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International Collaboration Activities on Disposal in Argillite R&D: DECOVALEX19 Task C – Geochemical and Reactive Transport Modeling

Fuel Cycle Research & Development

Prepared for

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Spent Fuel Waste Science and Technology

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REVISION HISTORY

Rev0	**September, 2019**

Acronym List

CTD	Closure Test Drift
DECOVALEX	DEvelopment of COupled models and their VALidation against EXperiments
DOE	Department of Energy
DOE-NE	DOE Office of Nuclear Energy
DR	Disposal Research
EBS	Engineered Barrier System
FCT	Fuel Cycle Technologies
GREET	Groundwater REcovery Experiment in Tunnel
H-C	Hydro-Chemical
JAEA	Japan Atomic Energy Agency
R&D	Research & Development
SF	Spent Fuel
SFWST	The Spent Fuel Waste Science and Technology
SNL	Sandia National Laboratories
THC	Thermal-Hydrological-Chemical
THMC	Thermal-Hydrological-Mechanical-Chemical
TUL	Technical University of Liberec
URL	Underground Research Laboratory

I. Introduction

International collaborations on nuclear waste disposal R&D are an integral part of the Spent Fuel Waste Science and Technology (SFWST) campaign within the DOE Fuel Cycle and Technology (FCT) program. These partnerships with international repository R&D programs provide key opportunities to participate in experiments developing laboratory/field data (underground research laboratories (URL)) of engineered barrier system (EBS) interactions (e.g., near-field) and characterization of transport phenomena in the host rock (e.g., far-field). The results of these experiments are used in the evaluation of coupled processes and their representation via state-of-the-art simulation approaches to evaluate repository performance. During the thermal heating period, increases in temperature from radionuclide decay in the spent fuel (SF) waste canisters will increase temperature in the surrounding EBS driving chemical and transport processes in the near- and far-field domains of the repository. URL heater-tests for extended periods of times (e.g., years) provide key information and data on thermal effects affecting engineered barriers in response to temperature and water saturation levels. Groundwater interactions with cementitious barriers are also important to in-drift chemistry and EBS performance during post-closure. Descriptions of the various URL experiments for various disposal design concepts according to the host country repository program and relevance to the US program is given elsewhere (Birkholzer et al., 2017; Jové Colón et al., 2016).

The DECOVALEX-2019 Task C involves collaboration with the GREET (Groundwater REcovery Experiment in Tunnel) at the Mizunami URL, Japan, which targets the development of monitoring methodologies of groundwater in granitic rock with applications to THMC simulations (Iwatsuki et al., 2005; Iwatsuki et al., 2015, 2017). Some of the goals of GREET is to conduct a facility-scale geochemical characterization study of short- and long-term effects of tunnel excavation activities, impacts on groundwater flow and transport, and influences on groundwater chemistry (Iwatsuki et al., 2015). The data obtained from these URL activities is then used in the development and evaluation of THC models to support post-closure safety and performance assessments of the repository environment.

The main goals of this report is to consolidate various aspects of the SNL hydro-chemical (HC) work so far as part of this DECOVALEX Task C collaborative international activity:

- Mixing model of 2.1.1 MSB2 monitoring borehole and related hydrochemical data.
- PFLOTRAN (Lichtner, 2013) 3D isothermal reactive transport modeling predictions of water chemistry in the 12MI33 monitoring borehole.
- PFLOTRAN 3D isothermal reactive transport modeling of the closure test drift (CTD) focusing on shotcrete – ground water interactions of the cementitious liner in the water-filled tunnel.
- This simulation effort is part of an inter-comparison exercise between different modeling teams (SNL, JAEA, TUL) participating in this task.

II. DECOVALEX-2019 Task C: GREET (Groundwater REcovery Experiment in Tunnel), Mizunami URL, Japan

This section describes an update to the PFLOTRAN reactive-transport model for DECOVALEX-2019 Task C described in Jové Colón et al. (2018). The Disposal in Argillite work package has expressed interest in the GREET (Groundwater REcovery Experiment in Tunnel, Mizunami URL, JAEA, Japan) URL project on the hydrochemical characterization of the site as part of the groundwater recovery activity from the closure test drift (CTD). The CTD is a tunnel section (46.5 m long × 5.0 m wide × 4.5 m high) of the URL sealed by plug and filled with groundwater (Fig. 1). A series of boreholes allow for monitoring water pressure and chemistry during the experiment. In FY17, geochemical modeling was applied to the analysis of dilution trends observed in monitoring borehole data through simulation of groundwater mixing. Interactions with cementitious barrier materials in the CTD were evaluated through 1D reactive-transport modeling for a water-filled tunnel scenario. The current study extends the work conducted on cement interactions in the flooded CTD to evaluate shotcrete liner interactions using a 3D model representation of this domain implemented in the reactive transport simulation code PFLOTRAN. pH and Cl^- concentration data obtained recently at the site will be used as a test to the model.

The GREET project task leader has kindly provided web access to the geochemical and hydrological data, as it becomes available, to be reviewed by the task participants. Hydrochemical data from the DECOVALEX-19 (Task C) was obtained from the JAEA team and/or information at the GREET website (http://www.jaea.go.jp/04/tono/miu/dataset/greet/greet.html).

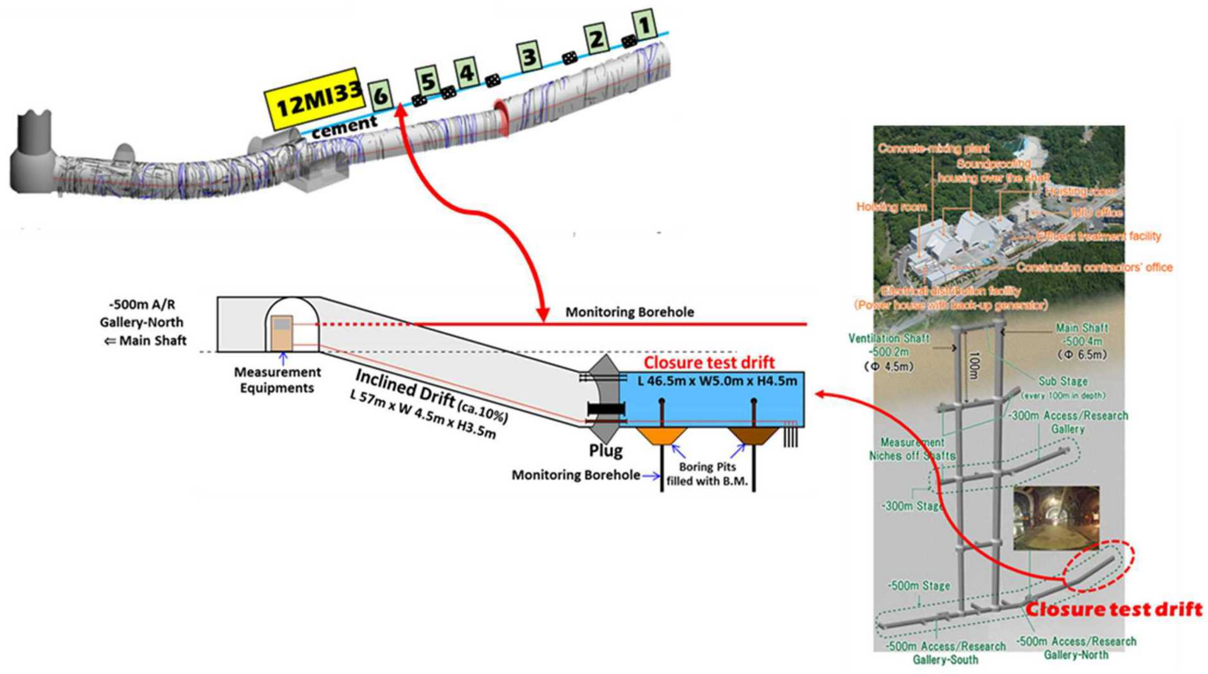

Figure 1. Diagrammatic picture of the closure test drift (CTD) at the Mizunami URL site, Japan. Upper schematic picture shows the inclined tunnel with CTD and the 12MI33 borehole with six monitoring zones. Figure content kindly provided by Dr. Teruki Iwatsuki (JAEA).

III MSB2 Monitoring Borehole and Hydrochemical Data: Simple Mixing Model

Extensive site characterization activities at the Mizunami URL site at various stages of its development provides an excellent opportunity for studying groundwater chemistry through data collection in monitoring boreholes, shafts, and galleries (Iwatsuki et al., 2005; Iwatsuki et al., 2015). The basement geology of the site is composed of Cretaceous granitic rocks that include the Toki Granite overlaid by Pliocene to Miocene sedimentary rocks (Iwatsuki et al., 2005). The general stratigraphy of the site along with locations for some of the monitoring boreholes is given in Fig. 2 (Iwatsuki et al., 2015). The groundwater at the site is hosted in aquifers within the sedimentary units. Iwatsuki et al. (2005) and Iwatsuki et al. (2015) provide a comprehensive description of the groundwater collection methodologies and geochemistry of the various monitoring boreholes. The focus of this preliminary geochemical assessment of the groundwater chemistry and mixing is on groundwater collected at the MSB-2 monitoring borehole. This vertical borehole extends to a depth of 173.5 meters below ground level (mbgl) and provides a large geochemical data set for testing simple groundwater mixing. This borehole has various sampling zones with increasing depth and characterization of major aqueous components for a period of up to 10 years. This resulted in hundreds of chemical analyses from multiple sampling periods.

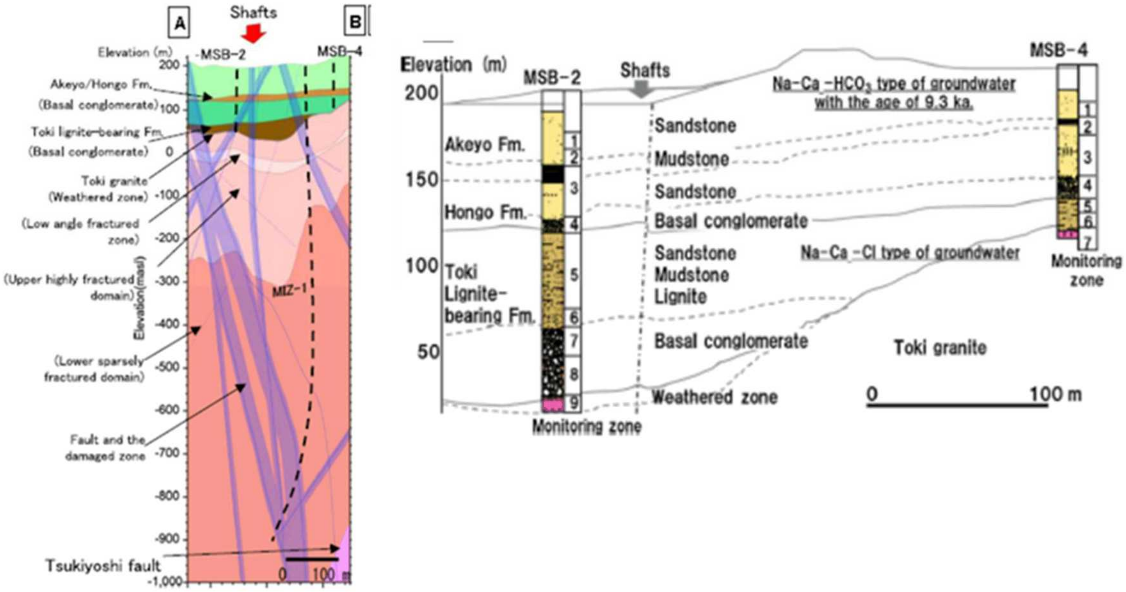

Figure 2. Generalized geologic and stratigraphic description of the the Mizunami URL site, Japan (Iwatsuki et al., 2015). Borehole MSB-2 shows the vertical monitoring zone sequence (1 through 9).

Reduction of groundwater discharge from the excavated shafts resulted in a temporary shaft flooding event which affected the groundwater chemistry in the boreholes. As described by Iwatsuki et al. (2015), the effect of this flooding event was the progressive mixing of groundwater throughout the vertical zones. The probable source of the flood water is a basal conglomerate unit conforming to zones 7 and 8 of the MSB-2 borehole (Iwatsuki et al., 2015). To test this suggestion, a simple model is being proposed where simulation of two water mixing is evaluated using the geochemical modeling. The advantage of using this approach is that interaction between waters, and potentially with other fluids and solids can be captured accounting for aqueous speciation as a function of the extent of mixing. The concentrations of Ca^{++} and SO_4^{--} are used as indicator species to evaluate the effect of mixing. The reason for choosing these two aqueous species is mainly due to their high correlation in their dilution trends and their seemingly unaffected concentrations by geochemical processes such as mineral-fluid interactions. However, Iwatsuki et al. (2015) notes that initial variations in Ca^{++} and SO_4^{--} are probably due mineral weathering at shallow depths but subsequent groundwater mixing and sampling tend to remove such effects. Notice in Fig. 3 the different levels of Ca^{++} concentrations between zones but with progressive dilution particularly for zones MSB-1, MSB-8, and MSB-9. Figs. 4 and 5 shows a comparison of Ca^{++} and SO_4^{--}concentration, respectively, in MSB-1 (zone 1) with monitoring times for the various zones in the vertical borehole.

The extent of dilution in a particular zone is dependent on the difference between aqueous ion concentrations in the zone and that of the predominantly diluent groundwater. As noted previously, the flood water source is probably a basal conglomerate unit in zones 7 and 8 (Iwatsuki et al., 2015). To test this suggestion, mixing simulation consisted in the dilution of MSB2-1 zone groundwater with that from the MSB2-7 zone. The computer code EQ3/6 (Wolery and Jarek, 2003) along with the YMP thermodynamic database are used to conduct the mixing simulations by "adding" groundwater compositions MSB2-7 into MSB2-1. As a starting point, the simulations are initiated groundwater compositions corresponding to times just after the shaft flooding period.

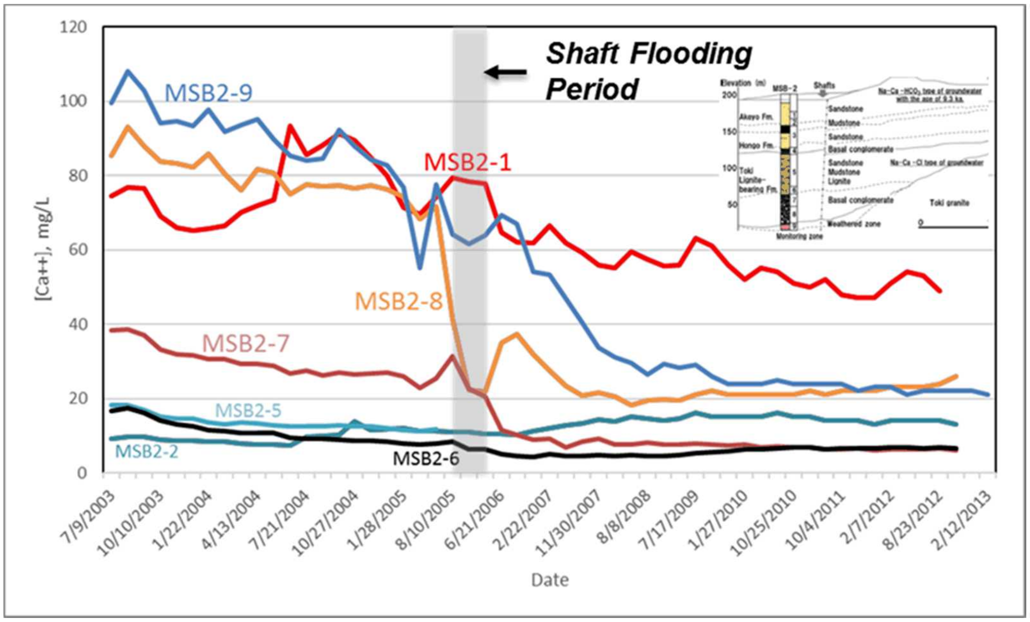

Figure 3. Ca concentration profiles with monitoring time for the sampling zones (1 through 9) in borehole MSB-2. Vertical gray band represents the shaft flooding period.

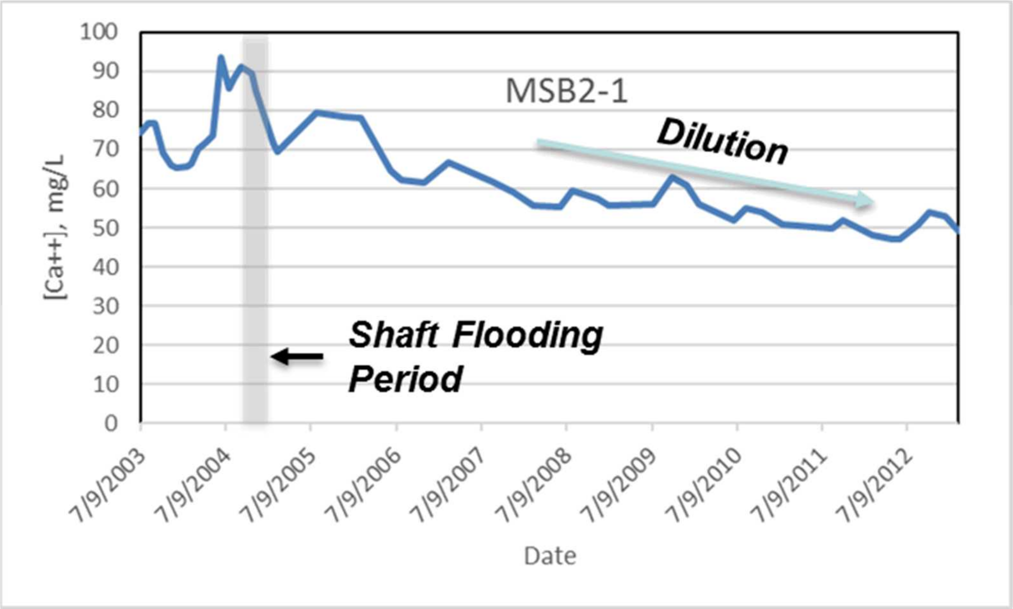

Figure 4. Ca^{++} concentration profiles with monitoring time for zone 1 in borehole MSB-2.

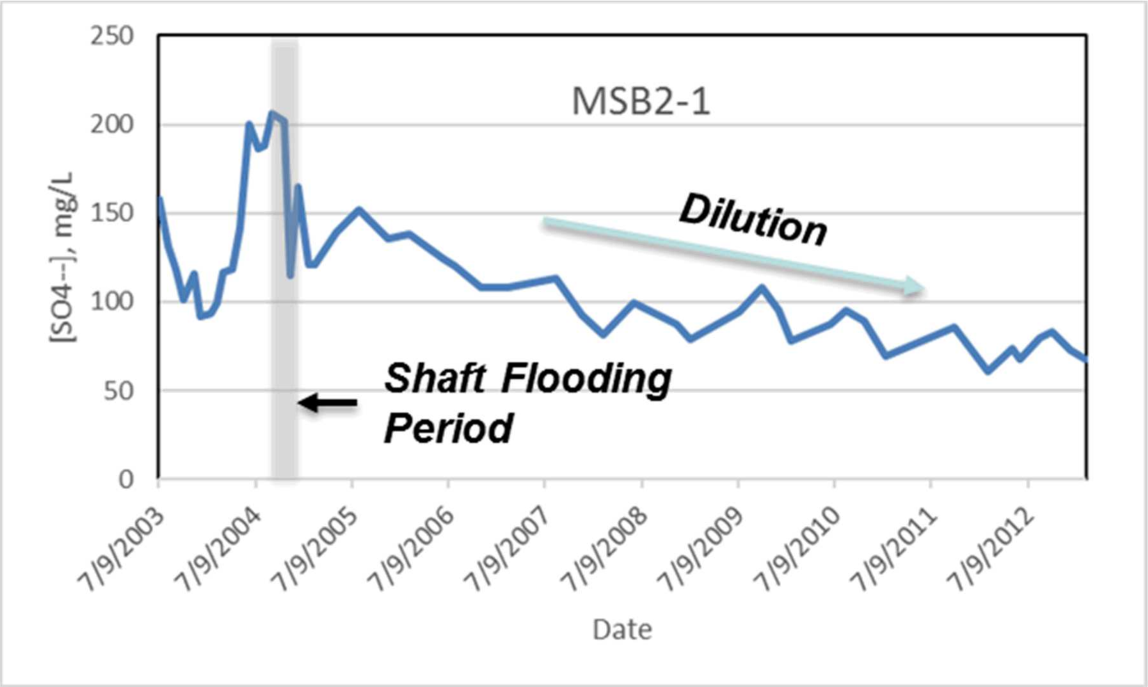

Figure 5. SO_4^{--} concentration profiles with monitoring time for zone 1 in borehole MSB-2.

The results of the groundwater mixing simulation in EQ3/6 is depicted in Fig. 6 in the form of Ca and SO_4 concentrations. As expected, the simulation shows a linear trend with progressive dilution noting the good correspondence between prediction and monitoring data. Such agreement suggests relatively fast and effective mixing through the length of the borehole by deeper groundwater sources percolating. It also suggests the absence of component sinks (e.g., mineral precipitation) in the course of mixing. Concentration predictions of Cl (not shown) overall shows increasing trends but at higher concentrations relative to those in the observed data. This suggest a more complex mixing probably involving contributions from other groundwater sources. However, the variability in Cl data is much larger and their overall concentrations are much smaller relative to Ca and SO_4 which needs to be taken into account when comparing data and simulations.

Applications of this geochemical modeling methodology to simulate the extent of fluid mixing is useful in the analysis of groundwater compositions and their potential interactions with other phases such as gases and minerals. It also provides a consistent geochemical evaluation methodology to exploit the extensive hydrochemical field data relevant to site characterization. Moreover, in the case of the Mizunami site, it provides the opportunity to evaluate the effects of hydrological and chemical disruption due to excavation and site construction activities.

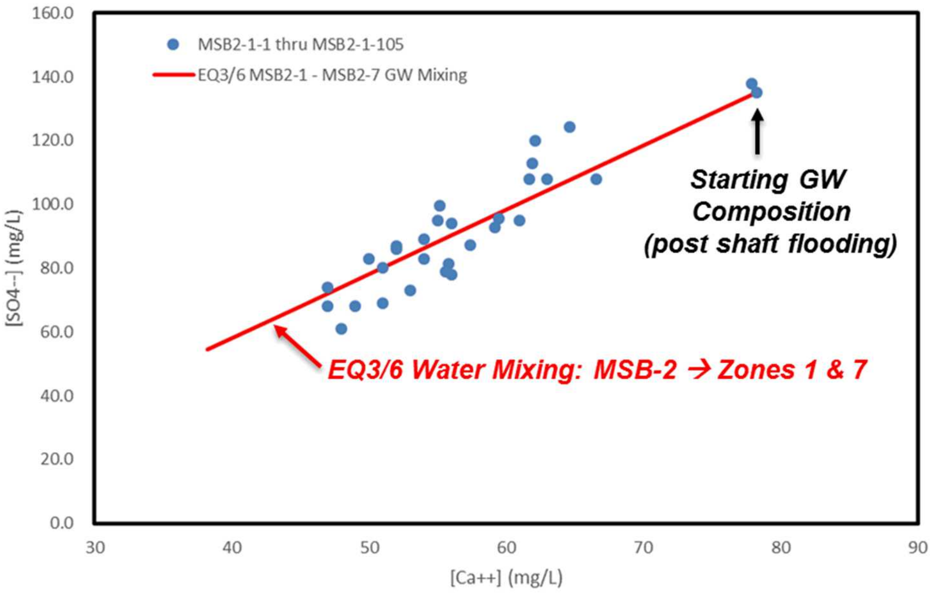

Figure 6. Comparison of predicted and observed Ca and SO4 concentration profiles for a mixing scenario between for zone 1 and zone 7 groundwaters in borehole MSB-2 (see text).

IV 12MI33 Monitoring Borehole

Fig. 1 shows the location of the monitoring borehole and associated sampling regions. The nearly horizontal borehole is about 107 meters long into the Toki granite extending parallel to the CTD. As illustrated in this figure, the monitoring borehole lies in the host rock parallel to the CTD and next to the inclined tunnel. Rock cores were obtained from the borehole for textural, mineralogical, and fracture characterization. Geochemical data was obtained from the monitoring borehole after the drift excavation. Initial PFLOTRAN 3D isothermal reactive transport simulations were conducted using homogeneous permeabilities for the granite without the effects of fractures. Subsequent simulations will incorporate heterogeneous permeability distributions obtained from the hydrological study. The initial groundwater chemistry was constrained as that reported by Iwatsuki et al. (2015) for the Toki granite at depths of 100 and 300 meters. Volume fractions for the Toki granite used in the simulations are based on the mineral normative abundances after Yamasaki and Umeda (2012). Fig. 7 describes measured and predicted pH at the six monitoring zones in borehole 12MI33. The groundwater in this region interacts with the granitic host rock, however, zone 6 is closer to the cement liner. Possible interaction with cementitious material is illustrated in Fig. 7 where sampled groundwaters in zone 6 reaches pH~11. The PFLOTRAN pH prediction is essentially the same for all six zones where there is initial small drop in pH and a subsequent slight increase with time. This trend is generally consistent with the scatter of the measured pH's from zones 1-5. However, the prediction for zone 6 doesn't capture the pH increase most likely because of limited interaction with the cement liner in the tunnel due to the distance or the need to include a cementitious liner in the borehole. Predictions for some of the solutes (not shown) show similar flat trends even for zone 6. Future PFLOTRAN simulations will add a cementitious liner material to the neighboring cells of the 12MI33 borehole to see if this pH trend can be represented by the model.

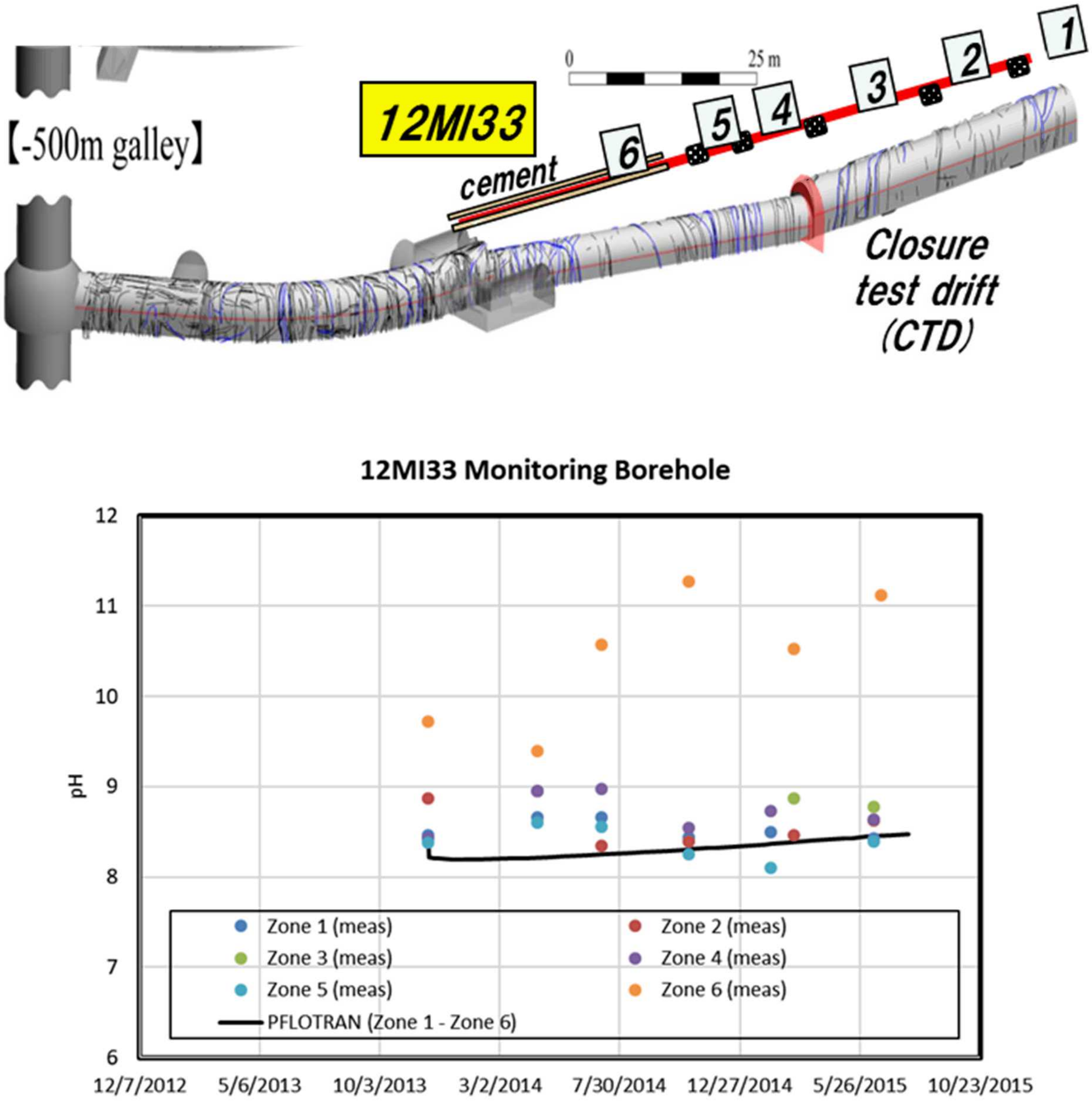

Figure 7. Schematic diagram of borehole 12MI33 (upper panel) with six monitoring zones. Measured and predicted pH (lower panel) profiles at monitoring zones 1 through 6.

V Closure Test Drift (CTD): 3D H-C Model of Shotcrete Liner Interactions

The Closure Test Drift (CTD) is a tunnel facility (Fig. 1) at 500 meters below ground level to investigate the effects of hydrological, geomechanical, and geochemical variations during drift excavation and post-closure in fractured granitic rock. The facility is equipped with monitoring probes for water sampling, hydraulic pressure, and rock displacement. Mapping of fractures was conducted during drift excavation. The CTD tunnel is lined with Mg-bearing ordinary Portland cement (OPC) shotcrete and is sealed by using a low-heat Portland cement plug (Iwatsuki et al., 2017). After closure, the tunnel was filled with water to study environmental changes including effects on hydrochemistry due to interactions with barrier materials such as shotcrete. Like FEBEX-DP and other international repository science activities, interactions with cementitious barrier materials (e.g., shotcrete) is important given its potential for alkaline reactions with other silicates (e.g., clay barriers, host rock) and the generation of high-pH pore solutions. These processes could lead to dissolution/precipitation processes at barrier interfaces that could affect solute (radionuclide) transport and clay barrier sorption properties. A 3D reactive transport representation (Fig. 8; YZ cross section) has been implemented on a hydrological model of the site near the CTD. The goal is to extend the hydrological model to capture the extent of high pH effects within the flooded tunnel and with distance from the cement-water interface.

A 3D reactive transport representation (Fig. 8; YZ cross section) has been implemented using the computer code PFLOTRAN on a hydrological model of the site near the CTD. The goal is to extend the hydrological model to capture the extent of high pH effects within the flooded tunnel and with distance from the cement-water interface. Such interactions in the water-filled zone may influence pore solution chemistry in the nearby monitoring boreholes where fractures in the excavated disturbed zone (EDZ) are present throughout the length of the CTD. The presented results make use of a hydrological model that does not include fractures. However, a hydrological model including heterogeneous permeability fields to represent fractures has been successfully coupled with the reactive-transport model. This effort is currently ongoing and will be described in a later section.

The 3D reactive reactive-transport model implementation is done in PFLOTRAN using similar parameters (e.g., material properties) to those adopted previously in the 1D evaluation of EBS material interactions (Jové Colón et al., 2016). The PFLOTRAN simulations were conducted in TH mode (coupled thermal-hydrological flow) assuming full saturation and transport by diffusion only. Thermodynamic data for cementitious phases such as CSH(1.6), portlandite, and ettringite were obtained from the THERMODDEM database (Blanc et al., 2012; Blanc et al., 2006). The composition of the cementitious domain resembles that of ordinary Portland cement (OPC) assuming a calcite aggregate (Jové Colón et al., 2016). The current updated model considers a Cl-bearing phase (Friedel salt) and a Mg-bearing (brucite) in the cementitious phase assemblage. The reason for adding these phases is to account for their presence in the shotcrete and to evaluate their effect on solution chemistry, particularly on Cl concentration.

Dissolution rates of cementitious solids were obtained from various sources as described in Jové Colón et al. (2016). The length of water-filled domain is about 47 m with a height of 5 m closely resembling the CTD dimensions. The cement plug thickness is 2 m and the shotcrete liner is 0.1 m. The flooded CTD domain is represented by a porous medium having a porosity of almost unity and a very high permeability. The groundwater in the flooded domain is assumed to have the same chemistry as that of the host granitic rock. This groundwater also represents the starting solution chemistry of the filled CTD. The simulations were performed over a period of 300-400 days.

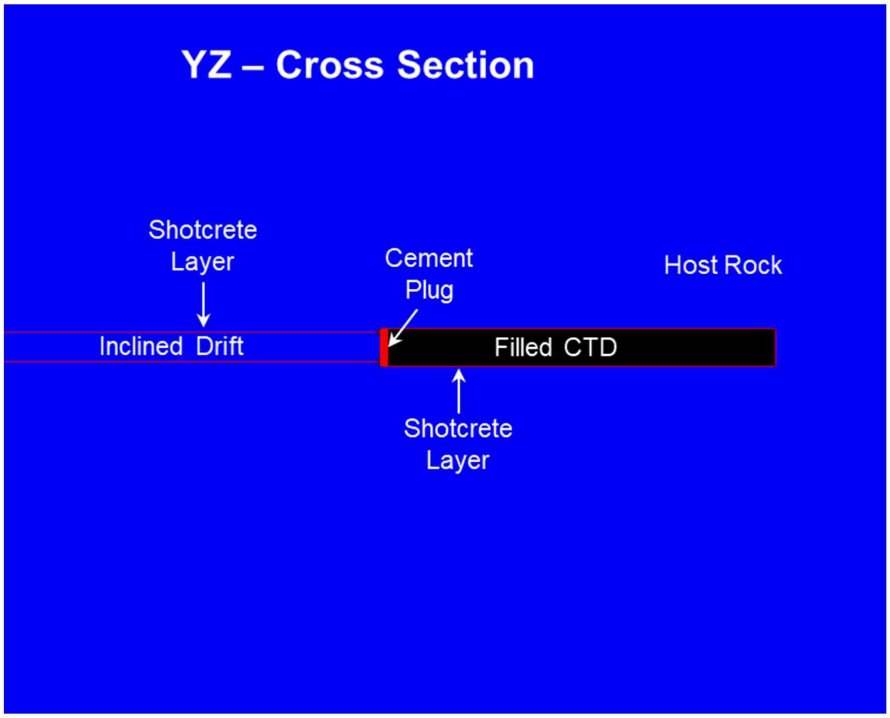

Figure 8. Schematic figure showing a YZ of the model domain in the PFLOTRAN reactive transport simulation of the CTD. Red areas delineate the shotcrete liner and cement plug. Observation points (not shown) are positioned at the tunnel length midpoint starting from the shotcrete-water interface up to a meter inside the water-filled tunnel.

Fig. 9 shows four time-snapshots (0, 60, 150, 300 days) of the pH mapping to represent the evolution of the reactive front from the shotcrete liner domain. As expected, pH increases with time from the interface into the water-filled CTD region and the host rock. After ~300 days of simulation time, the increase in pH because of the advancing front reaches ~0.5 m from the shotcrete interface into flooded CTD. About 1 m into the CTD, the pH remains close to the starting pH 8.9 for remainder of the simulation. The overall behavior of the reaction front described in these snapshots is very similar to that shown in Jové Colón et al. (2018).

The current stage of GREET effort involves the prediction of changes in groundwater chemistry to then be compared with data from monitoring boreholes from within the CTD and from the host rock within the excavated disturbed zone (EDZ). Fig. 10 (upper panel) shows the pH predictions from the PFLOTRAN reactive-transport model and the JAEA pH data. The measured pH data (purple dots connected by a line) show a rapid monotonic increase early in time then progressing towards a pH~10. Notice that measure pH data after 3/2016 show more variation with time (i.e., deviations from a monotonic increase) but still trending towards pH~10. The PFLOTRAN simulation results (solid curves) are shown for four observation points at a distance from the shotcrete interface (at the shotcrete interface, 0.4 m, 0.7 m, and 1 m) into the filled CTD. Notice that pH predictions at the observation point close to the shotcrete interface underestimate the measured data early times (<100 days). After 100 days, the model result is in good agreement with the measured pH trend progressing towards pH~10. As in previous results, predictions at 0.45 m show a slower pH increase due to diffusive transport from the shotcrete interface into the filled CTD. This increase reaches pH~10.3 towards the end of the simulation which is closer to the measured pH. Predictions of pH at 1 m from the shotcrete interface show a relatively small increase with time indicating the limited effect of the reaction front on groundwater pH towards the tunnel center axis.

The JAEA pH data was used to constrain the parameters in the transition state theory (TST) rate law in PFLOTRAN and adopted for portlandite dissolution kinetics (see Lichtner 2016). The observed trend in pH is assumed to be predominantly dependent on portlandite dissolution. The adjusted parameters are related to the primary chemical species (H^+ and Ca^{++}) in the prefactor term in the rate law for the mineral dissolution reaction of portlandite. The good agreement in the representation of the observed pH trend from the PFLOTRAN simulation suggests portlandite as the primary contributor to this change, even with the discrepancy at early times. More work is needed in the analysis of these parameters and the potential for other phases contributing to the overall pH change.

Fig. 10 shows the JAEA measured concentration of Na^+ (lower panel) decreasing with time with some level of scatter. The PFLOTRAN predictions at the shotcrete interface also represents this decrease in Na^+ concentration with time, in good agreement with the overall measured trend. The predictions of temporal changes in Na^+ concentration with distance from the shotcrete interface show similar decreasing profiles but with the expected effect of a diffusive front towards the CTD center.

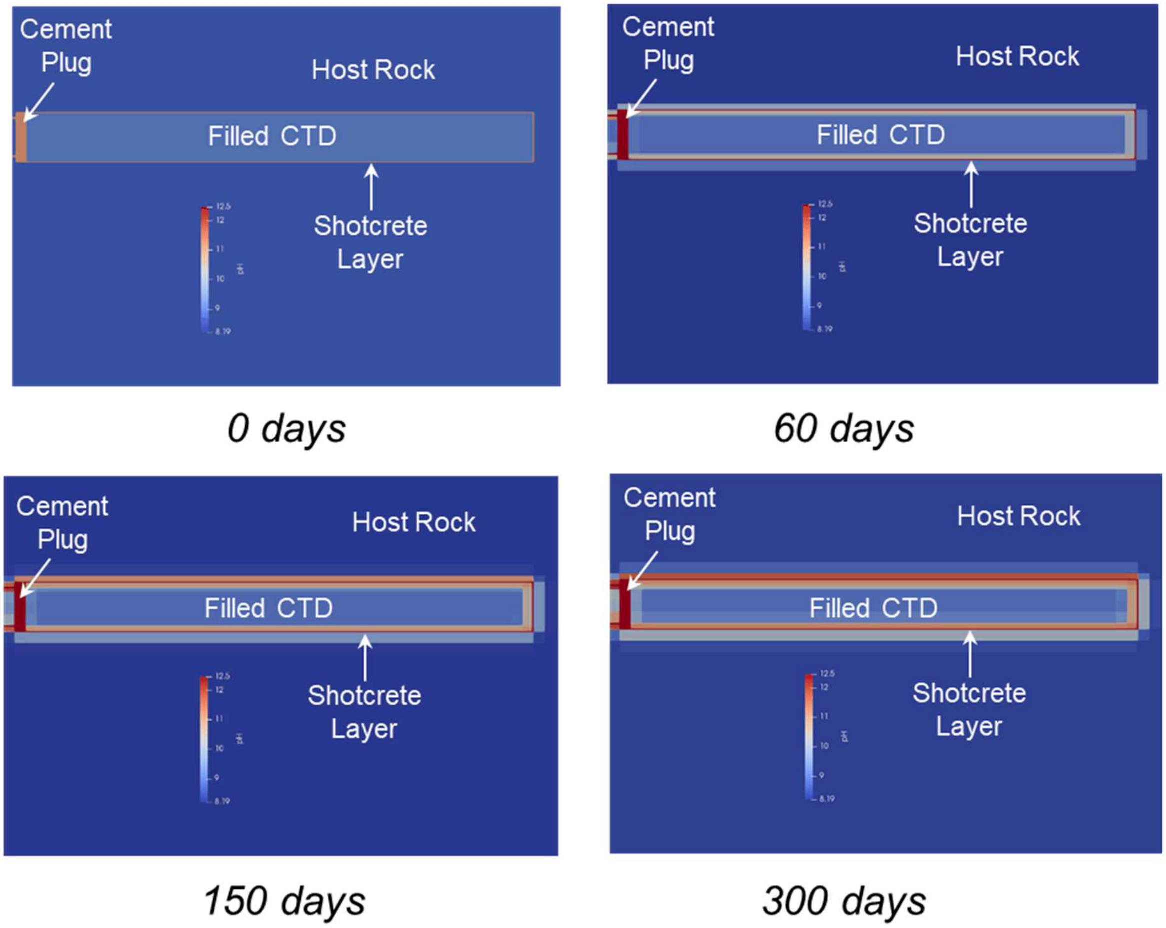

Figure 9. Predicted pH of the PFLOTRAN 3D reactive transport model of the CTD and surrounding host rock. The reaction front diffuses into the CTD and into host rock. pH color map scale ranges from 8.19 to 12.5.

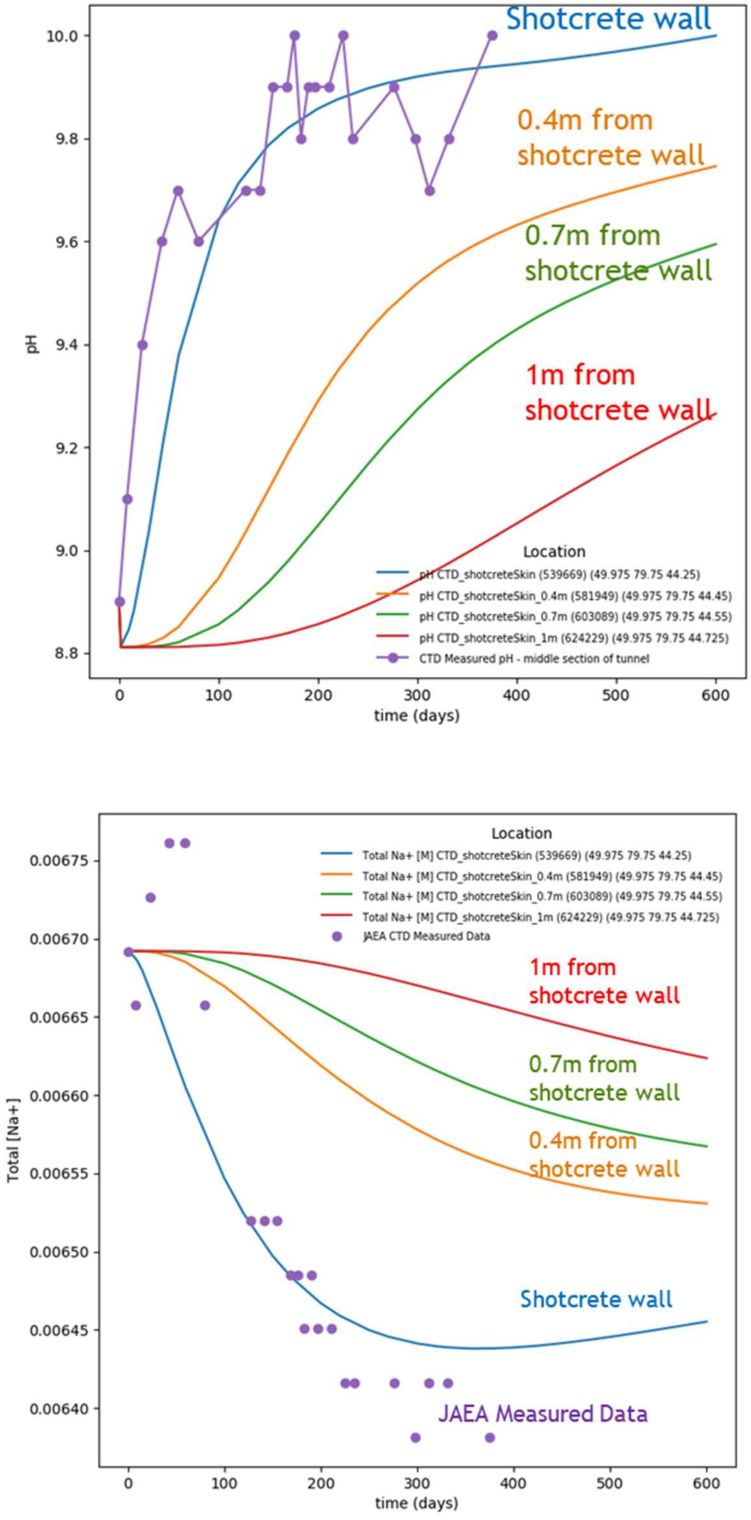

Figure 10. Measured and predicted pH (upper panel) and Na^+ concentration (lower panel) in moles/L profiles at the midpoint region of the CTD.

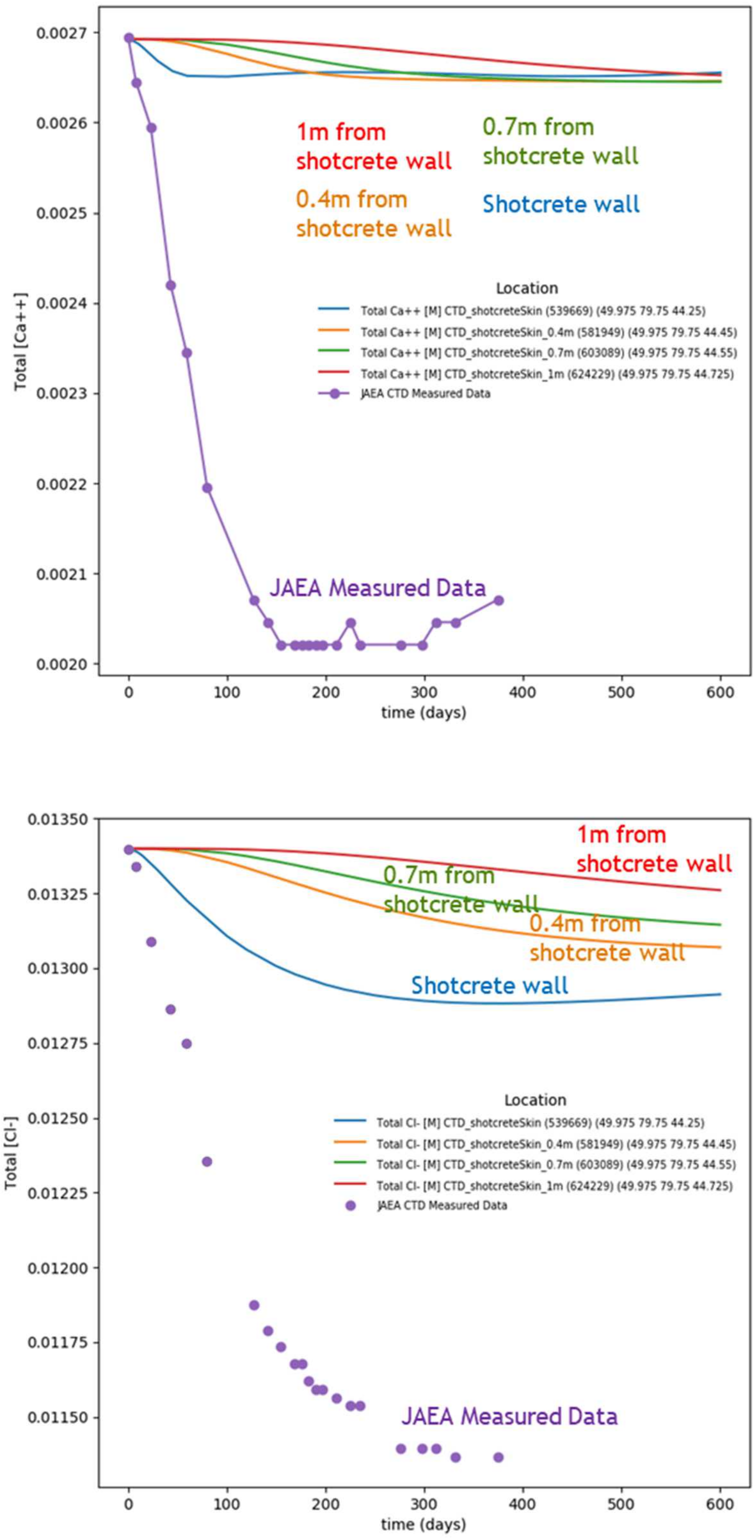

Figure 11. Measured and predicted Ca^{++} (upper panel) and Cl^- concentration (lower panel) profiles in moles/L at the midpoint region of the CTD.

Fig. 11 shows the temporal evolution of Ca^{++} and Cl^- measured concentrations in the CTD. Notice that both aqueous component concentrations show an initial (t ≤ ~150 days) sharp decrease to subsequently attain a nearly steady-state concentration. The PFLOTRAN simulation does produce an initial decrease in both Ca^{++} and Cl^- at the shotcrete interface observation point but much smaller in comparison. It is not clear what would cause such an initial large decrease, but possible reasons are groundwater mixing/dilution and/or Cl^- uptake by precipitation of a Cl-bearing cementitious phase. Both possibilities need further evaluation through monitoring and phase characterization activities, and reactive transport simulations, for example, focusing on evaluating the effects of hydrological characteristics (porosity and permeability) in shotcrete and host rock.

The next step is to combine the 3D H-C model with heterogeneous permeability distributions based on a fracture model. The Visualization Area domain, which is a CTD-scale domain recommended by the project has been adopted (Wang et al., 2017). The domain size is 100 m x 150 m x 100 m. To closely model geochemical processes in the CTD and related interfaces, a refined mesh was used for this analysis. Mesh refinements were added around the CTD to capture the cement plug and the shotcrete on the walls of the CTD. The mesh size is now 70 x 302 x 75, resulting in 1,585,500 grid blocks. Figs. 12 and 13 show a slice along the axis of the tunnel and mesh refinements at the CTD, respectively, to allow modeling of the shotcrete and cement plug.

Fracture characterization was conducted using the method detailed in Wang et al. (2017). Measured fracture data from tunnel walls and from packer tests in monitoring wells were used to develop the fracture model. A discrete fracture network (DFN) model was developed for the modeling domain for a selected number of realizations. For this study, the DFN “Realization 2” was used. The DFN permeability and porosity results for the selected realization were upscaled to the refined continuum mesh for use in flow and transport simulations. Figs. 14 and 15 show the upscaled permeability and porosity fields, respectively. An update to this report will include results of the reactive transport simulations with this heterogeneous permeability and porosity fields.

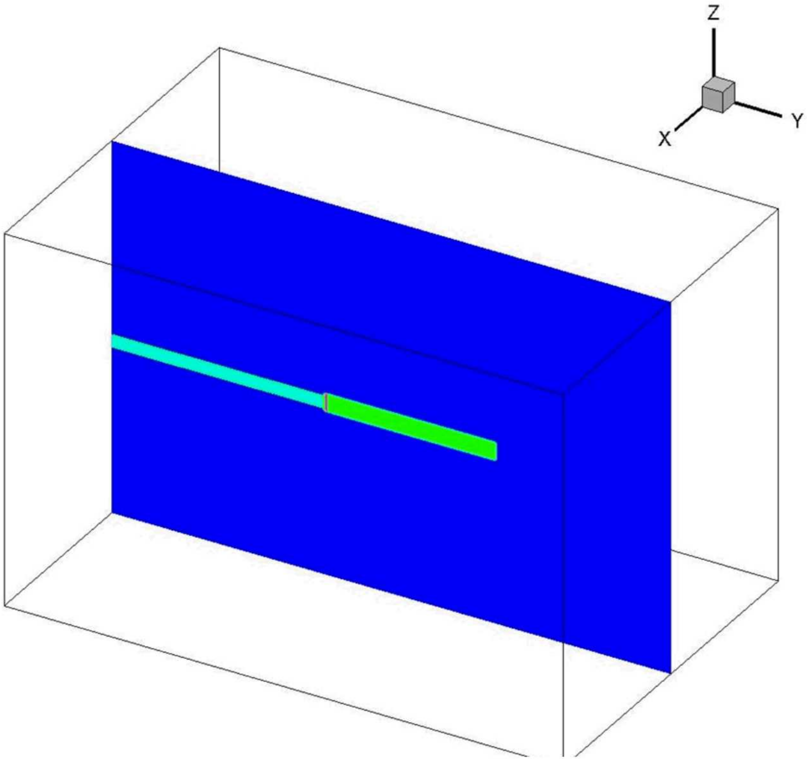

Figure 12. Vertical slice along the axis of the tunnel showing the CTD region (light green) and inclined drift (light blue).

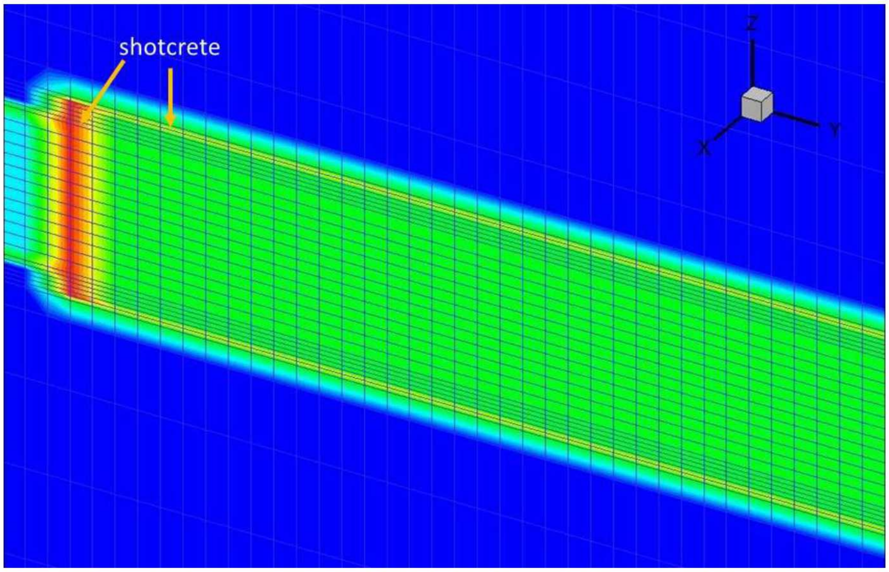

Figure 13. Mesh refinement showing shotcrete plug and lining around the CTD.

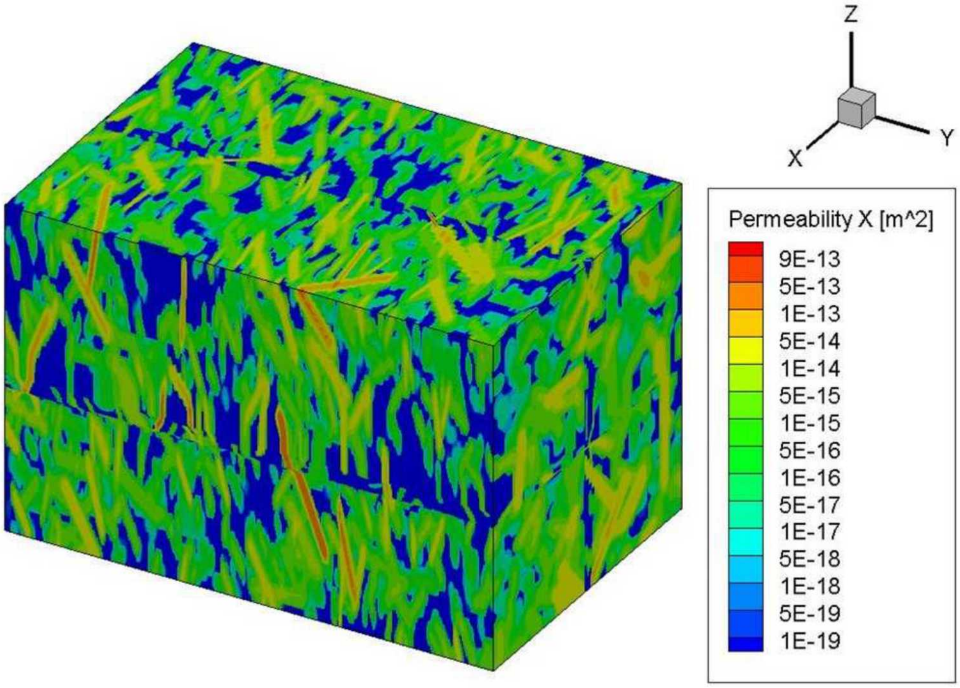

Figure 14. 3D domain representation of upscaled permeability field for DFN Realization 2.

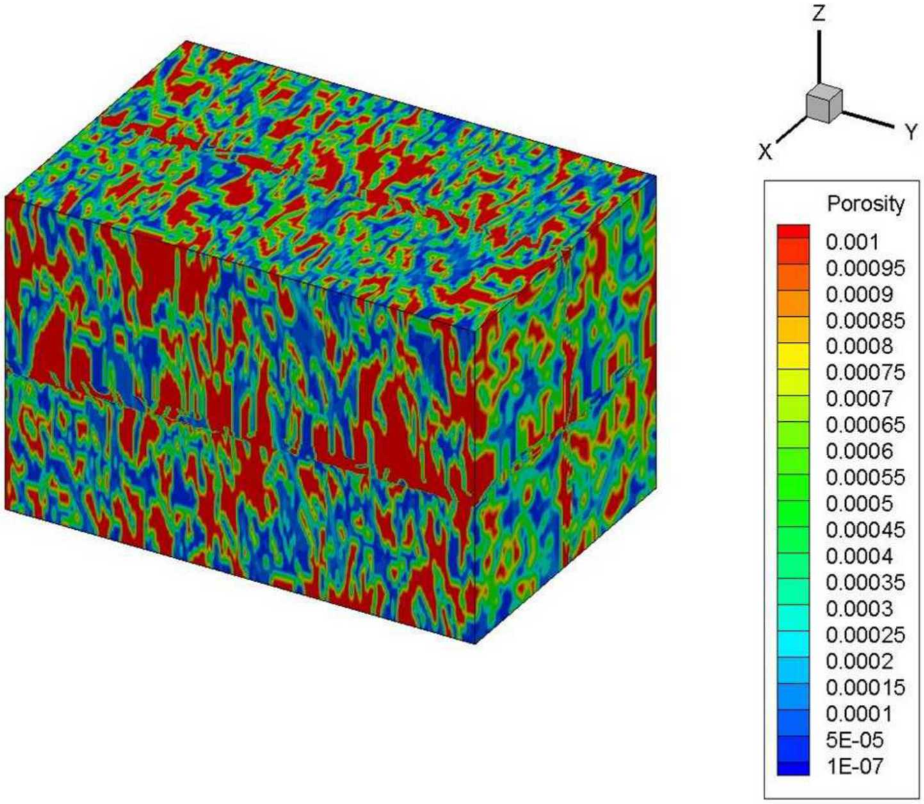

Figure 15. 3D domain representation of upscaled porosity field for DFN Realization 2.

VI. Conclusions

- **DECOVALEX-2019 Task C of GREET Experiment** – Geochemical modeling for groundwater mixing, monitoring borehole 12MI33, and 3D reactive transport modeling of the CTD:
    - Geochemical modeling has been applied to the analysis of dilution trends observed in monitoring borehole data through simulation of groundwater mixing. Applications of this modeling methodology to simulate the extent of fluid mixing is useful in the analysis of groundwater compositions and their potential interactions with other phases such as gases and minerals. It also provides a consistent geochemical evaluation methodology to exploit the extensive hydrochemical field data relevant to site characterization. Moreover, in the case of the Miizunami site, it provides the opportunity to evaluate the effects of hydrological and chemical disruption due to excavation and site construction activities.
    - The 3D reactive transport model was also used to model groundwater interactions in six zones of the monitoring borehole 12MI33. This borehole lies parallel to the CTD and near the inclined drift. PFLOTRAN pH predictions of zones 1-5 in the monitoring borehole show overall consistency with the measured data suggesting the control of the granitic host-rock on the groundwater chemistry. The high pH observed in zone 6 appears to be influenced by interactions with the nearby cement liner and could not be predicted by the current model. This probably suggest enhanced mixing at this zone.
    - 3D reactive transport modeling of shotcrete liner interactions was implemented on a hydrological model of the site domain comprising the CTD. PFLOTRAN predictions of pH and Cl^- from groundwaters sampled at the midpoint length of the CTD showed deviations from the measurements. The predicted pH overestimates the measured data at later times whereas the predicted Cl^- concentration prediction underestimates its decrease with time. Future work to assess the nature of these deviations will include exploring kinetic rate law and transport parameterizations to better represent the pH profile. Groundwater mixing/dilution and/or Cl^- uptake by precipitation of a Cl-bearing phase (e.g., Friedel's salt) will be explored to evaluate the observed decrease in Cl^- concentration with time.

VII. References

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