

**Coupled thermo-hydro-mechanical-chemical modeling of permeability change in porous  
rocks: The significant role of the pressure solution**

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## Abstract

When considering the safe isolation of high-level radioactive wastes, the long-term evolution of the hydraulic and transport behavior of the rocks of interest should be predicted prior to its operation because coupled thermal-hydraulic-mechanical-chemical (THMC) processes should be significantly active in such situations where relatively high ground pressure and temperature are induced. In this study, a coupled THMC numerical model has been developed to examine the long-term change in permeability of the porous sedimentary rocks that are assumed to be composed purely of quartz. Specifically, the chemo-mechanical process of the pressure solution was incorporated into the model. The developed model was validated by replicating the existing experimental measurements of the porosity reduction and the evolving silica concentration. Subsequently, by simulating the burial of high-level radioactive wastes in the deep subsurface, namely, by applying the simulated confining pressure and temperature conditions, the long-term evolution of the rock permeability was predicted. The model predictions clearly showed a significant influence of the pressure dissolution on the change in permeability with time. The predicted permeability of the rocks close to the wastes decreased by one order of magnitude in  $10^4$  years when considering the pressure dissolution, while the permeability changed little during the same period when the pressure dissolution was not considered. This reduction should delay the dispersion of the radioactive materials dissolved in the groundwater.

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30 **Keywords: Rock permeability, Coupled THMC model, Mineral dissolution, Pressure**  
31 **solution**

32

33 **Highlights:**

34 ➤ **A coupled THMC numerical model was developed to predict the long-term change in**  
35 **permeability.**

36 ➤ **The developed model considers the pressure solution.**

37 ➤ **The model was validated by replicating the existing experiments.**

38 ➤ **The model enables the long-term evolution of rock permeability to be predicted under**  
39 **arbitrary pressure and temperature conditions.**

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## 42 **1. Introduction**

43 When disposing high-level radioactive wastes in the deep subsurface, the influence of the  
44 disposal on the hydraulic property of the rocks of interest must be examined in advance and  
45 should be estimated with a certain level of precision. The rocks that work as natural barriers to the

46 migration of radionuclides should be influenced by the convolved phenomena, including the  
47 transfer of heat from the wastes, the groundwater flow, the variation in induced stresses, and the  
48 geochemical reactions, such as mineral dissolution and precipitation [1], [2]. Therefore, in order  
49 to predict the long-term evolution of the hydraulic property, a numerical model that can account  
50 for the coupled Thermo-Hydro-Mechanical-Chemical (THMC) processes is required. In particular,  
51 the precise modeling of the geochemical reactions, occurring at the interface between the grain  
52 particles composing the rocks and the pore water, is of significant importance to achieving precise  
53 predictions. To date, THMC numerical models have been developed to address such engineering  
54 issues as the geological isolation of CO<sub>2</sub> and radioactive wastes and energy recovery from  
55 geothermal reservoirs [3]-[9]. By using some of the above models, the long-term phenomena  
56 taking place in the artificial and natural barriers have been predicted by considering the specific  
57 geological conditions, the heat transfer, the water flow, the stress/deformation, and the  
58 geochemical reactions. In the geochemical calculations of the THMC models, the mineral  
59 dissolution and precipitation occurring on the free surfaces of the rocks [10] are typically  
60 considered, but the dissolution active at the grain contacts (e.g., pressure dissolution [11]-[18]) is  
61 not taken into account. In the literature, it is indicated that the pressure dissolution may change the  
62 hydraulic property over a long duration; and therefore, the phenomenon must be incorporated into  
63 the modeling process when evaluating the long-term integrity of the rocks in terms of the

hydraulic property. Recently, several THMC numerical models that can consider the process of the pressure dissolution have been proposed [7]-[9], but these models mostly address fracture media and do not estimate the evolution of the hydraulic property in porous rocks.

In this study, a new coupled THMC numerical model that incorporates the important process of the pressure dissolution, as well as the free-face dissolution and precipitation, was developed, and the validity of the model was examined by replicating the experimental measurements obtained from Elias and Hajash (1992) [19]. Subsequently, the long-term evolution of the permeability in porous rock was predicted under the expected stress and temperature conditions where high-level radioactive wastes are disposed. In particular, the influence of the pressure dissolution on the change in the rock permeability was examined intensively.

When any numerical model is developed, it may be dilemmatic to consider the balance between the simplicity and the precision of the model. Complex models that incorporate a number of equations to be solved may require time-consuming handling during pre- and post-processing, and lengthy calculation time. Therefore, simpler or more straightforward numerical models with satisfactory precision are preferred for general users. By focusing selectively on the geochemical process of the pressure dissolution, the minor objective of this study is to develop a relatively simple model.

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## 83    **2. Model description**

84       The coupled THMC model developed in this work enables the change in permeability of  
85   porous rocks to be followed with time by considering the interactions of the thermal, hydraulic,  
86   mechanical, and geochemical processes (i.e., heat transfer, groundwater flow in saturated porous  
87   media, stress/deformation, mass transport, and mineral dissolution/precipitation). The processes  
88   considered in this model are schematically summarized in **Figure 1**. As is apparent from this  
89   figure, the two-way interactions are taken into account between the T and H, the H and C, and the  
90   C and T components. In the M component, the stress distribution is calculated and then rendered  
91   to calculate a chemo-mechanical process, which is referred to as CM in **Figure 1**. In the C  
92   components, two different chemical processes are incorporated into the model; one is the  
93   free-surface dissolution/precipitation (CF) and the other is the pressure solution (CM). The  
94   pressure solution includes three serial processes - mineral dissolution at the stressed contacts,  
95   diffusive transport through the thin film of water, and re-precipitation of the mineral matter at the  
96   pore wall. The mineral dissolution at the stressed contacts is explicitly integrated into the  
97   proposed model as the CM component. It should be noted that we have proposed conceptual  
98   chemo-mechanical models to predict the change in permeability of porous and fractured rocks  
99   [20]-[24], and that this work is an attempt to fit the conceptual model into the coupled numerical

model and to conduct numerical simulations at a field scale instead of a representative element scale. It should be also noted that the interactions between the H and M and the M and T components are intentionally omitted in this work. These processes may influence the change in permeability, but the main focus of the current work is to examine the effects of the geochemical reactions (i.e., free-face dissolution/precipitation and pressure dissolution) on the change in permeability by simplifying the developed model.

## 2.1 Governing equations

The equations used to model each of the THMC processes are presented in this section. In this work, COMSOL Multiphysics [25] is utilized to solve the differential equations describing the THMC processes. The calculation procedure is shown in **Figure 2** and the details are described hereinafter. The coupled THMC processes are solved sequentially by exchanging the dependent variables (i.e., porosity/permeability, flow velocity, stress, temperature, and dissolution/precipitation rate constants).

The groundwater flow in saturated rocks is simply modeled by the conservation of water mass and by assuming the Darcian flow, given by

$$\frac{\partial(\rho_w \phi)}{\partial t} + \nabla \cdot (\rho_w \mathbf{u}) = f_m, \quad (1)$$

$$\mathbf{u} = -\frac{\mathbf{k}}{\mu}(\nabla p + \rho_w g \nabla D), \quad (2)$$

where  $\rho_w$  [kg m<sup>-3</sup>] is the density of the fluid,  $\phi$  [-] is the porosity,  $\mathbf{u}$  [m s<sup>-1</sup>] is the fluid velocity tensor,  $f_m$  [kg m<sup>-3</sup> s<sup>-1</sup>] is the source term for the flow,  $\mathbf{k}$  [m<sup>2</sup>] is the rock permeability tensor,  $\mu$  [Pa s] is the fluid dynamic viscosity,  $p$  [Pa] is the fluid pressure,  $g$  [m s<sup>-2</sup>] is the gravity acceleration, and  $D$  [m] is the potential head. The temperature-dependent variables of  $\rho_w$  and  $\mu$  are evaluated at arbitrary temperatures within the calculation scheme [25].

The heat transfer is evaluated by considering thermal convection and conduction without the radiation effect, as follows:

$$(\rho C_p)_{eq} \frac{\partial T}{\partial t} + \rho_w C_{p,w} \mathbf{u} \cdot \nabla T = \nabla \cdot (\mathbf{k}_{eq} \nabla T) + Q_h, \quad (3)$$

where  $T$  [K] is the temperature,  $(\rho C_p)_{eq}$  [J K<sup>-1</sup> m<sup>-3</sup>] is the equilibrium volumetric heat capacity,  $C_{p,w}$  [J kg<sup>-1</sup> K<sup>-1</sup>] is the heat capacity of the fluid,  $\mathbf{k}_{eq}$  [W m<sup>-1</sup> K<sup>-1</sup>] is the equilibrium thermal conductivity tensor, and  $Q_h$  [W m<sup>-3</sup>] is the heat source.  $(\rho C_p)_{eq}$  and  $\mathbf{k}_{eq}$  can be obtained from the following equations:

$$(\rho C_p)_{eq} = (1 - \phi) \rho_m C_{p,m} + \phi \rho_w C_{p,w}, \quad (4)$$

$$\mathbf{k}_{eq} = (1 - \phi) \mathbf{k}_m + \phi \mathbf{k}_w, \quad (5)$$

where  $\rho_m$  [kg m<sup>-3</sup>] is the density of the solid,  $C_{p,m}$  [J kg<sup>-1</sup> K<sup>-1</sup>] is the heat capacity of the solid, and  $\mathbf{k}_m$  and  $\mathbf{k}_w$  [W m<sup>-1</sup> K<sup>-1</sup>] are the thermal conductivity tensors of the solid and the fluid, respectively.

134 The numerical model enables the temperature-dependent variables of  $C_{p,m}$ ,  $C_{p,w}$ ,  $k_m$ , and  $k_w$  to be  
 135 followed at arbitrary temperatures [25].

136 The mechanical process of the rock structure is evaluated by the quasi-static equilibrium  
 137 equation and the typical Hooke's law, given by

$$138 \quad -\nabla \cdot \boldsymbol{\sigma} = \mathbf{F}_v, \quad (6)$$

$$139 \quad \boldsymbol{\sigma} = \mathbf{E} : \boldsymbol{\varepsilon}, \quad (7)$$

140 where  $\boldsymbol{\sigma}$  [Pa] is the stress tensor,  $\mathbf{F}_v$  [Pa m<sup>-1</sup>] is the body force,  $\mathbf{E}$  [Pa] is the elasticity tensor, and  $\boldsymbol{\varepsilon}$   
 141 [-] is the strain tensor. In this work, the thermal stress and the inelastic behavior are disregarded  
 142 for simplicity. A self-weight analysis is conducted to obtain the initial stress field, while the  
 143 change in stress distribution by the cavity excavation is calculated using these equations.

144 The advection-diffusion equation is used to calculate the solute transport behavior. The  
 145 mechanical dispersion and the retardation due to the sorption processes are not considered here.

$$146 \quad \frac{\partial(c_i \phi)}{\partial t} + \mathbf{u} \cdot \nabla c_i = \nabla \cdot (\phi \tau \mathbf{D}_{b,i} \nabla c_i) + R_i, \quad (8)$$

147 where  $c_i$  [mol m<sup>-3</sup>] is the concentration of solute  $i$ ,  $\tau$  [-] is the coefficient related to tortuosity,  $\mathbf{D}_{b,i}$   
 148 [m<sup>2</sup> s<sup>-1</sup>] is the diffusion coefficient tensor, and  $R_i$  [mol m<sup>-3</sup> s<sup>-1</sup>] is the solute source or sink of solute  
 149  $i$ . The diffusion coefficient is controlled by the system temperature and can be defined by an  
 150 Arrhenius-type equation [26], as

151 
$$D_{b,i} = D_{b,i}^0 \exp(-E_{D,i} / RT), \quad (9)$$

152 where  $D_{b,i}^0$  [ $\text{m}^2 \text{s}^{-1}$ ] and  $E_{D,i}$  [ $\text{J mol}^{-1}$ ] are the pre-exponential factor and the activation energy of  
 153 the diffusion of solute  $i$ , respectively, and  $R$  [ $\text{J mol}^{-1} \text{K}^{-1}$ ] is the gas constant.

154 The source/sink term,  $R_i$ , is calculated by considering both free-face dissolution/precipitation  
 155 and pressure dissolution, and can be expressed by

156 
$$R_i = R_i^{FF} + R_{diss,i}^{PS}, \quad (10)$$

157 where  $R_i^{FF}$  and  $R_{diss,i}^{PS}$  [ $\text{mol m}^{-3} \text{s}^{-1}$ ] are the rates of free-face dissolution/precipitation and  
 158 pressure dissolution, respectively. They are the physical quantities that describe the mineral  
 159 dissolution and precipitation per volume and time. The rate of the free-face  
 160 dissolution/precipitation is defined by [10]

161 
$$R_i^{FF} = k_+ A (a_{H^+})^n (1 - Q / K), \quad (11)$$

162 where  $k_+$  [ $\text{mol m}^{-2} \text{s}^{-1}$ ] is the mineral dissolution rate constant,  $A$  [ $\text{m}^2 \text{m}^{-3}$ ] is the specific surface  
 163 area,  $a_{H^+}$  [-] is the activity of  $H^+$ , and  $n$  [-] is the constant, which may be obtained from  
 164 experimental observations in the literature.  $Q$  [-] is the ionic activity product and  $K$  [-] is the  
 165 equilibrium constant. When  $Q/K < 1$ , free-face dissolution occurs; when  $Q/K > 1$ , free-face  
 166 precipitation occurs. The specific surface area is obtained by the measurement using the BET  
 167 method, given as follows:

$$A = A_{BET} \rho_m, \quad (12)$$

where  $A_{BET}$  [ $\text{m}^2 \text{ kg}^{-1}$ ] is the specific surface area determined by the BET method.

In this work, the rock is assumed to be composed purely of quartz, and subscript  $i$  in Eqs. (8) - (10) is omitted hereinafter. The equilibrium and the dissolution rate constants in Eq. (11) are obtained from PHREEQC [27] and Rimstidt and Barnes (1980) [28], respectively. These constants are temperature-dependent and are given via polynomial approximation and by an Arrhenious expression, as follows:

$$K = \sum_{m=0}^7 \alpha_m T^m, \quad (13)$$

$$k_+ = k_+^0 \exp(-E_{k_+} / RT), \quad (14)$$

where  $\alpha_m$  ( $m=0-7$ ) [-] is the constant,  $k_+^0$  [ $\text{mol m}^{-2} \text{ s}^{-1}$ ] is the pre-exponential factor, and  $E_{k_+}$  [ $\text{J mol}^{-1}$ ] is the activation energy of the mineral dissolution.

Incorporating the process of pressure dissolution into the developed model is the most important task in this work. As described above, we have developed conceptual models that describe the process [20]-[24]. The flux that represents the pressure dissolution is driven by the gradient in the chemical potential between the highly-stressed contacts and the less-stressed site of the pore walls [13], [26]. Dissolution is most conveniently defined in terms of a dissolution mass flux,  $\dot{M}_{diss}^{PS}$ , the rate of addition of dissolved mass into solution at the interface, given as [20]

$$\dot{M}_{diss}^{PS} = \frac{3V_m^2(\sigma_a - \sigma_c)k_+ \rho_g A_c}{RT}, \quad (15)$$

where  $V_m$  is the molar volume of the solid ( $2.27 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$  for quartz),  $\sigma_a$  [Pa] is the disjoining pressure [29] equal to the amount by which the pressure acting at the contacts exceeds the hydrostatic pore pressure,  $\rho_g$  is the grain density ( $2650 \text{ kg m}^{-3}$  for quartz),  $A_c$  [ $\text{m}^2$ ] is the area of the grain contact, and  $\sigma_c$  [Pa] is the critical stress, which defines the stress state where the compaction of the grain aggregate will effectively halt [20]. This stress is determined by considering the energy balance under applied stress and temperature conditions, given by [26], [30]

$$\sigma_c = \frac{E_m(1 - T/T_m)}{4V_m}, \quad (16)$$

where  $E_m$  and  $T_m$  are the heat and temperature of fusion, respectively ( $E_m = 8.57 \text{ kJ mol}^{-1}$ ,  $T_m = 1883 \text{ K}$  for quartz).

Based on Eq. (15), the rate of the pressure dissolution,  $R_{diss}^{PS}$ , is derived through the following procedure. Firstly, the strain rate due to the pressure dissolution is given as [20]

$$\dot{\epsilon}_{diss}^{PS} = \frac{\dot{M}_{diss}^{PS}}{d \rho_g A_c} = \frac{3V_m^2 k_+}{RTd} \left( \frac{\sigma_{eff}}{R_c} - \sigma_c \right), \quad (17)$$

$$\sigma_a = \frac{\sigma_{eff}}{R_c}, \quad (18)$$

where  $\dot{\epsilon}_{diss}^{PS}$  [-] is the strain state,  $d$  [m] is the grain diameter,  $\sigma_{eff}$  [Pa] is the effective stress exerted in the representative element, and  $R_c$  ( $0 < R_c < 1$ ) [-] is the contact-area ratio. In this work,

the FE analyses are conducted with 2-D meshes in the following sections. To this end, the effective stress is replaced with the von Mises stress that can boil any complex stress conditions down to a single representative scalar value. Therefore, Eq. (17) may be expressed as

$$\dot{\epsilon}_{diss}^{PS} \approx \frac{3V_m^2 k_+}{RTd} \left( \frac{\sigma_{VM}}{R_c} - \sigma_c \right), \quad (19)$$

$$\sigma_{VM} = \sqrt{\frac{3}{2} \boldsymbol{\sigma} : \boldsymbol{\sigma}}, \quad (20)$$

where  $\sigma_{VM}$  [Pa] is the von Mises stress. When the system is assumed to be simple cubic packing with uniformly sized contacting spheres (**Figure 3**), the volumetric rate induced by the pressure dissolution can be defined by

$$\dot{V}_{diss}^{PS} = \frac{\Delta d \cdot d^2}{\Delta t} = \dot{\epsilon}_{diss}^{PS} d^3 = \frac{3V_m^2 k_+ d^2}{RT} \left( \frac{\sigma_{VM}}{R_c} - \sigma_c \right), \quad (21)$$

where  $\dot{V}_{diss}^{PS}$  [ $\text{m}^3 \text{s}^{-1}$ ] is the volumetric rate of the pressure dissolution. The dissolution rate, with respect to the representative element, can be simply evaluated by dividing the volumetric rate by the molar volume, as

$$\frac{\dot{V}_{diss}^{PS}}{V_m} = \frac{3V_m k_+ d^2}{RT} \left( \frac{\sigma_{VM}}{R_c} - \sigma_c \right). \quad (22)$$

The volume of the representative element (**Figure 3**) is  $d^3$  [ $\text{m}^3$ ], and the number of grains per unit volume should be  $d^{-3}$  [ $\text{m}^{-3}$ ]. Finally, the rate of pressure dissolution is defined by multiplying Eq. (22) by  $d^{-3}$ , as follows:

$$R_{diss}^{PS} = \frac{3V_m k_+}{RTd} \left( \frac{\sigma_{VM}}{R_c} - \sigma_c \right). \quad (23)$$

As the pressure dissolution proceeds, contact-area ratio  $R_c$  increases and corresponding porosity  $\phi$  decreases. Therefore, the relation between  $R_c$  and  $\phi$  should be obtained to solve Eq. (23) with time.

By considering the geometrical scheme (see **Figure 3** and more details in Appendix A), it is given by

$$R_c = \frac{12}{\pi} (1 - \phi) - 2. \quad (24)$$

Consequently, the rate of pressure dissolution is rearranged by substituting Eq. (24) into Eq. (23), as follows:

$$R_{diss}^{PS} = \frac{3V_m k_+}{RTd} \left( \frac{\sigma_{VM}}{(12/\pi)(1 - \phi) - 2} - \sigma_c \right). \quad (25)$$

## 2.2 Modification of porosity and related permeability

In this work, the change in porosity is only induced by the free-face dissolution/precipitation and the pressure dissolution. The porosity rates evaluated by the two geochemical processes are defined by

$$\dot{\phi}^{FF} = V_m R^{FF}, \quad (26)$$

$$\dot{\phi}_{diss}^{PS} = -V_m R_{diss}^{PS}, \quad (27)$$

where  $\dot{\phi}^{FF}$  and  $\dot{\phi}_{diss}^{PS}$  [ $s^{-1}$ ] are the porosity rates of the free-face dissolution/precipitation and the

pressure dissolution, respectively. Therefore, the porosity at an arbitrary time is evaluated using

Eqs. (26) and (27), given by

$$\phi = \phi_i + \int \dot{\phi}^{FF} dt + \int \dot{\phi}_{diss}^{PS} dt, \quad (28)$$

where  $\phi_i$  [-] is the initial porosity. Once the porosity is calculated, the related permeability is also

evaluated by the Kozeny-Carman equation [31], as

$$k = k_i \frac{(1-\phi_i)^2}{(1-\phi)^2} \left( \frac{\phi}{\phi_i} \right)^3, \quad (29)$$

where  $k$  and  $k_i$  [m<sup>2</sup>] are the permeability at an arbitrary time and the initial permeability,

respectively.

### 3. Model verification

In the previous section, we proposed a coupled THMC model to describe the evolution of

porosity/permeability in porous media. In order to verify the proposed model, the model

predictions are compared with the laboratory experiments performed by Elias and Hajash (1992)

[19]. The compaction of quartz sand, with a mean grain diameter of 180-250  $\mu\text{m}$ , has been

completed under the constant effective stresses of 69.0, 34.5, and 17.2 MPa at 150°C. The

changes in porosity and the silica concentrations in the pore fluid were measured over time to

examine the chemical and physical processes associated with the pressure solution [19]. In this work, both the rates of porosity reduction and the evolving concentrations of silica in the pore fluid were predicted. The parameters utilized in the calculations are summarized in **Table 1**.

In the predictions, the domain whose porosity initially starts with 0.35, equivalent to that of the experiments [19], was set to be a square with side lengths of 0.01 m. The uniaxial confining pressures of 69.0, 34.5, and 17.2 MPa and the temperature of 150°C were applied as the boundary conditions and as the initial condition, respectively. The silica concentration within the domain was initially fixed at the equilibrium concentration of quartz at 150°C, which was obtained by Eq. (13), and was followed over time by considering the free-face dissolution/precipitation and/or the pressure dissolution of quartz. All the boundaries were assumed to be thermally and hydraulically the outflow boundaries. The initial contact-area ratio,  $R_{c0}$ , was evaluated by assuming the Herzian contacts, given by

$$R_{c0} = \left( \frac{3\sigma_{eff} \pi (1-\nu)^2}{4E} \right)^{2/3}, \quad (30)$$

where  $\sigma_{eff}$  [Pa] is the effective stress (i.e., 69.0, 34.5, or 17.2 MPa),  $\nu$  [-] is Poisson's ratio, and  $E$  [Pa] is Young's modulus. When the pressure dissolution proceeds, the contact-area ratio increases.

The change is obtained using Eqs. (24), (26), and (27), as

$$\begin{aligned}
R_c &= R_{c0} + \int \dot{R}_c dt \\
&= R_{c0} - \frac{12}{\pi} \int \dot{\phi} dt \\
&= R_{c0} - \frac{12}{\pi} \int (\dot{\phi}^{FF} + \dot{\phi}^{PS}) dt \\
&= R_{c0} - \frac{12}{\pi} (\int V_m \cdot R^{FF} dt - \int V_m \cdot R_{diss}^{PS} dt)
\end{aligned} \tag{31}$$

After every time step, the new  $R_c$  was updated and used for calculating the rate of the pressure dissolution,  $R_{diss}^{PS}$ , in the following time step (see **Figure 2**). Note that in these verification predictions,  $R_{diss}^{PS}$  was evaluated over time with Eq. (23) instead of Eq. (25) because  $R_c$  can be evaluated directly with Eq. (31). It should also be noted that the specific surface area in Eq. (11) cannot be obtained from the literature [19]. Therefore, by introducing roughness factor  $f_r$  [32], which is the ratio of the true (microscopic) surface area over the apparent (geometric) surface area, the model predictions were conducted. The relation between specific surface area  $A$  and roughness factor  $f_r$  is defined as follows:

$$A = f_r A_{geo}, \tag{32}$$

where  $A_{geo}$  [ $\text{m}^2 \text{m}^{-3}$ ] is the apparent specific surface area, which is simply given by the ratio of the surface area of the spherical grain of diameter  $d$  over the volume, as

$$A_{geo} = \frac{\pi d^2}{\frac{\pi d^3}{6}} = \frac{6}{d}. \tag{33}$$

In the model predictions, three kinds of roughness factors, namely, 10, 20, and 80, were utilized. The values are congruent with the magnitude indicated by Anbeek [1992] [33], who concluded

that it ranged from 2.5 to 11 for freshly created surfaces, and Sverdrup [1990] [34], who reported that it varied between 1.5 and 71 for 28 silicate minerals.

Predictions of the porosity reduction rates and the silica concentration rates normalized by the initial values are shown in **Figure 4** and **Figure 5**, respectively, together with the data measured in the experiments. Surprisingly, all the predicted porosity reduction rates with time closely match the experimental measurements (**Figure 4**). Note that changing the roughness factor has little effect on the evolution of the porosity; and thus, the predictions with different roughness factors are not shown in **Figure 4**. In contrast, the predicted silica concentrations are clearly dependent on which roughness factors are applied (**Figure 5**). The utilization of higher roughness factors results in the prediction of lower silica concentrations. The system in the pore fluid is always oversaturated with silica because that is initially equivalent to the equilibrium concentration, and the additional solute is supplied from the grain contacts via the pressure dissolution. Therefore, the rates of precipitation are augmented by the higher roughness factors, resulting in the lower silica concentrations. The predictions show some variations because of the different roughness factors, but they follow the tendency observed in the experiments well (i.e., the abrupt increase after applying the pressures and the gradual decrease with time). Overall, a comparison of the results of the porosity reduction and the evolving silica concentrations between the predictions and the experimental measurements gives us confidence to use the developed

model to examine the long-term evolution of the porosity/permeability in porous media due to the free-face dissolution/precipitation and the pressure dissolution, dependent on the applied pressure, temperature, and flow conditions.

#### **4. Long-term predictions of permeability**

The developed model was applied to predict the long-term evolution of the permeability in sedimentary rock near radioactive wastes within a simulated repository. It should be noted that although we used actual data from related literature in the following predictions, we do not anticipate any specific sites for high-level radioactive waste repositories.

##### ***4.1 Modelling conditions***

The calculation domain, of the rock density of  $1700 \text{ kg/m}^3$ , was set to be a rectangle with vertical and horizontal lengths of 700 and 12.2 m, respectively. The canisters of radioactive wastes were virtually installed as a heat source by setting them laterally at a depth of 450 m [35]. The horizontal length of 12.2 m was chosen for the domain because it may be one-half of the center-to-center spacing of each cavity, of the diameter 2.22 m [35] (**Figure 6**). The rock for the calculations was assumed to have been fully-saturated with water and to have been composed

purely of quartz, with the initial porosity of 0.40 [36]. The hydraulic and thermal gradients were set to be 1/1000 and 5°C/100 m, respectively [37]. The surface temperature was fixed at 15°C. The initial silica concentrations within the domain were assumed to be the equilibrium values, which were evaluated by Eq. (13). The change in pH was not considered and the initial value was set at pH = 7.

In this work, the Excavation Distributed Zone (EDZ) was modeled explicitly with respect to the rock permeability. The scientific and technical report, summarizing the HLW disposal construction in Japan [38], indicates that the EDZ in both sedimentary and crystalline rocks may range, in the radial direction, from the periphery of the excavated cavity to roughly 1 m. Therefore, the range of 0.8 m was modeled as the EDZ in our calculations (**Figure 6**). The permeability in the EDZ was increased by two orders of magnitude greater than the sound rock [35], [39]. Note that the thermal and the mechanical properties in the EDZ were assumed to be equivalent to those of sound rock, because those in the EDZ were ill-defined, and examining the changes in permeability due to geochemical processes is the most significant task in this work. In the actual calculations, the changes in the von Mises stresses, due to the excavation, were predicted by conducting a self-weight analysis (**Figure 7**). The evolved von Mises stresses, greater around the periphery of the cavity, as is apparent in **Figure 7**, are the driving-force for the pressure dissolution (see Eq. (25)). The heat source from the radioactive wastes was modeled by applying

the temperatures at the periphery of the cavity as the boundary conditions. The applied temperatures over time were obtained from the literature [38], as shown in **Figure 8**. The prediction period was set at  $10^4$  years after the excavation. All the boundaries, excluding the periphery of the cavity, were assumed to be thermally and hydraulically the outflow boundaries. The parameters utilized in the calculations are summarized in **Table 2**.

#### 4.2 Prediction results

In this work, the predictions were conducted for two different cases – one was done by considering the full processes illustrated in **Figure 2**, and the other was done by excluding only the pressure dissolution, in order to examine the effect of the pressure dissolution on the change in permeability with time. The former and the latter cases are called the “PS” and the “no-PS” conditions hereinafter. Calculations for the no-PS condition were performed by merely making  $R_{diss}^{PS}$  in Eq. (25) zero at all the calculation steps.

The change in the temperature distribution with time, predicted under the PS condition, is shown in **Figure 9**. The temperature in the EDZ increases with time; it increases to more than 80°C between  $10^1$  and  $10^2$  years. Subsequently, it decreases with time and reaches a steady temperature (i.e., ~45°C) after  $10^4$  years. This tendency is quite similar to the change in Si concentration with time (**Figure 10**), which is reasonable. As the equilibrium concentration of Si

is only controlled by the induced temperature, the changes over time should be similar. It should be noted that the predicted changes in both temperature and the Si concentration with time, under the no-PS condition, show no great difference from those under the PS condition. This is because the concentrations in the whole system approach the equilibrium values in a relatively short period, through free-face precipitation, when additional solute is supplied in the pore fluid due to the pressure dissolution, and through free-face dissolution, when the system temperature and the related equilibrium concentration increase. Consequently, the Si concentrations are equivalent to the equilibrium values throughout most of the calculation period.

The changes in permeability with time under the no-PS and the PS conditions are compared (**Figure 11** and **Figure 12**). Note that the permeability is normalized by the initial value. As is apparent from the figures, it changes little with time under the no-PS condition, while it decreases with time and the reduction appears after  $10^2$  years under the PS condition. Specifically, the reduction is significant within the EDZ. This is because the pressure dissolution, resulting in porosity reduction, is enhanced by the increase in the von Mises stress due to the cavity excavation (see **Figure 7**), and an additional reduction in porosity is caused by the free-face precipitation induced by the supply of the dissolved silica through the pressure dissolution. In order to further investigate the influence of the pressure dissolution on the permeability change within the EDZ, the changes with time at four specific locations, shown in **Figure 13**, are depicted

in **Figure 14**. Three of the four points are located within the EDZ, and the fourth one is 5 m away from the periphery of the cavity. No change in permeability is observed under the no-PS condition. In reality, the free-face precipitation of the secondary minerals, induced by the dissolution of the cement materials, may cause changes in the porosity/permeability, but it is not the case in this work. On the other hand, the permeability at No. 1 decreases by one order of magnitude in  $10^4$  years. However, the reduction is locally limited and is not observed at No. 4, which is located at one-fourth of the center-to-center spacing of each cavity (**Figure 14**). In the current predications, the decrease in permeability was observed only under the PS condition. This should result in the delay of the transportation of radioactive materials, and the influence needs to be examined quantitatively.

As a parametric study, predictions are made by varying the parameters of initial porosity  $\phi_i$  and critical stress  $\sigma_c$ , that should control the rate of the pressure dissolution (see Eq. (25)) to examine the influence on the change in permeability. Two different initial porosities, 0.40 and 0.45, are selected to simulate Horonobe mudstone in Japan [36], and three levels of critical stress, 15, 50, and 80 MPa, are set for the analysis. The change in permeability at observation point No. 1, shown in **Figure 13**, is shown in **Figure 15**. It is obvious that when a higher critical stress is applied, less change in permeability is observed. This is because the effect of the pressure dissolution becomes smaller when the difference between the von Mises stress and the critical

stress is smaller, as is clear from Eq. (25). In particular, at 80 MPa, the permeability hardly changes in the case of  $\phi_i = 0.40$ , and it decreases roughly 30 % for  $10^4$  years in the case of 0.45. From the above calculations, we have confirmed that choosing the right values for the critical stress is of great importance to achieving precise predictions.

## 5. Conclusions

A coupled THMC model was developed to investigate the long-term evolution of the permeability in sedimentary rocks. The model solves the heat transfer, the groundwater flow, the variation in induced stresses, and the geochemical reactions (i.e., the free-face dissolution/precipitation and the pressure dissolution), and their interactions. The changes in porosity and silica concentration in the quartz aggregates were examined to test the adequacy of the developed model in representing the experimentally observed behavior [19]. The predictions showed an excellent agreement with the experimental observations. Subsequently, the verified model was applied to examine the influence of the pressure dissolution on the evolution of the permeability in sedimentary rocks where a radioactive waste repository may be constructed, in considering the expected temperature, flow, and stress conditions. The predictions confirmed that the process of the pressure dissolution decreased the permeability especially close to the

excavated cavity by one order of magnitude smaller than the initial value, which should delay the transportation of the radioactive materials.

The developed model is straightforward and relatively simple because some interactions among the THMC processes are omitted, but it enables the long-term evolution of the permeability under arbitrary stress and temperature conditions to be followed over time with some precision. Generally, when considering coupling processes for solving complicated nonlinear problems, the uncertainty should be significant. Therefore, it is always important to ponder whether complex, fully-coupled models are necessary for achieving sufficiently high precision. In the near future, we will update the current model by taking into account the omitted processes among the THMC interactions (e.g., the hydraulic-mechanical interactions; see **Figure 1**), and examine whether or not the updates are indeed meaningful to the problems of interest.

## **Acknowledgments**

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in this work are available upon request from the authors.

## APPENDIX A: Relation between contact-area ratio and porosity

Solid volume  $V_s$ , in the representative elementary volume, is obtained by subtracting the sums of the volumes truncated between the contacts of two hemispheres from the volume of a sphere of diameter  $d$ , given by

$$V_s = \frac{1}{6} \pi h (3a^2 + \frac{3d^2}{4} + h^2), \quad (\text{A1})$$

where  $h$  is one-half of the domain height and  $a$  is the radius of the contact area. One-half of the domain height,  $h$ , is given by

$$h = \sqrt{\frac{d^2}{4} - a^2}. \quad (\text{A2})$$

The porosity,  $\phi$ , is obtained by subtracting the solid volume,  $V_s$ , divided by the total volume of the domain,  $V_t$ , from one, as follows:

$$\phi = 1 - \frac{V_s}{V_t} = 1 - \frac{\frac{1}{6} \pi \sqrt{\frac{d^2}{4} - a^2} (2a^2 + d^2)}{d^2 \sqrt{\frac{d^2}{4} - a^2}} = 1 - \frac{\pi (2a^2 + d^2)}{6d^2}. \quad (\text{A3})$$

The radius of the contact area is expressed by

$$a^2 = \frac{d^2}{4} R_c. \quad (\text{A4})$$

By substituting Eq. (A3) into Eq. (A2), porosity  $\phi$  is rearranged as

$$\phi = 1 - \frac{\pi \left( \frac{d^2}{2} R_c + d^2 \right)}{6d^2} = 1 - \left\{ \frac{\pi}{12} (R_c + 2) \right\}. \quad (\text{A5})$$

$$\Rightarrow R_c = \frac{12}{\pi} (1 - \phi) - 2. \quad (\text{A6})$$

447

448

449 **Nomenclature**

|     |                    |                                                                                    |
|-----|--------------------|------------------------------------------------------------------------------------|
| 450 | $A$                | specific surface area [ $\text{m}^2 \text{m}^{-3}$ ]                               |
| 451 | $A_{BET}$          | specific surface area determined by the BET method [ $\text{m}^2 \text{kg}^{-1}$ ] |
| 452 | $A_c$              | area of the grain contact [ $\text{m}^2$ ]                                         |
| 453 | $A_{geo}$          | apparent specific surface area [ $\text{m}^2 \text{m}^{-3}$ ]                      |
| 454 | $a_{H^+}$          | activity of $H^+$ [-]                                                              |
| 455 | $C_i$              | concentration of the solute $i$ [ $\text{mol m}^{-3}$ ]                            |
| 456 | $C_{p,m}$          | heat capacity of the solid [ $\text{J kg}^{-1} \text{K}^{-1}$ ]                    |
| 457 | $C_{p,w}$          | heat capacity of the fluid [ $\text{J kg}^{-1} \text{K}^{-1}$ ]                    |
| 458 | $D$                | potential head of the fluid [m]                                                    |
| 459 | $\mathbf{D}_{b,i}$ | diffusion coefficient tensor [ $\text{m}^2 \text{s}^{-1}$ ]                        |
| 460 | $d$                | grain diameter [m]                                                                 |
| 461 | $\mathbf{E}$       | elasticity tensor [Pa]                                                             |
| 462 | $E_{D,i}$          | activation energy of the diffusion of the solute $i$ [ $\text{J mol}^{-1}$ ]       |
| 463 | $E_{k^+}$          | activation energy of the mineral dissolution [ $\text{J mol}^{-1}$ ]               |
| 464 | $E_m$              | heat of fusion [ $\text{kJ mol}^{-1}$ ]                                            |
| 465 | $\mathbf{F}_v$     | body force [ $\text{Pa m}^{-1}$ ]                                                  |
| 466 | $f_m$              | source term for flow [ $\text{kg m}^{-3} \text{s}^{-1}$ ]                          |
| 467 | $f_r$              | roughness factor [-]                                                               |
| 468 | $g$                | gravity acceleration [ $\text{m s}^{-2}$ ]                                         |
| 469 | $K$                | equilibrium constant [-]                                                           |
| 470 | $\mathbf{k}$       | rock permeability tensor [ $\text{m}^2$ ]                                          |
| 471 | $\mathbf{k}_{eq}$  | equilibrium thermal conductivity tensor [ $\text{W m}^{-1} \text{K}^{-1}$ ]        |

|     |                                              |                                                                                                     |
|-----|----------------------------------------------|-----------------------------------------------------------------------------------------------------|
| 472 | $\mathbf{k}_m$                               | thermal conductivity tensor of the solid [ $\text{W m}^{-1} \text{K}^{-1}$ ]                        |
| 473 | $\mathbf{k}_w$                               | thermal conductivity tensor of the fluid [ $\text{W m}^{-1} \text{K}^{-1}$ ]                        |
| 474 | $k_+$                                        | dissolution rate constant [ $\text{mol m}^{-2} \text{s}^{-1}$ ]                                     |
| 475 | $\dot{M}_{diss}^{PS}$                        | rate of addition of dissolved mass into solution at the interface [ $\text{kg s}^{-1}$ ]            |
| 476 | $p$                                          | fluid pressure [Pa]                                                                                 |
| 477 | $Q$                                          | ionic activity product [-]                                                                          |
| 478 | $Q_h$                                        | heat source [ $\text{W m}^{-3}$ ]                                                                   |
| 479 | $R$                                          | gas constant [ $\text{J mol}^{-1} \text{K}^{-1}$ ]                                                  |
| 480 | $R_c$                                        | contact-area ratio [-]                                                                              |
| 481 | $R_i^{FF}$                                   | rate of free-face dissolution/precipitation of the solute $i$ [ $\text{mol m}^{-3} \text{s}^{-1}$ ] |
| 482 | $R_{diss,i}^{PS}$                            | rate of pressure dissolution of the solute $i$ [ $\text{mol m}^{-3} \text{s}^{-1}$ ]                |
| 483 | $R_i$                                        | solute source or sink of the solute $i$ [ $\text{mol m}^{-3} \text{s}^{-1}$ ]                       |
| 484 | $T$                                          | system temperature [K]                                                                              |
| 485 | $T_m$                                        | temperature of fusion [K]                                                                           |
| 486 | $\mathbf{u}$                                 | fluid velocity tensor [ $\text{m s}^{-1}$ ]                                                         |
| 487 | $\dot{V}_{diss}^{PS}$                        | volumetric rate of the pressure dissolution [ $\text{m}^3 \text{s}^{-1}$ ]                          |
| 488 | $V_m$                                        | molar volume [ $\text{m}^3 \text{mol}^{-1}$ ]                                                       |
| 489 | $V_s$                                        | solid volume [ $\text{m}^3$ ]                                                                       |
| 490 |                                              |                                                                                                     |
| 491 | <u>Greek letters</u>                         |                                                                                                     |
| 492 | $\boldsymbol{\varepsilon}$                   | strain tensor [-]                                                                                   |
| 493 | $\dot{\boldsymbol{\varepsilon}}_{diss}^{PS}$ | strain rate due to the pressure dissolution [ $\text{s}^{-1}$ ]                                     |

|     |                          |                                                                             |
|-----|--------------------------|-----------------------------------------------------------------------------|
| 494 | $\phi$                   | porosity [-]                                                                |
| 495 | $\dot{\phi}^{FF}$        | porosity rate of the free-face dissolution/precipitation [s <sup>-1</sup> ] |
| 496 | $\dot{\phi}_{diss}^{PS}$ | porosity rate of the pressure dissolution [s <sup>-1</sup> ]                |
| 497 | $\mu$                    | dynamic viscosity of the fluid [Pa s]                                       |
| 498 | $\nu$                    | Poisson's ratio [-]                                                         |
| 499 | $\rho_g$                 | grain density [kg m <sup>-3</sup> ]                                         |
| 500 | $\rho_m$                 | density of the solid [kg m <sup>-3</sup> ]                                  |
| 501 | $\rho_w$                 | density of the fluid [kg m <sup>-3</sup> ]                                  |
| 502 | $(\rho C_p)_{eq}$        | equilibrium volumetric heat capacity [J K <sup>-1</sup> m <sup>-3</sup> ]   |
| 503 | $\sigma$                 | stress tensor [Pa]                                                          |
| 504 | $\sigma_a$               | stress acting at the contact area [Pa]                                      |
| 505 | $\sigma_c$               | critical stress [Pa]                                                        |
| 506 | $\sigma_{eff}$           | effective stress [Pa]                                                       |
| 507 | $\sigma_{VM}$            | von Mises stress [Pa]                                                       |
| 508 | $\tau$                   | tortuosity [-]                                                              |
| 509 |                          |                                                                             |

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613 Table 2. Calculation parameters to simulate long-term permeability.

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Table 1. Calculation parameters to simulate experimental results.

| Diameter<br>$d$ [ $\mu\text{m}$ ]                               | Temperature<br>$T$ [ $^{\circ}\text{C}$ ]                                  | Effective stress<br>$\sigma_{\text{eff}}$ [MPa] | Critical stress<br>$\sigma_c$ [MPa] | Equilibrium constant<br>$K$ [ $\text{mol m}^{-3}$ ] |
|-----------------------------------------------------------------|----------------------------------------------------------------------------|-------------------------------------------------|-------------------------------------|-----------------------------------------------------|
| 215                                                             | 150                                                                        | 69.0, 34.5, 17.2                                | 73.2                                | 1.79                                                |
| Diffusion<br>coefficient<br>$D_b$ [ $\text{m}^2\text{s}^{-1}$ ] | Dissolution rate<br>constant<br>$k_+$ [ $\text{mol m}^{-2}\text{s}^{-1}$ ] | Young's modulus<br>$E$ [GPa]                    | Poisson's ratio<br>$\nu$ [-]        |                                                     |
| $1.12 \times 10^{-9}$                                           | $2.51 \times 10^{-9}$                                                      | 72.4                                            | 0.17                                |                                                     |

Table 2. Calculation parameters to simulate long-term permeability.

| Rock<br>type | Initial<br>permeability<br>$k_i$ [ $\text{m}^2$ ] | Young's<br>modulus<br>$E$ [GPa] | Poisson's<br>ratio<br>$\nu$ [-] | Initial<br>porosity<br>$\phi_i$ [-] | Thermal<br>conductivity<br>$k_{eq}$ [ $\text{W m}^{-1}\text{K}^{-1}$ ] | Heat capacity<br>$C_p$ [ $\text{J kg}^{-1}\text{K}^{-1}$ ] |
|--------------|---------------------------------------------------|---------------------------------|---------------------------------|-------------------------------------|------------------------------------------------------------------------|------------------------------------------------------------|
| EDZ          | $1.0 \times 10^{-13}$                             | 2.5                             | 0.30                            | 0.40                                | 1.60                                                                   | 1500                                                       |
| Sound        | $1.0 \times 10^{-15}$                             | 2.5                             | 0.30                            | 0.40                                | 1.60                                                                   | 1500                                                       |

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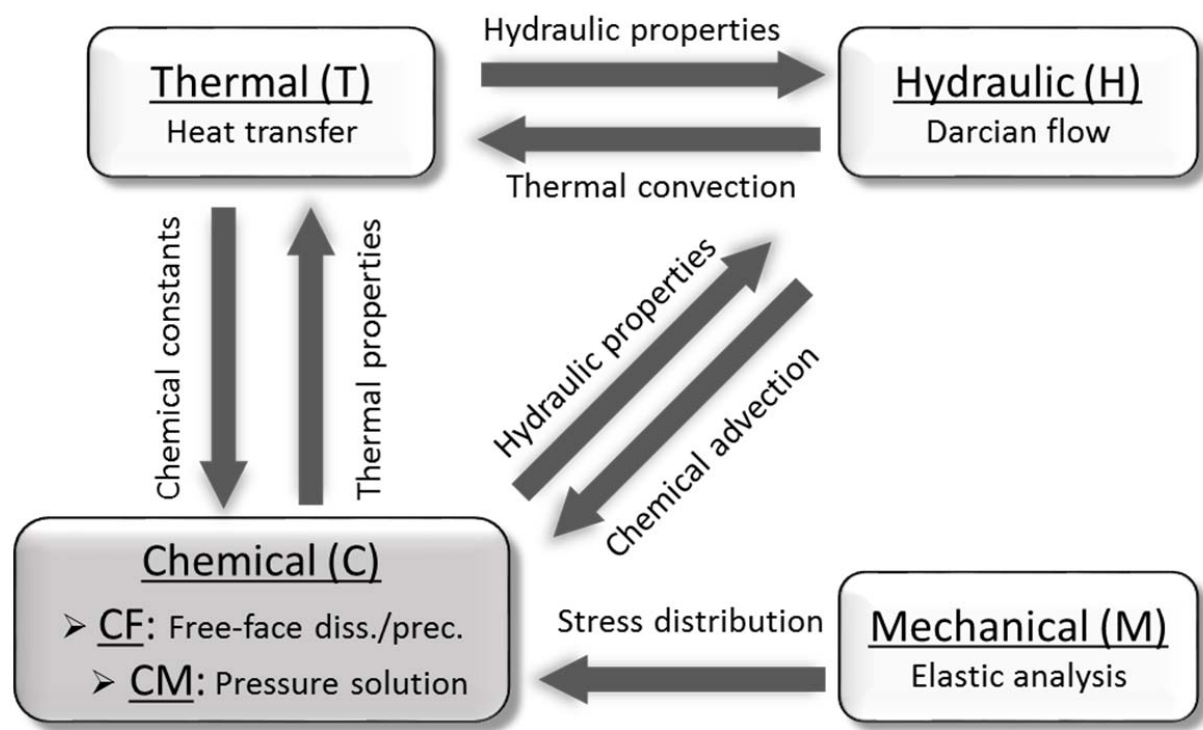
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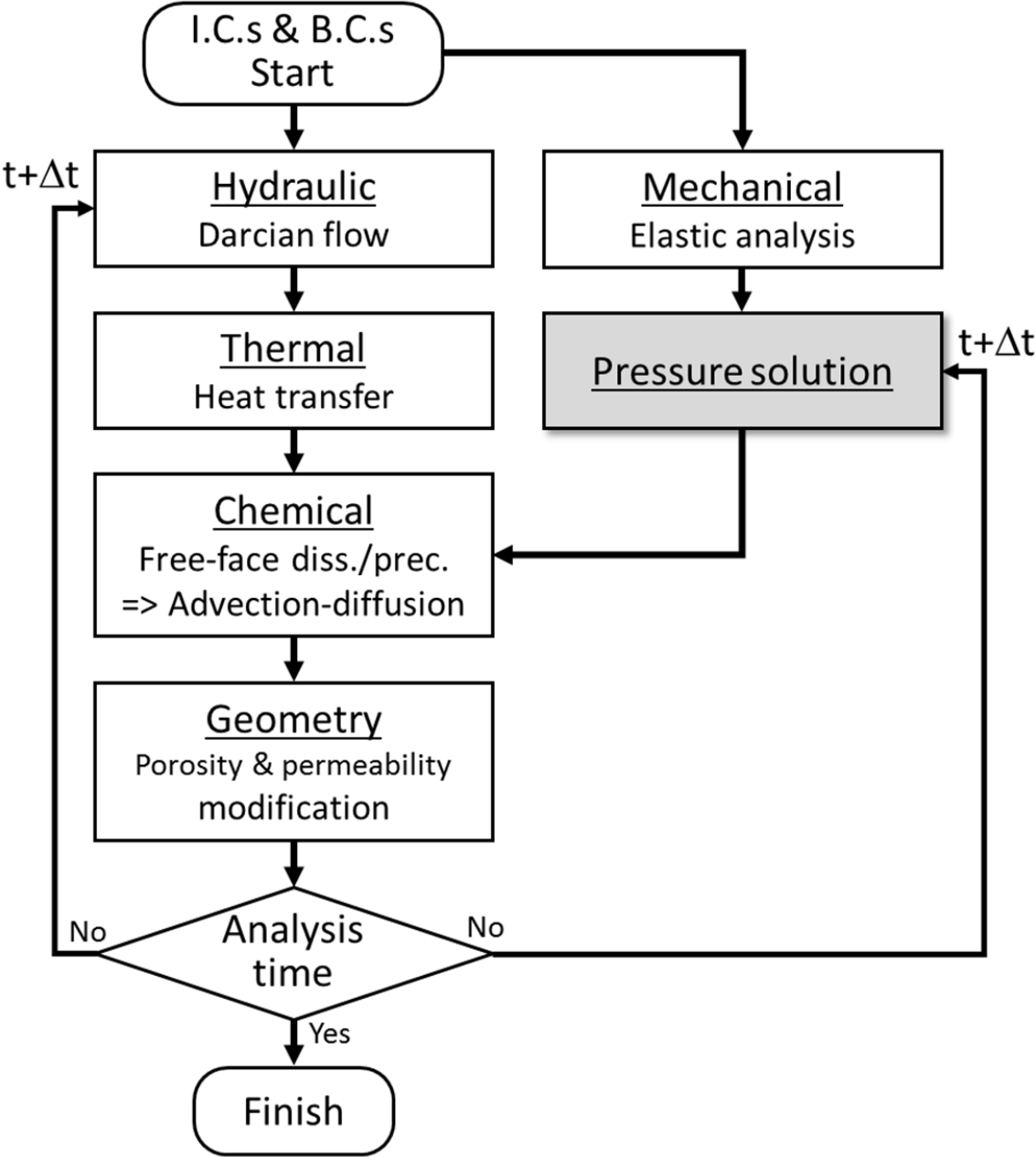


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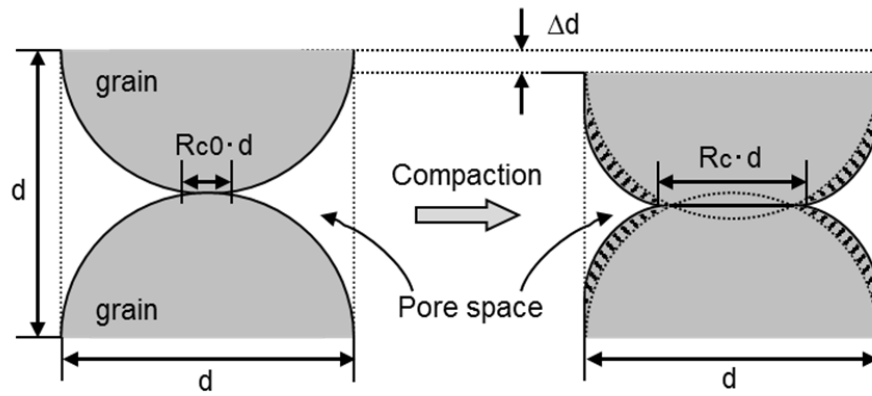
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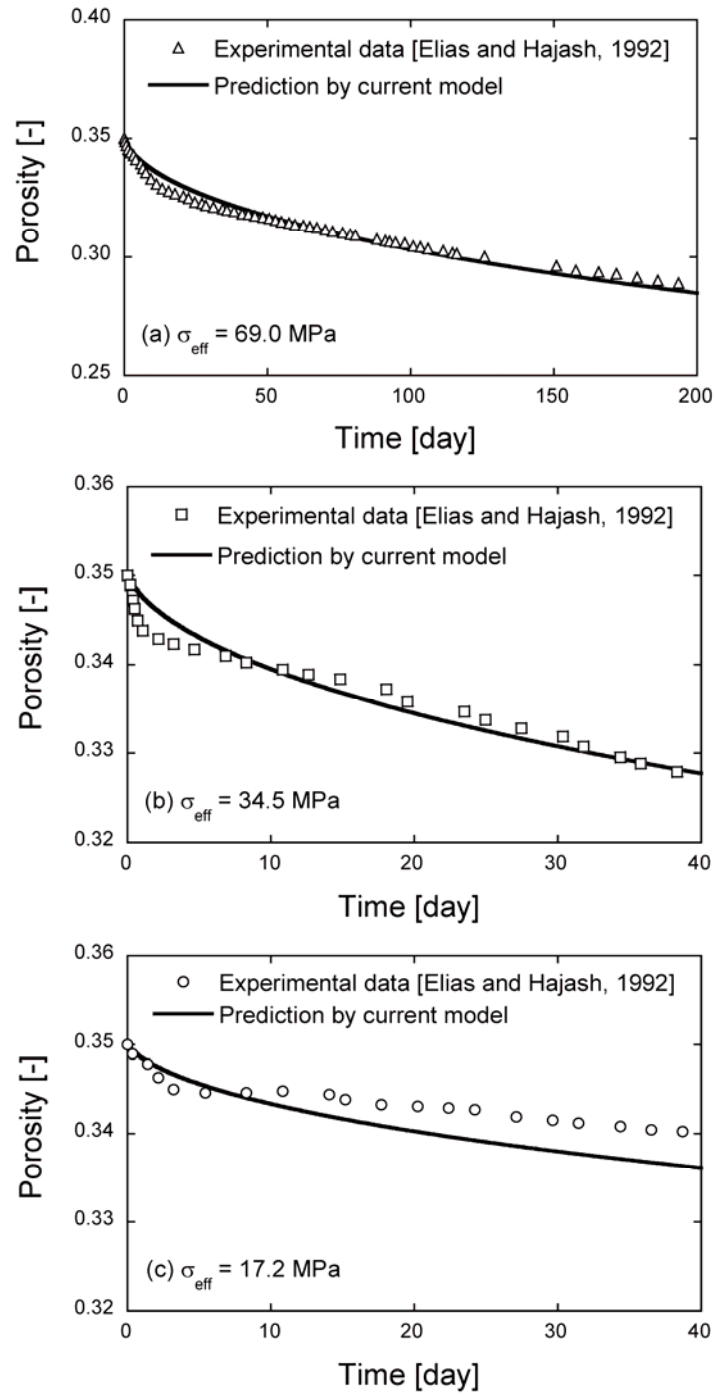


Figure 4. Comparison of porosity reduction with time between experimental data [19] and predictions of the model.

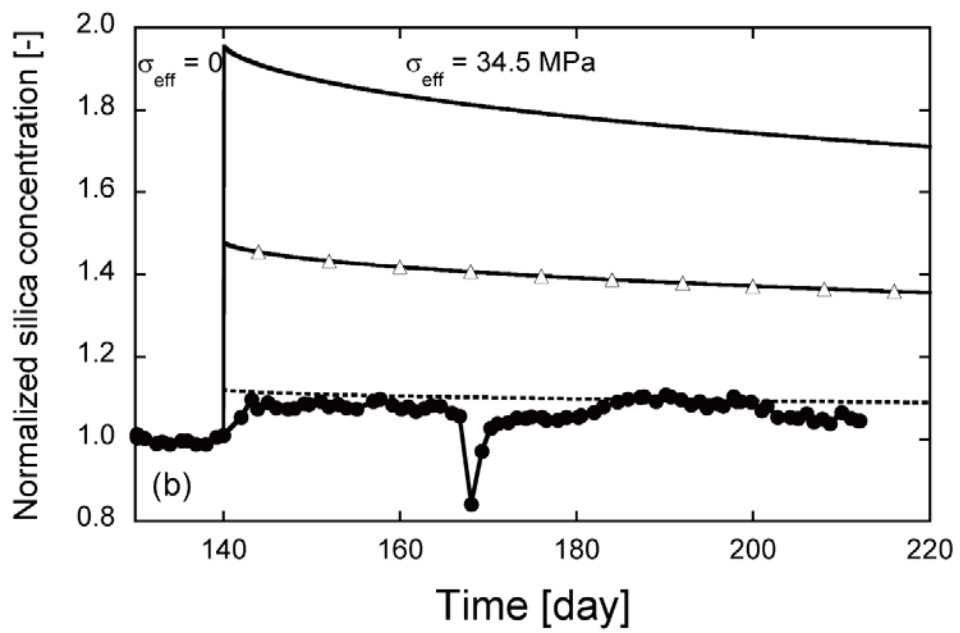
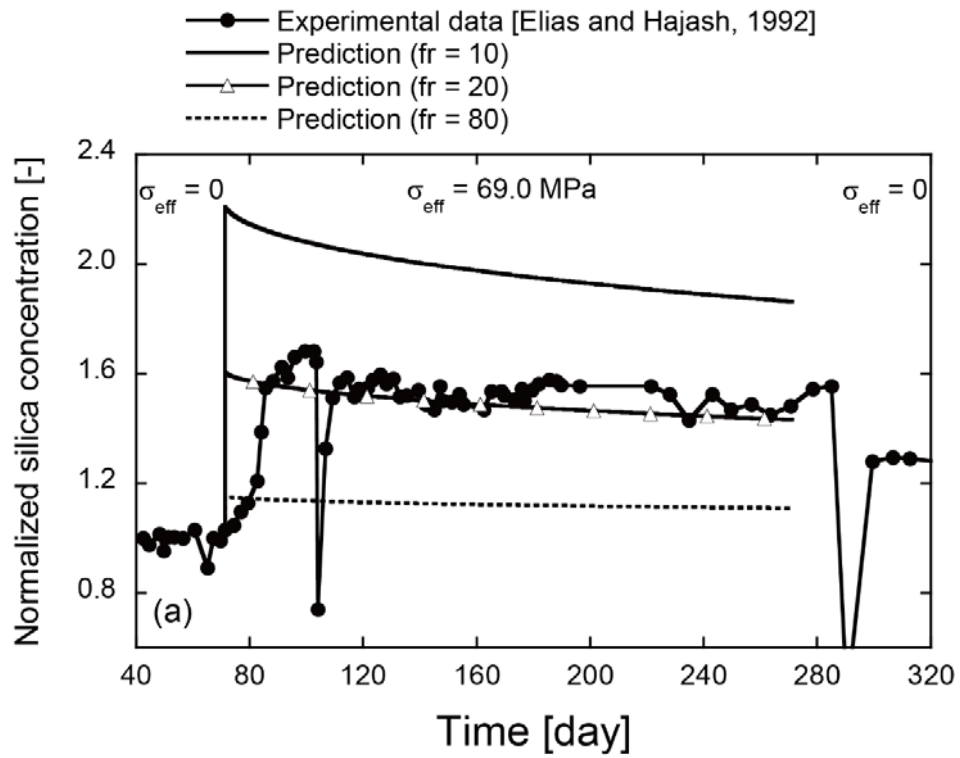
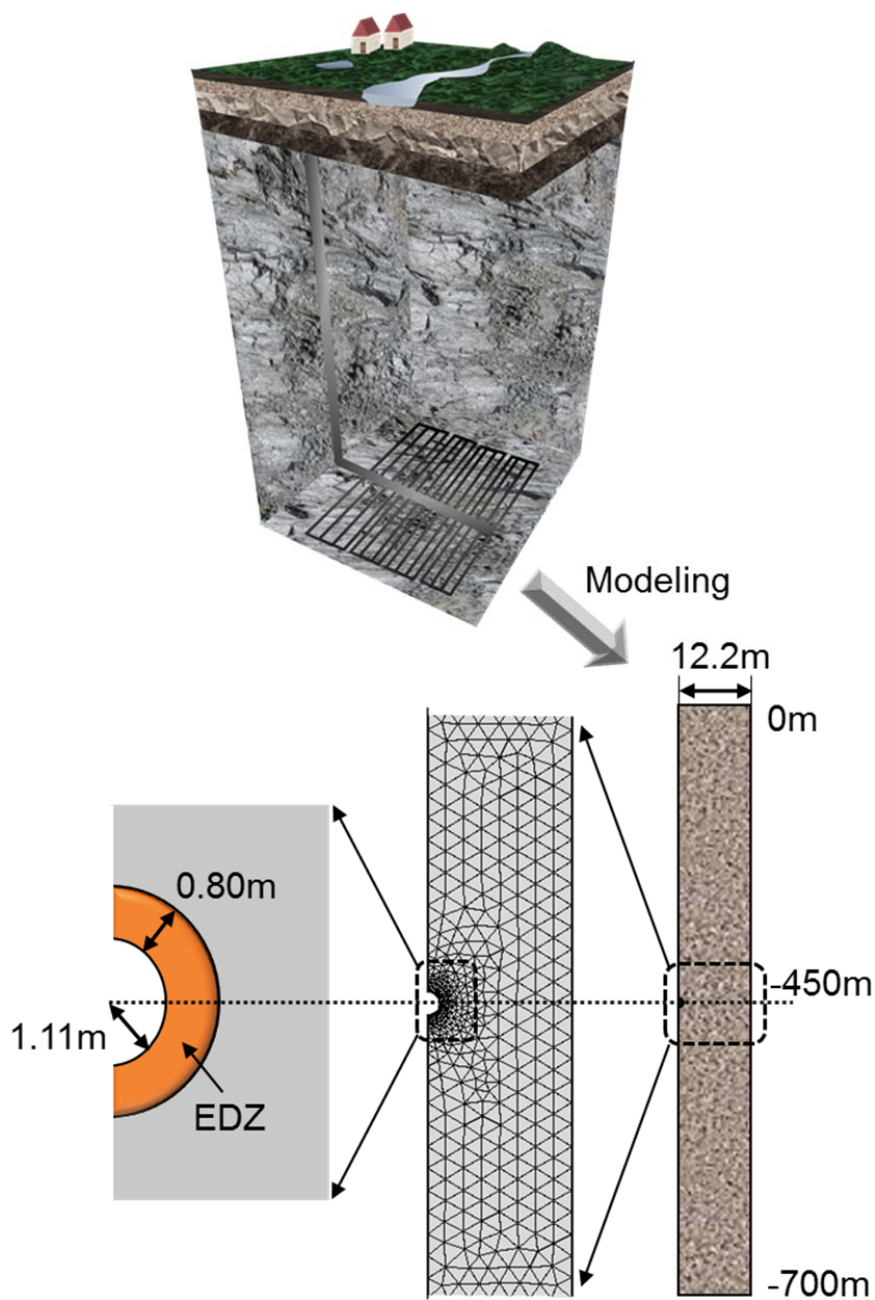


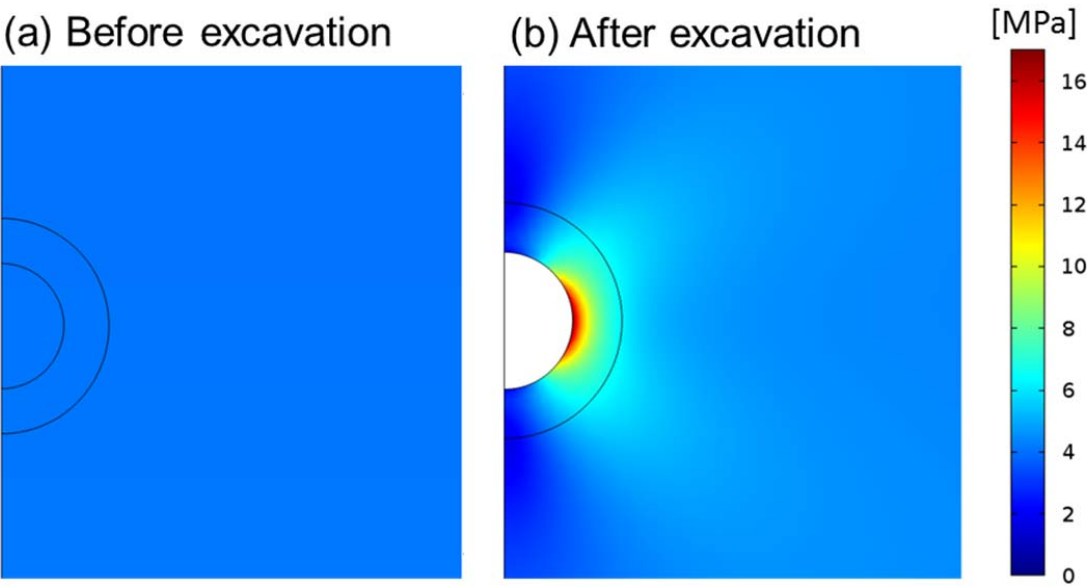
Figure 5. Comparison of silica concentration in pore fluid between experimental data [19] and predictions of the model.





681  
 682 Figure 6. Calculation domain. The calculation domain is a rectangle with vertical and horizontal  
 683 lengths of 700 and 12.2 m, respectively. The cavity, with a diameter of 2.22 m, is excavated by  
 684 lateral setting at a depth of 450 m. The EDZ ranges, in the radial direction, from the cavity wall to  
 685 0.8 m.

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687

688 Figure 7. Distribution of von Mises stress before and after cavity excavation.

689

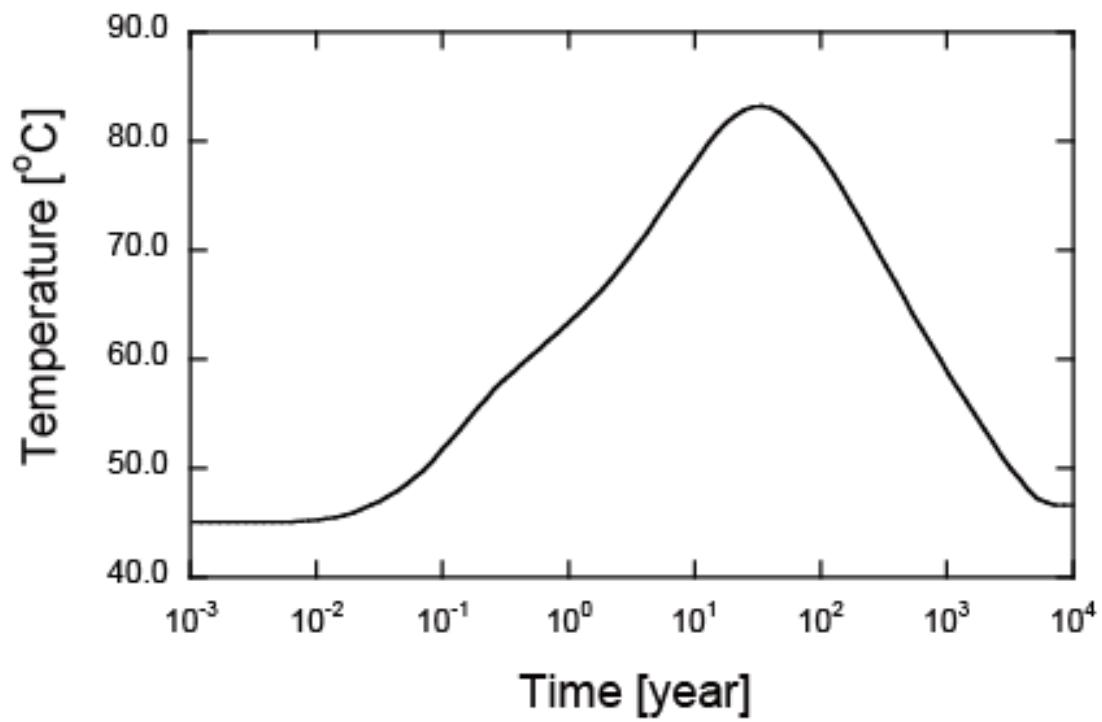
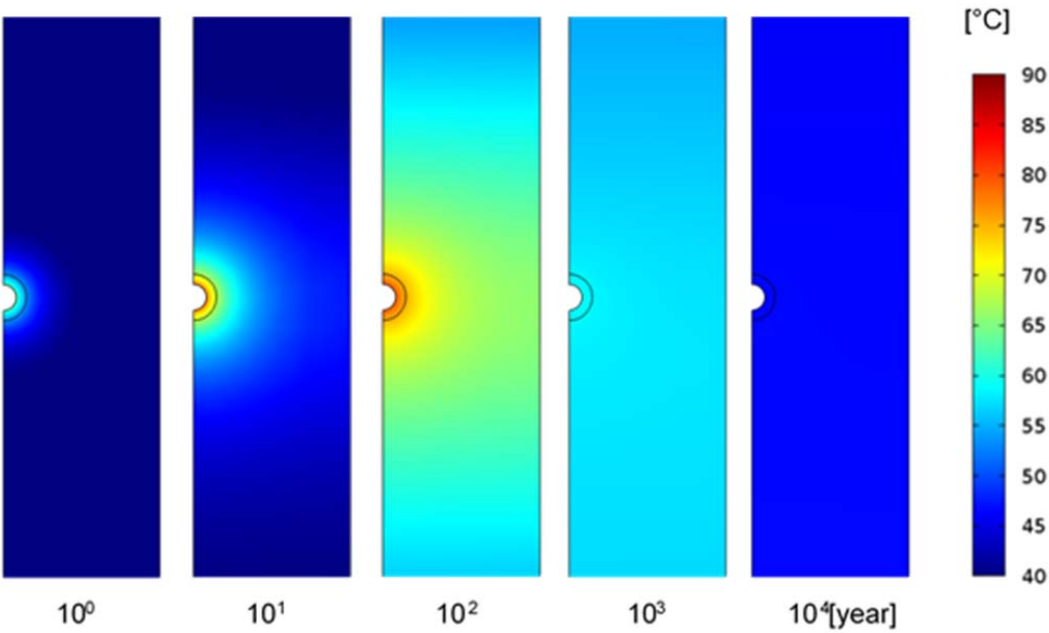


Figure 8. Temperature change with time that is used as the boundary condition applied on the periphery of the cavity [38].

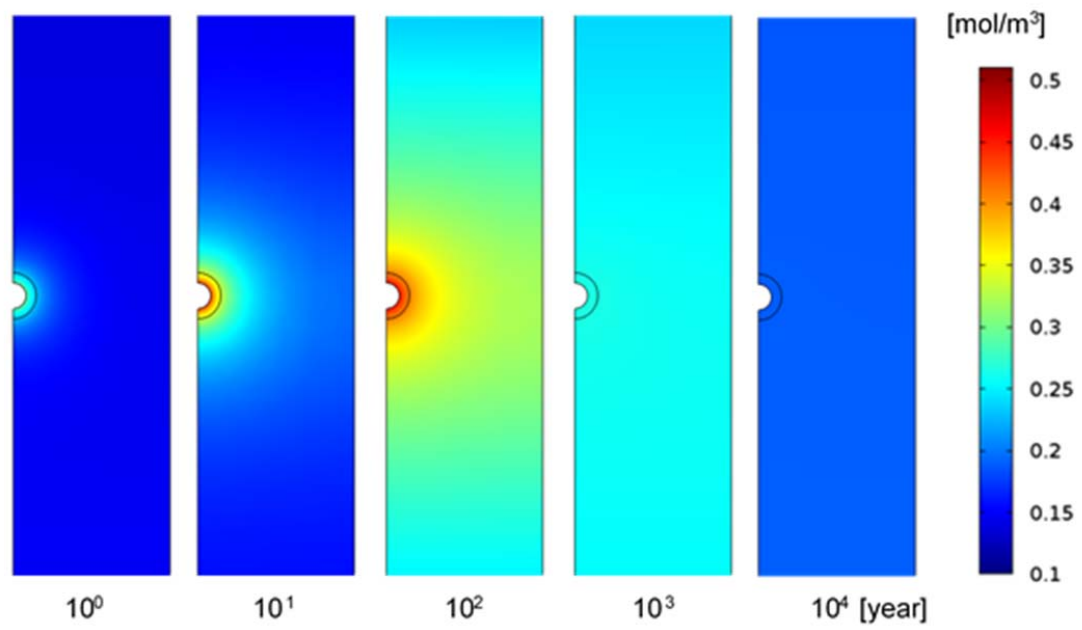
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698

699 Figure 9. Change in temperature distribution with time in the range of  $10^0$  to  $10^4$  years under the  
700 PS condition.

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702

703 Figure 10. Change in Si concentration distribution with time in the range of  $10^0$  to  $10^4$  years under  
 704 the PS condition.

705

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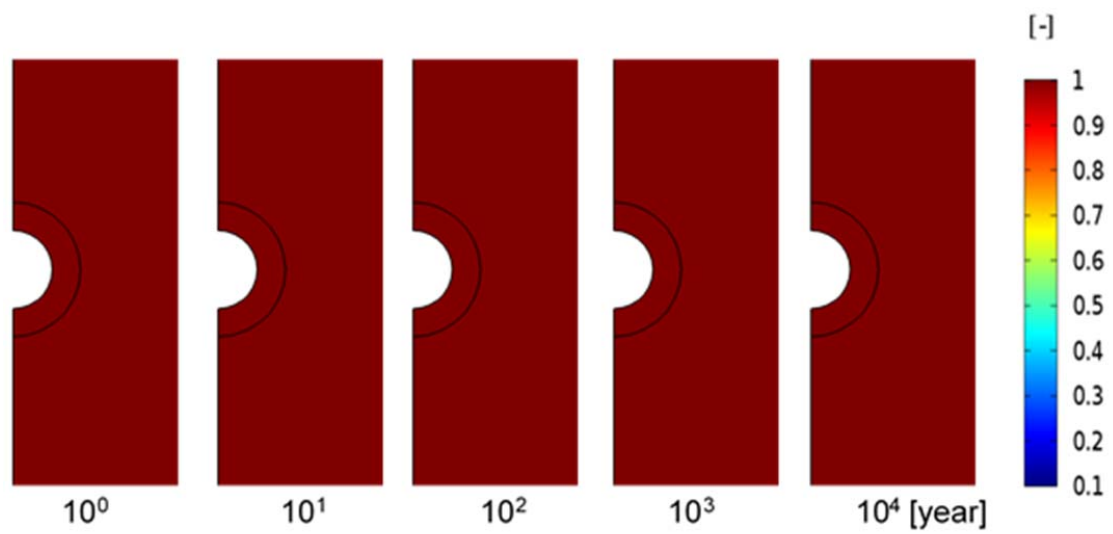


Figure 11. Change in normalized permeability with time in the range of  $10^0$  to  $10^4$  years under the no-PS condition. No permeability change is confirmed.

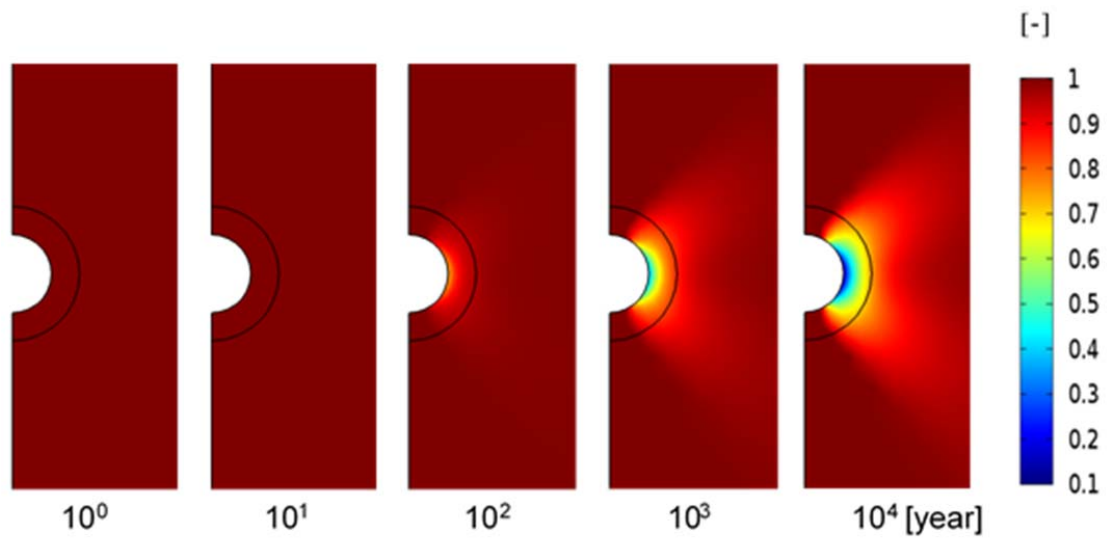
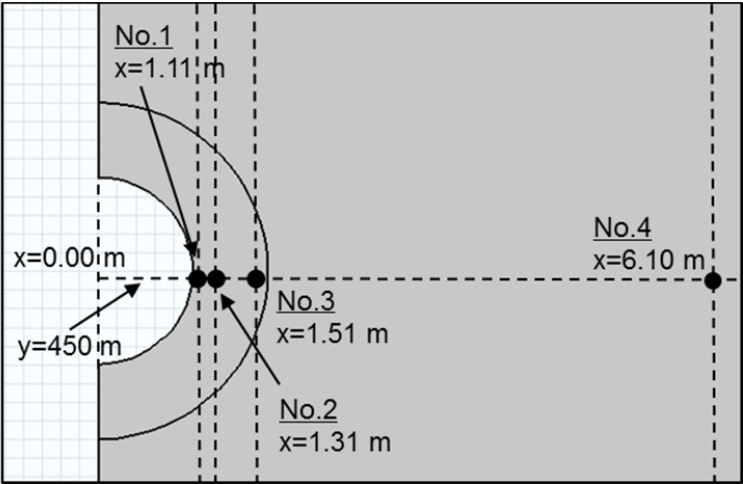


Figure 12. Change in normalized permeability with time in the range of  $10^0$  to  $10^4$  years under the PS condition. The permeability decreases with time. The reduction is especially significant around the periphery of the cavity.

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717

718 Figure 13. Specific locations where changes in permeability with time are observed.

719

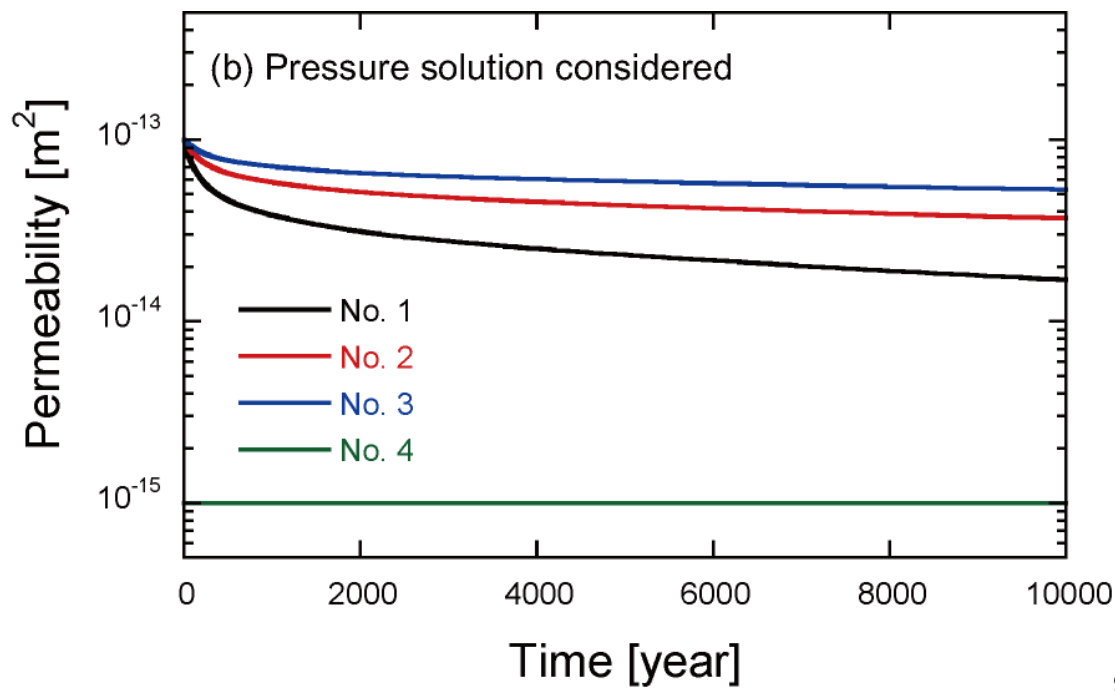
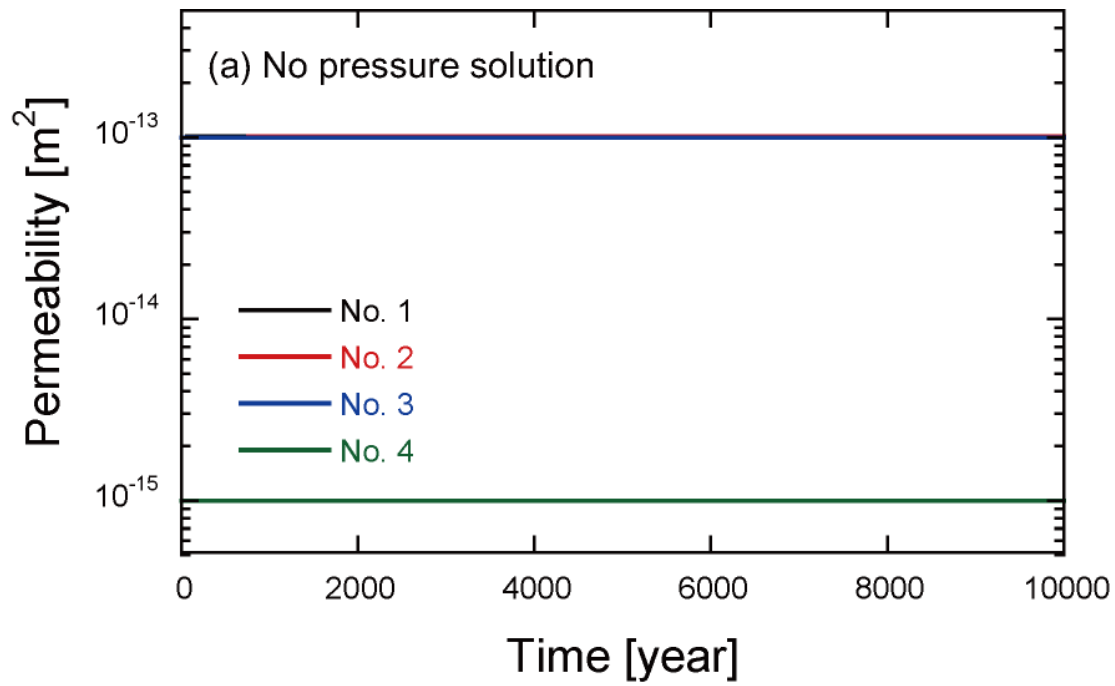


Figure 14. The permeability changes with time at specific locations indicated in Figure 13((a) the no PS condition and (b) the PS condition).

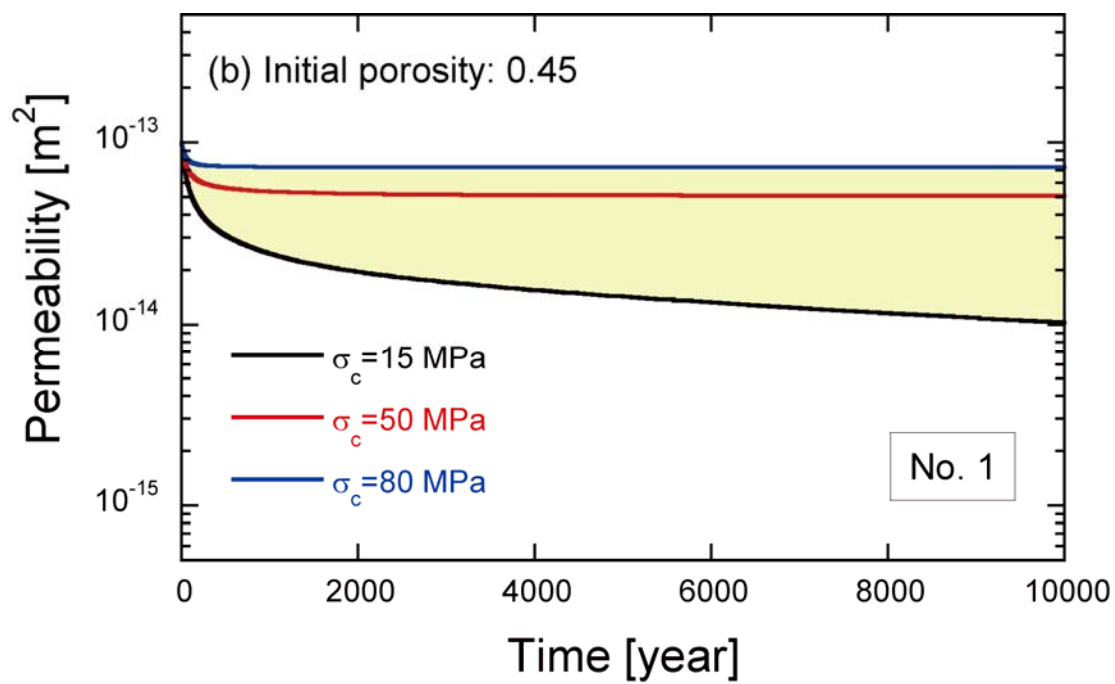
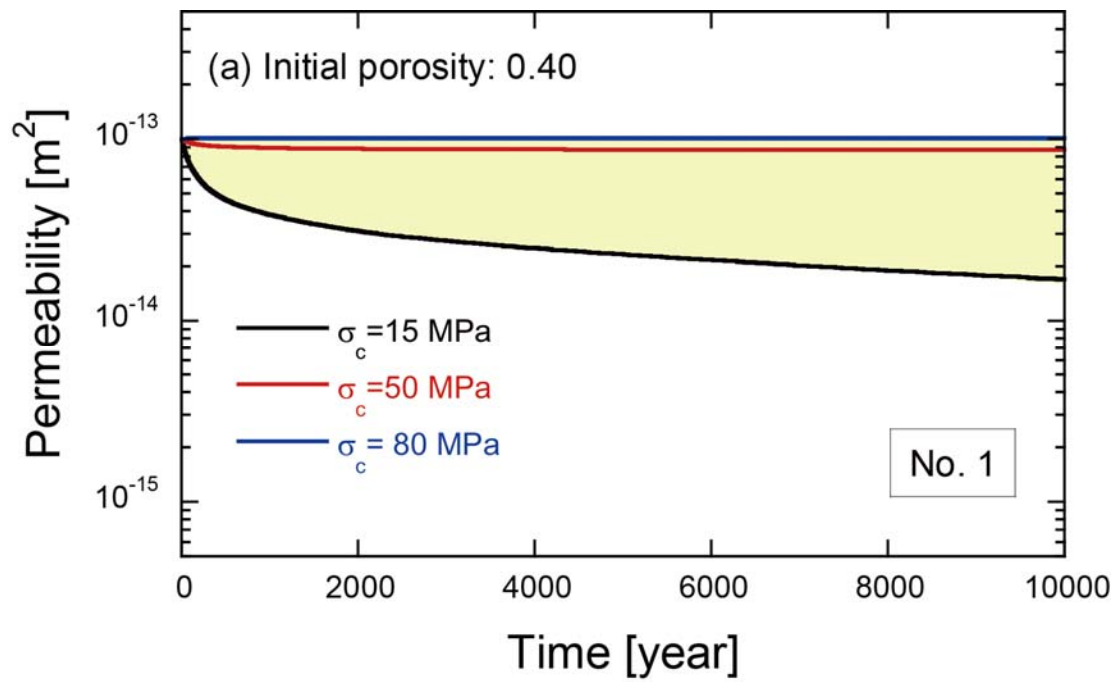


Figure 15. The permeability changes with time under the PS condition at No. 1, indicated in Figure 13((a) initial porosity of 0.40 and (b) 0.45).