SAND2017-5457PE

Spent Fuel and Waste Science and Technology

SFWST – Disposal in Argillite R&D

Barrier Material Degradation and Interactions

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SFWST Campaign – Working Group Meeting

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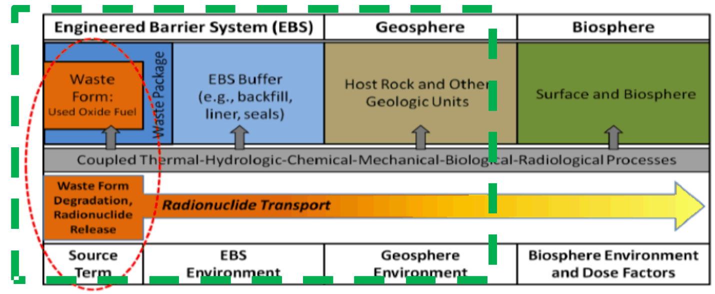
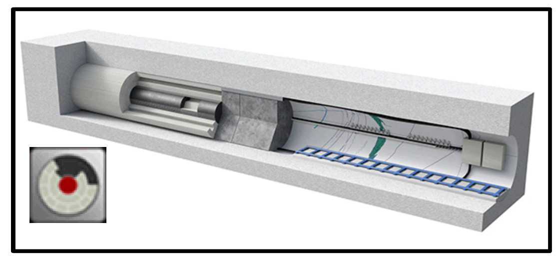
Argillite Disposal R&D

- **Reactive-transport modeling (THC) with decay heat effects**
- **Engineered barrier system (EBS) model integration with performance assessment (PA)**
- **Thermodynamic modeling of barrier material interactions (clay, cement, metal) and thermodynamic database (TDB) development**
- **Clay interaction experiments:**
  - **High temperature mineral phase stability, clay – metal interactions (waste package material (steel, Cu) corrosion)**
  - **Low-T RN sorption/diffusion in bentonite & modeling**
- **High temperature coupled thermal-hydrological-mechanical-chemical (THMC) modeling**
- **Spent fuel matrix degradation model development**
- **International collaborations: FEBEX-DP (GRIMSEL URL), DECOVALEX19, SKB EBS Task Force, Mont Terri/Bure URLs (France)**

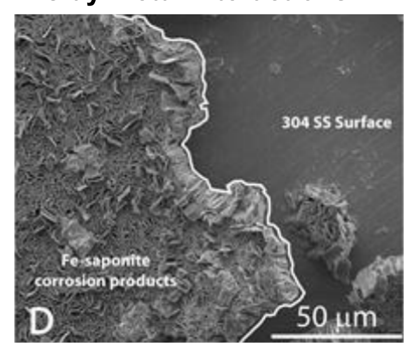
GDSA PA Level Of Integration



International Collaboration: FEBEX-DP



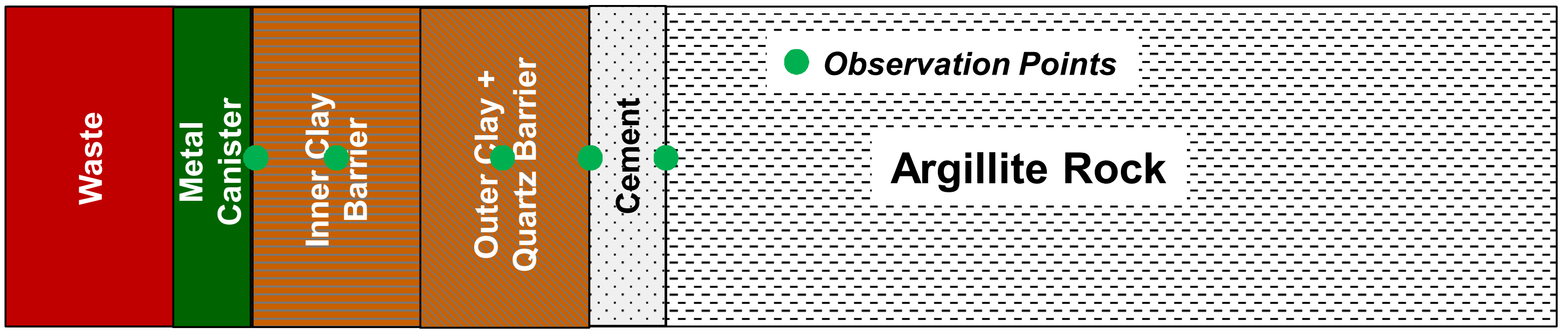
Clay-Metal Interactions



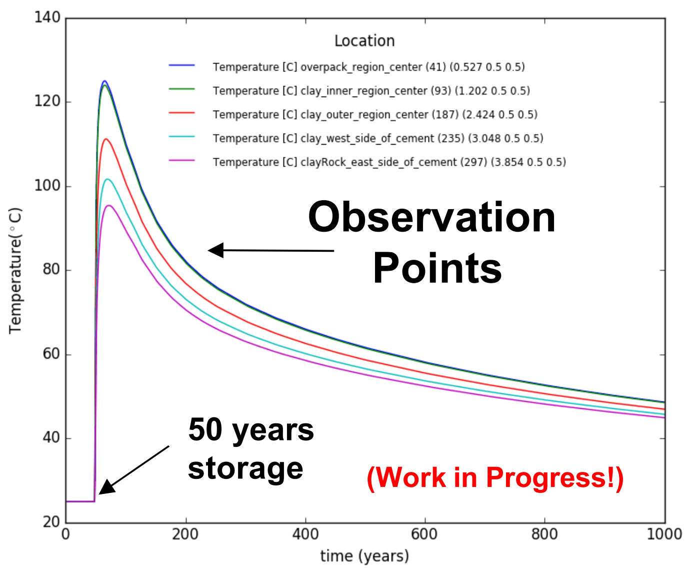
Steel Corrosion

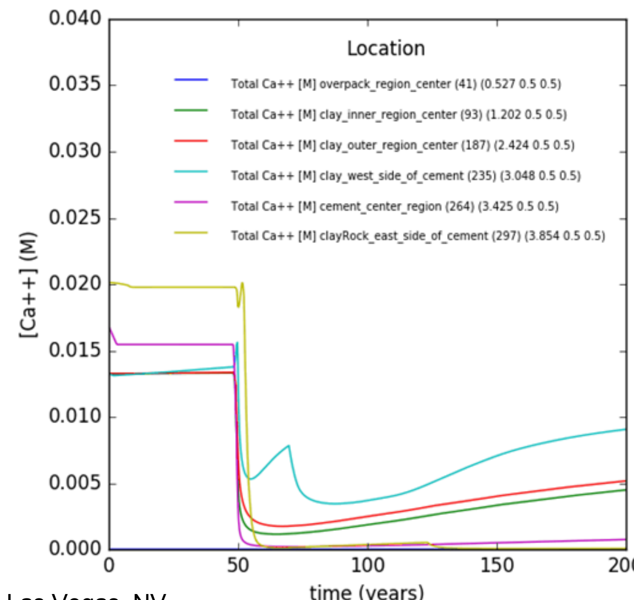
1D Reactive Transport of Layered EBS: Integration with GDSA-PA

PFLOTRAN 1D Reactive Transport Modeling

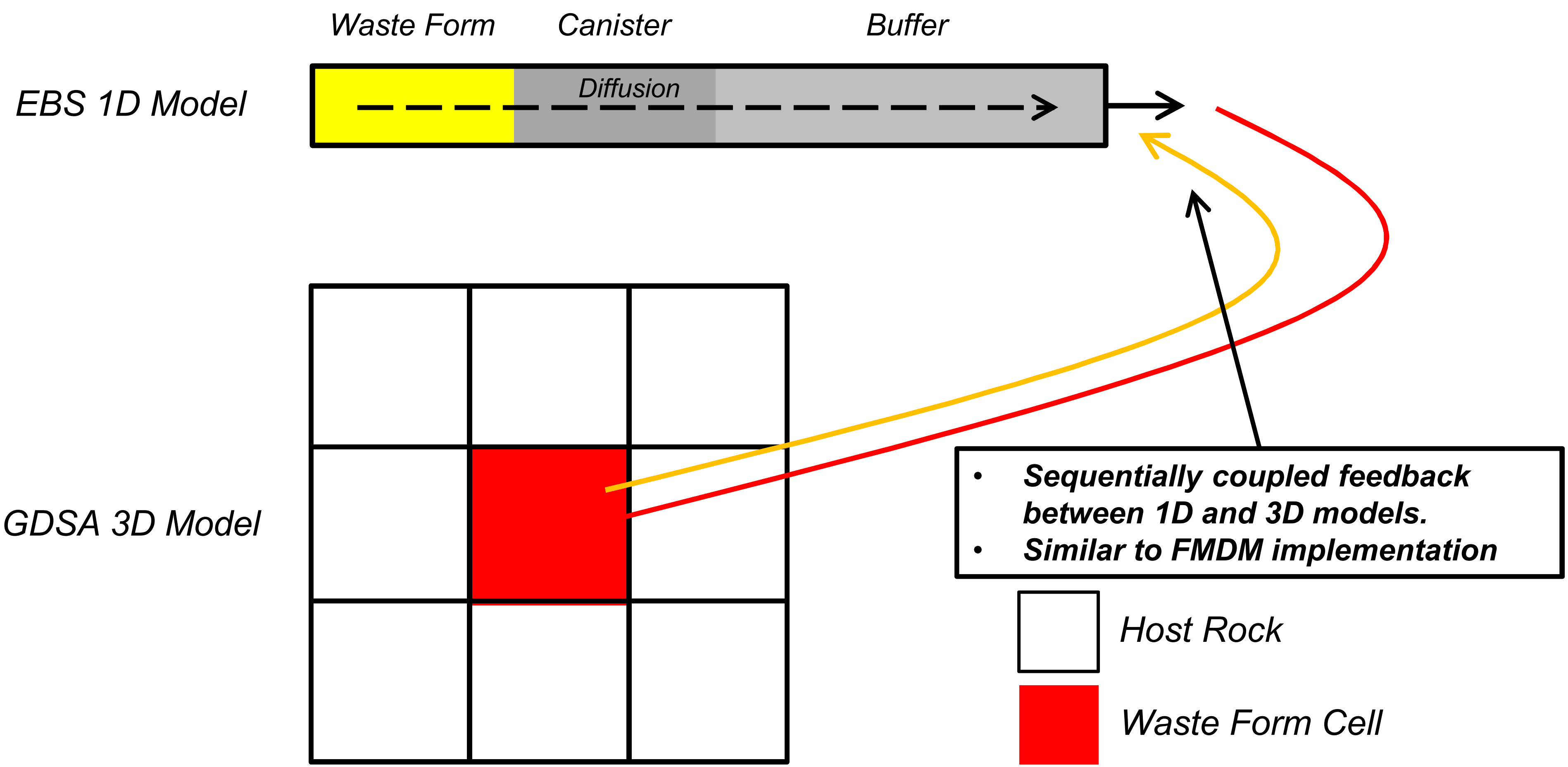


0.475 m 0.1 m 1.24 m 1.24 m 0.75 m >>10 m (RED Font: Domains Considered)



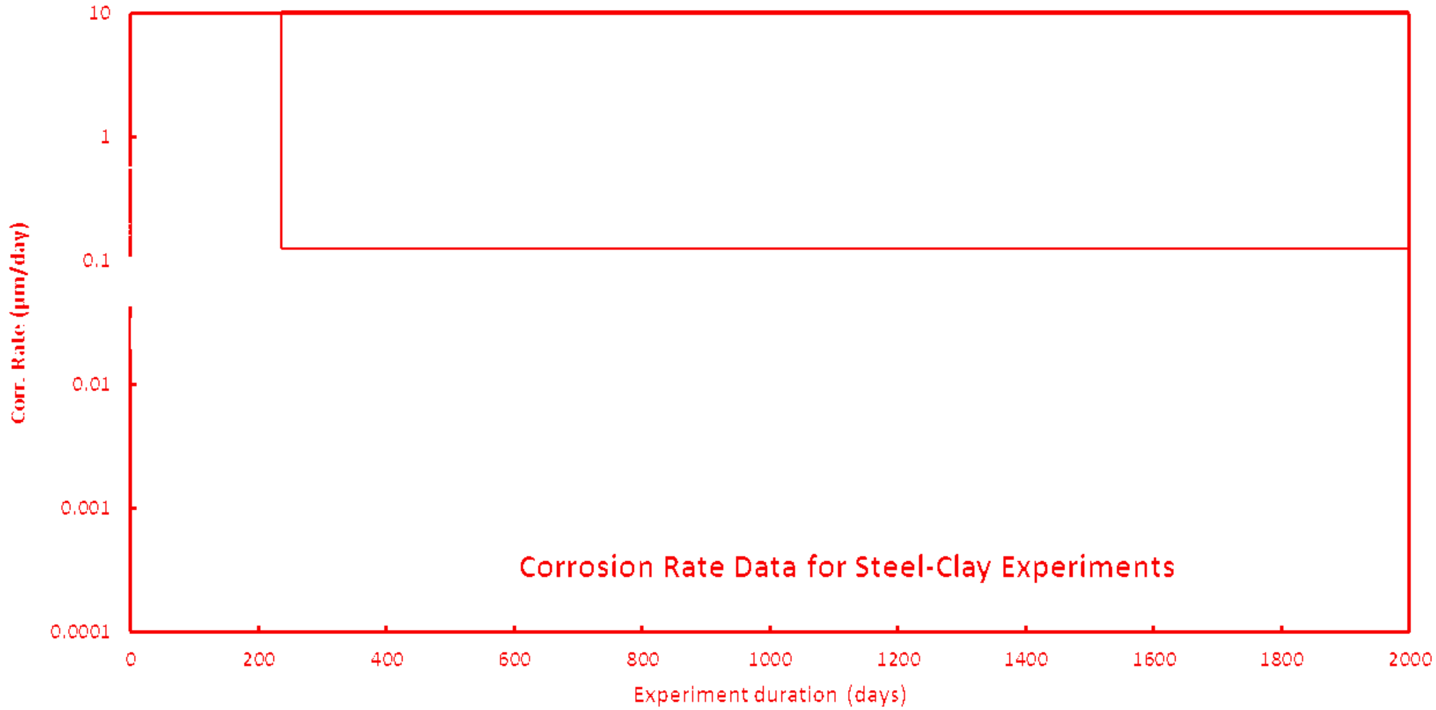


1D Waste Form-Canister-Buffer Model as Loosely Coupled Source Term within 3D Model



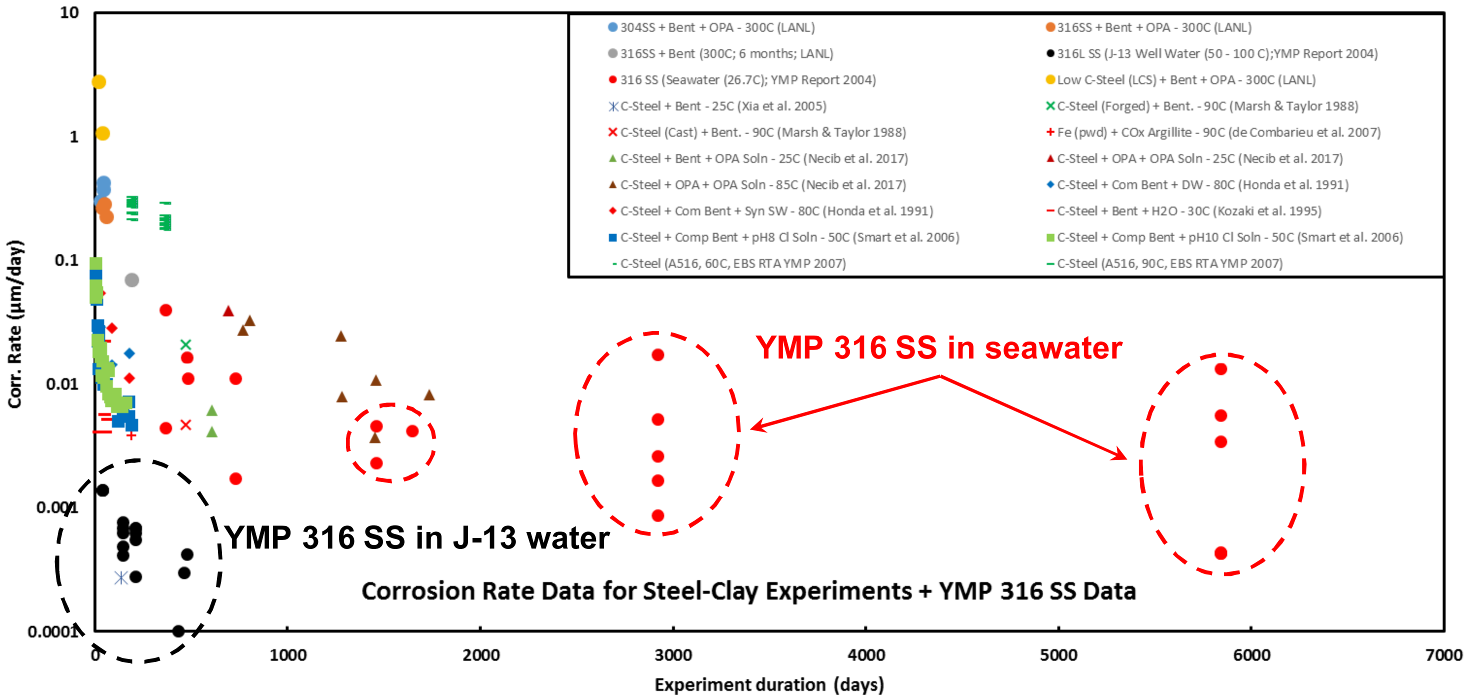
- ***Sequentially coupled feedback between 1D and 3D models.***
- ***Similar to FMDM implementation***

Corrosion Rate Data of Steel Barrier Materials



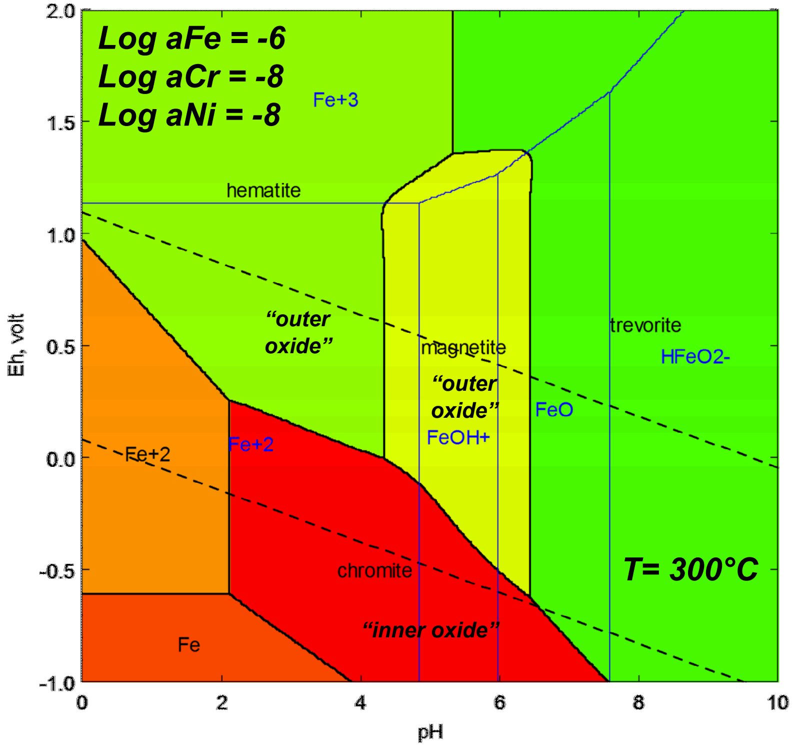
- **Corrosion rate data compilation:**
  - **LANL Exp's: Uniform Corr. Rate for C-steel and stainless steel (316L SS)**
  - **Compare trends → f(Experimental duration)**
  - **Evaluate upper/lower bounds**
  - **Decrease in corrosion rate with time**

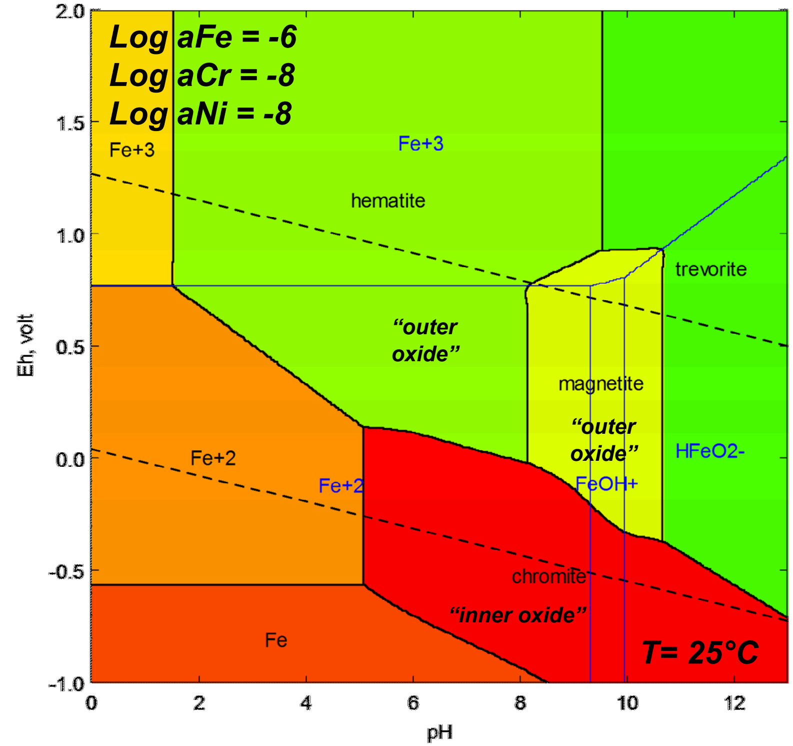
Corrosion Rate Data of Steel Barrier Materials (Cont.)

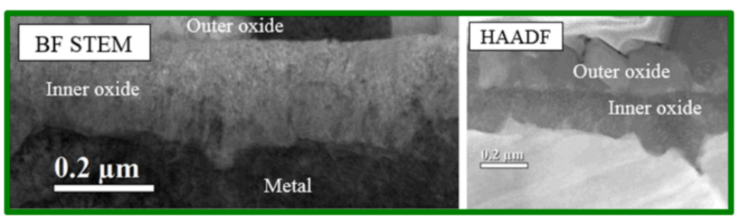


- **Corrosion rate data compilation:**
  - Overlay of selected YMP aqueous corrosion data (316 SS) (BSC 2004)
  - Data trends plot within bounds of existing data sets
  - Reasonable basis for GDSA-PA corrosion rate distributions

Thermodynamic Analysis of Steel Corrosion





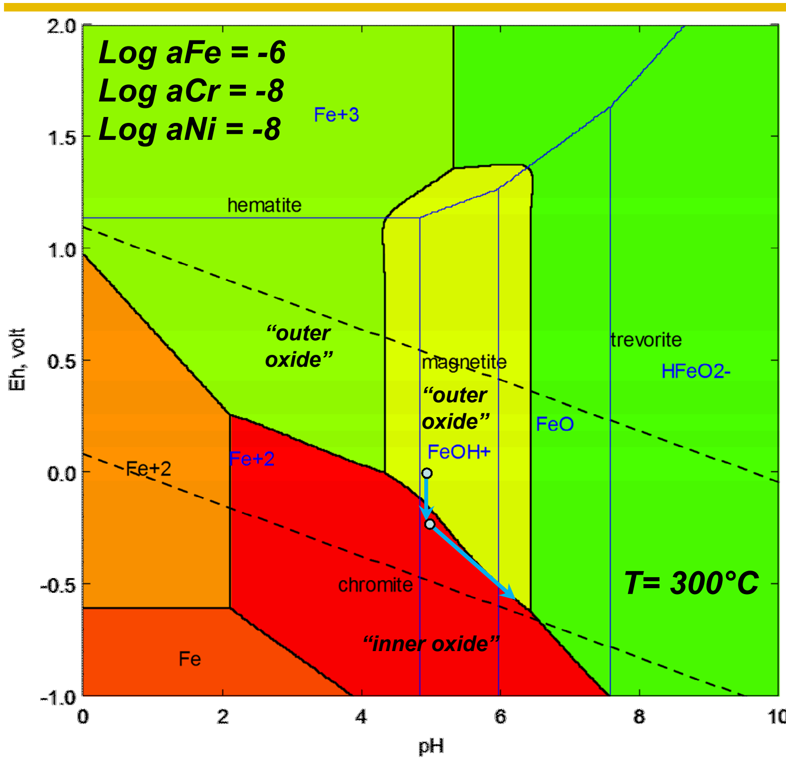


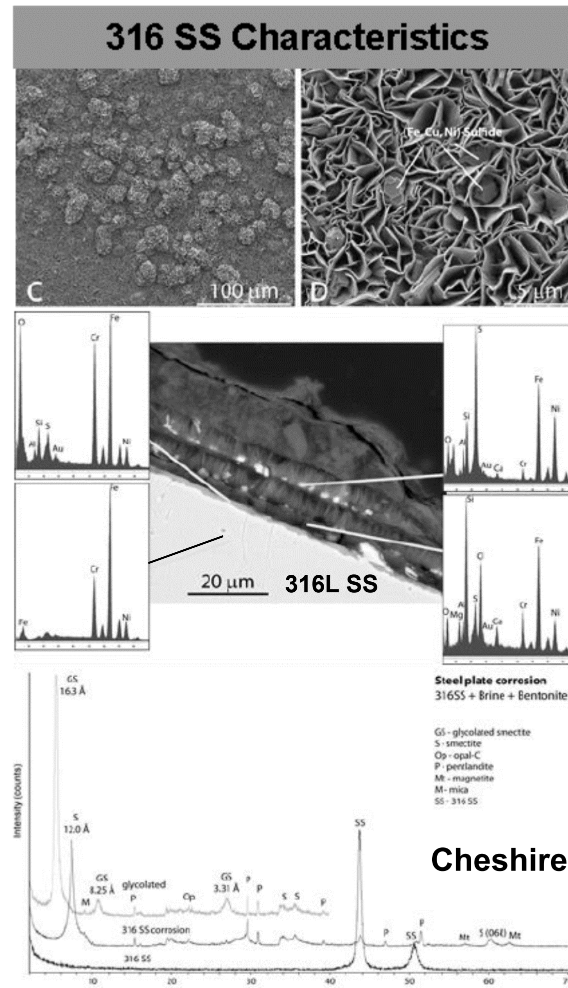
316L SS
T = 320°C
Unirradiated

DOE NEUP Report DE-AC07-05ID14517 (Jiao, Was, and Bartels – 2015)

- **Thermodynamic analysis:**
  - Eh-pH (Pourbaix) relations (CHNOSZ)
  - Updates to thermodynamic data (chromite)
  - EQ3/6 reaction path modeling
  - Temperature effects

Thermodynamic Analysis of Steel Corrosion (Cont.)

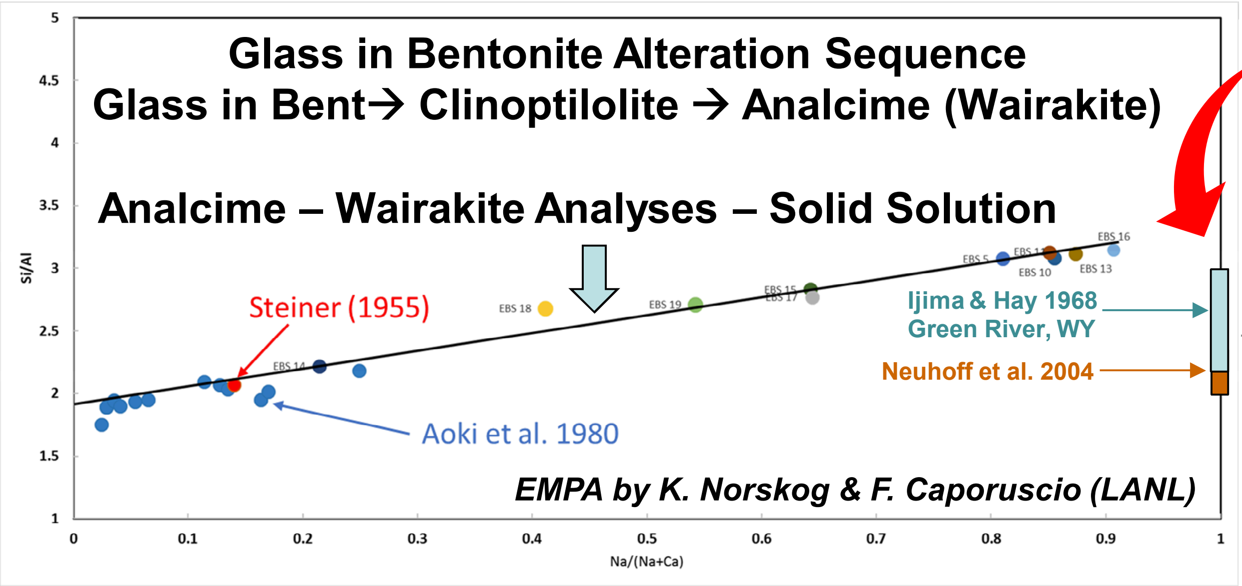


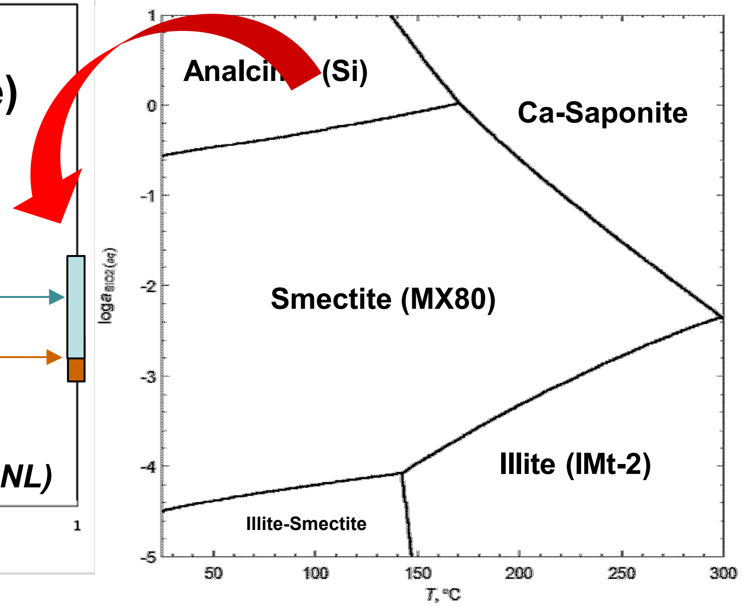


Cheshire et al. (2014)

- **Reaction path modeling:**
  - **316 SS composition**
  - **Dilute water starting solution**
  - **T = 25, 288 & 295°C**
- **Preliminary Results** ***Work in progress!!!***
  - **Reduce conditions & chromite sat.**
  - **Increase in pH & magnetite sat.**

Bentonite Alteration at High Temperatures: Zeolite Stability





- **Bentonite Alteration and Zeolite Stability:**
  - Glass alteration in bentonite → high Si
  - Formation of analcime – wairakite zeolites
  - High Si → prevents illite stability?
- **TODO**
  - Use analcime-wairakite analysis to advance solid solution
  - Analysis of analcime – wairakite equilibria

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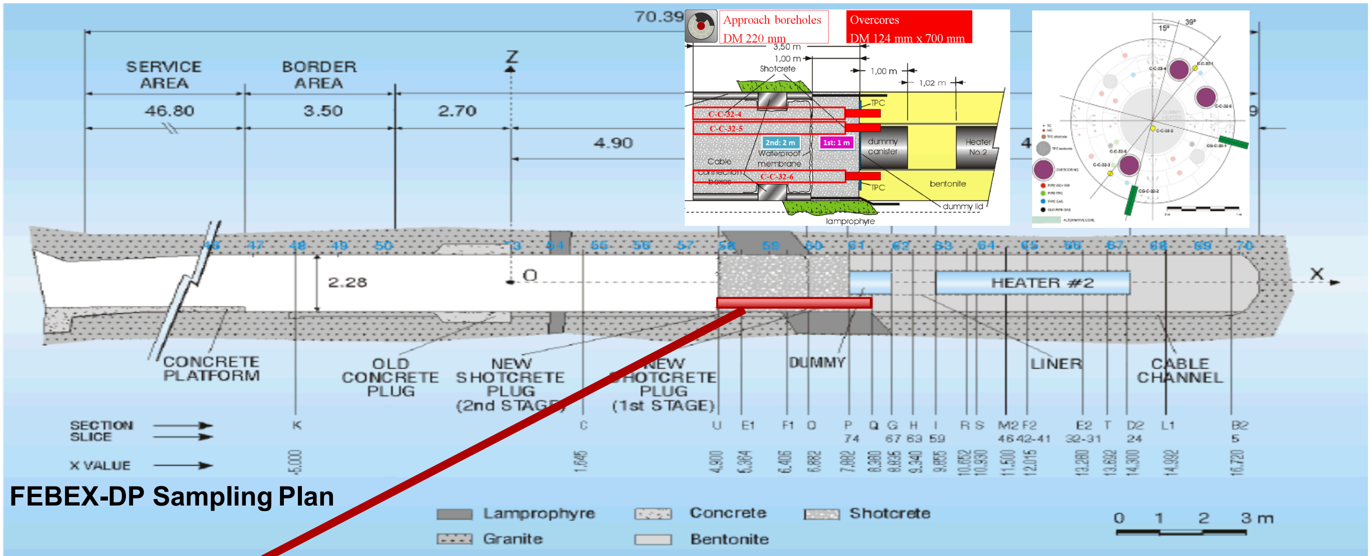
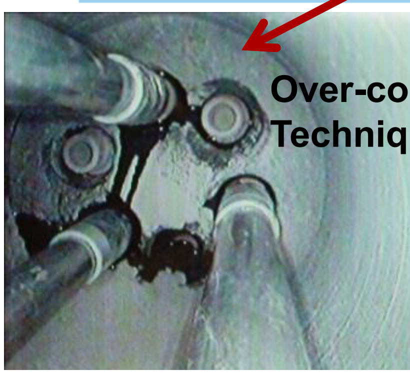
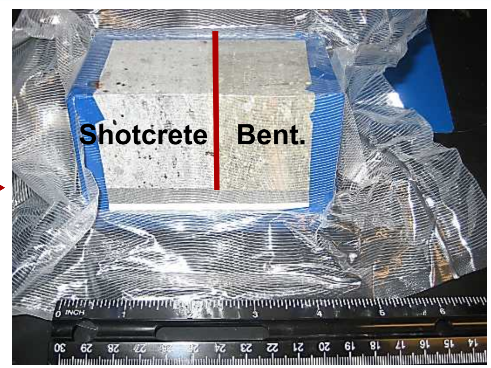
International Collaborations: FEBEX-DP (Grimsel URL)



FEBEX-DP Sampling Plan



Mäder (2014)



CFJC (SNL)

- **Shotcrete/bentonite interface sampling**
- **Characterization studies cement/bentonite interactions**
  - **Phase identification (SEM-EDS, XRD)**
  - **X-ray CT Scan: micron-scale structures**

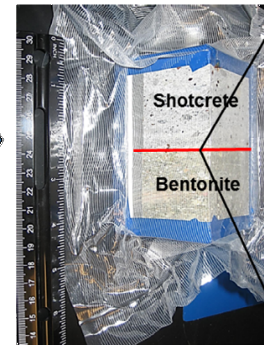
International: FEBEX-DP Bentonite – Concrete Interface Characterization (Cont.)

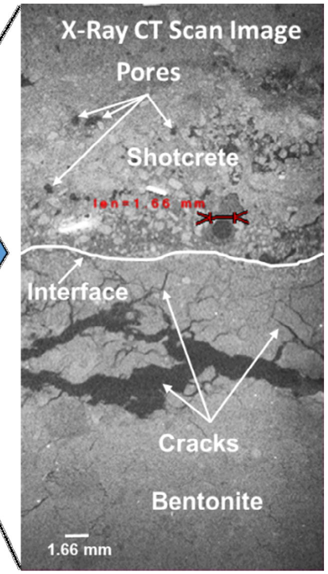
High Level of Core Preservation During Extraction

Overcoring Technique

Mäder (2014); CI Report

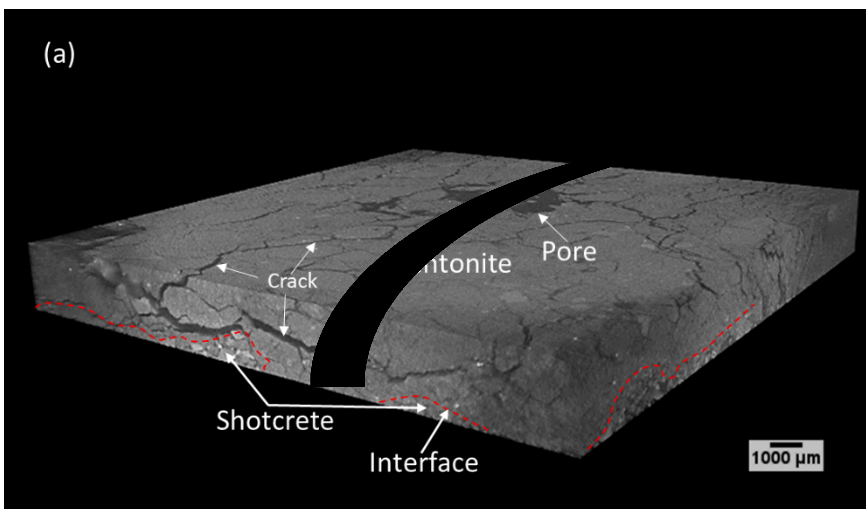
Overcore Specimen

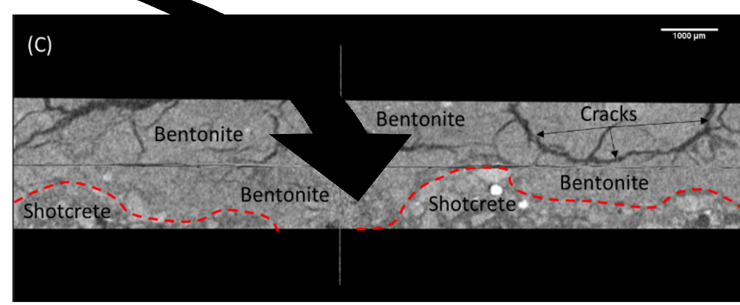




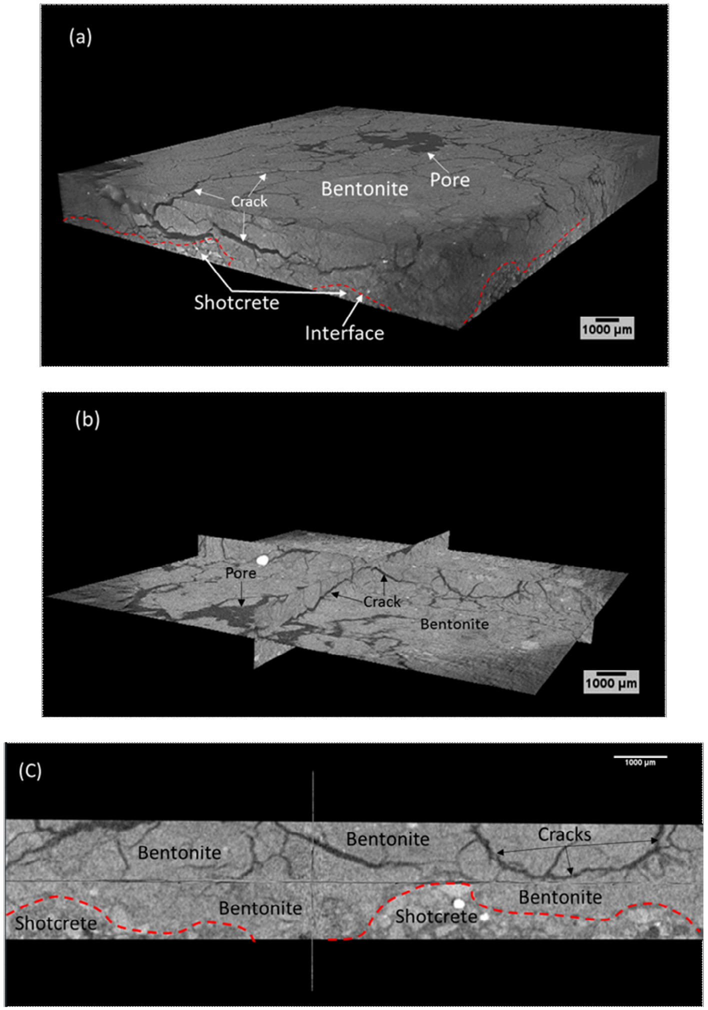
Imaging by J. Eric Bower (SNL)

Computerized Tomography (CT)





International Collaborations: FEBEX-DP Bentonite – Concrete Interface Characterization (X-ray CT Scan; Cont.)



Main Features:

– Occurrence of microcracks and pore spaces – connected in many cases
– "Craquelure" or "chickenwire" microcrack pattern (desiccation)
– Some embedded granular material in bentonite matrix with radiating cracks
– Heterogeneous microcrack spatial distribution → localized regions with no cracks

Crack – Pore pathways:

Bentonite:

- Continuous and discontinuous pore-microcrack networks (2D & 3D)
- Large pores tend to be connected to microcracks

Shotcrete:

- Bentonite: Large pores tend to be connected to microcracks
- No or little microcracks
- Isolated pores except at the interface

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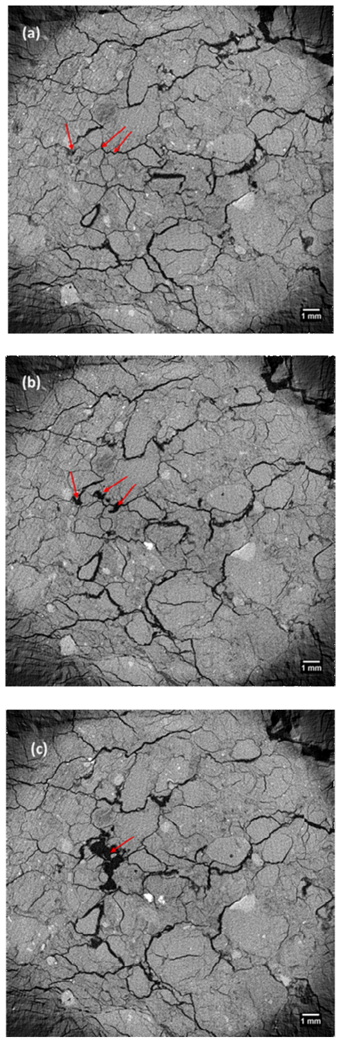
International Collaborations: FEBEX-DP Bentonite – Concrete Interface Characterization (X-ray CT Scan; Cont.)

Red arrows: microcrack segments evolving into pores



2D Slice Stack

Z direction

- **2D – 3D Stacked Image Evaluation:**
  - **Microcrack aperture enlargement/shrinking**
  - **Crack segments and junctions evolving into pores**
  - **Microcrack pathways can be highly heterogeneous**

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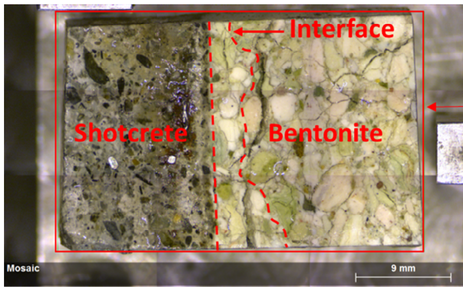
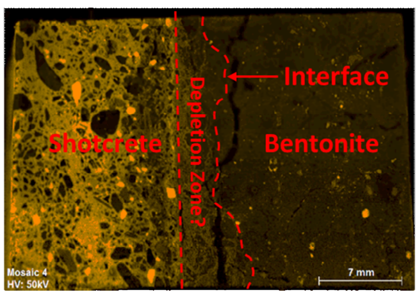
International Collaborations FEBEX-DP: Bentonite – Concrete Interface Characterization (micro-XRF; Cont.)

Thin Section

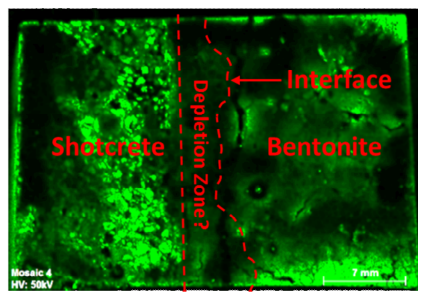


- 34.744 mm x 23.88 mm Scan Area,
- 30µm Spot to Spot Distance,
- 25µm Spot Size,
- X-ray Energy 50kV/200µA
- ~90 min to complete sample

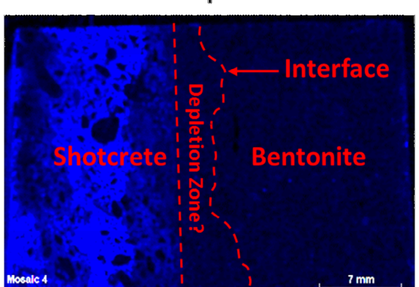
Ca Map



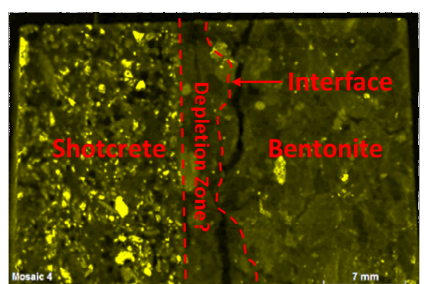
Si Map



S Map



K Map



- **Main Features**
  - Compositional map at thin section (mm) scale – Scanning at the µm scale
  - Sharp compositional changes at the bentonite-shotcrete interface
  - Consistent spatial correlation among various elements across interface
- **Ca, K, S, and Si gradients**
  - Depletion on shotcrete side of the interface → Leaching?
  - Bentonite seems compositional homogeneous at the interface
  - Limited reaction front?

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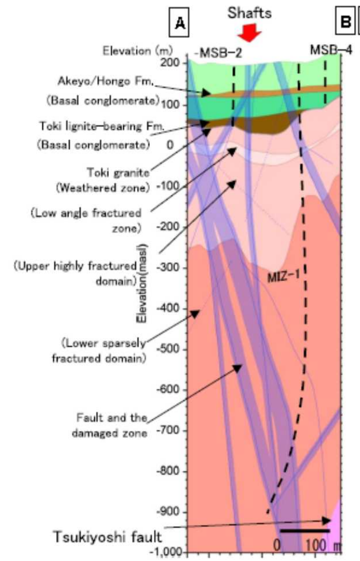
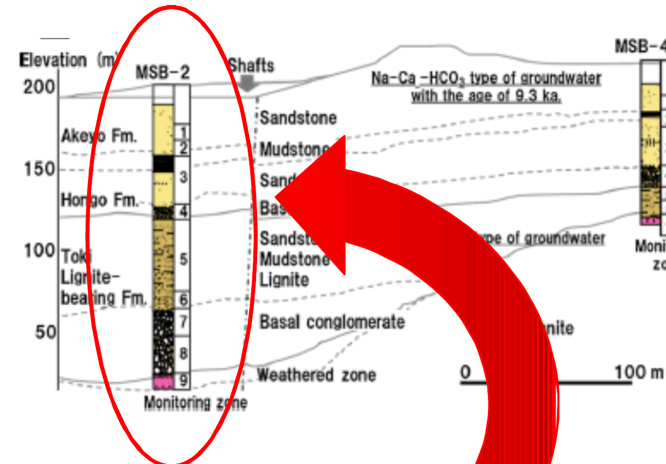
Evaluation of Geochemical Trends in Groundwater Chemistries in Crystalline Rock

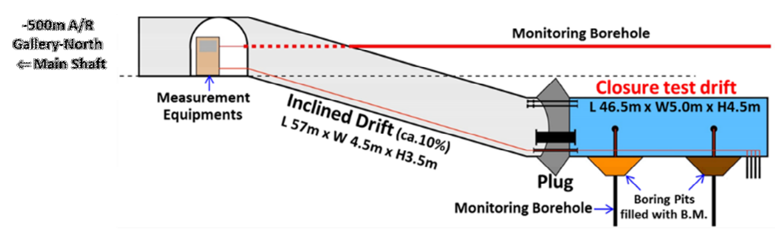
- **GREET (Groundwater REcovery Experiment in Tunnel)**
- **Geochemical evaluation of groundwater site data (JAEA GREET website; Iwatsuki et al., 2005 & 2015)**
- **DECOVALEX-19 Task C:**
  - **Current focus: geochemical evaluation of groundwater chemistry trends**
  - Evaluation of monitoring hydrological and geochemical site data (e.g., Closure Test Drift - CTD)
  - Interactions with host-rock and barrier materials



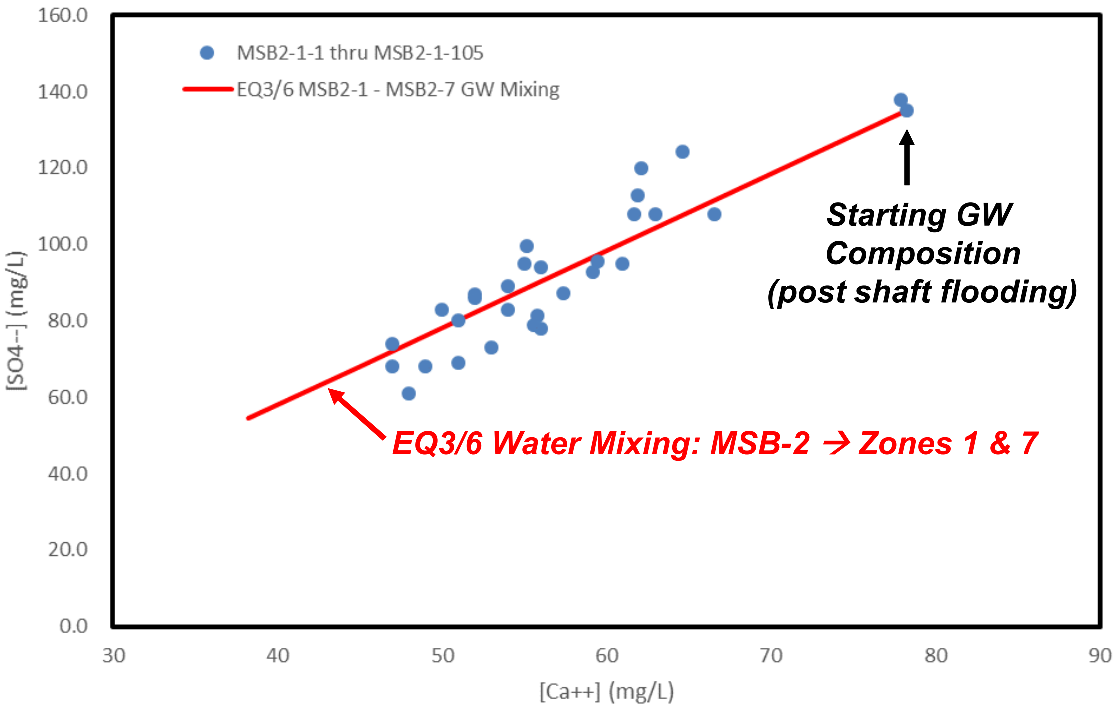


Monitoring Borehole MSB-2 Evaluation

Closure Test Drift - CTD



GREET: EQ3/6 GW mixing Simulation: MSB-2 monitoring borehole (Zones 1 & 7)



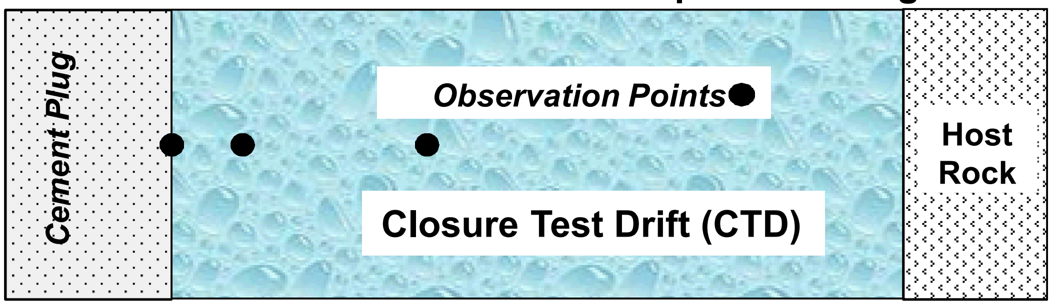
TODO Next:

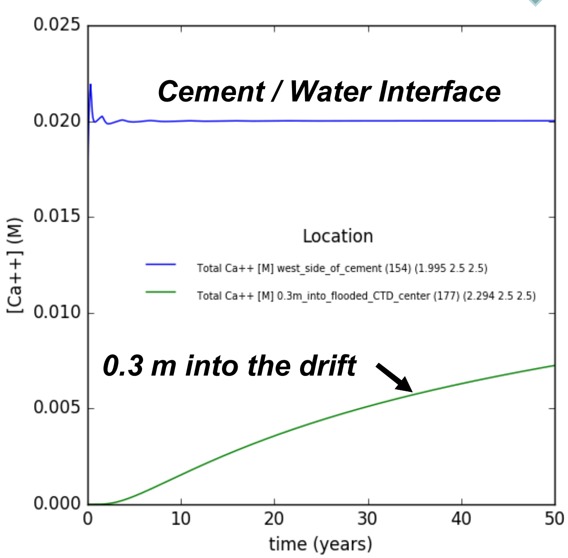
- *Consider different starting GW compositions: MSB2-1 & MSB2-4*
- *Consider other GW chemistries: MSB4, WR's, Galleries*
- *Simulate mineral saturation effects: e.g., calcite*

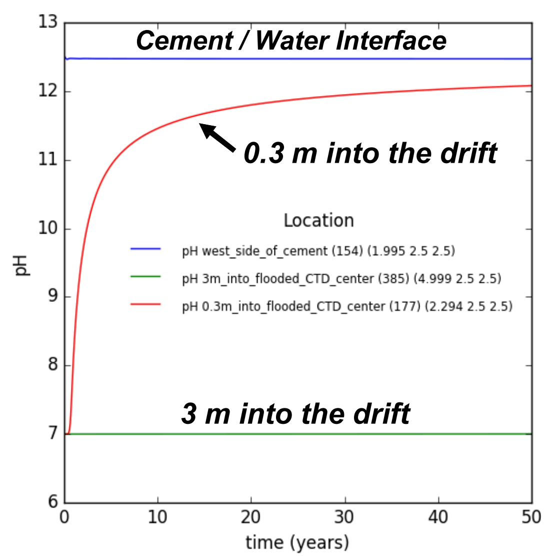
- **Evaluate dilution trends:**
  - EQ3/6 simulation of MSB-2 GW mixing of Zones 1 & 7
  - Test flood water provenance: likely from MSB-2, Zones 7 & 8 (Iwatsuki et al. 2015)
- **Simulation Results**
  - Ca vs SO_4 dilution trend is represented by the GW mixing for MSB-2, Zones 1 & 7
  - Simulation predicts increases in [Na] & [Cl] as observed but at higher concentrations
  - Assess discrepancies in predicted trends
    - *Fresh water input?*
    - *Mixing with a more dilute water?*

Closure Test Drift (CTD): H-C Model

PFLOTRAN 1D Reactive Transport Modeling







- *H-C (Reactive-transport - RT) modeling*
  - ***PFLOTRAN** RT simulation tool*
    - *1D reactive-transport model*
    - *Cement plug / CTD region*
    - *Flooded CTD region modeled as a high porosity / high permeability domain*
    - *Diffusion only*
    - *OPC cement composition*
    - *Diluted "fresh" water composition in flooded domain*
    - *THERMODDEM thermodynamic database including cement phases*
  - *Effects of cement interactions on bulk water chemistry*
    - *As expected, large changes in pore & bulk fluid composition at the vicinity of the cement / water interface (see Figs.)*
    - *Increases in Ca & pH can be significant even at 30 cm from the interface*
    - *Next: Sensitivity analyses on transport parameters, kinetic rates, aqueous species profiles*

FY17 - FY18 Outlook

- **GDSA-PA integration of RT modeling of EBS in PFLOTRAN**
  - 1D – 3D EBS implementation
  - 2D – 3D EBS RT model baseline
- **Clay – Metal interactions at high temperatures**
  - Submit paper on steel-clay interaction (corrosion) paper
  - Bentonite alteration:
    - *Zeolite formation & stability*
    - *Thermodynamic Modeling*
  - Preparation of steel corrosion rate paper
- **Thermodynamic database development and applications to geochemical modeling**
- **International Collaborations**
  - SKB TF, FEBEX-DP
  - DECOVALEX2019 – Task C: Groundwater Recovery experiment (GREET) at Mizunami URL, Japan, Closure Test Drift (CTD)

ACKNOWLEDGMENTS

- **This work supported by the DOE-NE Spent Fuel Waste Science and Technology campaign, Fuel Cycle Technologies R&D program.**
- **Kate E. Norskog (LANL) conducted compositional analysis (EMPA) bentonite alteration mineralogy.**

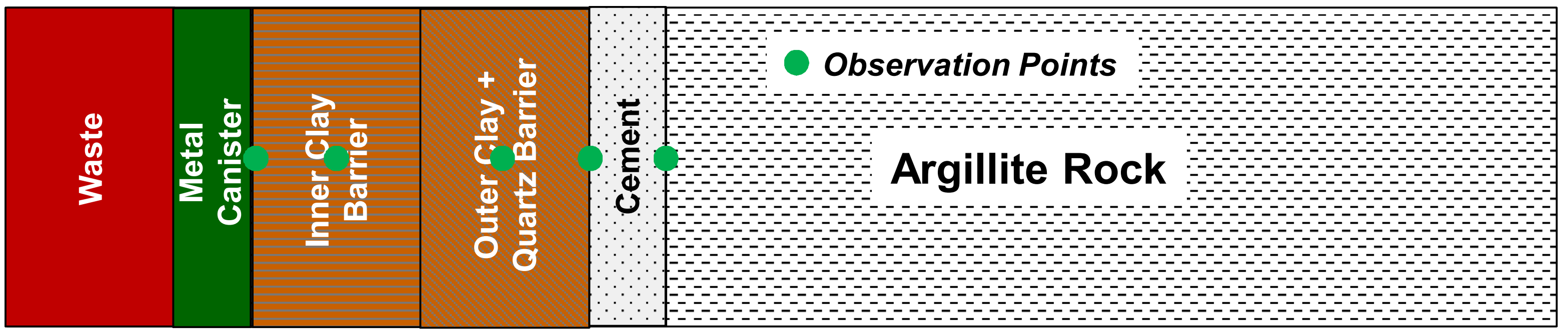
BACKUP SLIDES

Slide Title

- **Bullets, Numbers, Text, Pictures**

1D Reactive Transport of Layered EBS: Integration with GDSA-PA

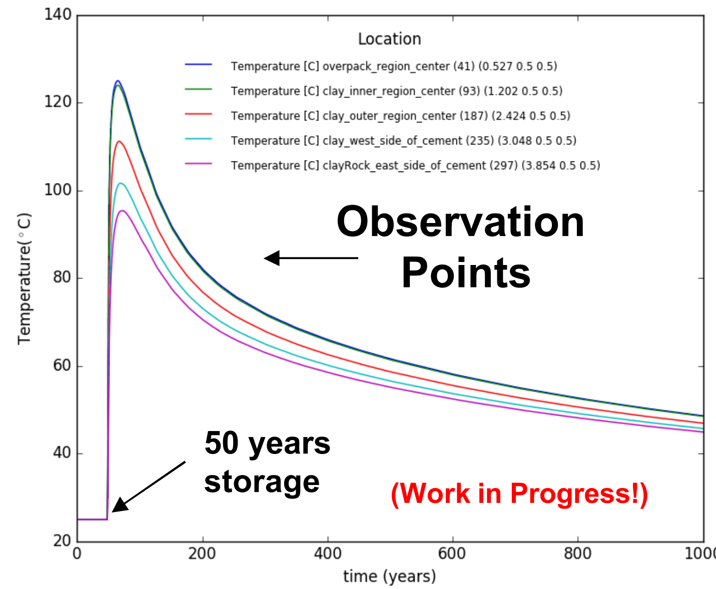
PFLOTRAN 1D Reactive Transport Modeling



0.475 m 0.1 m 1.24 m 1.24 m 0.75 m >>10 m (RED Font: Domains Considered)

- **1D reactive transport (RT) PFLOTRAN calculations:**
  - 24 minerals, 4 initial pore solution chemistries
  - Efficient model scoping in High Performance Computing (HPC) platforms
  - Evolution of mineral volume fraction and aqueous speciation with time: equilibrium & kinetics
- **Temperature effects case:**
  - SNF decay heat profile
  - Peak temperature: 125°C
  - Capture mineral phase transitions:

  gypsum → anhydrite + 2 H_2O



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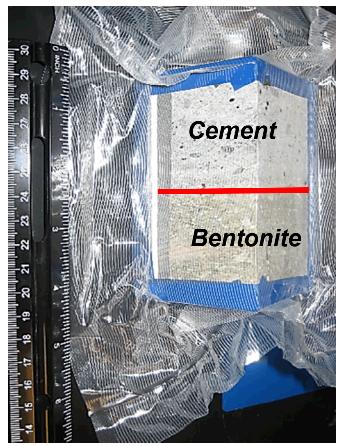
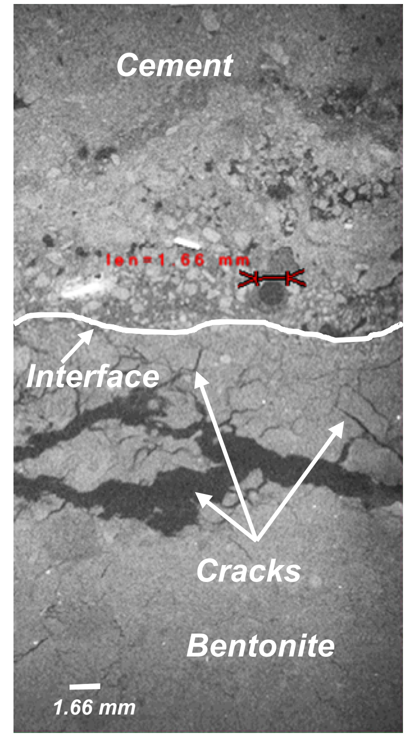
International Collaborations: FEBEX-DP Bentonite – Concrete Interface Characterization (X-ray CT Scan)

- **X-ray CT Scan:**
  - **Non destructive**
  - **Can manage hand-size samples**
  - **Scan rate resolution: 10.5 microns**
- **Can resolve important features:**
  - Cracks
  - Large pores
- **3D image analysis**
  - Continuous pores and cracks
  - “Heavy” minerals: oxides, sulfides

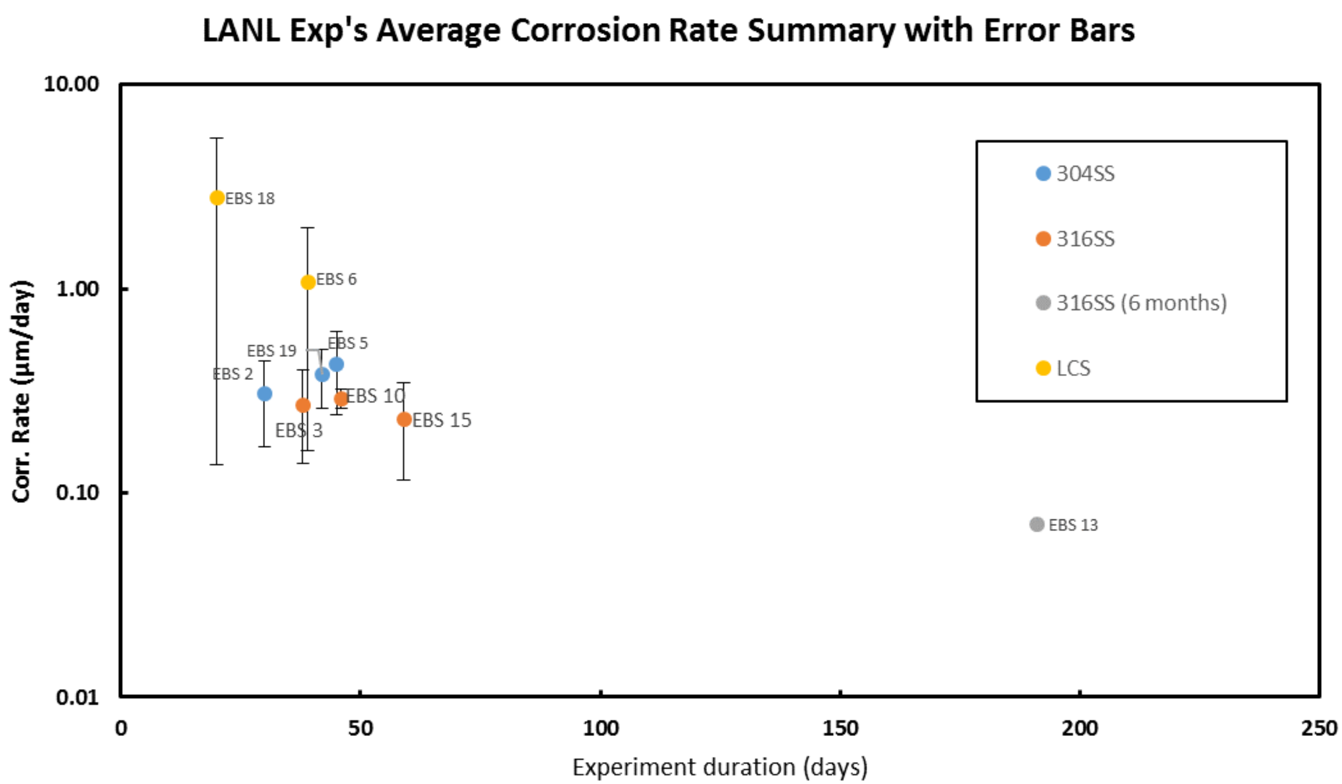
Core Specimen





Imaging by J. Eric Bower (SNL)

LANL Corrosion Rate Data of Steel Barrier Materials



- **Corrosion rate data compilation:**
  - **C-steel and stainless steel (316L SS)**
  - **Low C-steel show largest spread in rate data**

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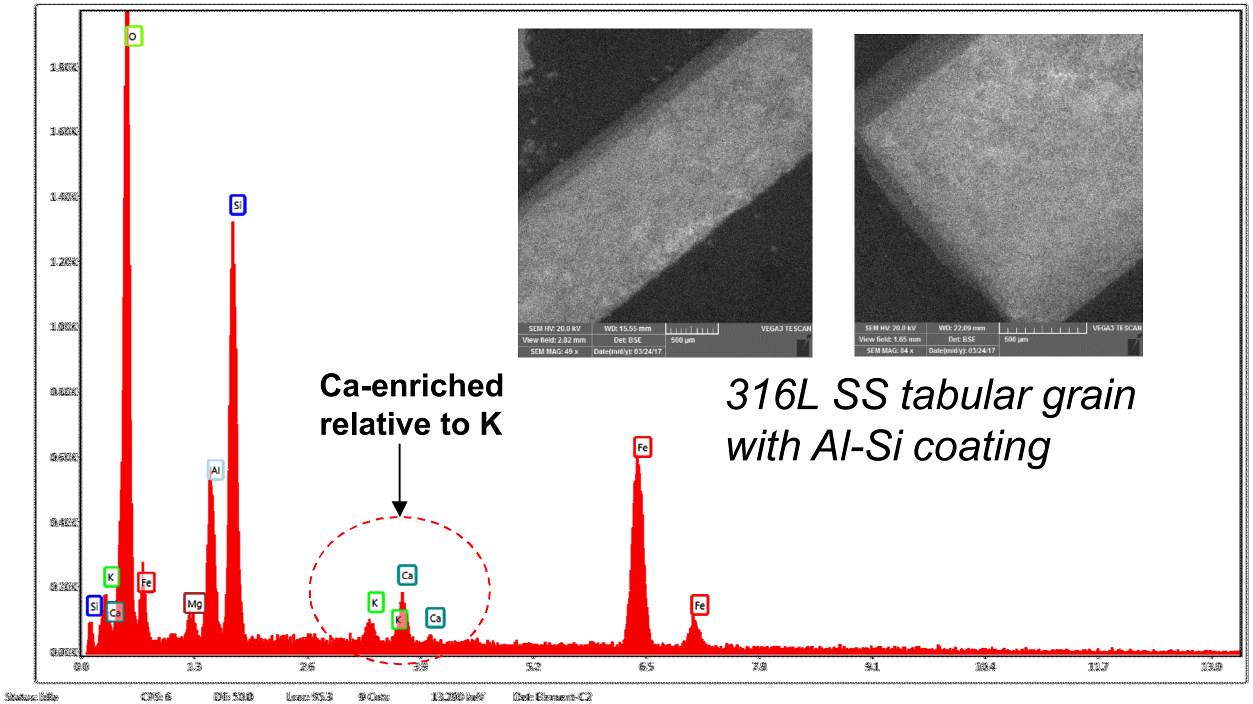
LANL Experiment EBS-Cors-5: Opalinus Clay & OPA Synthetic Brine



- **LANL experiments conducted at 150°C and 150 bars**
- **Opalinus clay (OPA) + 316L SS + OPA brine**
- **SEM-EDS analyses on tabular grain:**
  - Tabular grain: Ca, minor K, Mg, Fe, Si, Al
  - EDS Spot analyses: fairly homogeneous spectra across grain surface
- **Fe-rich clay?, saponite?, chlorite coating?**
- **Planned FIB/SEM for this sample**