{l}} \\
= \frac{\sum_{j}^{n} 2\chi_{j} f_{r,j} k_{+,j} (1-R_{c}) (1-SI_{j}) A_{i}^{l} \cdot V_{m,j}}{A_{i}^{l}} \\
= \sum_{j}^{n} 2\chi_{j} f_{r,j} V_{m,j} k_{+,j} (1-R_{c}) (1-SI_{j})$$
(15)

$$\dot{b}^{PS} = \sum_{j}^{n} \dot{c}_{j}^{PS} \cdot b$$

$$= \sum_{j}^{n} \frac{-3\chi_{j}f_{r,j}k_{+,j}V_{m,j}^{2}}{RTb} \left(\frac{\sigma_{n}}{R_{c}} - \sigma_{c}\right) \cdot b$$

$$= \sum_{j}^{n} \frac{-3\chi_{j}f_{r,j}k_{+,j}V_{m,j}^{2}}{RT} \left(\frac{\sigma_{n}}{R_{c}} - \sigma_{c}\right)$$
(16)

where \dot{M}_{j}^{FF} [mol s⁻¹] is the flux of mineral *j*, supplied by the free-face dissolution/precipitation at the fracture wall per time in the representative element, and $\dot{\varepsilon}_{j}^{FS}$ [s⁻¹] is the strain rate due to the pressure dissolution at the contacting asperities within the fracture. Within the fracture, the contact area ratio should also change in conjunction with the changes in fracture aperture. The relationship linking the fracture aperture and the contact area ratio of the fracture asperities may be represented by the following function (Yasuhara et al., 2011):

$$b = b_r + (b_0 - b_r) \exp\left[-\frac{(R_c - R_{c0})}{a}\right]$$
(17)

where b_r [m] is the residual fracture aperture, b_0 [m] is the initial fracture aperture, R_{c0} is the initial contact area ratio of the fracture asperities, and a [-] is a constant. The hydraulic aperture of a rock fracture is derived by utilizing the mechanical aperture and the contact area ratio of the fracture asperities (Walsh, 1981).

$$b_h{}^3 = \frac{(1 - R_c)}{(1 + R_c)} b^3 \tag{18}$$

2.2. Numerical implementation

The computational procedure for the presented model is depicted in Fig. 2. In this work, the aforementioned governing equations are solved in space and time by using the numerical computing system that allows for the linking of COMSOL MULTIPHYSICS and PHREEOC (Ogata et al., 2020). The interface to link the two codes was constructed using MATLAB scripts. Previously, as programs to link COMSOL and PHREEO, MATLAB scriptsbased (e.g., Wissmeier and Barry, 2011) and Java scriptsbased (Nardi et al., 2014) interfaces were constructed. The interface used in this study is almost the same as theirs in terms of the fundamental scheme connecting COMSOL and PHREEQC. The difference is that ours has been extended to handle not only the basic dissolution/precipitation of minerals (i.e., free-face dissolution/precipitation), but also the mineral dissolution driven by the effective stress (i.e., pressure dissolution).

In the calculation procedure of this work, by utilizing a non-iterative sequential split operator approach (Azad et al., 2016), the transport process (Eq. (4)) is divided into two processes: (a) the solute transport process by advection and diffusion, and (b) the kinetic reaction process (i.e., the dissolution/precipitation process of the multiple minerals). The following is a description of the specific calculation steps of the model.

(a) After setting the initial and boundary conditions for the numerical analysis, the solute transport process (see



Fig. 2. Computational procedure of proposed model.

Eq. (19)) is calculated in COMSOL for time step Δt with the fluid flow process (see Eq. (1)).

$$\frac{\partial(c_q^k \varphi)}{\partial t} + \boldsymbol{u} \cdot \nabla c_q^k = \nabla \cdot (\tau \varphi \boldsymbol{D} \nabla c_q^k)$$
(19)

where c_q^k [mol m⁻³] is the concentration of solute q in the pore water derived from the solute transport step. Then, solute concentrations and the values of the selected variables required for the calculation of the geochemical reaction rates of the pressure dissolution and the free-face dissolution/precipitation (i.e., system temperature T, mechanical aperture of the fracture b^k , effective stress σ_n , and the contact area ratio of the fracture asperities R_c^k) at each finite element mesh node in the analysis domain are outputted to PHREEQC.

(b) After step (a), firstly, the detailed chemical composition of the pore water at the end of the solute transport process is determined using PHREEQC as the initial condition for computing the kinetic reaction for time step Δt . Then, the pressure dissolution rate, R_i^{PS} (Eq. (10)), and only the part of the formula of the free-face dissolution rate R_i^{FF} (Eq. (9)), excluding the part related to the saturation index (i.e., $\frac{2\chi_j f_{r_j} k_{+j}}{b}$), are calculated in MATLAB, and they are inputted to PHREEQC to compute the kinetic reaction. It is noted that the saturation index of each mineral, required to fully calculate R_i^{FF} , is obtained during the computing of the reaction in PHREEQC. Through the computation of the kinetic reaction in PHREEQC, the updated solute concentrations of pore water, induced by the pressure dissolution and the free-face dissolution/precipitation at each finite element mesh node in time step Δt , are determined as follows:

$$c_q^{k+1} = c_q^k + r_q \Delta t, \tag{20}$$

where c_q^{k+1} [mol m⁻³] is the concentration of solute q in the pore water that is updated by the kinetic reaction process.

(c) Afterward, the changes in the fracture aperture due to the pressure dissolution and free-face dissolution/precipitation $(\Delta b^{FF}, \Delta b^{PS})$ in time step Δt are calculated based on each reaction rate (R_j^{PS}, R_j^{FF}) obtained in step (b), and finally the updated properties of the fracture geometry (i.e., the mechanical aperture of the fracture, b^{k+1} , and the contact area ratio of the fracture asperities, R_c^{k+1}) and fracture permeability are also computed. The abovementioned processes after step (b) are calculated in MATLAB. Then, the solute concentrations, the properties of the fracture geometry, and the fracture permeability at each finite element mesh node, derived from steps (b) and (c), are set as the initial conditions of the following transport process in COMSOL. By continuously iterating steps (a)-(c), the reactive transport process can be solved.

3. Model verification

In order to verify the correctness of the implementation of the model by linking the two numerical tools (COMSOL

and PHREEQC), a numerical analysis was performed for a 1D reactive transport problem assuming the fully saturated isothermal condition that mimics a laboratory column experiment as a benchmark. This benchmark case was introduced by Nardi et al. (2014). The analysis domain with a length of 0.08 m, divided into 160 nodes, is fully water-saturated under the isothermal condition. In this problem, the infiltrating water is injected from an inlet and the concentration of dissolved species within the domain are changed by the reactions between the infiltrating water and the five minerals composing the domain (calcite, K-feldspar, albite, illite, and pyrite). The initial contents of these minerals within the domain are 6.065 mol/L (calcite), 0.239 mol/L (K-feldspar), 0.289 mol/L (albite), 0.144 mol/L (illite), and 1.17 mol/L (pyrite). The flow velocity $(2.78 \times 10^{-6} \text{ m/s})$ and the diffusion coefficient within the pore water $(5.56 \times 10^{-9} \text{ m}^2/\text{s})$ are given uniformly within the domain. Regarding the reaction forms, all the minerals follow kinetic dissolution, except for the calcite, and the calcite is in equilibrium with the initial water composition.

The initial and infiltrating water compositions are listed in Table 1. All the formulas and parameters for the kinetic dissolution utilized in this benchmark are set to be equal to those of the PHREEQC source code by Nardi et al. (2014). Changes in the pH, pe, and concentrations of Al and K at the outlet of the domain computed by the proposed model, together with the PHREEQC solution, are shown in Fig. 3 (a), (b), (c), and (d), respectively. When the target of an analysis is a 1D problem, assuming the isothermal condition and constant fluid velocity, such as the present case, PHREEQC by itself can accurately calculate the solute transport as well as geochemical reactions. Thus, if COM-SOL and PHREEQC are correctly linked, the computed results are consistent with the solutions obtained utilizing PHREEQC alone.

Table 1

Compositions of initial and infiltrating water for benchmark analysis of 1D reactive transport problem.

| Compositions of dissolved species and pH | Initial water | Infiltrating water | |
|--|-----------------------|-----------------------|--|
| Al [mol/L] | 5.11×10^{-9} | 1.00×10^{-8} | |
| Br [mol/L] | 1.75×10^{-5} | 0 | |
| C [mol/L] | 4.94×10^{-3} | 1.90×10^{-4} | |
| Ca [mol/L] | 1.40×10^{-3} | 3.04×10^{-4} | |
| Cl [mol/L] | 1.10×10^{-2} | 9.03×10^{-4} | |
| F [mol/L] | 3.16×10^{-5} | 1.60×10^{-5} | |
| Fe [mol/L] | 7.18×10^{-6} | 5.37×10^{-5} | |
| K [mol/L] | 2.50×10^{-4} | 7.16×10^{-4} | |
| Mn [mol/L] | 3.46×10^{-6} | 0 | |
| Mg [mol/L] | 7.40×10^{-4} | 1.99×10^{-4} | |
| Na [mol/L] | 1.31×10^{-2} | 3.04×10^{-4} | |
| P [mol/L] | 3.87×10^{-6} | 0 | |
| S [mol/L] | 9.59×10^{-4} | 4.80×10^{-4} | |
| Si [mol/L] | 1.99×10^{-4} | 2.50×10^{-6} | |
| Sr [mol/L] | 0 | 6.84×10^{-7} | |
| pH [-] | 7.52 | 7.30 | |



Fig. 3. Comparisons of results between proposed model and PHREEQC for changes in (a) pH, (b) pe, and concentrations of (c) Al and (d) K.

All of the results by the proposed model agree well with the solutions obtained using PHREEQC alone, and they indicate that the computational framework of the proposed model has been accurately implemented.

4. Model validation

4.1. Simulating experimental results

In order to validate the proposed model, the results of experiments with flow-through granite specimens (Kinoshita and Yasuhara, 2012) are replicated by applying the model. The cylindrical specimens used for the experiments include an artificial single fracture, as seen in Fig. 4. The specimens are made from granite sampled from depths of 330 m to 350 m in Mizunami City, Gifu Prefecture, Japan. Two experiments, namely, E-4 and E-7, are conducted using granite specimens (E-4: 29.8 mm in diameter \times 57.4 mm in length and E7: 29.7 mm in diameter \times 62.1 mm in length); the experimental conditions of each experiment are summarized in Table 2. Under the confining pressure of 5 MPa, temperatures of 25-90 °C, and differential water pressure of 0.1-0.13 MPa, E-4 is conducted using deionized water (pH \sim 6) as the permeant. Under the confining pressure of 5.0 MPa, temperatures of 25-90 °C, and differential water pressure of 0.015-0.05 MPa, E-7 is conducted using a NaOH aqueous solution (pH \sim 11) as the permeant. During the experimental period, equivalent hydraulic aperture $\langle b_h \rangle$ and equivalent permeability $\langle k \rangle$ are continuously obtained from the measured flow rate via parallel plate approximation, as follows:



Fig. 4. Schematics of flow-through experiment (left side) from Yasuhara et al. (2011) and granite specimen (right side).

Table 2 Experimental conditions.

| Specimen | E-4 | E-7 |
|--------------------------|------------|-------------|
| Confining pressure [MPa] | 5.0 | 5.0 |
| System temperature [°C] | 25-90 | 25-90 |
| pH of permeant | ~ 6.0 | ~ 11.0 |

$$\langle b_h \rangle = \left(\frac{12\mu l Q_f}{w\Delta p}\right) \tag{21}$$

$$\langle k \rangle = \frac{\langle b_h \rangle^2}{12} \tag{22}$$



Fig. 5. Analysis domain discretized by finite element and boundary conditions for simulations of E-4 and E-7.

Table 3

Parameters used in simulations.

| Parameter | Value |
|--|------------------------------------|
| Critical stress σ_c [MPa] | 100 (Yasuhara et al., |
| | 2011) |
| Residual aperture b_r [µm] | 0.40 (Yasuhara et al., |
| | 2011) |
| Initial contact area ratio R_{c0} [-] | 0.04 (Yasuhara et al., |
| | 2011) |
| Constant <i>a</i> [-] | 0.025 (Yasuhara et al., |
| | 2011) |
| Pre-exponential factor of diffusion of solute | 5.2×10^{-8} (Revil, 1999) |
| $[m^2/s] D_b^0$ | |
| Activation energy of diffusion of solute | 13.5 (Revil, 1999) |
| $[kJ/mol] E_D$ | |
| Longitudinal dispersion coefficient α_L | 0.001 (Renchao et al., |
| | 2018) |

where $Q_f [m^3 s^{-1}]$ represents the measured flow rates, Δp [Pa] is the differential water pressure, w [m] is the width of each specimen, and l [m] is the length of each specimen.

In addition, through the analysis of fluid samples taken from the flow outlet using inductively coupled plasma atomic emission spectrometry (ICP-AES), the concentrations of the effluent elements (Si, Al, K, Fe, Ca, Na, and Mg) are determined.

4.2. Setup of numerical simulations

In the current work, an attempt is made to reproduce the measured data on the evolution of the equivalent permeability of the granite fractures and the effluent element



Fig. 6. Comparisons of changes in fracture permeability with time between measurements and predictions for (a) E-4 and (b) E-7.

| rable 4 |
|---------|
|---------|

| Parameters of kinetic dissolution rate constants for minerals derived from Palandri and Kharaka | (2004 |). |
|---|-------|----|
|---|-------|----|

| Parameter | Quartz | K-feldspar | Anorthite | Albite | Biotite | | |
|-----------------------|--------|------------|-----------|--------|---------|------------------|--|
| | | | | | | Amorphous silica | |
| $\log k_1^{298.15K}$ | _ | -10.66 | -3.50 | -10.16 | -9.84 | _ | |
| $\log k_2^{298.15K}$ | -13.99 | -12.56 | -9.12 | -12.56 | -12.55 | -12.77 | |
| $\log k_3^{298.15K}$ | _ | -21.2 | _ | -15.6 | _ | - | |
| E_1 [kJ/mol] | _ | 51.7 | 16.6 | 65 | 22.0 | - | |
| E_2 [kJ/mol] | 87.6 | 38.0 | 17.8 | 69.8 | 22.0 | 68.7 | |
| E_3 [kJ/mol] | _ | 94.1 | 1.411 | 71.0 | _ | _ | |
| n_1 | _ | 0.50 | _ | 0.457 | 0.525 | _ | |
| <i>n</i> ₃ | _ | -0.823 | _ | -0.572 | _ | _ | |

concentrations (Si, Al, K, Fe, Ca, Na, and Mg) for E-4 and E-7 using the proposed model. As shown in Fig. 5, the fracture is expressed as a one-dimensional domain with a length corresponding to that of the specimens. As the mineral compositions of the analysis domains for E-4 and E-7, five minerals are considered after referring to the literature (Yasuhara et al., 2011), namely, quartz (50 vol%), Kfeldspar (25 vol%), albite (10 vol%), anorthite (10 vol%), and biotite (5.0 vol%). Amorphous silica is considered as a secondary mineral based on observations made in previous flow-through experiments performed under conditions similar to those of E4 (Yasuhara et al., 2011). For the solute transport process, eight elements are considered, namely, Si, Al, K, Fe, Ca, Na, Mg, and C. As some amount of CO₂ may generally be dissolved in the permeant, it should be considered in the setting of the water composition at the inlet boundary. For E-4, only the C concentration at the inlet boundary is set to have the non-zero value of 6.57×10^{-6} mol/L. The value of the inlet concentration of C is determined by a back analysis of the chemical composition using PHREEQC. For E-7, the inlet concentration of Na is set to be 1.0×10^{-3} mol/L corresponding to the inflow of the NaOH aqueous solution, while the other element concentrations are set in the same way as those in E-4. Differential pressures of 0.1–0.13 MPa and 0.015–0.05 MPa are given at the inlet and outlet boundaries of the domain for E-4 and E-7, respectively. The isothermal condition within the entire domains varies from



Fig. 7. Comparisons of element concentrations (E-4) between measurements and predictions: (a) Si, (b) Al, (c) K, (d) Fe, (e) Ca, (f) Na, and (g) Mg.

25 °C to 90 °C, according to the temperature history with time during the experiments. In the simulations for E-4 and E-7. the initial hydraulic aperture and the contact area ratio of the fracture asperities are assumed to be homogeneous within the entire domains. The values for the initial hydraulic aperture are determined from the experimental data for E-4 and E-7. As the initial contact area ratio, residual aperture, and constant a, represented in Eq. (17), were not obtained from the target experiments, they are set to have the values nearly equivalent to those defined by Yasuhara et al. (2011). The critical stress is assumed to be 100 MPa for both E-4 and E-7, which is nearly equivalent to their uniaxial compressive strength. The utilized parameters, mentioned above, are listed in Table 3. These parameter values were determined by referring to the literature (Revil, 1999; Yasuhara et al., 2011; Renchao et al., 2018). Furthermore, the kinetic dissolution rate constants (see Eqs. (12) and (13)), for the minerals considered in the calculations derived from Palandri and Kharaka (2004), are summarized in Table 4. Based on previous experimental works, the roughness factor of the quartz, K-feldspar, albite, and anorthite is given as 7.12 (Yasuhara et al., 2011), while that of the biotite is given as 512 (Kalinowski and Schweda, 1996).

4.3. Comparisons with experimental results

Comparisons of the changes in fracture permeability over time between the measurements and the predictions for (a) E-4 and (b) E-7 are shown in Fig. 6(a) and (b), respectively. From the figures, it can be confirmed that the predictions follow the trends of the actual permeability reduction well for both E-4 and E-7. The comparisons of the measured permeability between E-4 and E-7 imply that the degree of the drop in permeability, enhanced by the increasing temperature of E-7, is more significant than that of E-4. This phenomenon is properly reproduced by the model. In both experiments, the predicted results tend to be slightly different from the actual permeability data after the changes in temperature. After the increase in temperature from 25 °C to 90 °C in the cases of E-4 and E-7, the measured permeability is slightly overestimated by the prediction. On the other hand, after the decrease in temperature from 90 °C to 25 °C in the case of E-7, the measured permeability is slightly underestimated. The above-mentioned gaps after the increase and decrease in temperature may be related to the thermal expansion and shrinkage (release of expansion), respectively, because these effects of thermal-induced deformations of the rock fracture are not considered in the proposed model.

Predictions of the concentration histories for the seven elements (Si, Al, K, Fe, Ca, Na, and Mg), together with the corresponding measured data for E-4, are shown in Fig. 7. The figure shows that the predicted concentrations for five of the elements (Si, Al, Fe, Ca, and Mg), excluding K and Na, are similar to the actual data, except when the temperature changes. In particular, the predicted Al and Ca concentrations coincide well with the actual histories. Moreover, in terms of the increase in effluent concentration during the temperature fluctuation, the predictions underestimate the measured results for most elements (Si, Al, Fe, Ca, and Mg). This difference is probably related to the underestimation of the drop in permeability by the predictions. As drops in permeability should cause an increase in travel time of the fluid and a decrease in pore volume within the fracture, they may result in an increase in effluent concentration.

The predicted K and Na concentrations are apparently underestimated throughout the experimental period. These mismatches for the K and Na concentrations are unexplainable at this stage. The relationships for all the element concentrations, between the measurements obtained from E-4 and the predictions, are depicted in Fig. 8. This figure indicates that the predicted concentrations for four of the elements (Al, Fe, Ca, and Mg) can reproduce most of the corresponding measured data within a discrepancy of roughly-one order.

The predicted evolutions in concentration for all seven elements (Si, Al, K, Fe, Ca, Na, and Mg), together with the corresponding experimental data for E-7, are shown in Fig. 9. From this figure, it can be confirmed that predicted concentrations for five of the elements (Si, Fe, Ca, Na, and Mg), excluding Al and K, are close to the measurements. Among the above-mentioned five elements, the predicted concentrations for Fe, Ca, and Na show good agreements with the actual data. In terms of the Na concentration, throughout the experimental periods, the measured value is almost equivalent to the concentration contained in the inflow solution (NaOH aqueous solution).



Fig. 8. Comparisons of element concentrations between measurements and predictions for E-4.



Fig. 9. Comparisons of element concentrations (E-7) between measurements and predictions: (a) Si, (b) Al, (c) K, (d) Fe, (e) Ca, (f) Na, and (g) Mg.

The overestimation of the Al concentration may be attributed to an unaccounted contribution of the mineral precipitations related to element Al at the free-walls within the fractures. In the case of E-7, as a high concentration of the Na is maintained, due to the continuous inflow of the NaOH aqueous solution, the albite containing element Na may reach the supersaturated state and the precipitation of albite may occur continuously, which should be further examined. Comparisons of the element concentrations, between the measurements obtained from E-7 and the predictions, are shown in Fig. 10. As is apparent from the figure, the predicted concentrations for all the elements (Si, Fe, Ca, and Mg), except for Al and K, match the actual data within about one order of difference.

All the results of the comparisons between the predictions and the measurements for E-4 and E-7 imply that the proposed model in this study will be a useful tool that enables the prediction of the evolution of the fracture permeability of rock and the reactive transport behavior within rock fractures due to the mineral reactions depend-



Fig. 10. Comparisons of element concentrations between measurements and predictions for E-7.

ing on the fluid pH under coupled THMC conditions. At this stage, however, some unpredictable phenomena still remain, such as the changes in the K and Na concentrations for the E4 experiment and the change in the Al concentration for the E-7 experiment. Therefore, further detailed investigations are needed to more fully address the reactive transport process with the kinetic reactions of multi-minerals.

5. Conclusion

The current study has presented a reactive transport model by considering the reactions of multi-minerals (pressure dissolution, fee-face dissolution, and secondary mineral precipitation), depending on the temperature, stress, and fluid pH conditions as well as the changes in permeability of the rock fractures induced by those reactions. Then, to validate the presented model, it was applied to replicate the changes in permeability and effluent element concentrations obtained from two flow-through experiments in single granite fractures performed with permeants of different pH levels, including the alkaline state (pH ~ 11) under stressed and temperature-elevated conditions. The computed alterations in fracture permeability accurately tracked the actual histories of the permeability reductions measured from both experiments and appropriately reflected the observed differences in the reduction rates depending on the pH levels of the permeant. As for the effluent element concentrations, the computed results matched the measured data relatively well.

Considering the results of all the comparisons done in this work between the experimental data and the predictions, the validity of the presented model for predicting the changes in permeability and reactive transport process within rock fractures induced by the geochemical reactions, depending on the temperature, stress, and fluid chemistry conditions (e.g., fluid pH and solute concentrations), has been confirmed. Moreover, the validation provides confidence for the use of the proposed model for advancing the understanding of the flow and transport behavior within fractured rocks under convolved conditions in geological repositories of HLW where the formation of alkaline environments can be expected.

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