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International Collaboration Activities on Engineered Barrier Systems

Fuel Cycle Research & Development

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Spent Fuel Waste Science and
Technology

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Acronym List

BRIE	Bentonite Rock Interaction Experiment
CIEMAT	Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas
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
EDS	Energy Dispersive Spectroscopy
EMPA	Electron Microprobe Analysis
FCT	Fuel Cycle Technologies
FEBEX-DP	Full-scale Engineering Barrier Experiments – Dismantling Project
FEPs	Features, Events and Processes
GTS	Grimsel Test Site
HLW	High Level Waste
JAEA	Japan Atomic Energy Agency
mSEM	Multi – Scanning Electron Microscopy
PA	Performance Assessment
QA	Quality Assurance
R&D	Research & Development
SEM	Scanning Electron Microscopy
SFWST	The Spent Fuel Waste Science and Technology
SNL	Sandia National Laboratories
URL	Underground Research Laboratory
XRF	X-ray Fluorescence
µ-XRF	micron X-ray Fluorescence

I. Introduction

The Spent Fuel Waste Science and Technology (SFWST) campaign from the DOE Fuel Cycle and Technology (FCT) program has been engaging in international collaborations between repository R&D programs for nuclear waste disposal to leverage on the extensive research investigations and laboratory/field data of engineered barrier system (EBS) components (e.g., near-field) and characterization of transport phenomena in the host rock (e.g., far-field) processes from state-of-the-art underground research laboratories (URL) experiments. Thermal heating from radionuclide decay in the waste canisters will generate increases in temperature that will drive chemical and transport processes in the near- and far-field domains of the repository. URL sites provide the ideal setting to conduct heater test experiments to simulate the thermal effects of heat-generating nuclear waste in disposal galleries and surrounding host rock.

A brief description of the types of URL experiments according to the disposal design concepts of the host country repository program with relevance to EBS configurations and barrier materials of interest to the US program is given elsewhere (Birkholzer et al., 2016; Jové Colón et al., 2016). Current engagements include participation in in the FEBEX-DP collaboration which is a concerted effort of various international partners working on the evaluation of sensor data and *post-mortem* characterization of barrier materials obtained during heater dismantling. Such information is used in model development and validation implemented in computational tools to simulate coupled THM and THC coupled processes. The current phase of FEBEX-DP focuses on the dismantling of heater #2 (see Fig, 1) conducted during 2015 with the goal of disassembling all the remaining sections of the FEBEX "in situ test" after 18+ year of heating and sensor/probe data (García-Siñeriz et al., 2016; Martinez et al., 2016). This dismantling activity involves sampling of barrier bentonite, steel liner, sensors, embedded metallic components (e.g., metal coupons), and near-field sections with tracer components (see GTS website http://www.grimsel.com/gts-phase-v/febex/febex-i-introduction-).

In addition to investigations on EBS materials and interactions, extensive site characterization such as the Mizunami URL in Japan (Iwatsuki et al., 2005; Iwatsuki et al., 2015) in granitic host rock provides key hydrochemical monitoring data at various depths of the site. 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. Such facility-scale geochemical characterization is key to the study of short- and long-term effects of excavation activities in tunnels, impacts on groundwater flow and transport, and variability of groundwater chemistry with depth (Iwatsuki et al., 2015). This information is then used in models to support the safety and performance assessments of the repository environment within the post-closure period. The current phase of GREET is focused on the Closure Test Drift (CTD) hydrological and geochemical monitoring along with evaluation of the obtained data.

The main goal of this report section is:

- DECOVALEX Task C:
    - Provide a preliminary evaluation of the MSB-2 borehole hydrochemical data through a geochemical modeling approach. A simple water mixing model is used to simulate water titration scenarios to generate solution concentration profiles.
    - 1D Reactive transport modeling of cement – water interaction in the CTD to represent interaction between the CTD cement plug and the water-filled tunnel.
- FEBEX-DP:
    - Analysis of a FEBEX-DP bentonite sample using Multi-SEM (mSEM) analytical techniques. The mSEM technique is currently being tested on a cement – bentonite

sample to resolve secondary mineralization within small-scale features such as pores and cracks.
  - Expanded analysis of micro-XRF aSnalyses for elemental distribution at the interface region.

II. FEBEX-DP: Analysis of Micro-XRF (μ-XRF) Data of the Shotcrete-Bentonite Interface

The FEBEX-DP project currently entails the dismantling of heater #2 (see Fig. 1) performed during 2015 with the goal of carefully retrieving barrier material samples from the remaining sections of the FEBEX "in situ test" after 18+ year of heating which also includes sensor/probe data (García-Siñeriz et al., 2016; Martinez et al., 2016). This disassembling activity involves sampling of barrier bentonite, steel liner, sensors, embedded metallic components (e.g., metal coupons), and near-field sections with tracer components. The FEBEX bentonite is composed of 93% smectite with 2% quartz, 3% plagioclase, and 2% cristobalite plus minor accessory phases such as calcite and K-feldspar (Huertas et al., 2000; Missana and García-Gutiérrez, 2007). SEM/EDS analyses and micro-X-ray fluorescence (μ-XRF) conducted at Sandia National Laboratories on samples obtained from the FEBEX-DP phase include: 1) overcore sample from the shotcrete plug – bentonite interface, and samples from sections 49 and 58 (see Fig. 2) corresponding to spatial domains near and far from the heater zone, respectively. Fig. 3 shows the location for sample C-C-32-6 overcore (section 32) used in this characterization study.

This part of the report focuses on further evaluation of collected μ-XRF data of the shotcrete – bentonite interface. This data is in the form of elemental maps for Ca, S, Si, K, and Al. X-ray CT image analysis on epoxied overcore samples was described in Jové Colón et al. (2016) and will not be discussed here. Similarly, SEM/EDS characterization conducted on bentonite samples from Section 49 (samples BM-D-49-1,2,3) nearby the corroded steel mesh surrounding the heater revealed sparse Al-silicate grains rich in Fe. The extent of the corroded region into the bentonite is rather limited which might explain the relatively low level of Fe alteration in the bentonite. The main objective of this characterization study is to (1) identify spatial heterogeneities of barrier materials near and far from EBS interfaces that can inform process models (e.g., porous media transport), and (2) analyze the extent of chemical variations and heterogeneities (e.g., reaction fronts) at EBS interfaces and bulk barrier materials. An earlier analysis of the μ-XRF elemental maps was given in Jové Colón et al. (2016) based on preliminary evaluation of the data. Further analysis of these elemental maps has been conducted to generate line scan profiles which is the focus of this section.

II.A Discussion: μ-XRF Elemental Map Data

The extent of barrier alteration due interactions with fluids and other materials can affect porosity enhancement and reduction (i.e., clogging) of engineered barrier materials and associated interfaces. These interactions mainly involve mineral dissolution and precipitation along with transport which has been a topic of investigation particularly in the assessment of engineered barrier alteration in reactive-transport models (Marty et al., 2015; Wilson et al., 2015; Xie et al., 2015).

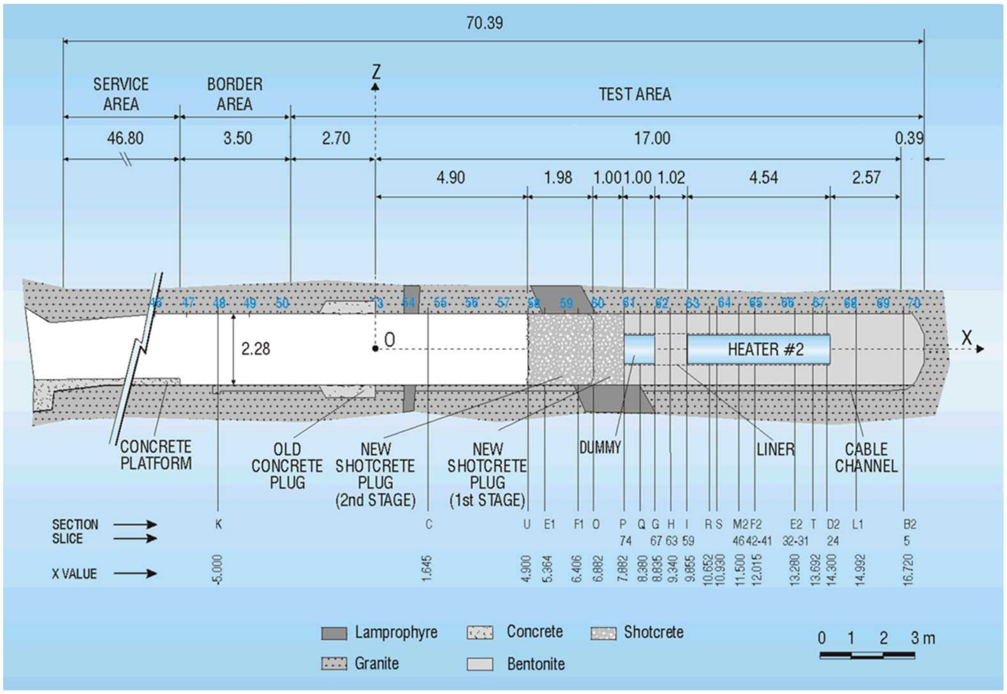


Figure 1. Schematic layout of the FEBEX "in-situ" field test after the first partial dismantling showing the configuration of heater #2 at the GTS URL (García-Siñeriz et al., 2016).

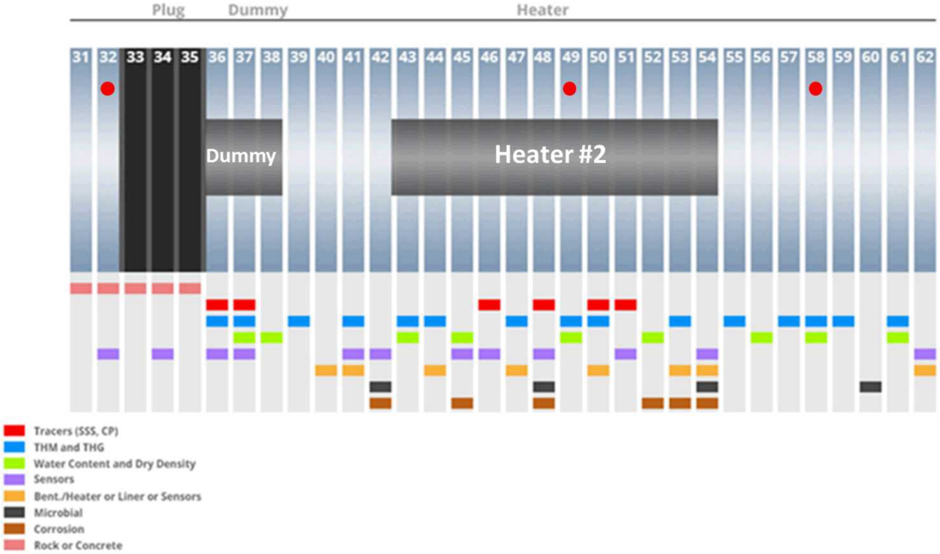


Figure 2. Schematic configuration of sampling zones (indicated by vertical light blue bars) for the FEBEX-DP project. Filled red circles indicate zones for samples obtained by Sandia National Laboratories (SNL). Source: FEBEX-DP website (members area): http://www.grimsel.com/gts-phase-vi/febex-dp/febex-dp-introduction.

For example, Wilson (2017) evaluated Fe-bentonite interactions as part of the FEBEX-DP project where observations of metal corrosion interactions with bentonite were evaluated through geochemical modeling. The swelling capacity in bentonite could be impacted by alteration to a non-swelling Fe-bearing phase. Likewise, interactions of shotcrete with clay rock could lead to clogging/sealing – a phenomena that has been observed as a result of cement carbonation (Gaboreau et al., 2012). However, these “clogged” zones have been described by the authors as heterogeneous along the interface and with varying levels of mineralogical alteration. With this in mind, SEM/EDS (or electron microprobe analysis – EMPA) and µ-XRF are excellent techniques to conduct spatial characterization of compositional heterogeneities at the shotcrete-bentonite interface and granular separates through elemental mapping, line scans, and spot analyses. Although the overall compositional characterization of solids is possible with SEM/EDS and µ-XRF, unequivocal identification of many phases is not possible at this time. Still, elemental profiles can describe the extent of alteration between dissimilar materials across their interfaces.

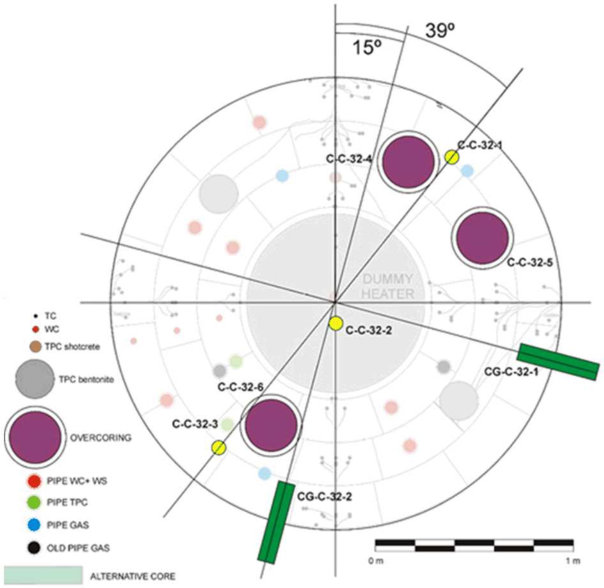
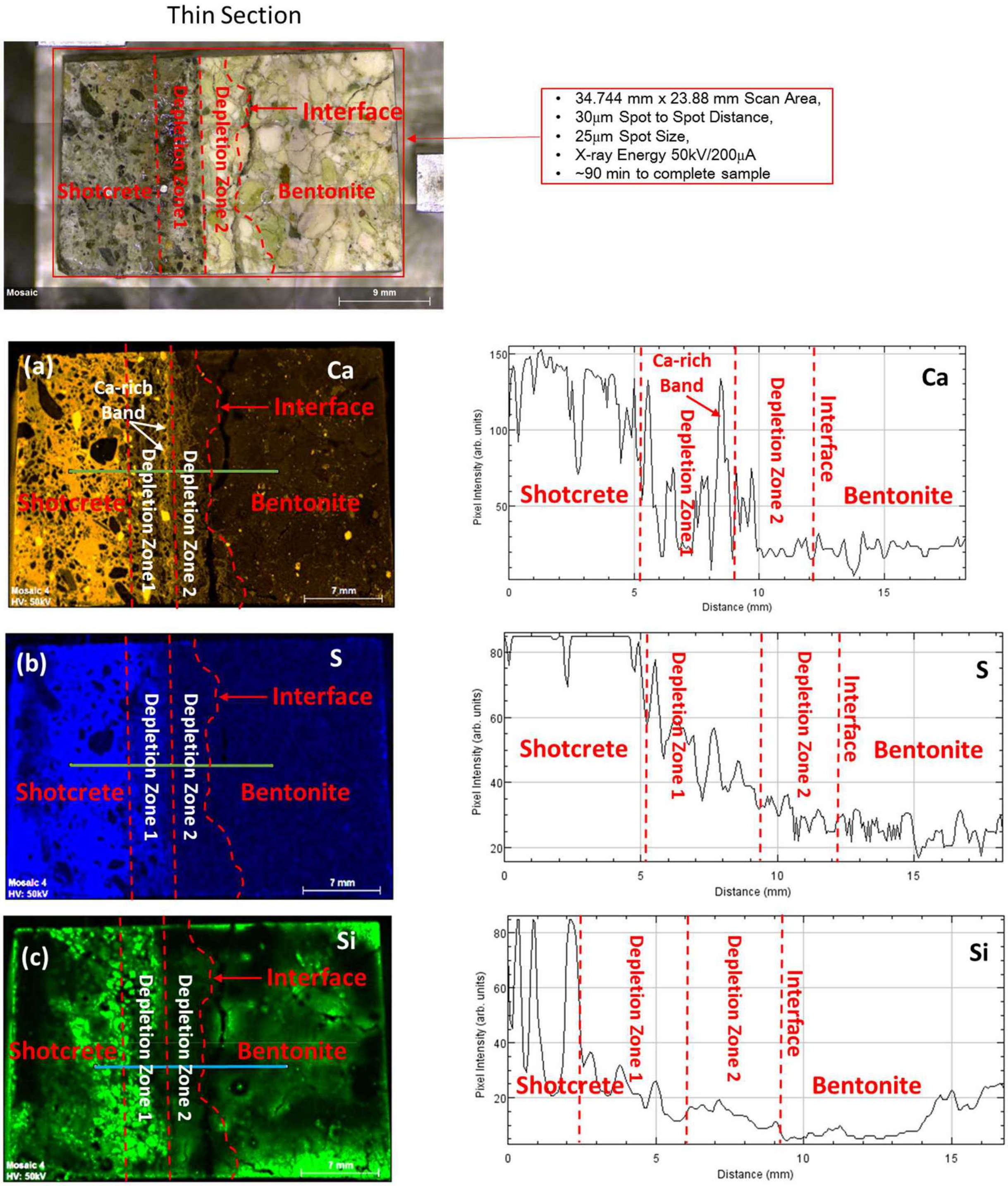


Figure 3. Schematic diagram of sampling locations of the shotcrete plug (C-C-32-6) for the FEBEX-DP dismantling section 32. See Fig. 2 for section location. (source: FEBEX-DP website (members area): http://www.grimsel.com/gts-phase-vi/febex-dp/febex-dp-introduction.)

As shown by Jové Colón et al. (2016), BSEI and an EDS analyses through SEM of the shotcrete-bentonite interface show a rather heterogeneous granular texture of the shotcrete with angular grains having a fairly wide size range embedded in a fine-grained matrix. The bentonite region shows cracks resembling the craquelure pattern observed in the CT imaging analysis along with some minor accessory grains. Although line scans an SEM/EDS X-ray maps are powerful probing tools for elemental distributions, the domain size can be rather small and compositional changes in the scale of millimeters to even centimeters can be difficult to assess. Therefore, µ-XRF analysis is being used to characterize compositional features of this interfacial domain at the thin section scale.

Ca and Si are ubiquitous component in many of both FEBEX bentonite and shotcrete phases and their overall distribution should serve as an indicator of alteration at the interface as shown in Fig. 4 (Jové Colón et al., 2016). EDS X-ray maps and line scans indicate the absence of pervasive alteration or mineralization in the analyzed interface regions. Similarly, analysis of textures using BSEI and EDS at the micron level also indicates little or no alteration along the interface. However, this micron level characterization is confined to a small area limiting the assessment of compositional trends from the bulk phases towards the interface. For this reason, compositional analysis using µ-XRF were conducted on the same polished thin section used in the SEM/BSEI/EDS analyses. µ-XRF has the advantage of minimal sample preparation and scanning sample areas from mm^2 to cm^2 at a high spatial resolution for a large suite of elements. This technique is more flexible and better suited for the specimen sizes collected from the dismantling phase activities where other microscopic techniques (e.g., SEM/EDS), although useful, would otherwise be much more laborious. The analyses were performed using a Bruker M4 Tornado µ-XRF mapping system. The instrument was equipped with a micro-focused Rh source (50 kV, 600 µA) with a poly-capillary optic (~30 µm spot-size). The detector system employed a silicon-drift detector to collect fluorescence spectra from the specimen. The specimen was secured to the x-y translation stage within the M4 chamber, and XRF spectra were collected under vacuum conditions (~10^{-3} Torr). The XRF-mapping dataset for the thin-section specimen was collected as a large datacube with full X-ray spectra (4096 channels, 0 to 40 keV range) collected at each pixel in a 2D array. The step-size employed for the micro-XRF spatial map was 50 µm. This resulted in a 502 × 860 matrix for the map which covered an area ~24 × ~35 mm^2, thus incorporating the entire cross-sectioned specimen. Total data collection time was ~90 minutes. The dimensionally of the datacube (502 × 860 × 4096) was greater than 1.7 billion elements, and encompassed a file size of 747 MB. Elemental maps for individual atomic species were generated within the M4 software package. Micro-XRF maps were generated for the elements Ca, Al, Si, K, Fe, S, Cl, Cu, Mn, Pd, Zn, Zr, and Ti. Image analyses and generation of line scan profiles were performed using the ImageJ/Fiji software package (http://imagej.net/Fiji; http://fiji.sc/).

Fig. 4 shows µ-XRF maps for Ca, Si, and S indicating little or virtually no alteration in the bentonite side. This observation is consistent with the SEM/EDS X-ray map analyses described previously. These compositional maps also suggest the existence of an apparent millimeter-scale depletion zones in shotcrete towards the bentonite interface. Jové Colón et al. (2016) described this as a depletion zone indicated by the gradation of pixel intensities in the image map from the bulk shotcrete towards the bentonite interface. Further evaluation of this image maps through the generation of line scans indicate the appearance of two regions within this depletion zone confined mainly to the shotcrete side. The region labeled “Depletion Zone 1” represents the beginning of sharp decrease in the shotcrete component roughly. “Depletion Zone 2” outlines the depleted region approaching a more stable behavior. The separation of regions in this depleted zone in shotcrete as it approaches the bentonite interface is somewhat arbitrary but it demonstrates the stabilization of elemental gradients down to a scale of a few millimeters. Similar to SEM/EDS observations, depletion zone doesn’t appear to traverse the bentonite side suggesting a reaction zone confined mainly to the shotcrete side. The line scans also display the magnitude of the rather heterogeneous elemental profile for both shotcrete and bentonite. For example, Ca and Si line scan profiles can vary extensively (dips and rises) in shotcrete making the data look rather noisy. This is probably due to the aggregated and/or composite nature of concrete or the presence of polishing artifacts (e.g., gaps, holes) in the making of the thin section. The profile for S whose source is mainly shotcrete show similar levels of variation towards the interface. No S-rich phases were detected at the interface. Ca in the bulk shotcrete can vary extensively based on multiple line scan transects but a common feature is the appearance of a thin Ca-rich band within “Depletion Zone 1”. This feature was presumably observed in the SEM/EDS analysis line scans. The origin of such feature is not known but it could be hypothesized as leached out material from shotcrete, maybe during emplacement. No other element profiles exhibit such enrichment in this narrow region or any correlation within the variability of the data. Si displays the largest variation in the bulk but the depletions zones show similar behavior as the other elements. Multiple line scan transects across the sample yield similar variation for Si in the bulk and depletion zones noting an increase in the bentonite side, close to the interface and towards the bulk phase. The behavior of Si suggests more Si transport at the interface even when solid precipitation is not discerned from the data. The extent of the depletion zone is small, on the order of 7-8 mm. More information needs to be gathered from the bulk phase domains to better assess component variability within and away from the interface which would be the next step in this investigation.



- 34.744 mm x 23.88 mm Scan Area,
- 30µm Spot to Spot Distance,
- 25µm Spot Size,
- X-ray Energy 50kV/200µA
- ~90 min to complete sample

Figure 4. µ-XRF maps for Ca, S, and Si at the shotcrete-bentonite interface – panels (a), (b), and (c), respectively. Apparent depletion zones 1 and 2 close to the shotcrete-bentonite interface are delineated by red-dashed lines. Horizontal lines (green in (a) and (b); blue in (c)) are the line scan transects for each elemental map shown on the right. “Depletion Zone 1” shows the inception of a sharp element depletion whereas “Depletion Zone 2” trends towards a more stable behavior.

Towards this goal, the MultiSEM or mSEM technique has been has been explored for the fast acquisition of high resolution SEM/EDS/BSEI information from length scales ranging from nanometers to micrometers. mSEM is essentially an SEM with 61 parallel electron beams allowing for remarkably fast data acquisition at a high level resolution. The analyses were performed using a Zeiss MultiSEM 505 scanning electron microscope. The sample surface was ion milled using a broad beam setup. Multiple scans across the interfacial and bulk regions revealed various features previously identified using standard SEM for a similar sample from the same core. Porous structures were identified in shotcrete near the interface with bentonite showing newly-formed euhedral solids with a blocky morphology (Fig. 5). This Mg-rich phase appears to be growing from the pore walls towards the center. Mg is a common component on the shotcrete fine-grained matrix and appears to be transported throughout the interface. The blocky fillings could be an example of pore clogging in association with carbonate material. However, it's difficult to determine if the pore filling precipitation occurred before, during, or after the shotcrete emplacement. Comparisons with the EDS Ca map and crystal morphology within the pore suggests mineral precipitation after shotcrete emplacement. The identity of the phase is unknown but its composition (Mg, C, O) and morphology are indicative of Mg-carbonate (magnesite?). Carbonate-rich zones are common throughout this domain suggesting possible shotcrete carbonation as a result of high pH reactions along with CO_2 uptake. Plans for future analyses will target more of the pore filling mineralization and bulk phase analyses away from the shotcrete/bentonite interface.

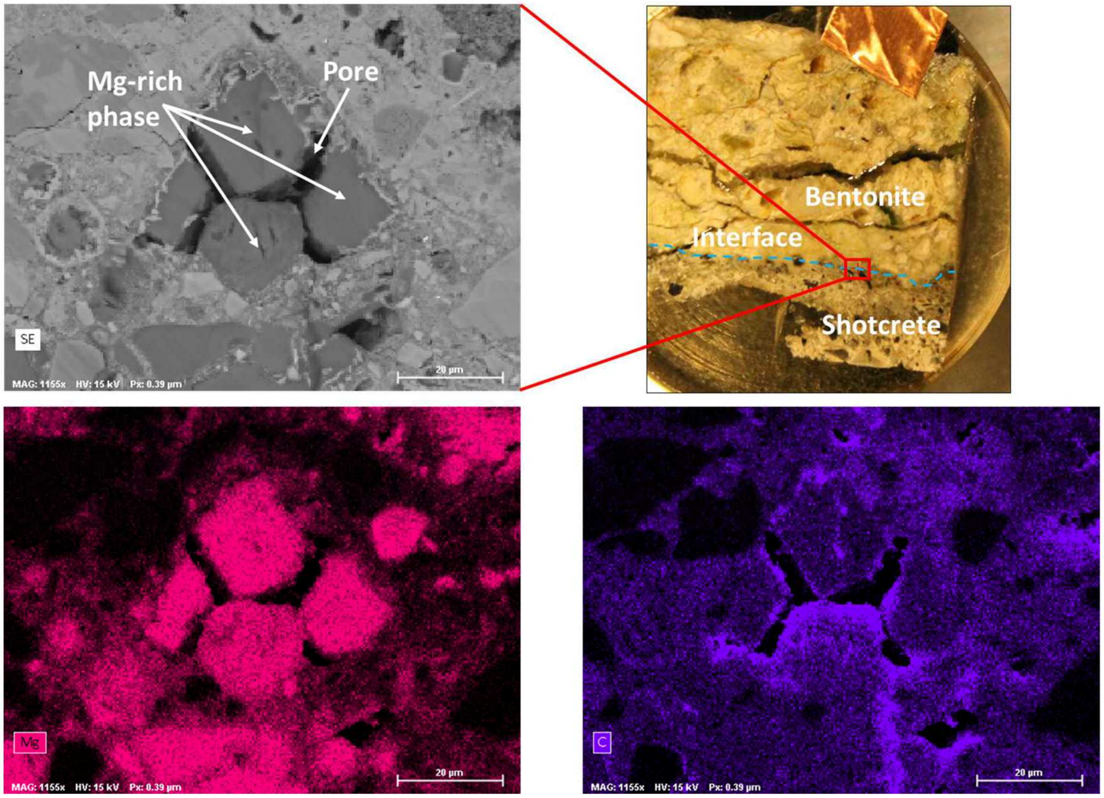


Figure 5. mSEM micrograph, optical photograph, and EDS element maps for Mg and C collected near the interface region. Texture and solid phase compositions indicate this analyzed region is mainly shotcrete. The interface location is approximated by the blue line shown in the optical photograph.

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

The DECOVALEX-2019 project phase started this year with seven tasks (A-G) targeting various THMC issues based on experimental and URL field data. 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. A series of boreholes allow for monitoring water pressure and chemistry during the experiment. The goals of the GREET project as defined by the JAEA website are (http://www.jaea.go.jp/04/tono/miu/dataset/greet/greet.html):

- "To understand the recovery process and mechanism of geological environment during facility closure.
- To verify the HMCB simulation methodology for recovery process in fractured granite.
- To develop the monitoring technique for facility closure phase and the appropriate closure method taking recovery process into account."

The focus of GREET within the DECOVALEX-2019 project is to "develop the simulation procedure and technique to estimate the post closure environments in fractured media (asymmetric media)". Within this focus, an initial evaluation of groundwater chemistry data from a monitoring borehole (MSB2) currently available has been conducted to assess data quality and trends by conducting speciation calculations using geochemical code tools and databases. Also, a 1D reactive-transport model has been developed to study the interaction between the cement plug at the CTD and the flooded tunnel to assess the effects of high pH waters as a result of interactions with cementitious materials. Such interactions in a flooded zone can impact chemical gradients in the host rock pore solution and neighboring groundwater monitoring boreholes. The GREET project task leader has kindly provided access to geochemical and hydrological data to be reviewed by the participants which has stimulated good communications exchanges. 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).

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. 6 (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 (1-9; see Figs. 6 and 7) 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.

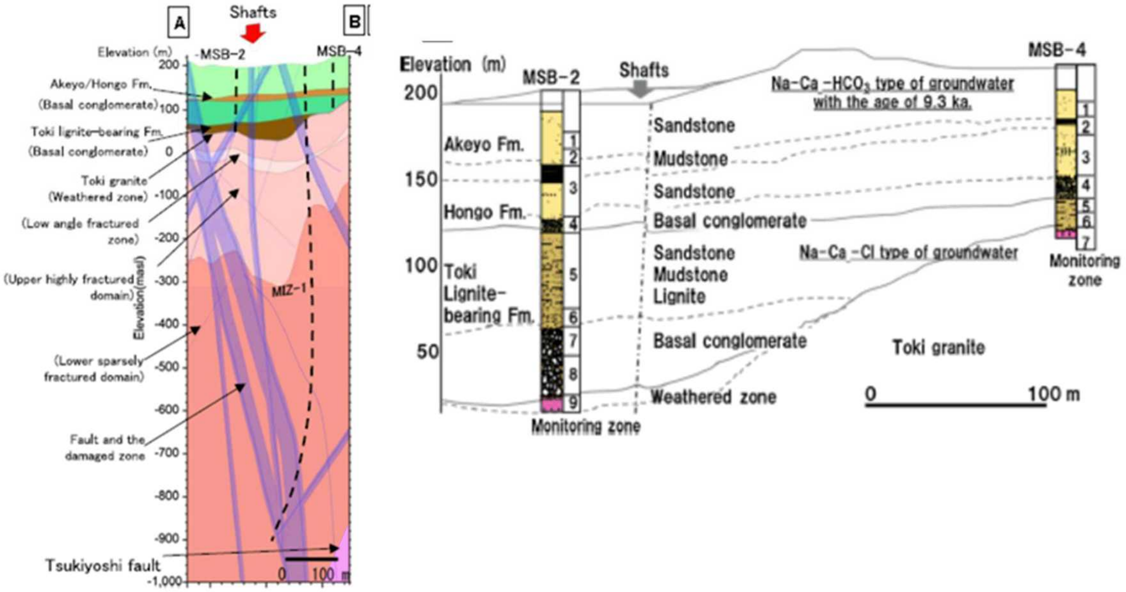


Figure 6. Generalized geologic and stratigraphic description of the the Mizunami URL site, Japan (Iwatsuki et al., 2015). Borehole MSB-2 shows the vertical monitoring zone sequence (1 through 9).

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. 7 the different levels of Ca^{++} concentrations between zones but with progressive dilution particularly for zones MSB-1, MSB-8, and MSB-9. Figs. 8 and 9 shows a comparison of Ca^{++} and SO_4^{--}concentration 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.

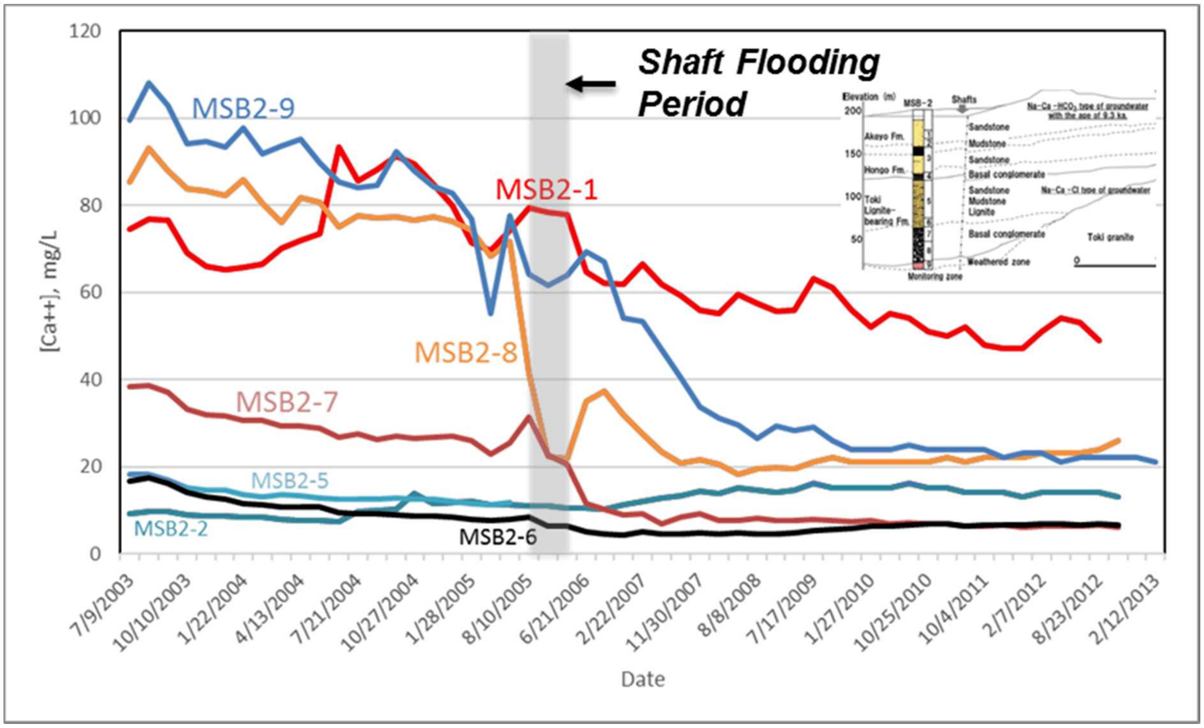


Figure 7. Ca concentration profiles with monitoring time for the sampling zones (1 through 9) in borehole MSB-2. Vertical gray band represents the shaft flooding period.

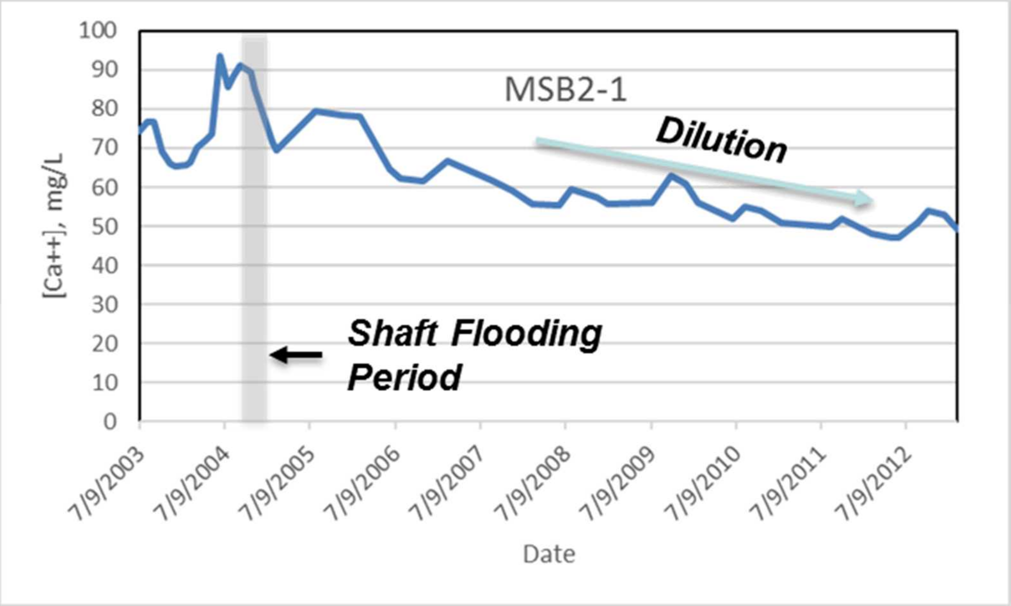


Figure 8. Ca concentration profiles with monitoring time for zone 1 in borehole MSB-2.

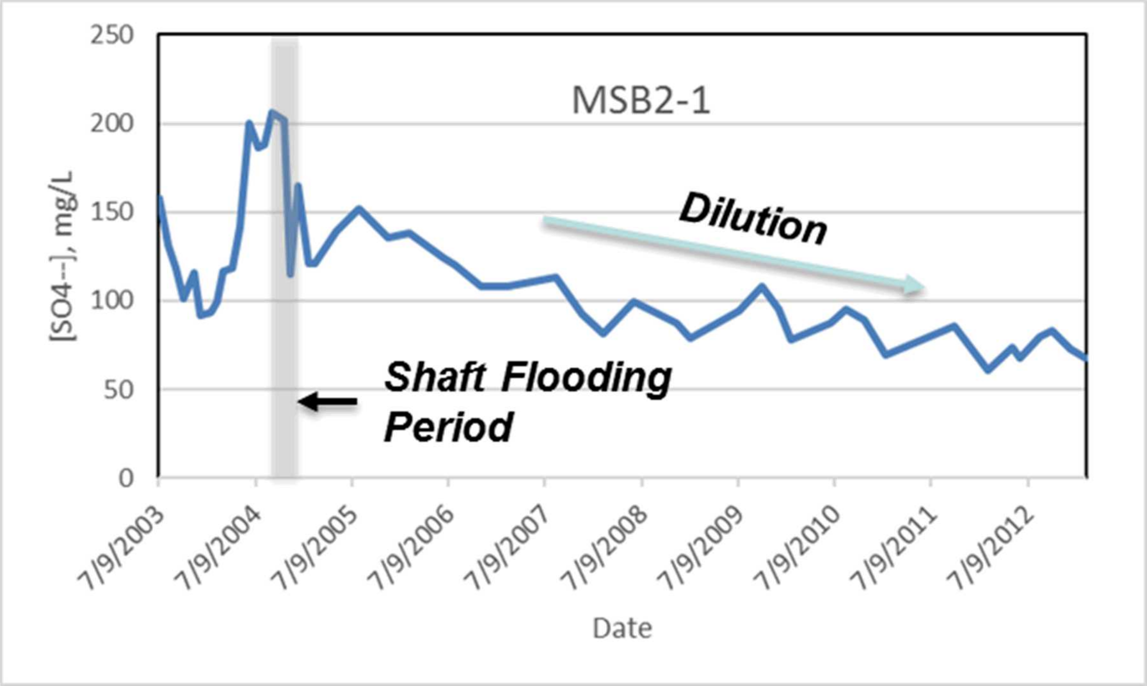


Figure 9. SO_4 concentration profiles with monitoring time for zone 1 in borehole MSB-2.

The results of the groundwater mixing simulation in EQ3/6 is depicted in Fig. 10 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 Miizunami site, it provides the opportunity to evaluate the effects of hydrological and chemical disruption due to excavation and site construction activities. The next step will be to apply this to compositional data of groundwaters collected in horizontal boreholes within the galleries. Iwatsuki et al. (2015) observed variations in water chemistry sampled at the galleries where they suggested the influence of mixing between water with different levels of salinity.

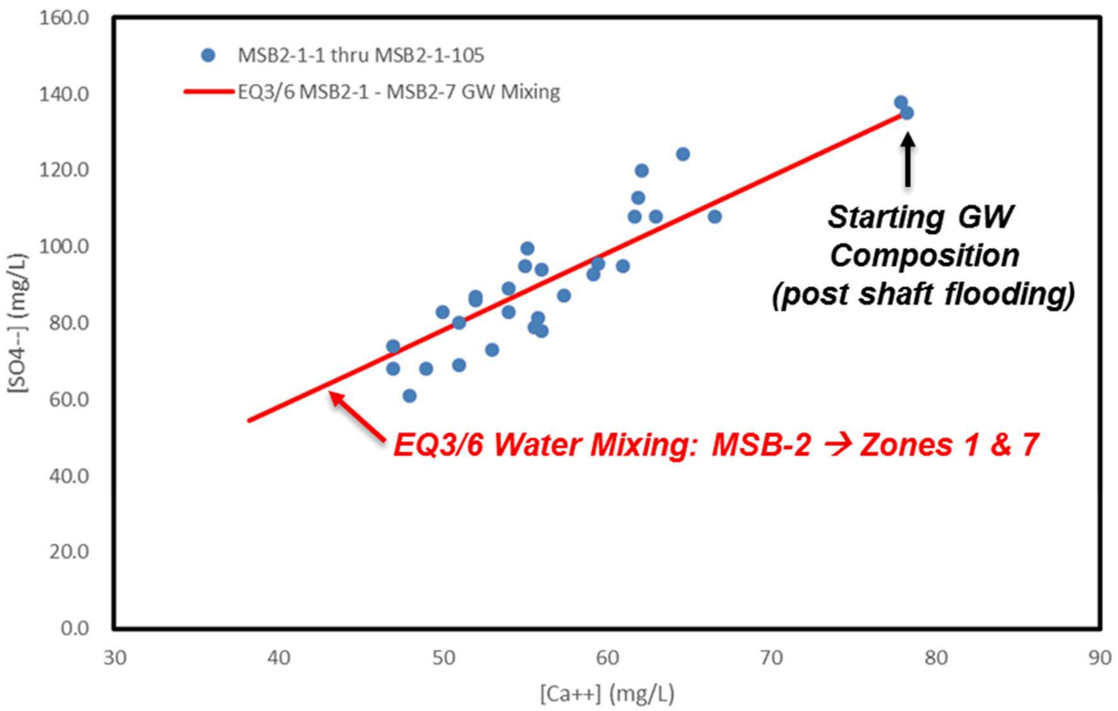


Figure 10. Comparison of predicted and observed Ca and SO_4 concentration profiles for a mixing scenario between for zone 1 and zone 7 groundwaters in borehole MSB-2 (see text).

Closure Test Drift (CTD): H-C Model

The Closure Test Drift (CTD) is a tunnel facility (Fig.11) at 500 meters below ground level to investigate the effects of hydrological, geomechanical, and geochemical variations during drift excavation and closure in fractured granitic rock. The facility is equipped with monitoring probes for water sampling, hydraulic pressure, rock displacement, and mapping of drift fractures. The CTD tunnel is lined with Ordinary Portland Cement (OPC) shotcrete and is sealed by using a low-heat Portland cement plug (Iwatsuki et al., 2017). After closing, the tunnel was filled with water to study environmental changes including effects on hydrochemistry due to interactions with barrier materials such as shotcrete. Similar to 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 transport and clay barrier sorption properties.

A 1-D reactive transport model (Fig. 12) has been developed to mimic the conditions between the cement plug and water-filled tunnel. The goal is to have a relatively simple model to characterize the extent of alkaline or high pH effects with distance from the cement-water interface. Such interactions in the water-filled zone may influence pore solution chemistry in the nearby monitoring borehole (12MI33) where fractures in the excavated disturbed zone (EDZ) can be pervasive throughout the length of the CTD. Moreover, pH measurements in the monitoring borehole 12MI33 show elevated values suggesting the influence cementitious material in the sampled pore solution.

The 1D reactive reactive-transport model in PFLOTRAN is similar to that developed previously in the 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 (diffusivity constant = 1.0×10^{-9} m^2/s).

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). 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 46.5 m with a height of 5 m closely resembling the CTD dimensions. The cement plug thickness is 2 m. The 1D domain is discretized into 970 cells. The flooded domain is represented by a porous medium having a porosity of almost unity and a very high permeability. The pore solution in the cement phase The simulations were performed for a time period of 10 years.

The results are shown Fig. 13 in the form of selected solution concentration profiles for pH, H_4SiO_4(aq), Ca^{++}, and SO_4^{--} as a function of time and distance from the interface (0, 0.3 m, and 1 m). As expected, the pH near the interface is pH~12.5 due to the equilibria with the cementitious material. With distance from the interface into the water-filled CTD region, pH increases with time as expected even at a distance of about a meter. H_4SiO_4(aq) concentration near the interface decreases rapidly due to leaching and mixing with a highly depleted water. However, its concentration increases slightly with distance from the interface. Similarly, near the interface, SO_4^{--} concentration increases at early times but then decreases within about a year of simulation time. Like H_4SiO_4(aq), SO_4^{--} concentration increases with time further away from the interface. Ca^{++} concentration also experiences a similar behavior near the interface showing a rapid increase at early times. The rapid increase in these solutes is interpreted as pore solution equilibration with cement, dissolution cementitious phases, and pore solution interaction with a relatively dilute groundwater. These processes result in cement leaching inducement along with transport away from the cement interface. Ca^{++} concentration remain relatively constant throughout the simulation period (unlike H_4SiO_4(aq) and SO_4^{--}) due to the predominance of Ca-bearing cementitious phases during dissolution. This also explains the higher increases in Ca^{++} concentration with distance from the interface.

The observed cement leaching behavior in this simple 1D model provides key observations for barrier material interactions in a water-filled tunnel and outlines the importance of solute transport even for the bounding case of diffusion. A monitoring borehole located within the fractured granite rock (e.g., 12MI33) but at some distance from the CTD will likely experience some of the effects of groundwater interaction with barrier materials such as cements. This assumes of course the likelihood of some level of communication between the groundwater in the CTD and that of the bounding host rock. Depending on the EBS design concept (e.g., shotcreted drift walls), this reactive transport analysis can explain variations in groundwater chemistry within monitoring zones, particularly for crystalline fractured rock. The extent of these effects will be investigated in conjunction with the crystalline work package team in this Task C with the application of fracture models to describe hydrologic conditions at this site and excavation effects. The goal is to add chemistry to this hydrological model and then compare monitored solute concentrations at the site with model results. Solutes like Cl are often used as tracers which is very useful in constraining key hydrologic transport parameters. Work is planned to use tracer data from the site to evaluate the effects of excavation activities on host rock hydraulic behavior.

The importance of high pH in groundwater as a result of interactions with cementitious barrier materials is on its effect on silicate solubility and sorption properties of clay barrier material. Moreover, the behavior of high pH interactions in the EDZ for the case of fractured crystalline host rock deserves further investigation given the availability for fast pathways into the disposal galleries. Shaft flooding episodes at the Mizunami URL are indicative of relatively rapid water mixing between different levels of the granitic host rock and the overlying sedimentary units. Therefore, the likelihood of barrier material interactions with circulating groundwaters is high, thus strongly influencing the potential for radionuclide transport in this type of deep geologic repository setting.

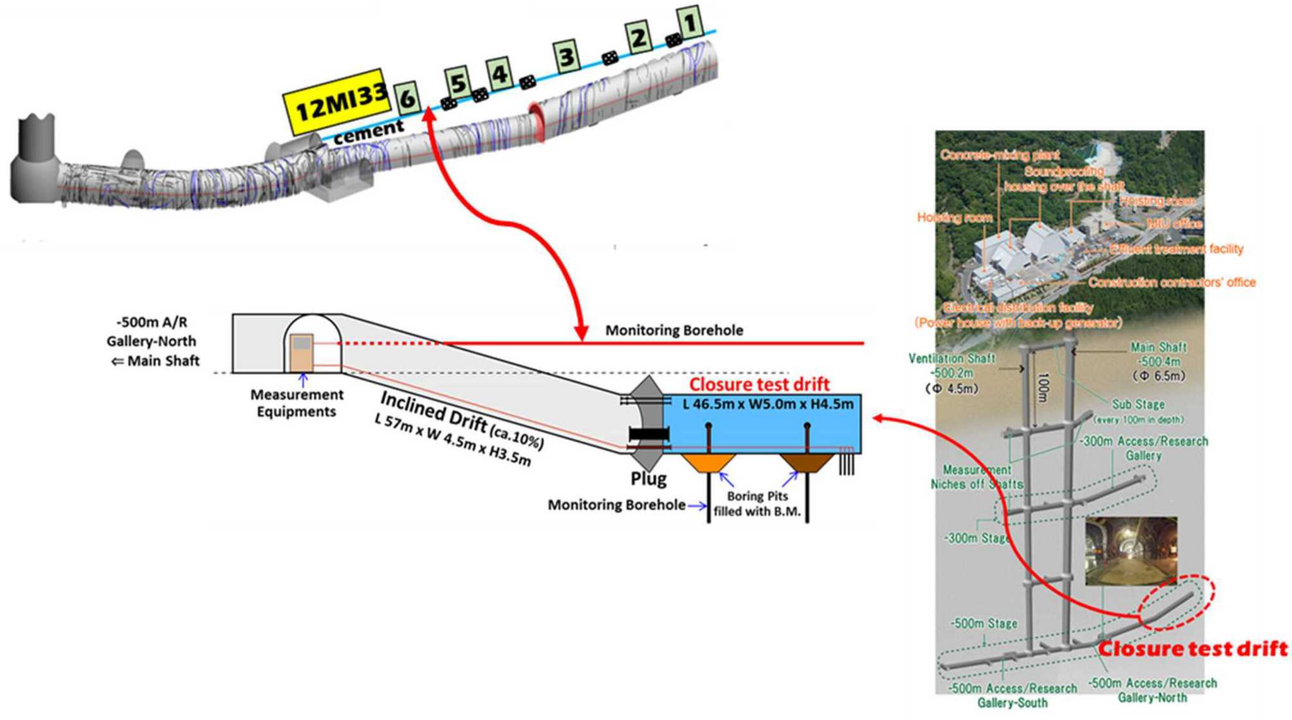


Figure 11. Diagrammatic picture of the closure test drift (CTD) at the Mizunami URL site, Japan. Upper schematic picture shows the inclined tunnel with CTD and the 12MI33 monitoring borehole. Figure content kindly provided by Dr. Teruki Iwatsuki (JAEA).

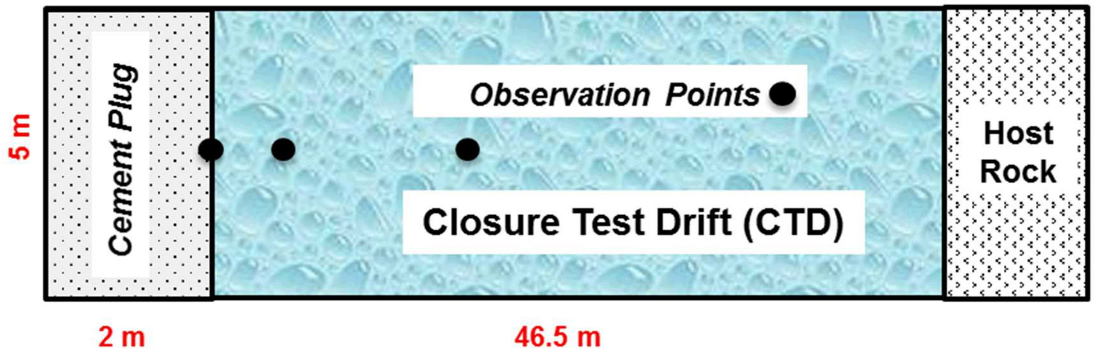


Figure 12. Schematic figure showing the 1D model domain considered in the PFLOTRAN reactive transport simulation of the CTD. Observation points are positioned near the cement plug to evaluate the effect of cement interactions in the water-filled domain (see text).

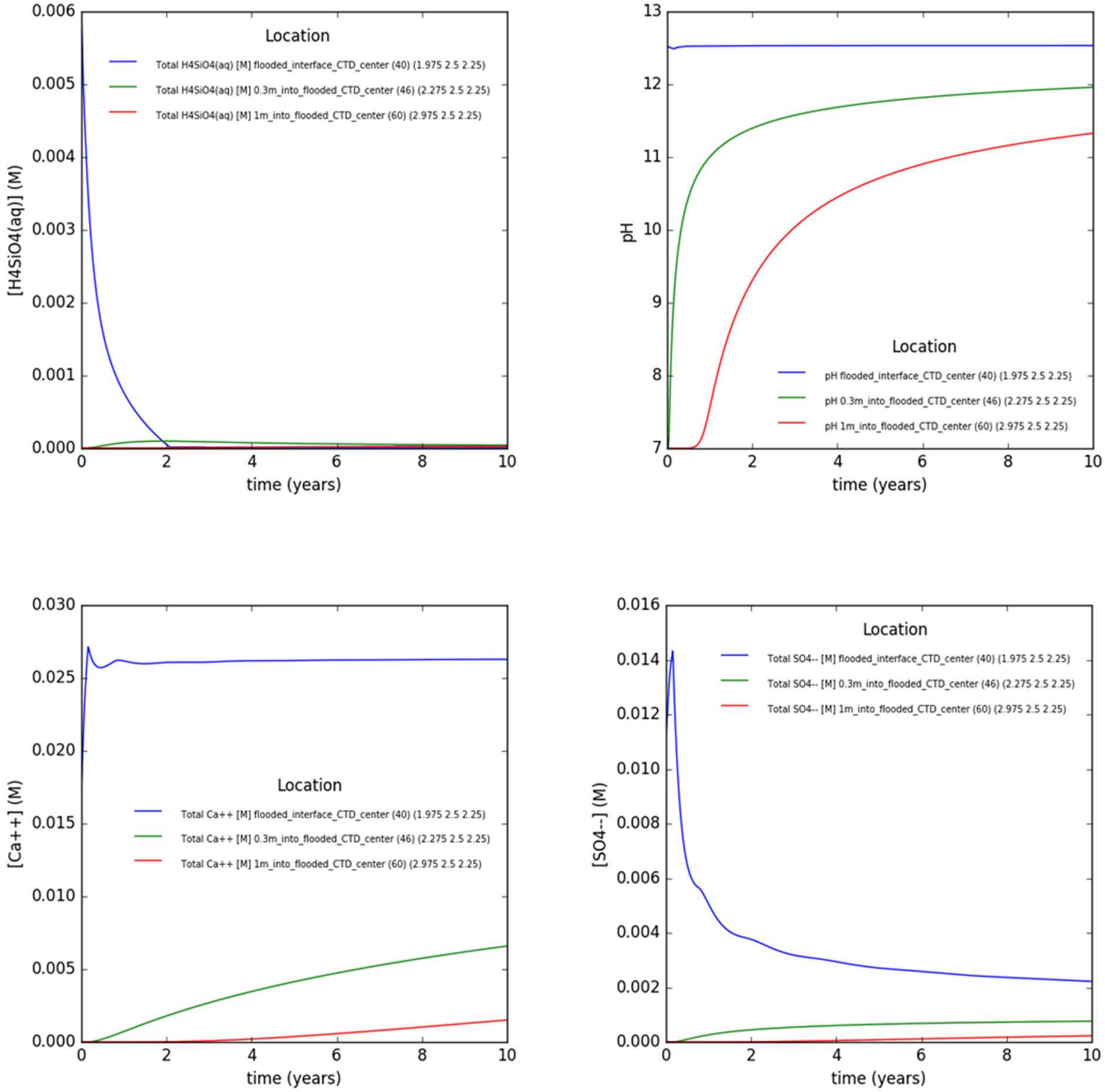


Figure 13. Solute concentration profiles from the 1D PFLOTRAN simulation results for pH, H_4SiO_4(aq), Ca^{++}, and SO_4^{--} as a function of time and distance from the interface (0, 0.3 m, and 1 m – see text).

V. Conclusions

- Analysis of elemental line scan profiles retrieved from μ-XRF data collected for the FEBEX-DP bentonite-shotcrete overcore sample suggests the extent of depletion zones between the bulk domains to be on the order of 7-8 mm. These elemental line scans also suggest Ca leaching with some level of accumulation in the interface region as Ca-rich bands. These Ca-rich zones were previously observed using SEM/EDS analysis but were better resolved at thin-section scale using μ-XRF data.
- SEM/EDS analyses still support the idea that much of the alteration appears to be confined mainly to the shotcrete region. mSEM/EDS analyses revealed the formation of Mg-rich phases with carbonate within pores suggesting pore clogging and secondary mineralization near the shotcrete-bentonite interface. However, it's difficult to discern the timing for such mineralization and appears to be localized in the "shotcrete-rich" region where Mg in the cement matrix is more abundant. The presence of carbonate-rich zones is indicative of cement carbonation but such observation is still preliminary needing further analysis of the sample.
- DECOVALEX-2019 Task C of GREET Experiment: Geochemical modeling has been 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 has been evaluated through 1D reactive-transport modeling for a water-filled tunnel scenario. Solute concentration profiles relative to locations from the cement interface as a function of time describe the progression of the cement leaching as a result of pore solution equilibration with cementitious material along with dissolution and transport away from the cement plug interface. This work serves as a preamble to scope the extent of high pH zones in the CTD in support of future HC transport models to describe the influence of cement-water interactions in the host rock groundwater chemistry.

VI. FY18 Work

Planned work on **FEBEX-DP** samples for FY18 (and the remainder of FY17):

- Extend mSEM/EDS analysis focusing on the pore-clogging and secondary mineral precipitation in the bentonite/cement interface region. This includes the distribution of carbonate and Mg-bearing phases. Expand compositional characterization into the bulk bentonite and cement regions from the FEBEX-DP sample collection.
- In addition to the above, further phase characterization of bentonite from the heated zone towards wall rock. Past observations suggest limited C-steel/clay interactions close to the heater zone. Phase properties between bentonite samples far and close to the heater should be investigated.
- Reactive-transport work on DECOVALEX-2019 Task C (GREET) will be integrated with hydrological simulations in fractured rock conducted with the crystalline work package team. That is, looking a tracer transport and adding chemistry to the hydrology model evaluating the effect of the CTD excavation at the Mizunami URL site in Japan.

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