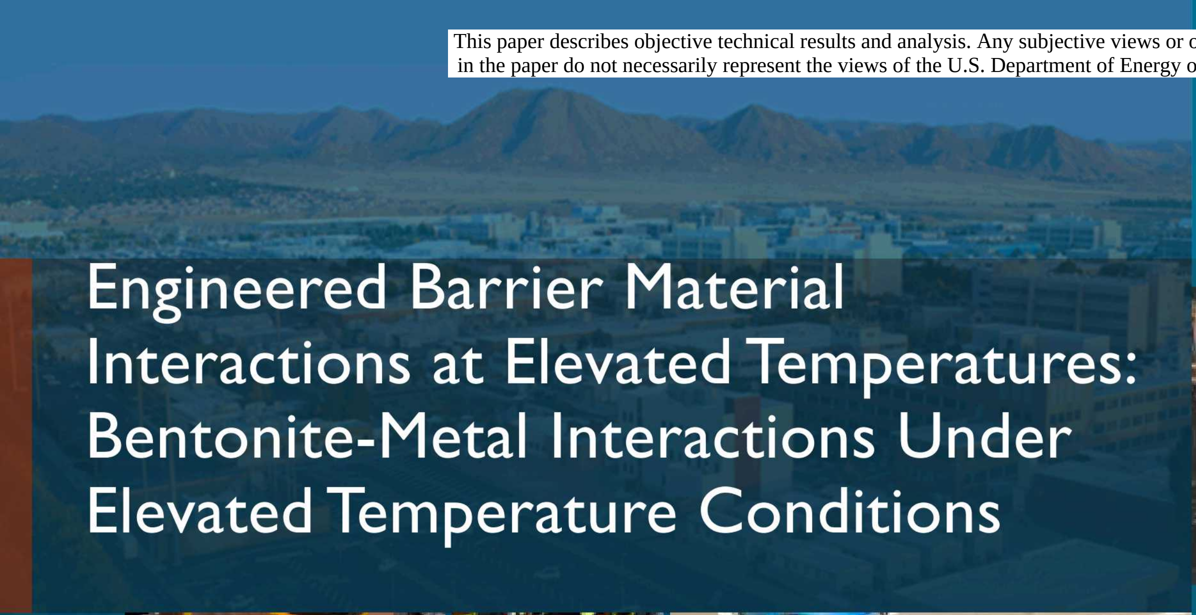
SAND2019-4150C



Engineered Barrier Material Interactions at Elevated Temperatures: Bentonite-Metal Interactions Under Elevated Temperature Conditions

PRESENTED BY

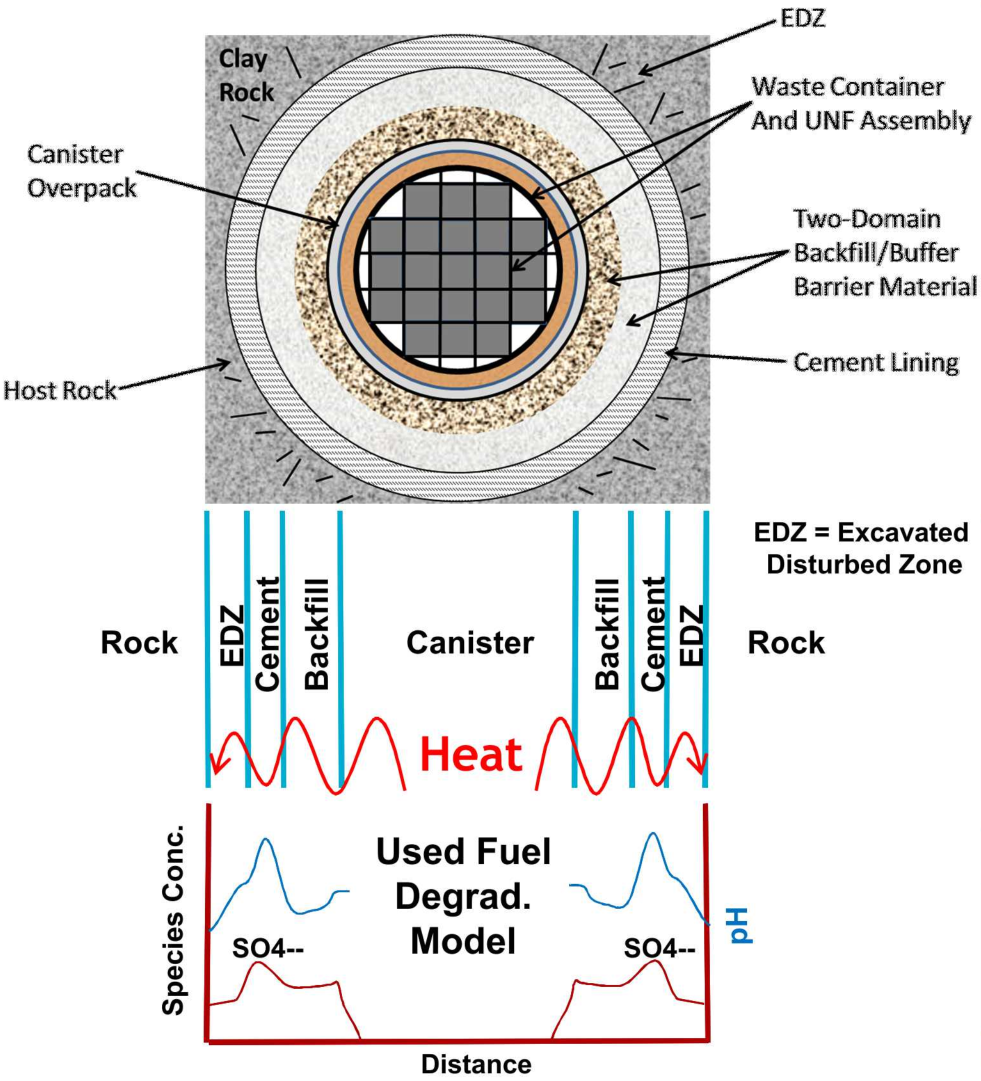
Dr. Carlos F. Jové Colón (SNL)

Drs. Florie A. Caporuscio, Kirsten Sauer (LANL)
Dr. Michael Cheshire (ORNL)

SAND2019-XXXX

EBS Interactions & Canister Heating

- **Evaluate chemical interactions with EBS barrier materials by hydrothermal experiments**
  - Steel/copper corrosion in the presence of bentonite clay
  - Influence of backfill bentonite composition and secondary phases (e.g., pyrite) on corrosion (e.g., S attack)
  - Phase transformation and alteration mineralogy at the metal – clay interface
- **Thermodynamic modeling & reactive transport**
  - Phase equilibria modeling
  - Reactive transport modeling of the near-field environment



Goals

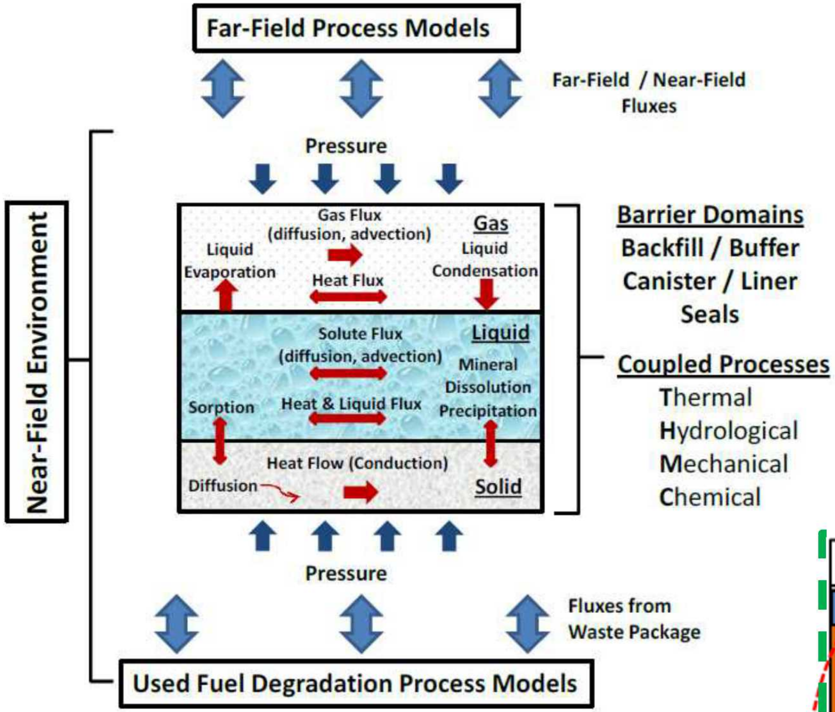
- **Investigate the effects of temperature on bentonite clay barrier interactions:** clay phase change / degradation, smectite swelling, and structure / composition
    - ❖ Dual Purpose Canisters (DPC's) – High capacity canister (up to 37 SNF PWR assemblies); can generate peak T>200°C in disposal scenarios.

- **Inform fluid-solid chemical models** to assess barrier material interactions

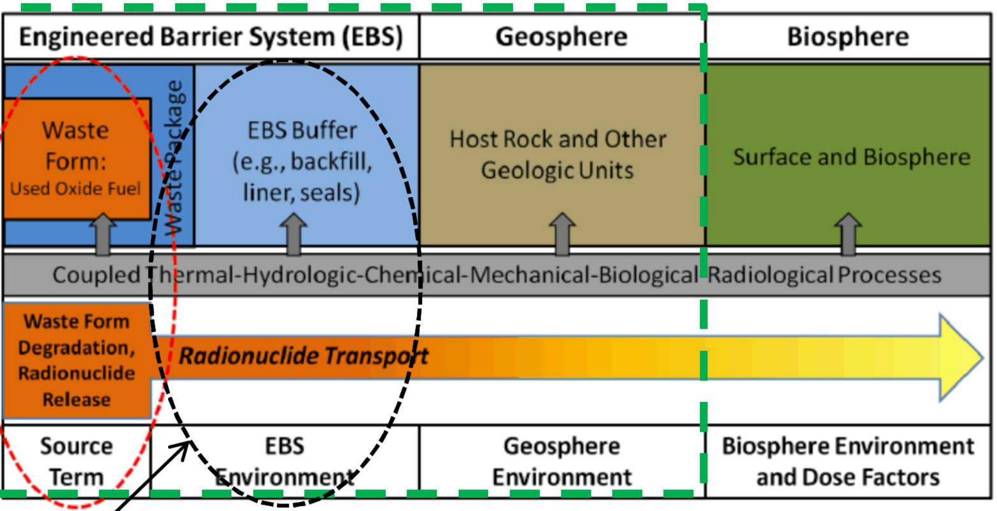
- **Investigate effects of clay phase exposure to elevated temperatures** on sorption and diffusion (e.g., FEBEX-DP)

- **Improve representation of barrier phase interactions at elevated temperatures** in sub-models that support performance assessment (PA) models for waste repositories

Coupled Processes in the Near- and Far-Field



GDSA PA Level Of Integration



Waste form Interactions

EBS Interactions

Modified After Sassani et al. 2013

Experimental Setup

Experimental Conditions

- Unprocessed Wyoming bentonite
- *f*(O_2) buffered at ≈ IM (iron-magnetite)
- 304 SS, 316 SS, low carbon steel, copper
- Synthetic STRIPA brine, 1900 ppm
- 150 – 300°C, 150 - 160 bars, weeks-months

Hydrothermal Apparatus

Photo courtesy of F. Caporuscio (LANL)

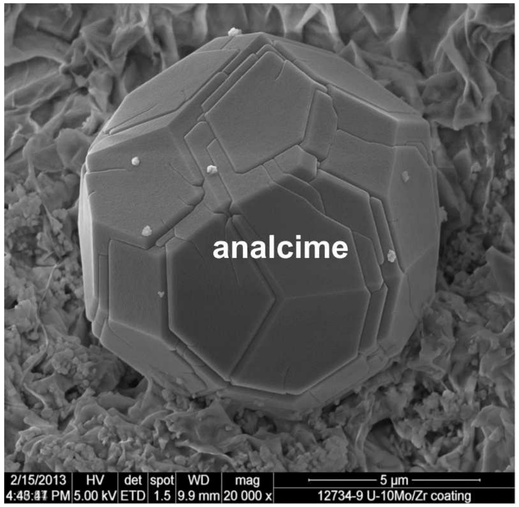
Synthetic STRIPA brine

Species	Concentration (mg/L)
Ca^{2+}	89
Cl^-	1045
K^+	583
Na^+	167
Si	1
SO_4^{2-}	47
Sr^{2+}	0.05
TDS	1934
pH	8.59

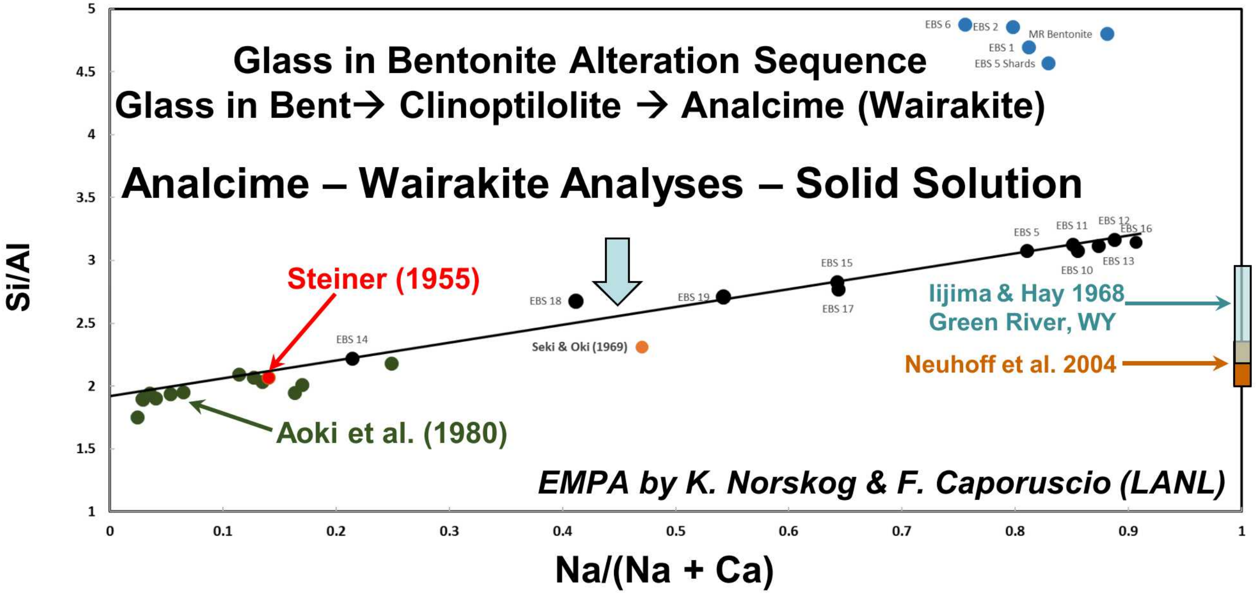
Based on V2 (69-4), Frape et al. (2003)

Authigenic zeolite produced from clinoptilolite / glass in bentonite

Analcime (Bentonite only)



Jové Colón et al. (2017)



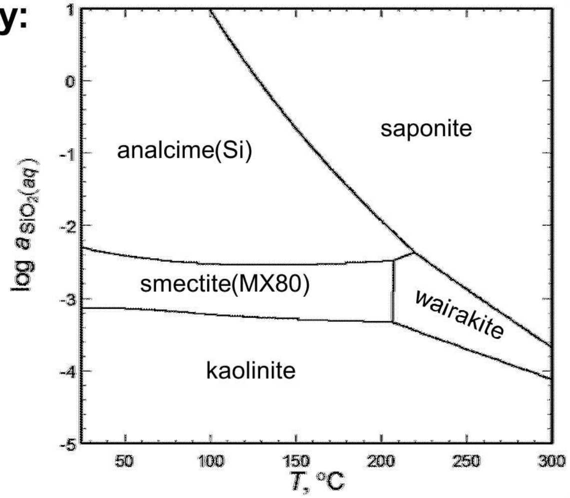
Wairakite-rich zeolite (Opalinus clay + Bentonite)

Bentonite Alteration and Zeolite Stability:

- Glass alteration in bentonite → high Si
- Formation of clinoptilolite, analcime – wairakite zeolites
- Analcime-wairakite solid solution
    - Expands zeolite stability?

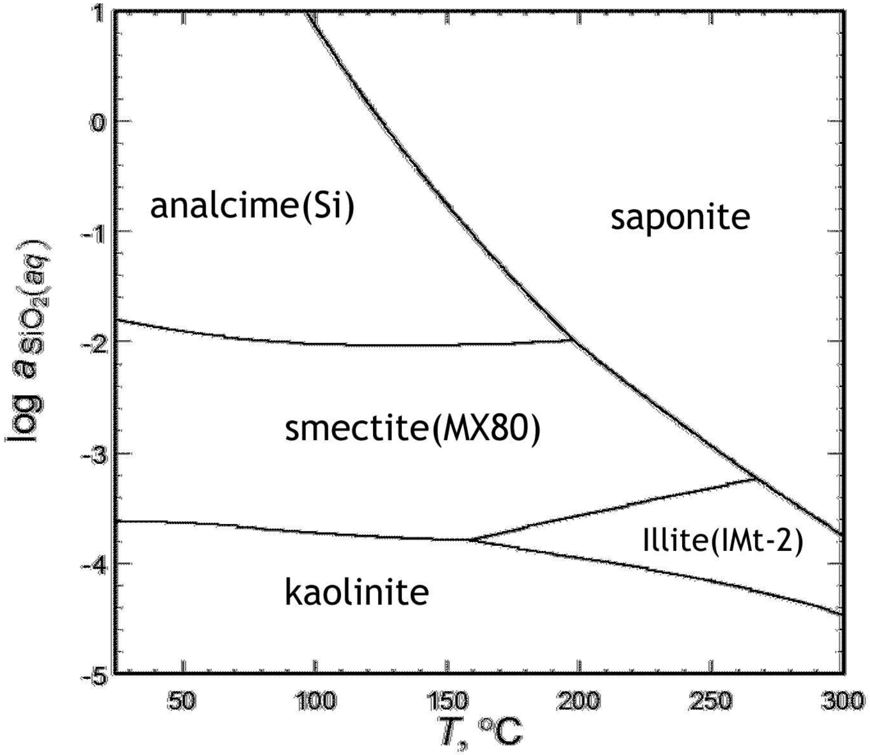
Thermodynamic Analysis:

- Clay-zeolite phase equilibria (CHNOSZ)
- Constrain on aqueous activities of clay/zeolite in solution
- NEXT: Reaction path & solid solution modeling



Jové Colón et al. (2017)

Illite Stability



Activity Phase Diagram:

- Thermodynamic data sources: Neuhoff et al. (2004), Gailhanou et al. (2007, 2012, 2013), Blanc et al. (2015)

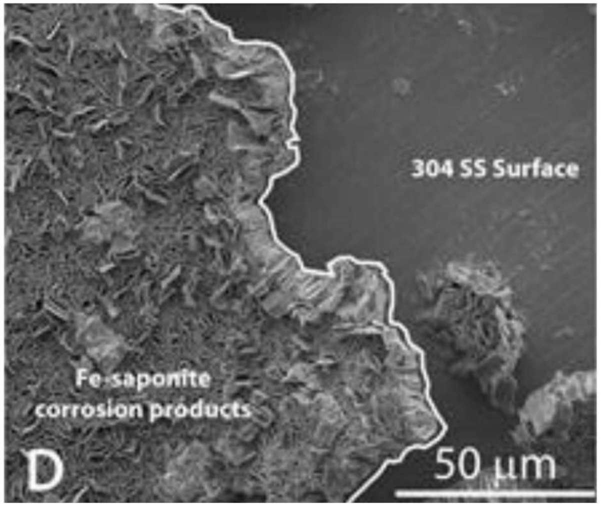
- Activity phase diagrams constructed with CHNOSZ (Dick 2008). Aqueous activities constrained to represent experiments and to obtain stable phase topology

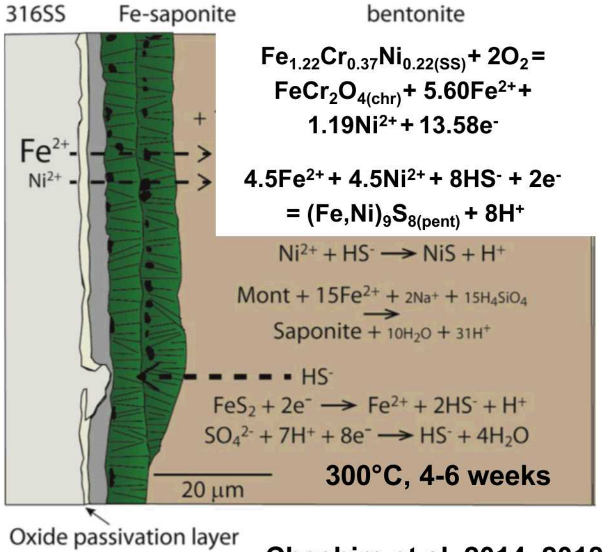
Little or no illite formation

- Low K in solution
- High Si in solution:
  - Favors analcime, smectite, saponite stability
- Ca-bearing solutions favors wairakite formation at elevated temperatures
- Existing illite in wall rock, bentonite may aid in illite nucleation
- Thermodynamic analysis consistent with saponite growth at high temperatures

Waste Canister Degradation: 304 & 316L Stainless Steel – Clay Interactions

- **Experiment**
  - **T = 300ºC; STRIPA brine**
  - **Wyoming Bentonite**
  - **316 stainless steel (SS), 304 SS, low-C steel, copper**
- **Uniform corrosion – no pitting:**
  - **$Fe_{1.22}Cr_{0.37}Ni_{0.22(SS)} + 2O_2 = FeCr_2O_{4(chr)} + 5.60Fe^{2+} + 1.19Ni^{2+} + 13.58e^-$**
- **Corrosion products**
  - **Chromite passivation layer**
  - **Fe-rich smectite (Fe-saponite growth)**
  - **Chlorite**
  - **Early Pentlandite $(Fe,Ni)_9S_8$ formation**
  - **Millerite (NiS)**
- **316 SS - more extensive passive layer**





$Fe_{1.22}Cr_{0.37}Ni_{0.22(SS)} + 2O_2 = FeCr_2O_{4(chr)} + 5.60Fe^{2+} + 1.19Ni^{2+} + 13.58e^-$

$4.5Fe^{2+} + 4.5Ni^{2+} + 8HS^- + 2e^- = (Fe,Ni)_9S_{8(pent)} + 8H^+$

$Ni^{2+} + HS^- \longrightarrow NiS + H^+$

$Mont + 15Fe^{2+} + 2Na^+ + 15H_4SiO_4 \longrightarrow Saponite + 10H_2O + 31H^+$

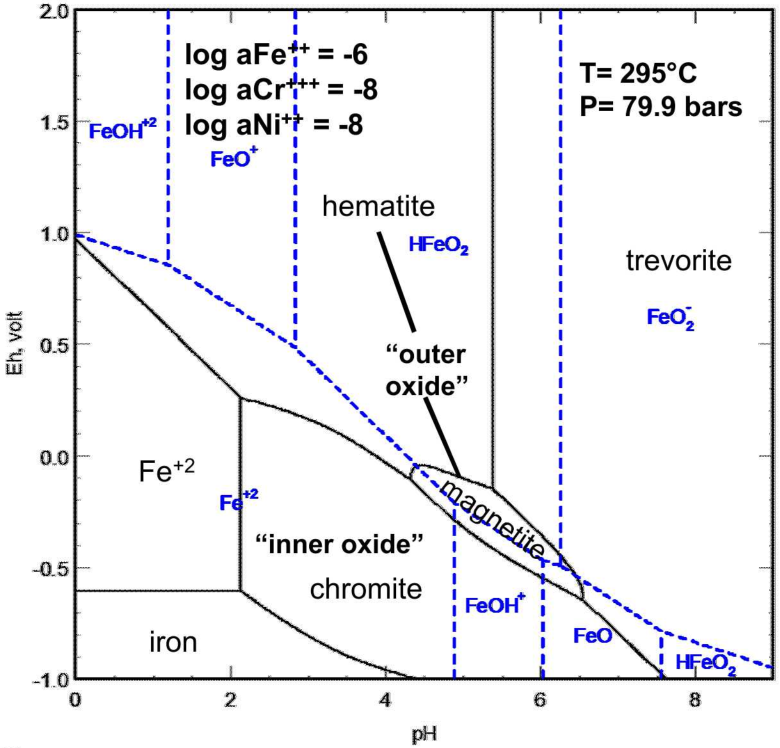
$FeS_2 + 2e^- \longrightarrow Fe^{2+} + 2HS^- + H^+$

$SO_4^{2-} + 7H^+ + 8e^- \longrightarrow HS^- + 4H_2O$

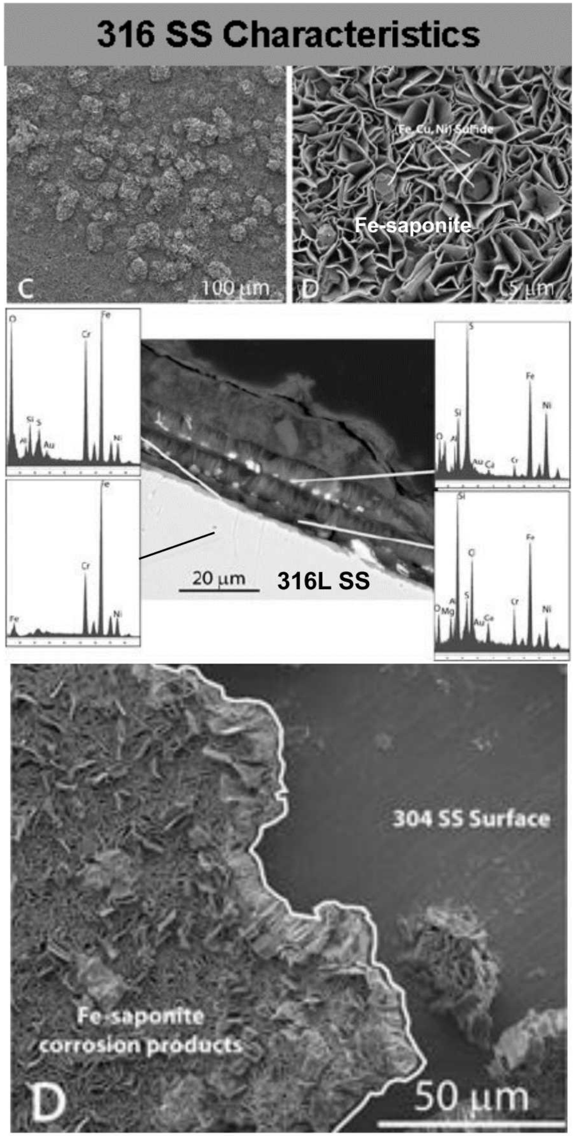
300°C, 4-6 weeks

Cheshire et al. 2014, 2018

Waste Canister Degradation: 304 & 316L Stainless Steel – Clay Interactions



Cheshire et al. (2014, 2018)



Remarks

- Fe-Saponite growth perpendicular to metal substrate
- S is generated from pyrite degradation in bentonite
- Concurrent surface sulfide precipitation with Fe-saponite

Waste Canister Degradation: Low Carbon Steel – Clay

Results

Corrosion Products:

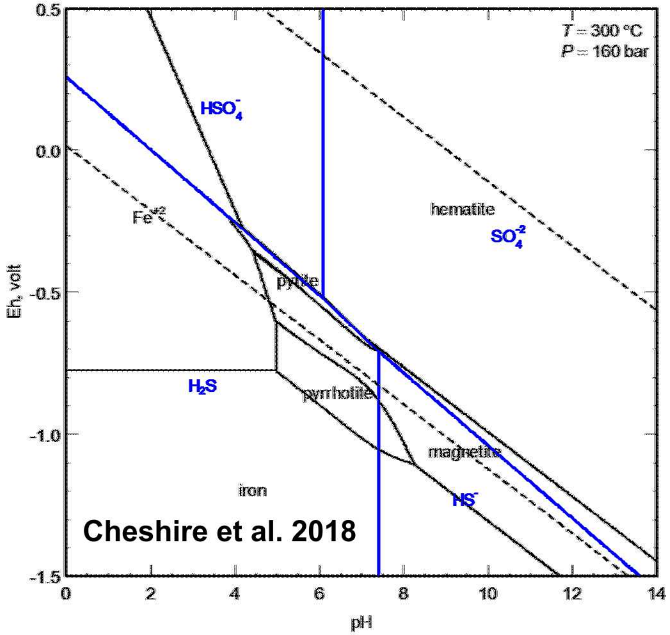
- **Fe-smectites (Fe-saponite)**
- **Pyrrhotite ($Fe_{1-x}S$)**

13 – 56 µm thick corrosion layer

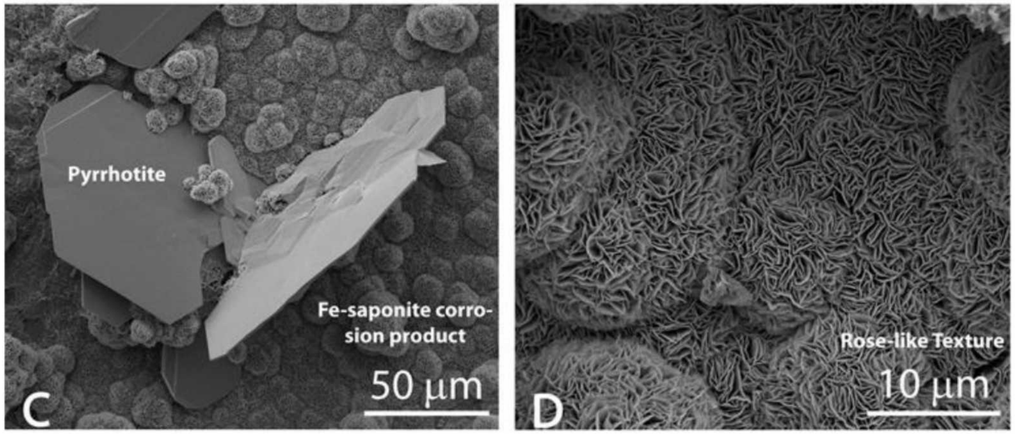
~20 µm pitting corrosion

No passivation layer - corrosion expected to continue

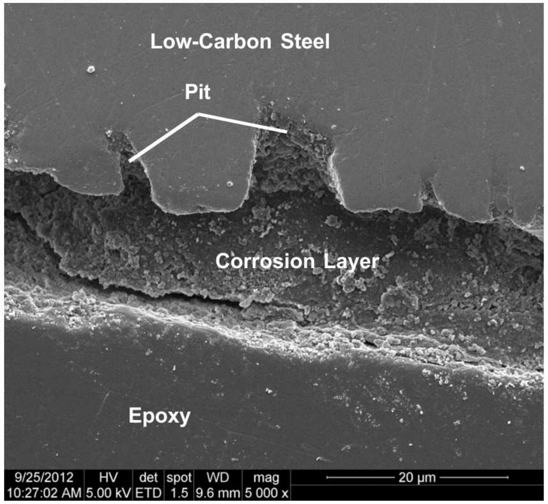
Extensive Fe_3O_4 layers develops



Cheshire et al. 2018



Cheshire et al. 2014



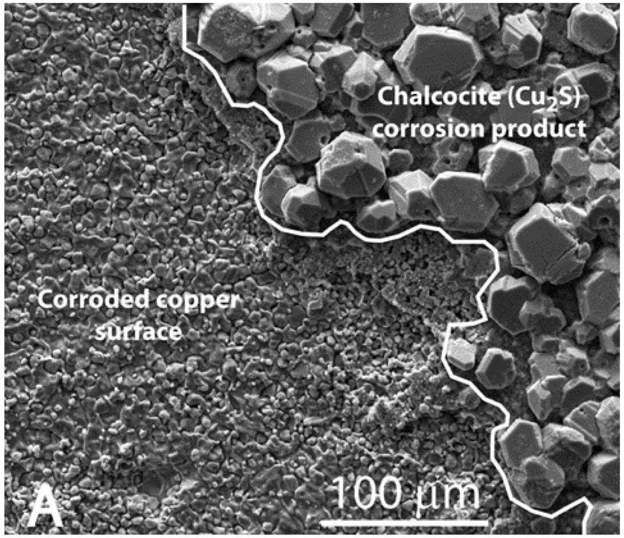
Ramped-up temperature exp's:

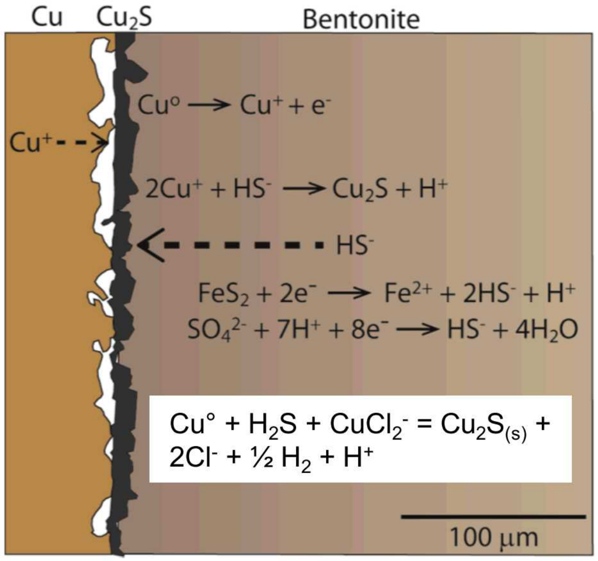
- **T = 25/100/200/300/25 °C,**
- **5 weeks duration**

Sources: Cheshire et al. 2014, 2018; Jové Colón et al. 2015

Waste Canister Degradation: Copper – Clay Interactions

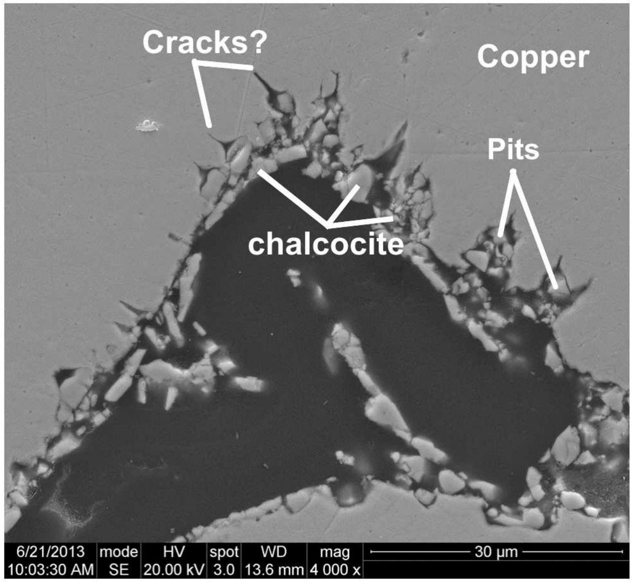
- Copper has been considered as canister and/or cladding/coating material
- Sulfide-induced corrosion (anoxic):
  - Pyrite (FeS_2) decomposition from bentonite
- Primary corrosion product → Chalcocite (Cu_2S):
  - $Cu^{\circ} + H_2S + CuCl_2^- = Cu_2S_{(s)} + 2Cl^- + \frac{1}{2} H_2 + H^+$
  - ~13 μm thick chalcocite layer
- Degradation texture resembles pitting corrosion



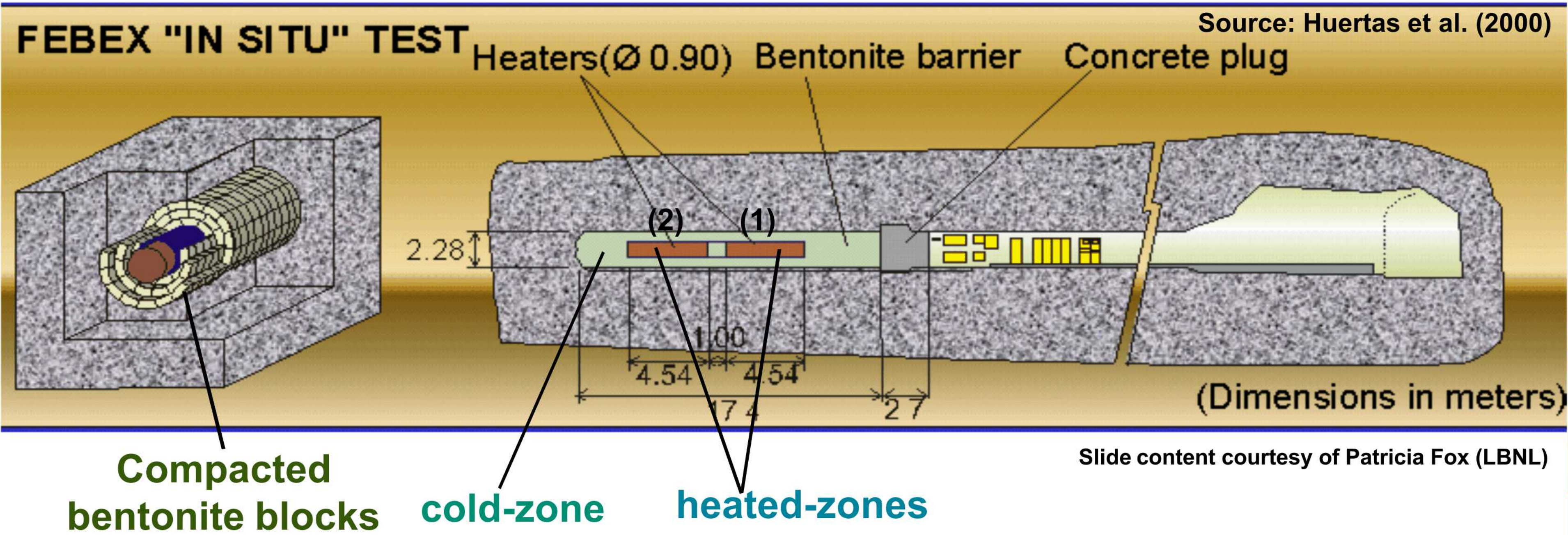


$Cu^{\circ} + H_2S + CuCl_2^- = Cu_2S_{(s)} + 2Cl^- + \frac{1}{2} H_2 + H^+$

Cheshire et al. 2014



FEBEX Full Scale Heater Test Experiment



Source: Huertas et al. (2000)

Slide content courtesy of Patricia Fox (LBNL)

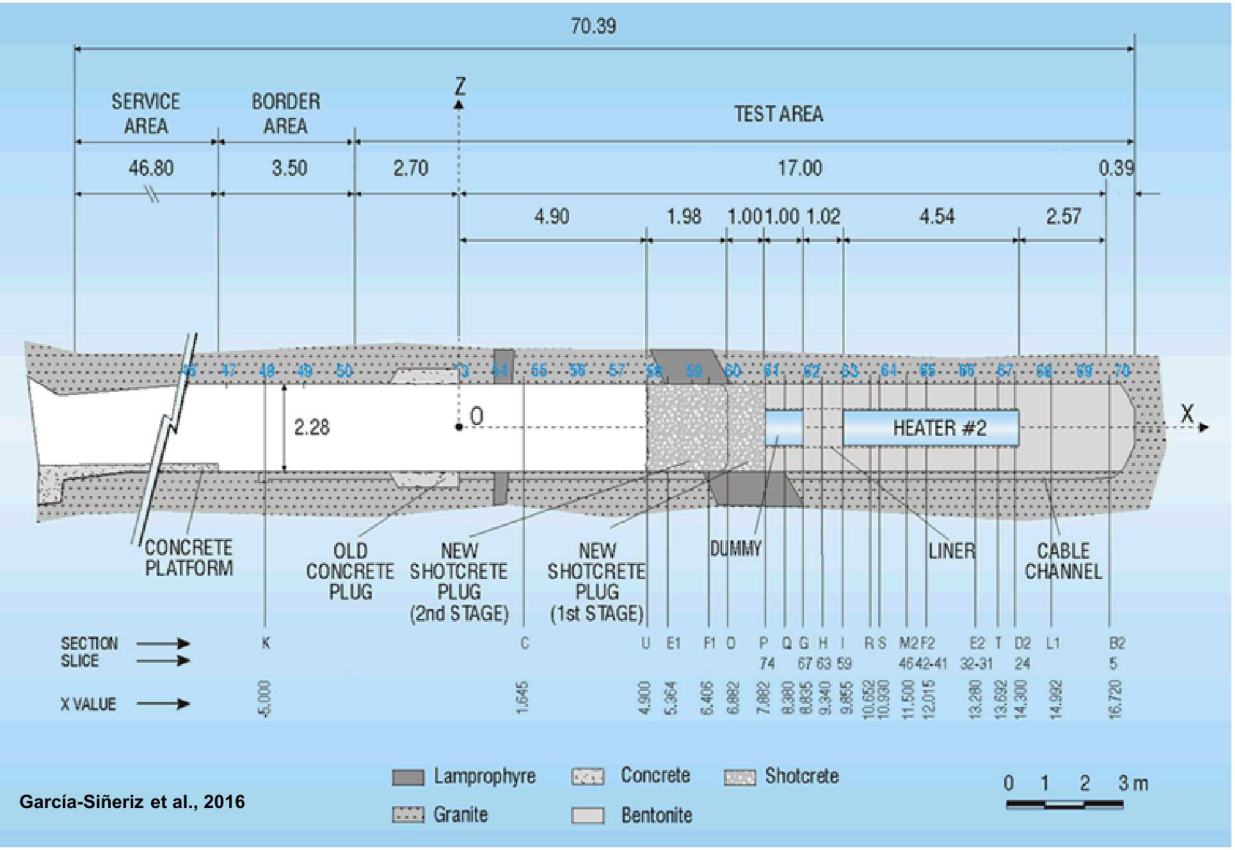
Compacted bentonite blocks

cold-zone

heated-zones

- Conducted by ENRESA under auspices of the EU at the Grimsel Test Site (GTS) in Switzerland
- Bentonite was compacted into blocks at 1650 kg/m^3 dry density and placed in a radial arrangement surrounding 2 heaters
- Heaters operated at a maximum of 100 °C – Heater 1 operated for 5 years; heater 2 operated for 18 years
- FEBEX-DP samples were obtained from heater 2 dismantling in 2015 after 18 years of heating
- Unique opportunity for long-term full-scale heater test and sample / data availability

FEBEX-DP Experiment: Sampled Sections

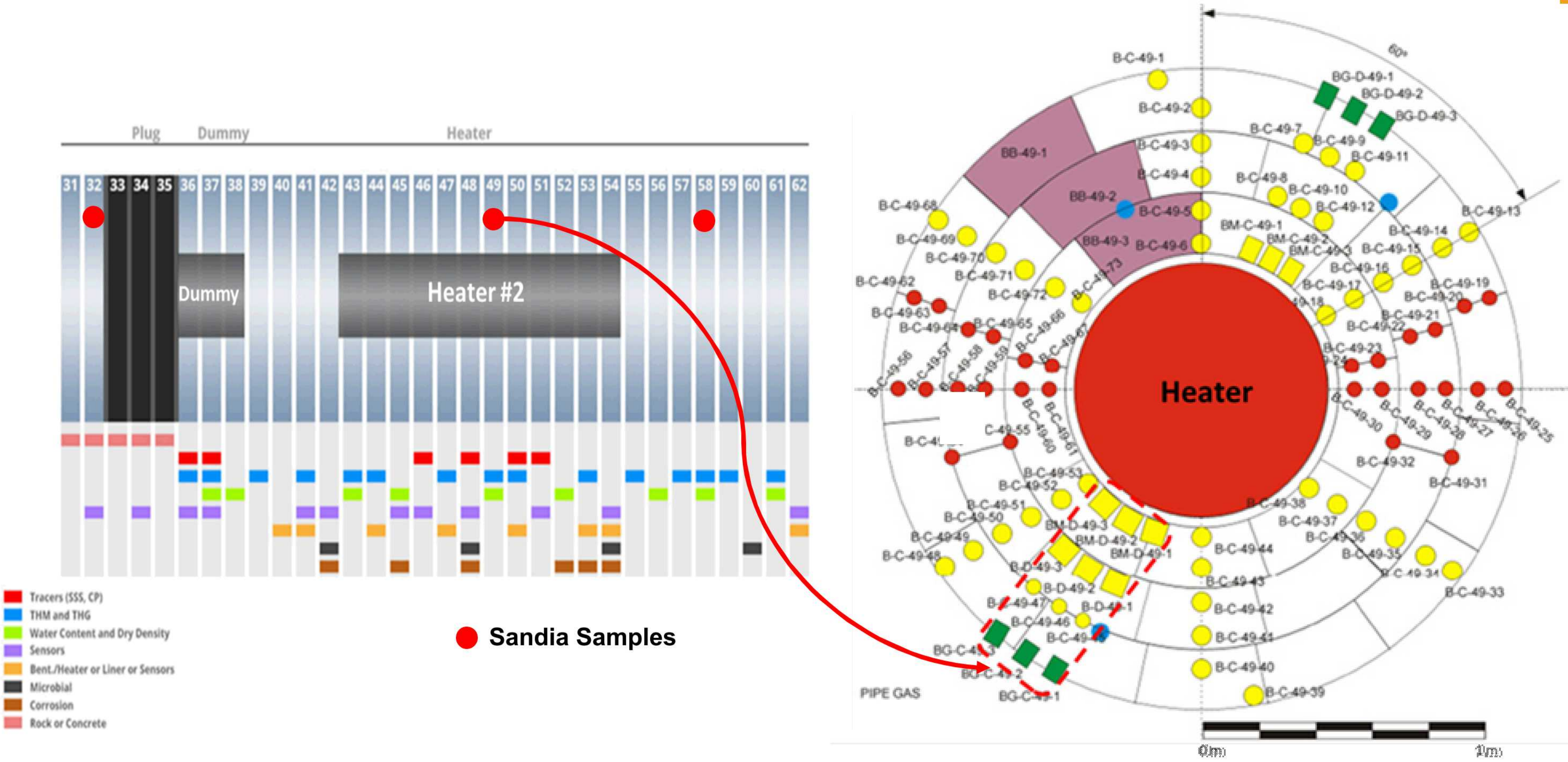


García-Siñeriz et al., 2016

FEBEX-DP Sampling

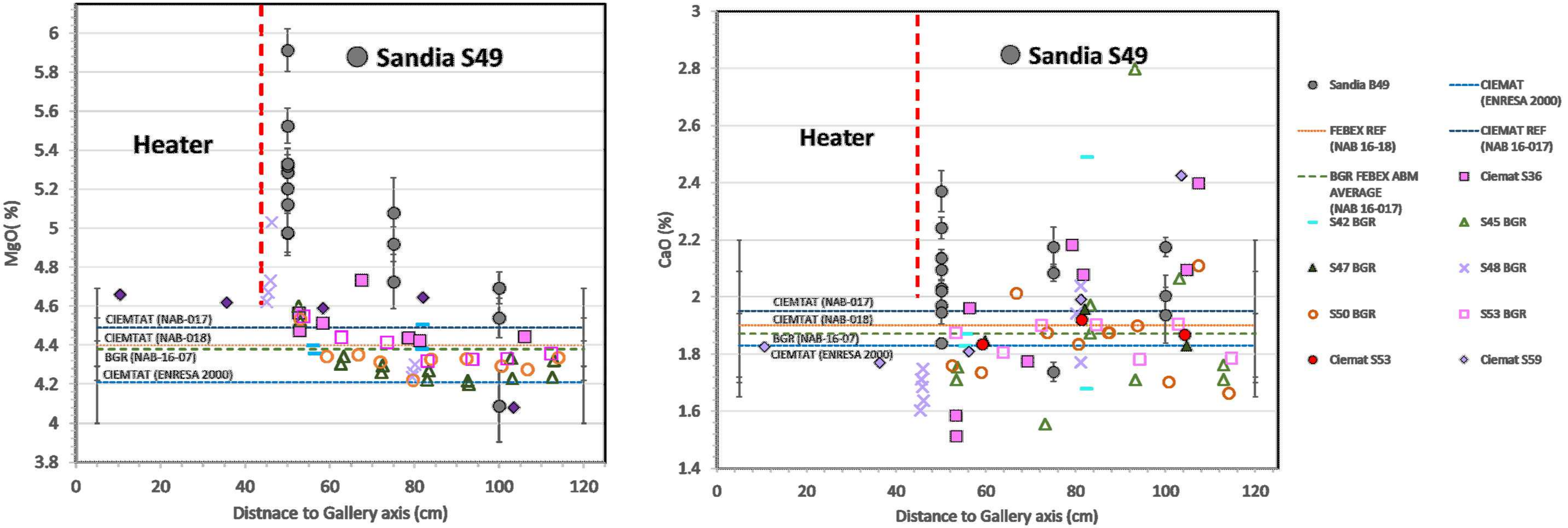
- **<u>Section 49</u> samples (near longitudinal central area of heater)**
- **Bentonite samples from close to the heater towards the outer parts of the barrier**
- **X-Ray Fluorescence (XRF) bulk composition, X-ray CT-scan, μ-XRF, SEM-EDS, X-Ray Diffraction (XRD), Thermogravimetric analysis (TGA)**

FEBEX-DP Experiment: Sampled Sections



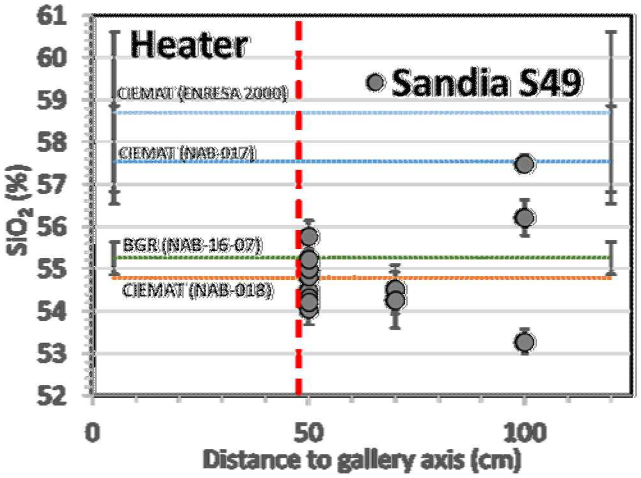
Section 49

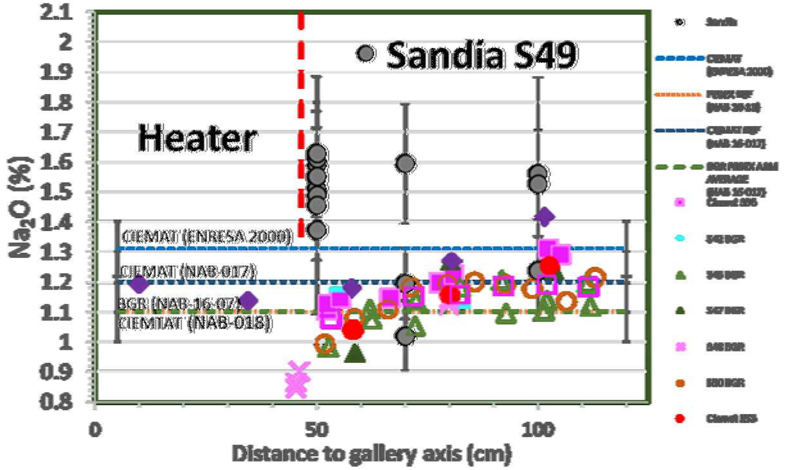
FEBEX-DP Bulk Bentonite Samples: X-ray Fluorescence (XRF)

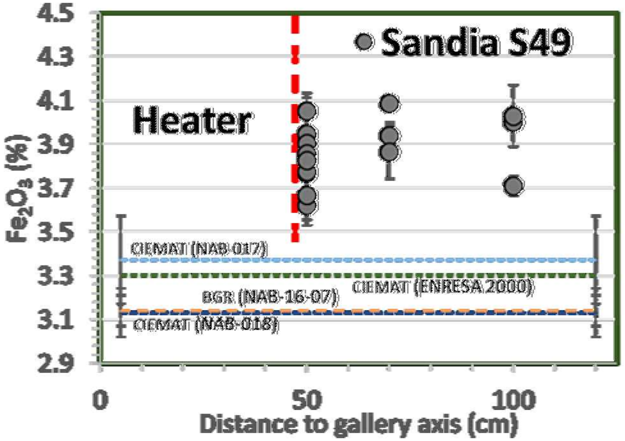


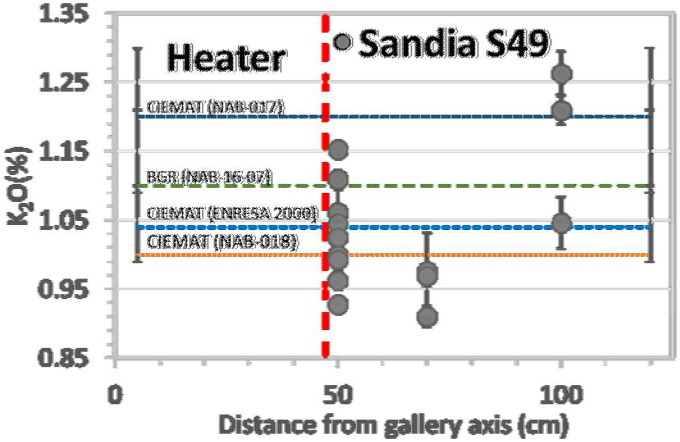
- Mg enrichment towards the heater surface – zones of increasing dry out conditions
- Bulk MgO content far from heater nominally within the bounds of other lab analyses
- Overall, CaO content is relatively variable close to the heater surface
- Mg enrichment(?):
  - Enhanced Mg content due to elevated temperatures?
  - SEM-EDS didn’t reveal newly-formed Mg-bearing phases within the clay matrix

FEBEX-DP Bulk Bentonite Samples: X-ray Fluorescence (XRF)



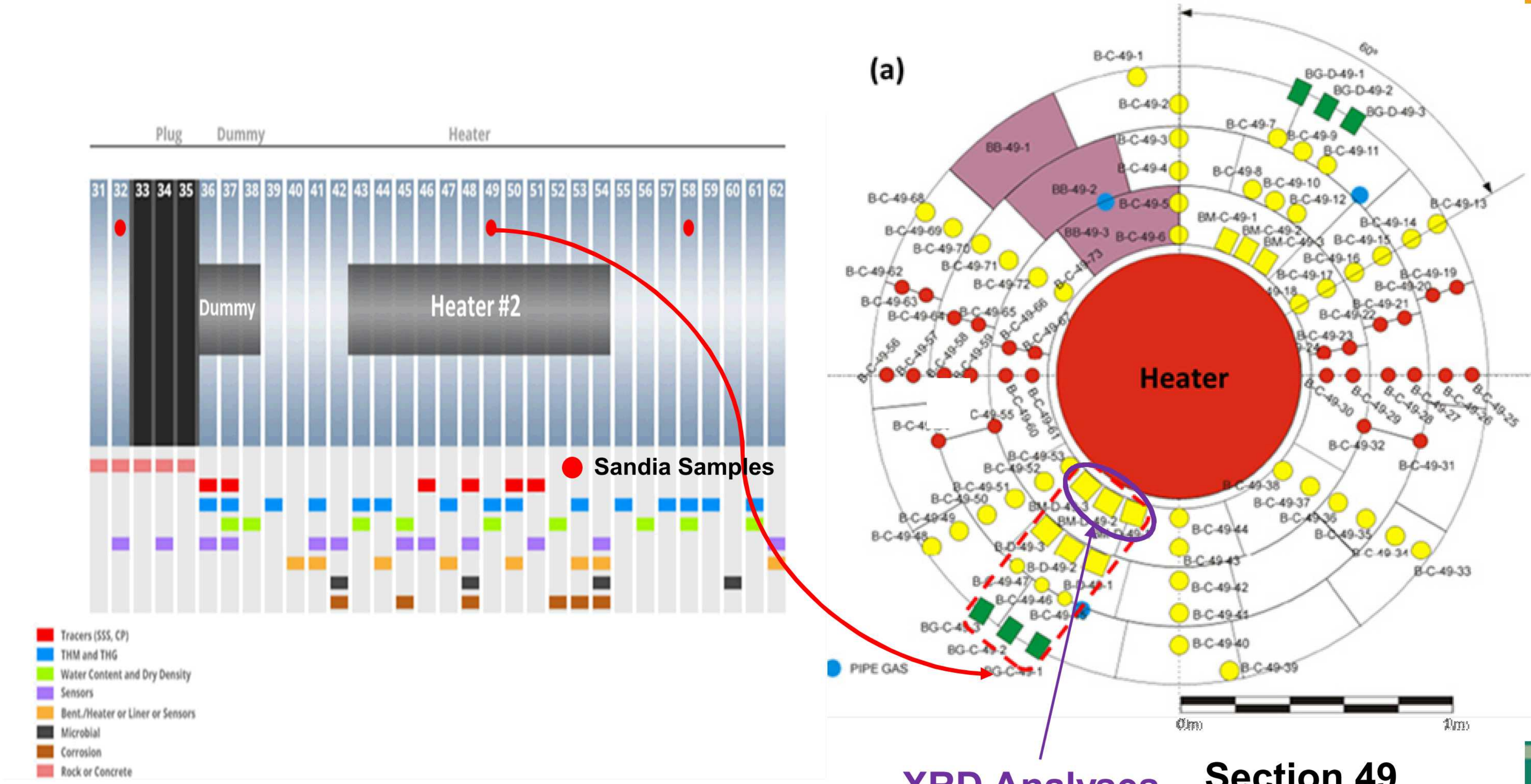






- Large uncertainties on Na_2O content – Issues with detection limits
- Slightly enriched in Fe_2O_3 relative to reference bentonite compositions
- Fe_2O_3, SiO_2, & K_2O fall within the range of reference bentonite compositions

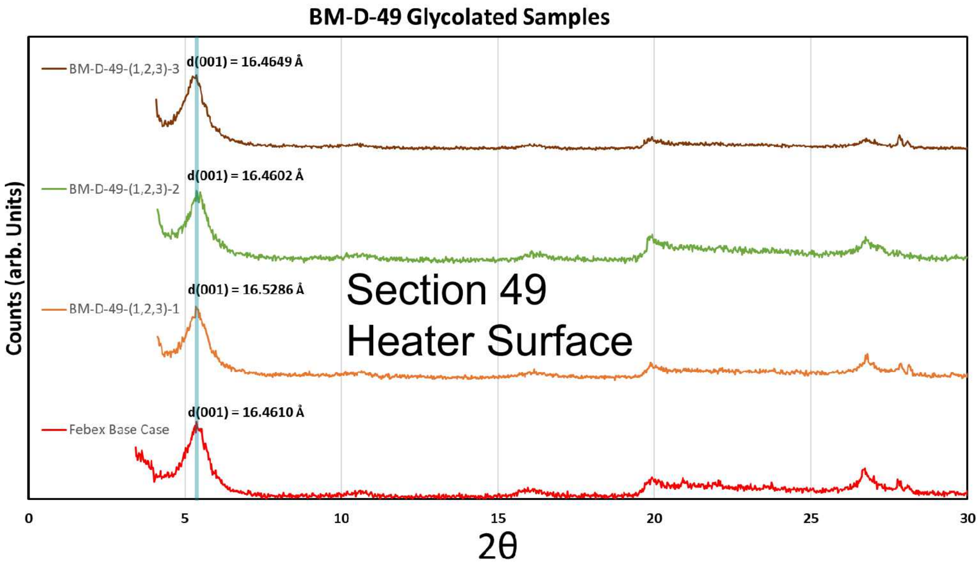
FEBEX-DP Experiment

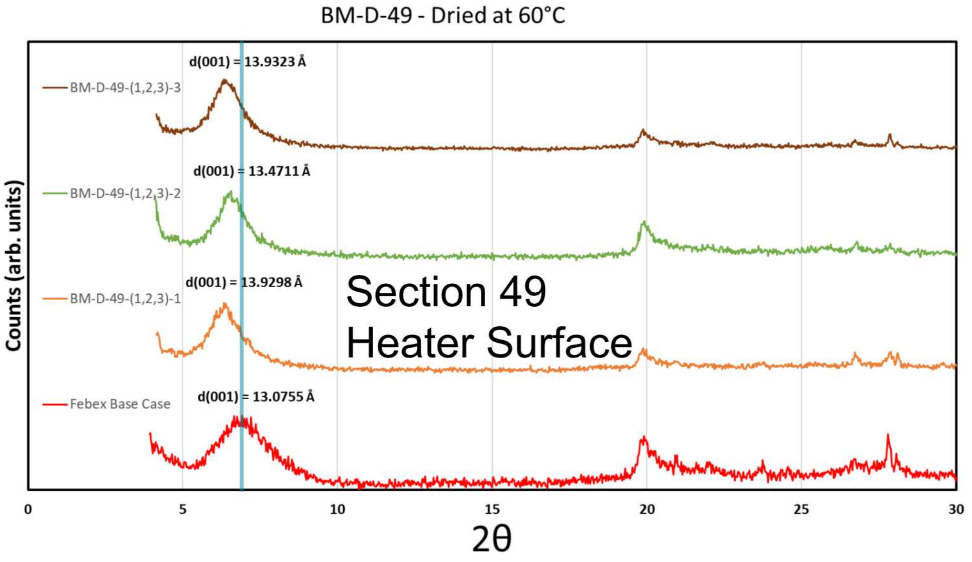


XRD Analyses samples close to heater surface

Section 49

FEBEX-DP: Bentonite X-ray Diffraction (XRD)

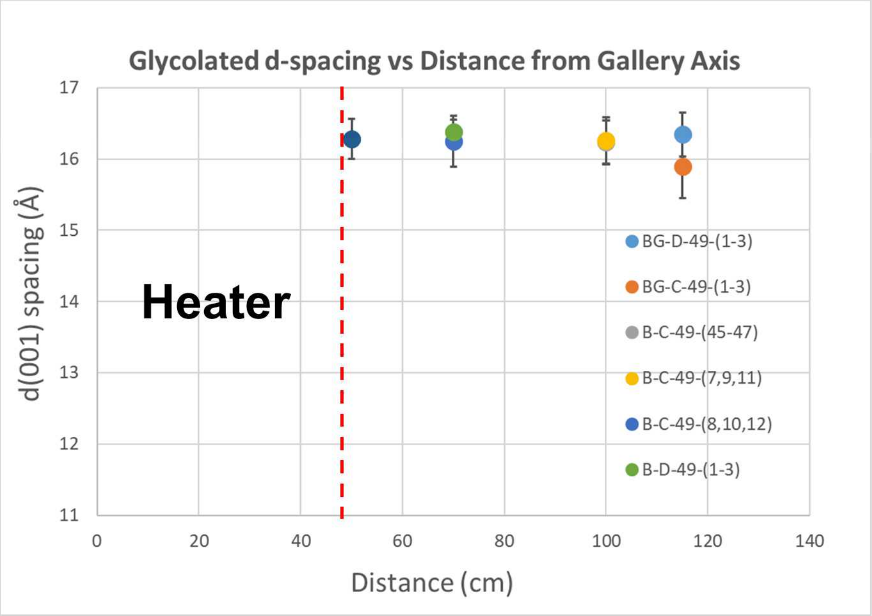


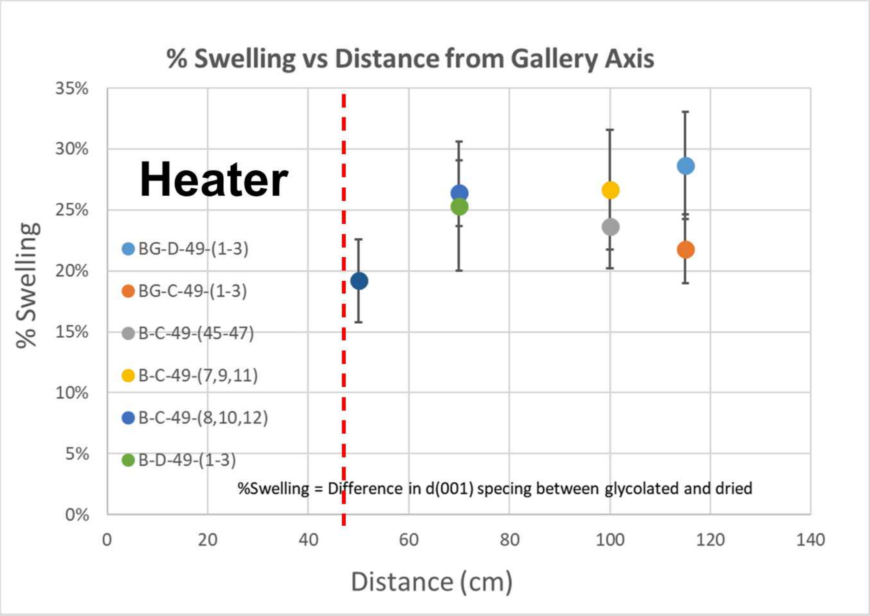


Smectite Clay Structural Characterization:

- Comparison of XRD spectra across sampled domains
- Evaluate d(001) spacings as a function of distance from heater surface
- Smectite d(001) spacings close to the heater surface showed most differences relative to base case FEBEX bentonite
- d(001) spacings from glycolated samples (max. clay expansion) are similar for samples close and far from heater surface
- However, consistent d(001) spacing deviations are observed for dried samples
- Overall, XRD profiles are similar to those reported by others in the FEBEX-DP project

FEBEX-DP: Bentonite X-ray Diffraction (XRD)





- No apparent effect of elevated temperatures on d(001) spacing for glycolated clay samples
- Slight decrease in swelling extent for samples in contact or close to the heater surface
- Prolonged exposure of bentonite to T = 95 – 100 ºC causes some changes in swelling
  - **Correlate with compositional changes in clay close to heater surface**

Summary

- Bentonite-metal interfacial interactions at elevated temperatures:
  - ➢ Produces zeolites (analcime) and sulfide phases
  - ➢ Fe-saponite growth perpendicular to the metal substrate
  - ➢ Little or no illite forms in the experiments and URL heater tests
  - ➢ More work is needed to assess metal passivation effects
  - ➢ Thermodynamic analysis of clay-metal and clay-zeolite equilibria is consistent with experimental observations
- Characterization studies of *post mortem* FEBEX-DP bentonite samples:
  - ➢ Mg-enrichment in clay observed in bentonite close to the heated surface
  - ➢ Slight decrease in bentonite swelling also observed close to the heated surface

Studies on Bentonite Teams

Sandia National Laboratories (SNL)

Carlos F. Jové Colón, Clay Payne, Andrew Knight, Melissa Mills, Jessica Kruichak

Los Alamos National Laboratory (LANL)

Florie Caporuscio, Michael Cheshire (now at ORNL), Kirsten Sauer, Katherine E. Norskog (now at Tulane U.)

Lawrence Berkeley National Laboratory (LBNL)

Patricia Fox, Jonny Rutqvist, Liange Zheng, Jens Birkholzer, Ruth Tinnacher (now at CSU, East Bay), Peter Nico

Acknowledgement

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Questions?

References

Aoki, M. and H. Minato, Lattice constants of wairakite as a function of chemical composition. American Mineralogist, 1980. 65(11-12): p. 1212-1216.

Birkholzer, J., B. Faybishenko, L. Zheng, J. Rutqvist, P. Dobson, P.M. Fox, P. Reimus, H. Viswanathan, C.F. Jove-Colon, Y. Wang, K. Kuhlman, K. McMahon, and M. Zavarin, International Collaboration Activities in Different Geologic Disposal Environments (SFWD-SFWST-2017-000013), in Prepared for US Department of Energy, Spent Fuel and Waste Disposition Campaign (SFWD-SFWST-2017-000013)2017, (National Laboratory Report No. LBNL-2001063): Berkeley, California. 236 pp.

Cheshire, M., F.A. Caporuscio, M.S. Rearick, C.F. Jové Colón, and M.K. McCarney, Bentonite evolution at elevated pressures and temperatures: An experimental study for generic nuclear repository designs. American Mineralogist, 2014. 99: p. 1662-1675.

Cheshire, M.C., F.A. Caporuscio, C.F. Jové Colón, and K.E. Norskog, Fe-saponite growth on low-carbon and stainless steel in hydrothermal-bentonite experiments. Journal of Nuclear Materials, 2018. 511: p. 353-366.

Fernandez, A.M., B. Baeyens, M. Bradbury, and P. Rivas, Analysis of the porewater chemical composition of a Spanish compacted bentonite used in an engineered barrier. Physics and Chemistry of the Earth, 2004. 29(1): p. 105-118.

García-Siñeriz, J.L., H. Abós, V. Martínez, C. De la Rosa, U. Mäder, and F. Kober, FEBEX DP: Dismantling of heater 2 at the FEBEX "in situ" test: Description of operations - Arbeitsbericht NAB 16-11, 2016, National Cooperative for the Disposal of Radioactive Waste (NAGRA): Wettingen, Switzerland. p. 1-136.

Huertas, F., J.L. Fuentes-Cantillana, F. Jullien, P. Rivas, J. Linares, P. Fariña, M. Ghoreychi, N. Jockwer, W. Kickmaier, M.A. Martínez, J. Samper, E. Alonso, and F.J. Elorza, *Full-scale engineered barriers experiment for a deep geological repository for high-level radioactive waste in crystalline host rock (FEBEX project): Final report. EUR 19147, 2000: European Commission, Brussels.*

Iijima, A. and R. Hay, Analcime composition in tuffs of Green River Formation of Wyoming. American Mineralogist, 1968. 53(1-2): p. 184.

Jerden, J., E. Lee, V.K. Gattu, and W.L. Ebert, Results from In-Package Alloy Electrochemical Corrosion Experiments: Implications for Long-Term Spent Fuel Degradation (ANL/CFCT-19/2), 2019, Argonne National Laboratory: Illinois, USA. 55 pp.

Jové Colón, C.F., International Collaboration Activities on Engineered Barrier Systems (FCRD-UFD-2016-000628), 2016, Sandia National Laboratories: Albuquerque, NM, SAND2016-8935 R. 26 pp.

Jové Colón, C.F., Y. Wang, T. Hadgu, L. Zheng, J. Rutqvist, H. Xu, K. Kim, M. Voltolini, X. Cao, P.M. Fox, P.S. Nico, F.A. Caporuscio, K.E. Norskog, M. Zavarin, T.J. Wolery, C. Atkins-Duffin, J.L. Jerden, V.K. Gattu, and W.L. Ebert, Evaluation of Used Fuel Disposition in Clay-Bearing Rock (SFWD-SFWST-2017-000006), 2017, Sandia National Laboratories: Albuquerque, NM. SAND2017-10533 R. 442 pp.

Mäder, U., K. Detzner, F. Kober, H. Abplanalp, T. Baer, and V. Cloet, FEBEX-DP - Plug Overcoring and Concrete-Bentonite Interface Sampling Prior to Dismantling, in Arbeitsbericht NAB 16-10, 2016, NAGRA: Wettingen, Switzerland.

Neuhoff, P.S., G.L. Hovis, G. Balassone, and J.F. Stebbins, Thermodynamic properties of analcime solid solutions. American Journal of Science, 2004. 304(1): p. 21-66.

Sassani, D.C., C.F. Jové Colón, P. Weck, J.L. Jerden, K.E. Frey, T. Cruse, W.L. Ebert, E.C. Buck, and R.S. Wittman, Used Fuel Degradation: Experimental and Modeling Report (FCRD-UFD-2013-000404), 2013, U.S. Department of Energy (DOE), Sandia National Laboratory Report SAND2013- 9077P: Albuquerque, New Mexico USA., 123 pp.

Seki, Y. and Y. Oki, Wairakite-analcime solid solutions from low-grade metamorphic rocks of the Tanzawa Mountains, Central Japan. Mineralogical Journal, 1969. 6(1-2): p. 36-45.

Steiner, A., Wairakite, the calcium analogue of analcime a new zeolite mineral. Mineralogical Magazine, 1955. 30(230): p. 691-698.

Villar, M.V., A.M. Fernandez, E. Romero, A. Dueck, J. Cuevas, M. Plotze, S. Kaufhold, R. Dohrmann, R.J. Iglesias, T. Sakaki, M. Voltolini, L. Zheng, K. Kawamoto, and F. Kober, FEBEX-DP Post-mortem THM/THG Analysis Report, in NAGRA Arbeitsbericht NAB 16-17, 2017, NAGRA: Wettingen, Switzerland. 187 pp.

Villar, M.V., R.J. Iglesias, and J.L. García-Siñeriz, State of the in situ Febex test (GTS, Switzerland) after 18 years: a heterogeneous bentonite barrier. Environmental Geotechnics, 2018: p. 1-13.

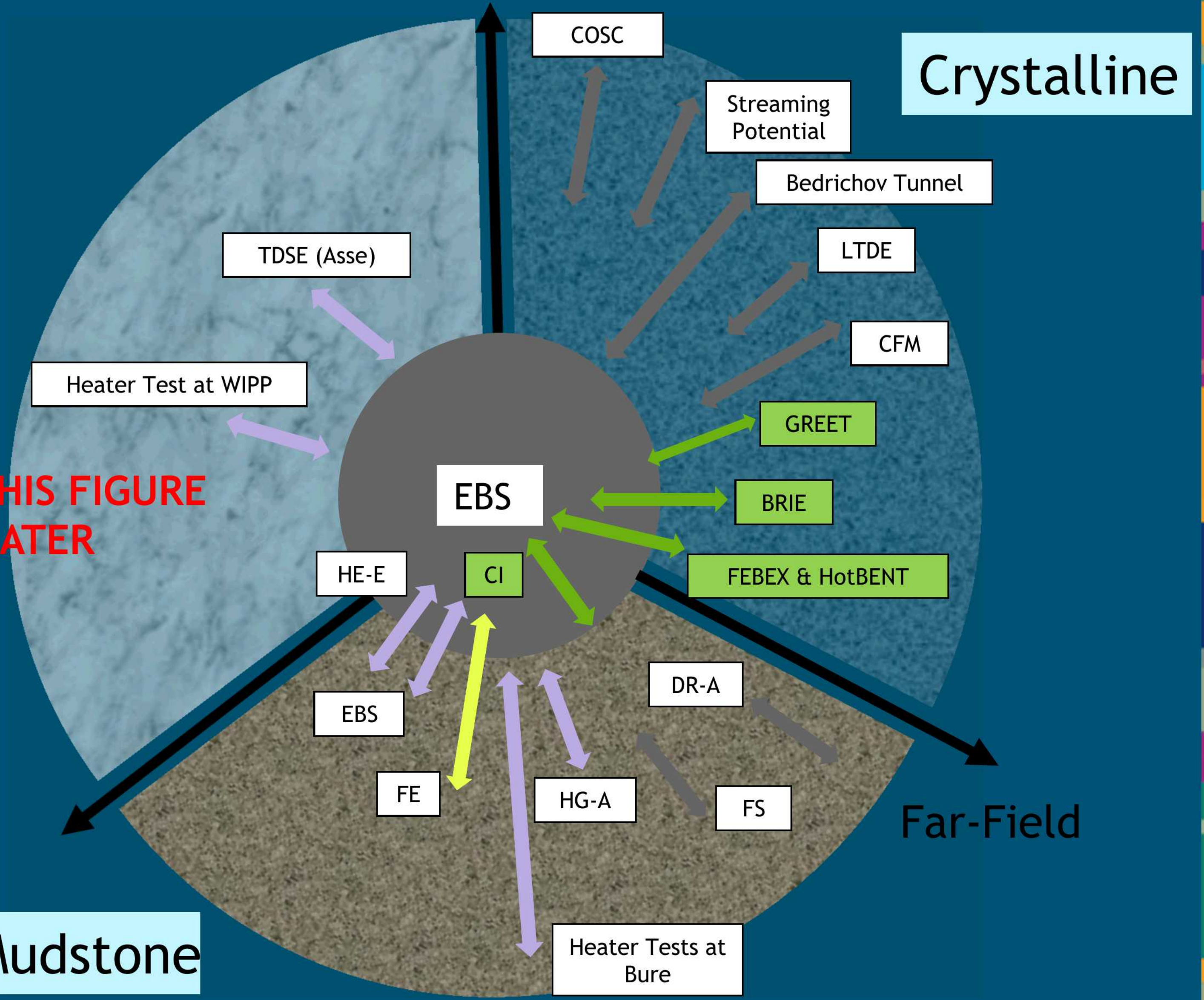
EXTRA SLIDES

EBS fits in the DOE Underground Research Laboratory (URL) Portfolio

Key R&D Issues

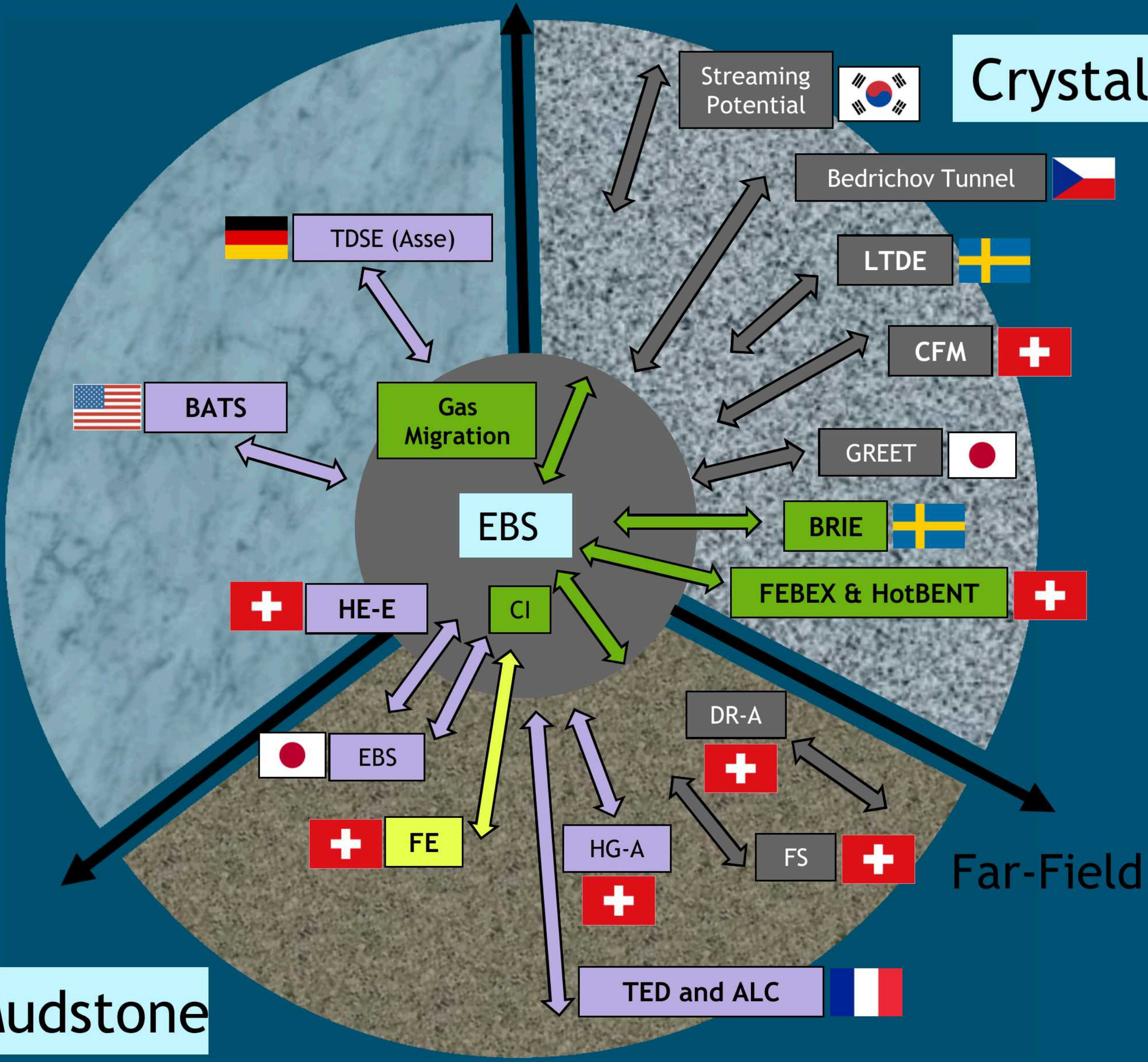
- Near-Field Perturbation
- Engineered Barrier Integrity
- Radionuclide Transport
- Demonstration of Integrated System Behavior

FINAL VERSION OF THIS FIGURE WILL BE PROVIDED LATER



International URL Portfolio in a Nutshell

Key R&D Issues
Near-Field Perturbation
Engineered Barrier Integrity
Flow and Radionuclide Transport
Demonstration of Integrated System Behavior



Repository Phases and Relevant Processes

Key R&D Issues

- Near-Field Perturbation
- Engineered Barrier Integrity
- Flow and Radionuclide Transport
- Demonstration of Integrated System Behavior

BATS

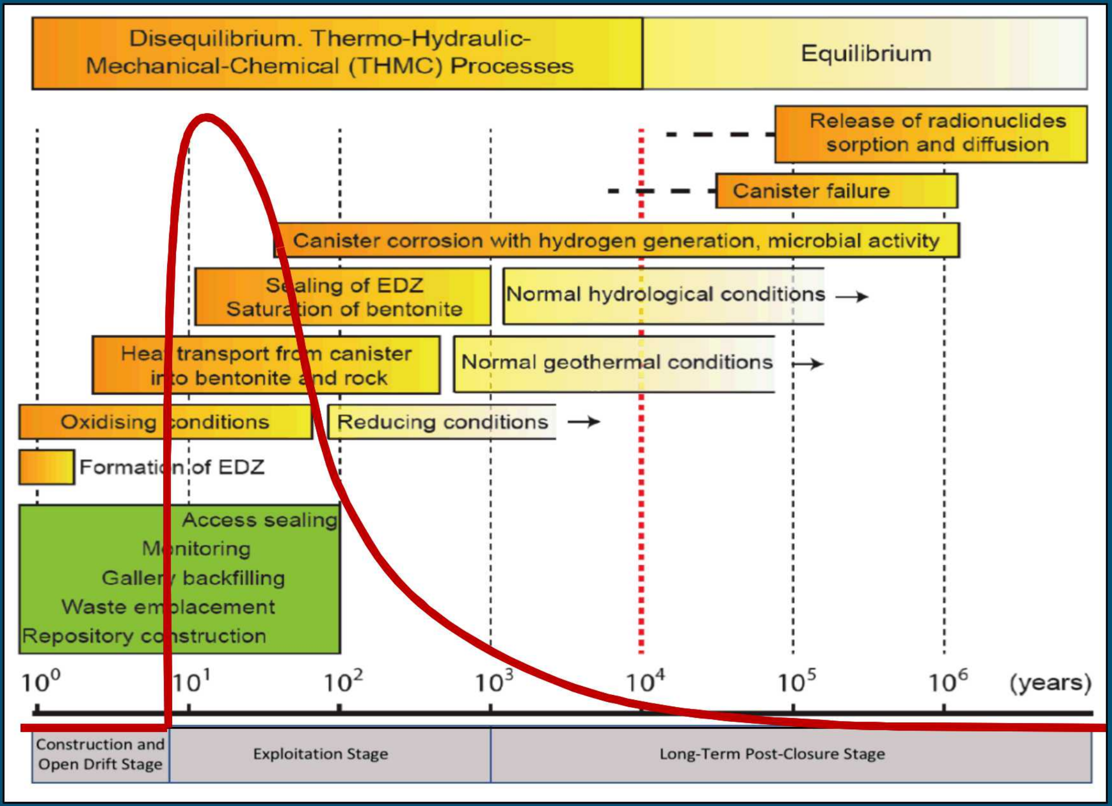
FEBEX & HotBENT

BRIE

Gas Migration

CFM

LTDE

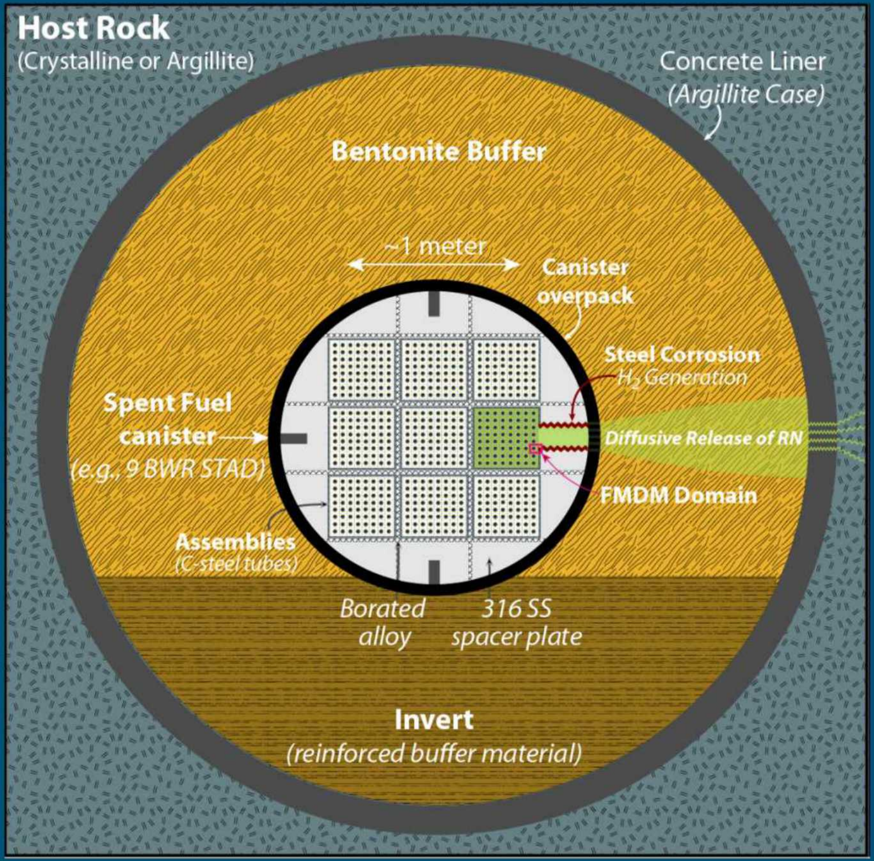


TED, ALC, HE-E

FE

What is the Engineered Barrier System (EBS)?

- **EBS definition from the US Nuclear Regulatory Commission (10 CFR 60.2)**
  - “Engineered barrier system means the waste packages and the underground facility”
- **EBS definition from to the NEA/OECD EBS State-Of-The-Art Report (2003):**
  - “The “engineered barrier system” represents the man-made, engineered materials placed within a repository, including the waste form, waste canisters, buffer materials, backfill and seals.”



Generic EBS concept with bentonite barrier showing a canister breaching scenario (Jerden et al. 2019)

Thermal Implications on Transport in Bentonite Team

Sandia National Laboratories (SNL)

Carlos F. Jové Colón, Clay Payne, Andrew Knight, Melissa Mills
Jessica Kruichak, Ed Matteo (EBS)

Los Alamos National Laboratory (LANL)

Florie Caporuscio, Michael Chesire (now at ORNL), Kirsten Sauer

Lawrence Berkeley National Laboratory (LBNL)

Patricia Fox, Jonny Rutqvist, Liange Zheng, Jens Birkholzer, Ruth Tinnacher (now at CSU, East Bay), Peter Nico

Lawrence Livermore National Laboratory (LLNL)

Mavrik Zavarin, Enrica Balboni, Thomas J. Wolery

Argonne National Laboratory (ANL)

James Jerden, William Ebert

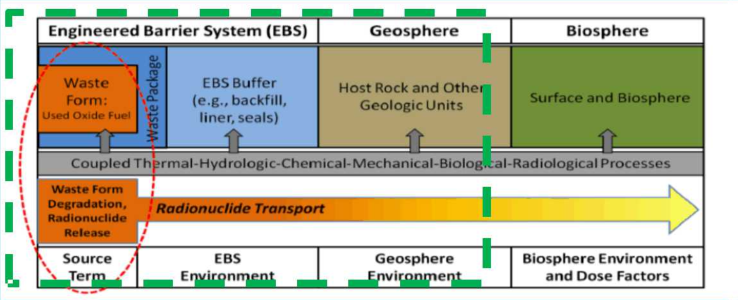
Pacific Northwest National Laboratory (PNNL)

Edgar Buck

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) 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 URL (Switzerland)**

GDSA PA Level Of Integration



Engineered Barrier System (EBS) | Geosphere | Biosphere

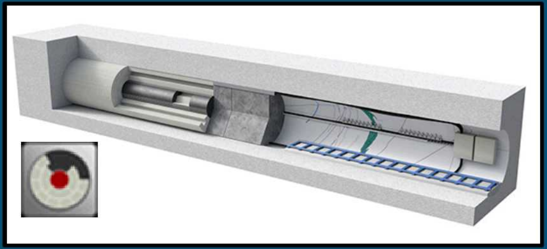
Waste Form: Used Oxide Fuel
Waste Package
EBS Buffer (e.g., backfill, liner, seals)
Host Rock and Other Geologic Units
Surface and Biosphere

Coupled Thermal-Hydrologic-Chemical-Mechanical-Biological-Radiological Processes

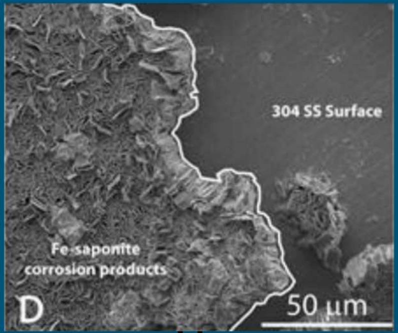
Waste Form Degradation, Radionuclide Release
Radionuclide Transport

Source Term
EBS Environment
Geosphere Environment
Biosphere Environment and Dose Factors

International Collaboration: FEBEX-DP



Clay-Metal Interactions

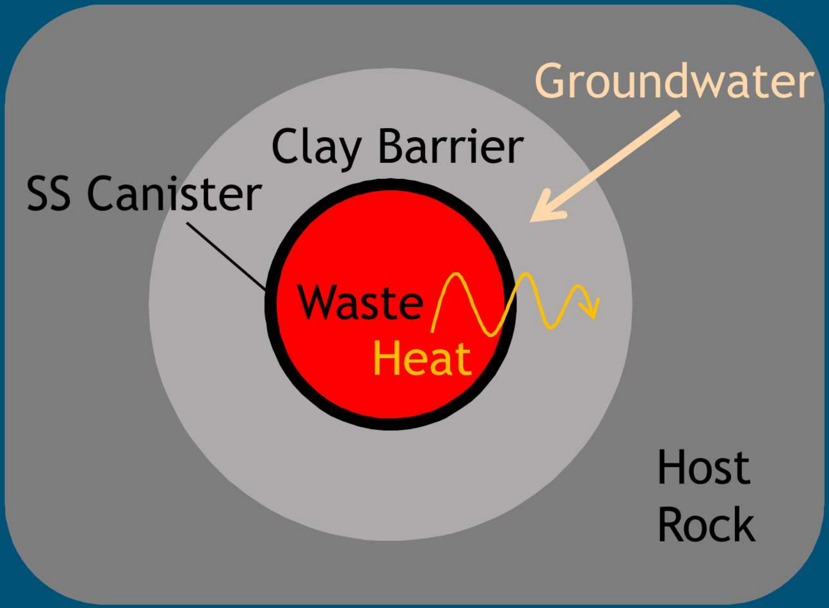


Steel Corrosion

Understanding radionuclide adsorption to clay under realistic waste-disposal scenarios

- Heat-generating waste canisters increase temperatures of surrounding engineered barriers
- Groundwater Intrusion from surrounding host rock

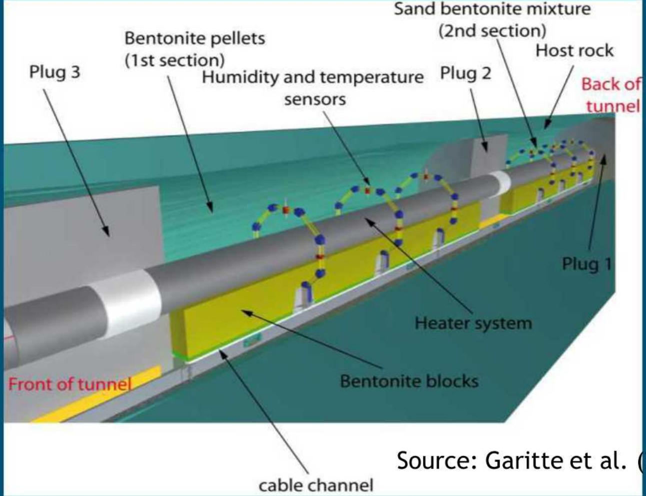
- Variable saturation across clay barrier
- Changes in pore water chemistry
- Changes in accessory mineral assemblage (e.g., calcite, pyrite)
- Changes in clay structure/composition (e.g., illitization, ion exchange)



- Changes in aqueous radionuclide (RN) speciation
- Changes in mineral sorption capacity
- Changes in swelling behavior

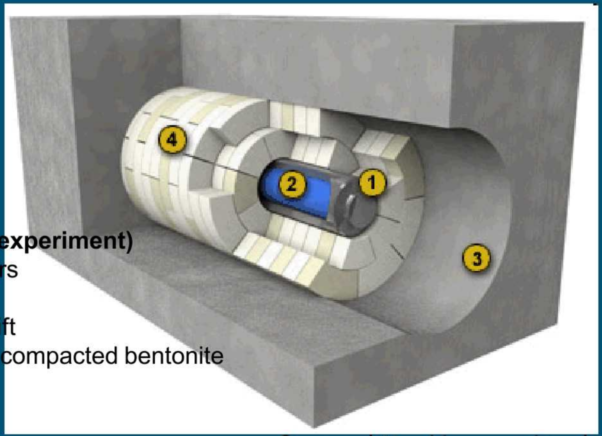
What has been done for EBS? (Cont.)

- International Activities:
  - **Underground Research Laboratories (URLs)**:
    - Mt. Terri (Opalinus Clay, Switzerland)
    - Grimsel (Granite, Switzerland)
    - Tournemire (Argillite, France)
    - Meuse/Haute-Marne (BURE) (Callovo-Oxfordian Clay, France)
    - FEBEX (Mock-Up, Spain; Granite, Site-Scale, Grimsel site, Switzerland)
    - KAERI/KURT (Granite, South Korea)
    - Horonobe (Mudstones) and Mizunami (Granite) Sites (Japan)
  - **International Collaborations**
    - DECOVALEX (Development of Coupled Models and their Validation Against Experiments, International Collaboration)
    - SKB EBS Task Force



Source: Garitte et al. (2011)

HE-E heater test at Mont Terri



FEBEX (in situ experiment)
(1) Steel canisters
(2) Waste
(3) Horizontal drift
(4) High-density compacted bentonite blocks

Source: http://www.grimsel.com

For more details, see Birkholzer et al. (2017)

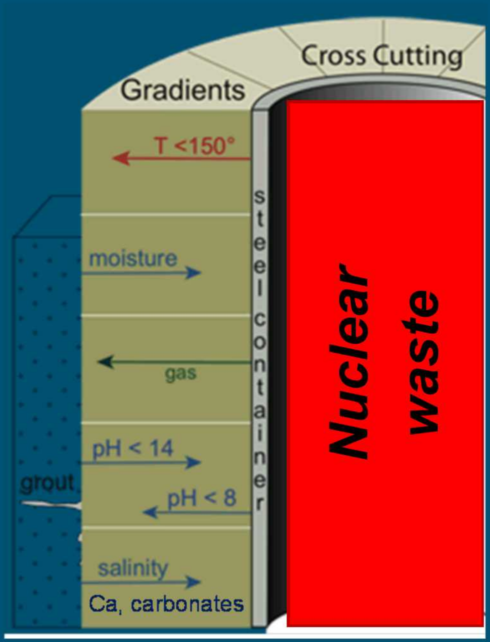
Conceptual Model for Transport in Bentonite

The long-term management of nuclear waste requires reliable predictions of radionuclide transport through engineered barrier systems (EBS).

⇨ **Compacted bentonite (montmorillonite)** is the proposed backfill material in EBS.

⇨ **Diffusion** will be the dominant transport mechanism in EBS that contributes to radionuclide dose in the environment.

⇨ **Gradients of chemical solution conditions and temperature** are expected over time and across EBS.



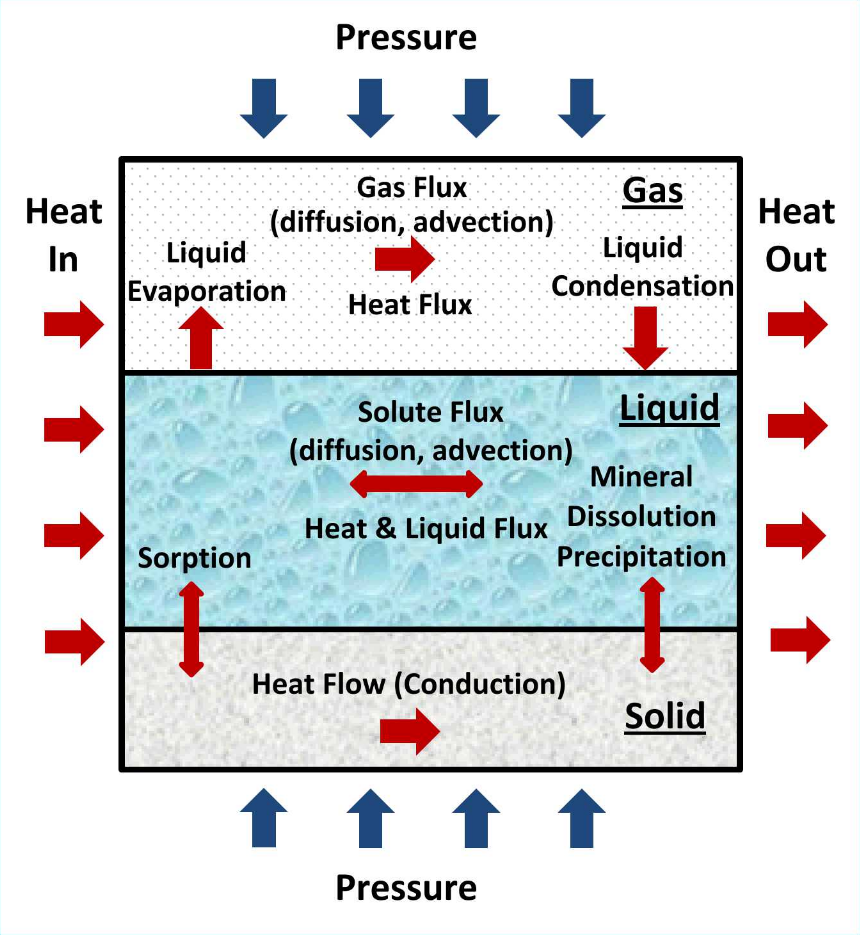
Goals:

- **Decrease the uncertainty** in actinide sorption / diffusion sub-models that are part of performance assessment models for waste repositories.
- **Investigate effects of changing chemical conditions and temperatures** on uranium(VI) sorption and diffusion.

SFWST Needs for EBS?

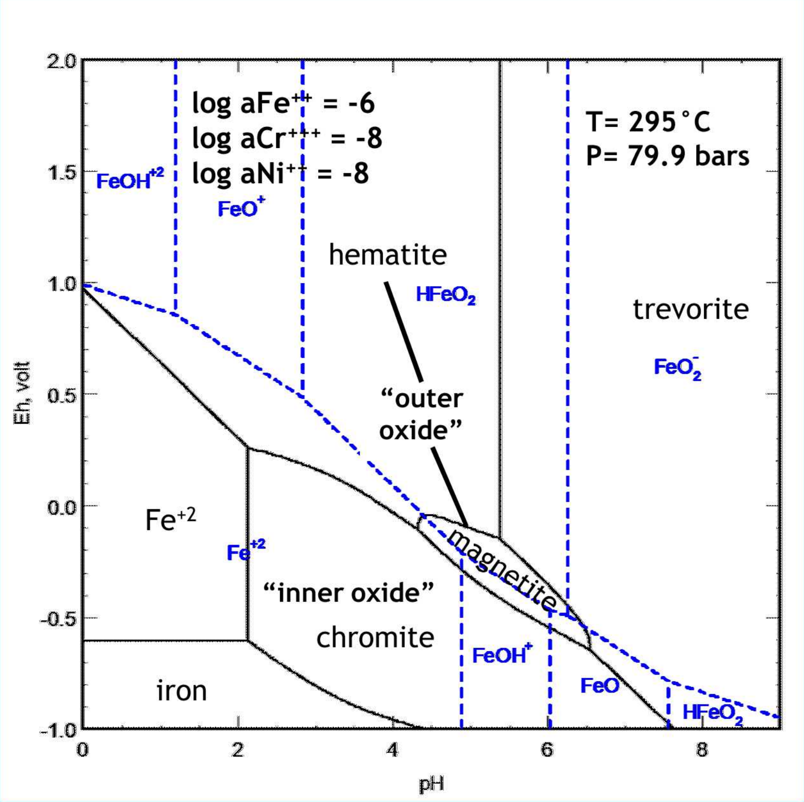
- Highest ranked issues:
  - Waste Form
  - THM Processes
  - Waste Container
  - Radionuclide speciation and solubility
  - Buffer/Backfill material
- **THMC processes** relevant to interactions at **EBS interfaces:**
  - **Loci for important degradation processes in the near-field**
  - **Shares a boundary with far-field region**
  - **THMC models must assess the generic aspects of EBS design concepts**

THMC Processes in the EBS

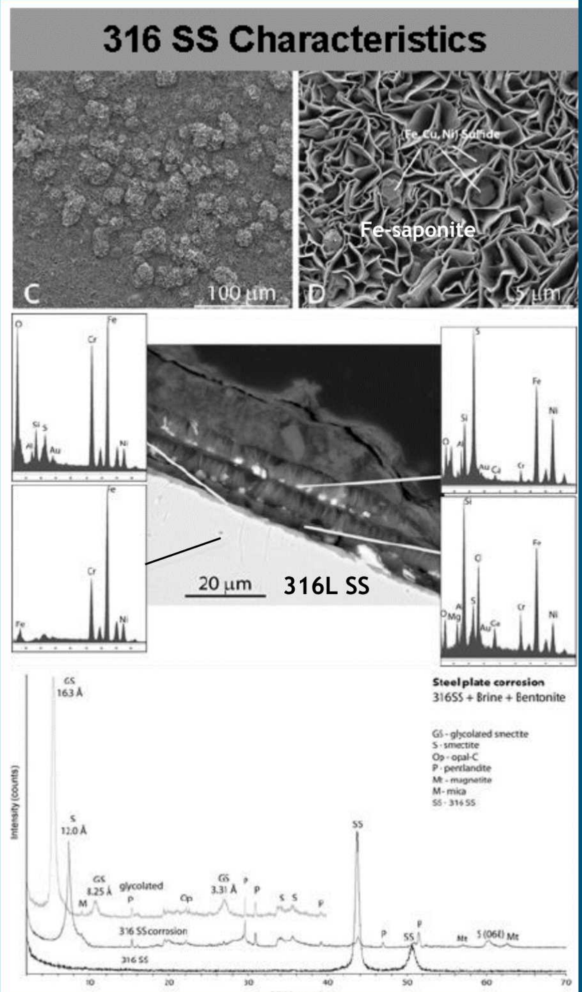


Modified After Olivella et al. (2011)

Bentonite – Metal Interaction Experiments



Cheshire et al. (2014)



Experiment

- T = 300ºC
- STRIPA Brine
- Wyoming Bentonite
- 316 Stainless Steel (SS), 304SS, low-C steel

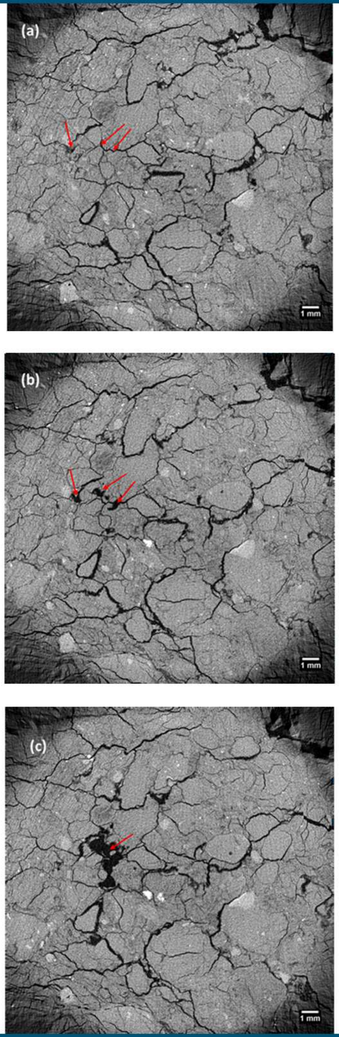
Results

- Fe-Saponite growth perpendicular to metal
- Concurrent sulfide precipitation
- Observations consistent with thermodynamic relations

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

ack

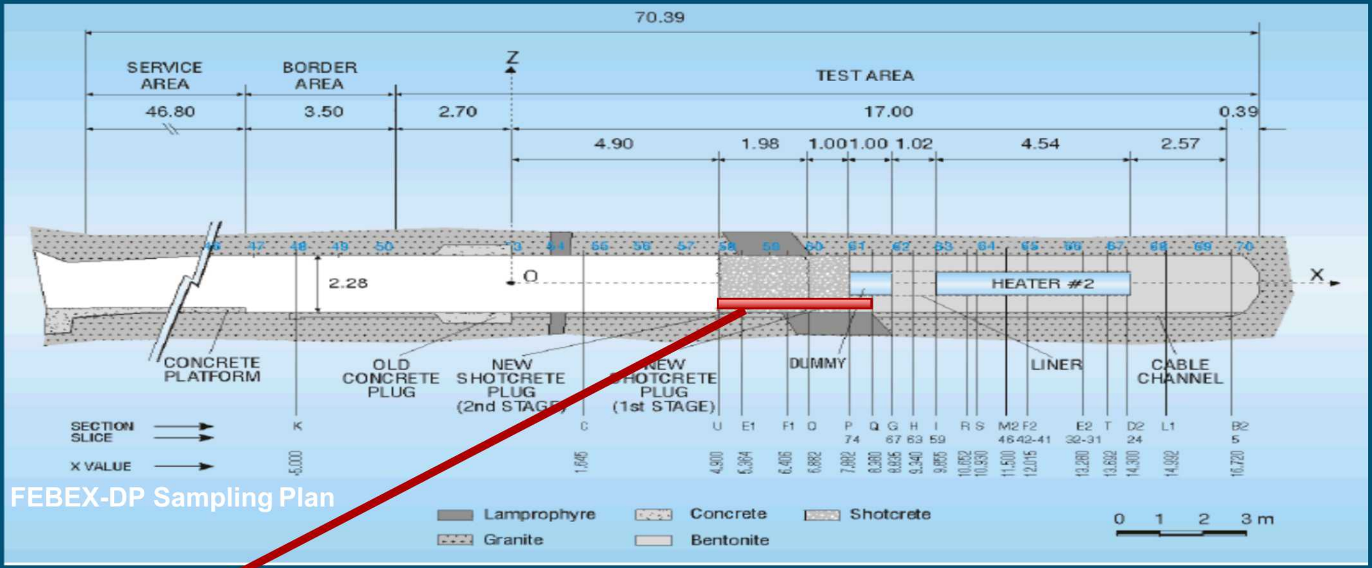
n



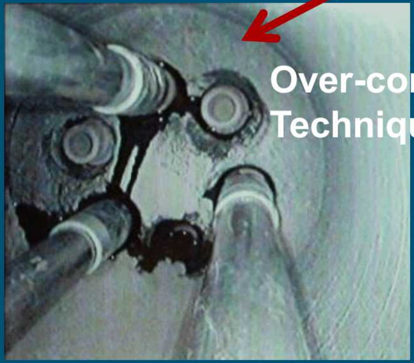
Red arrows: microcrack segments evolving into pores

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

FEBEX-DP: Shotcrete – Bentonite Interface Core Extraction



FEBEX-DP Sampling Plan



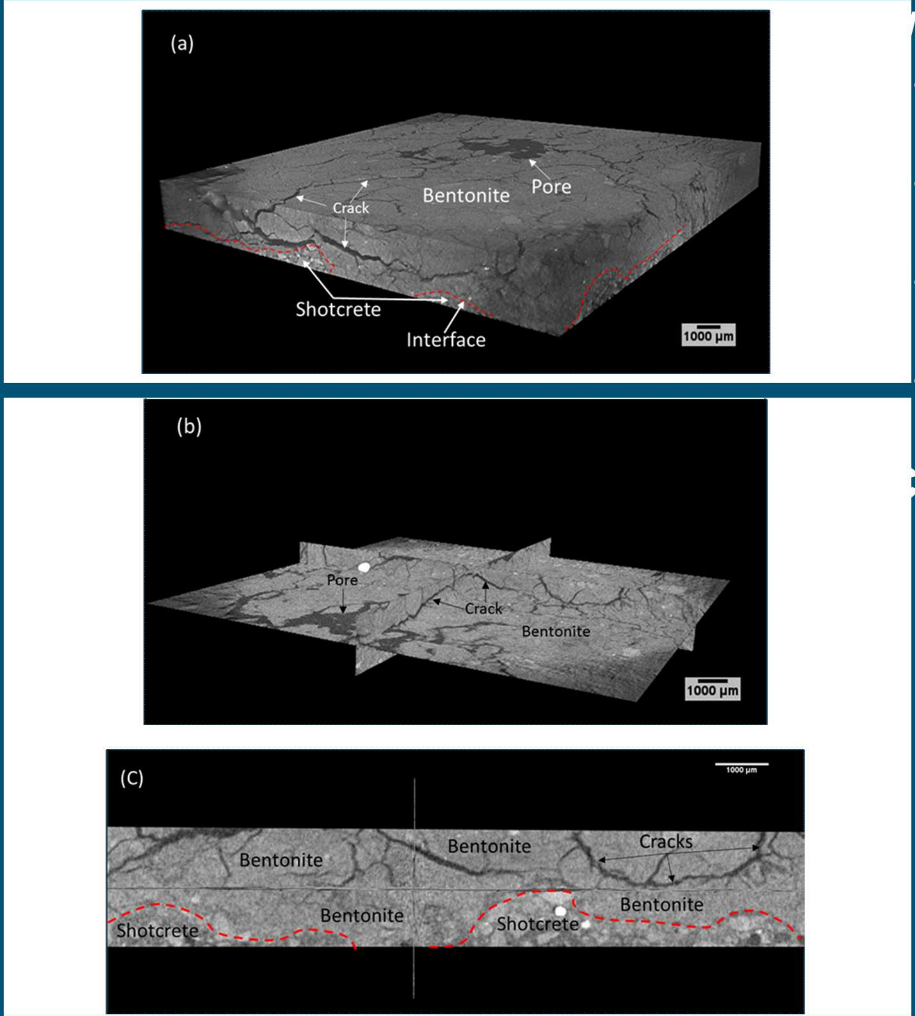
Over-coring Technique

Mäder et al. (2016)

C. F. Jove Colon (SNL)

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

Bentonite – Concrete Interface Characterization (X-ray CT Scan)



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:

<u>Bentonite:</u>

Continuous and discontinuous pore-microcrack networks (2D & 3D)

Large pores tend to be connected to microcracks

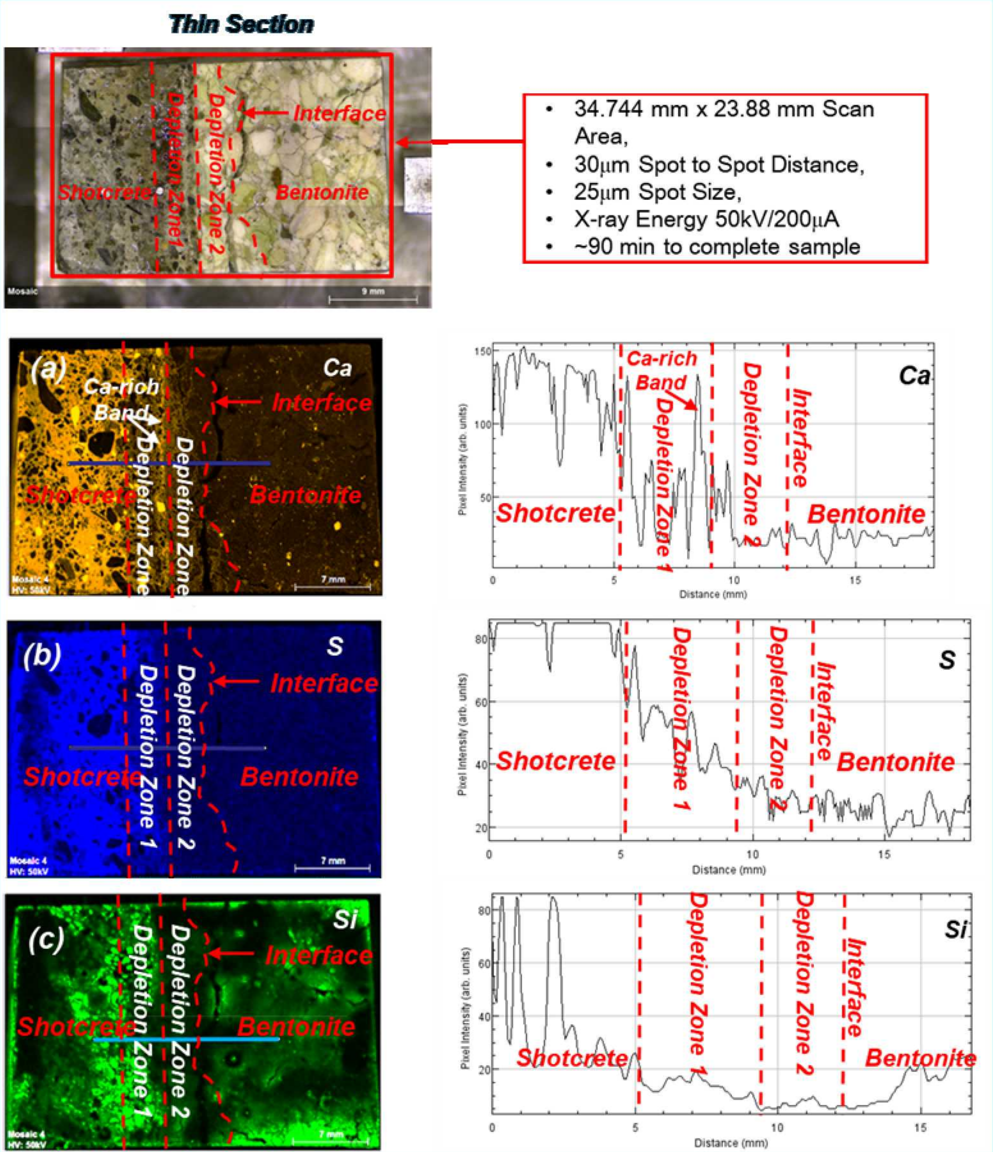
<u>Shotcrete:</u>

Bentonite: Large pores tend to be connected to microcracks

No or little microcracks

Isolated pores except at the interface

Shotcrete - Bentonite Interface Characterization (μ-XRF)



- 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

Main Features

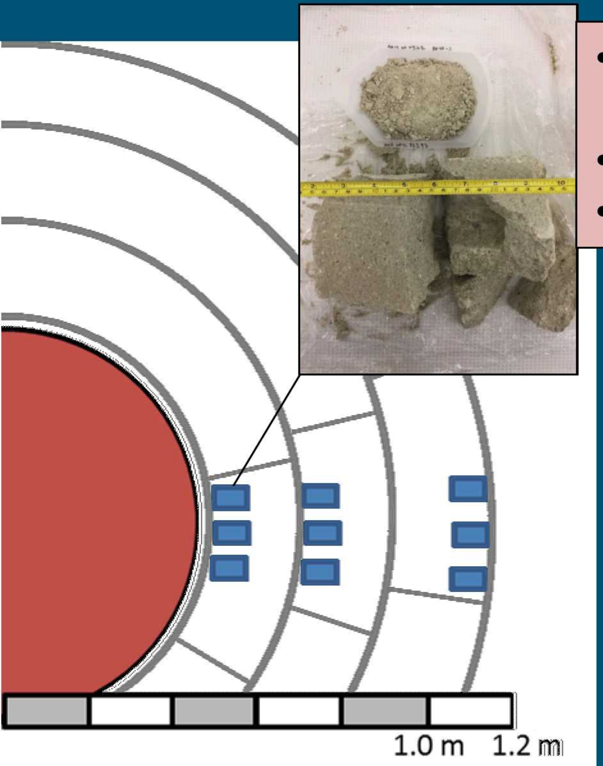
- Compositional map at thin section (mm) scale – Scanning at the μm scale
- Sharp compositional changes at the bentonite-shotcrete interface
- Consistent spatial correlation among various elements across interface

Compositional Gradients

- Depletion on shotcrete side of the interface → Leaching?
- Bentonite seems compositional homogeneous at the interface
- Limited reaction front?

Jové Colón et al. (2017)

U(VI) adsorption experiments: FEBEX-DP clay samples that experienced different temperature and moisture regimes



Heated Zone:

- 50 cm from axis (Section 48)
- T= 95°C
- Moisture Content≅18%

Cold Zone:

- 50 cm from axis (Section 59)
- T= 20°C
- Moisture Content ≅ 25%

<u>Original FEBEX Bentonite Mineral Composition</u>*
92 % smectite (illite-smetite mixed layer, with ~11% illite layers)
2% plagioclase
2% quartz
2% cristobalite
<1% potassium feldspar, calcite, trydimite, Fe- and Al-oxides

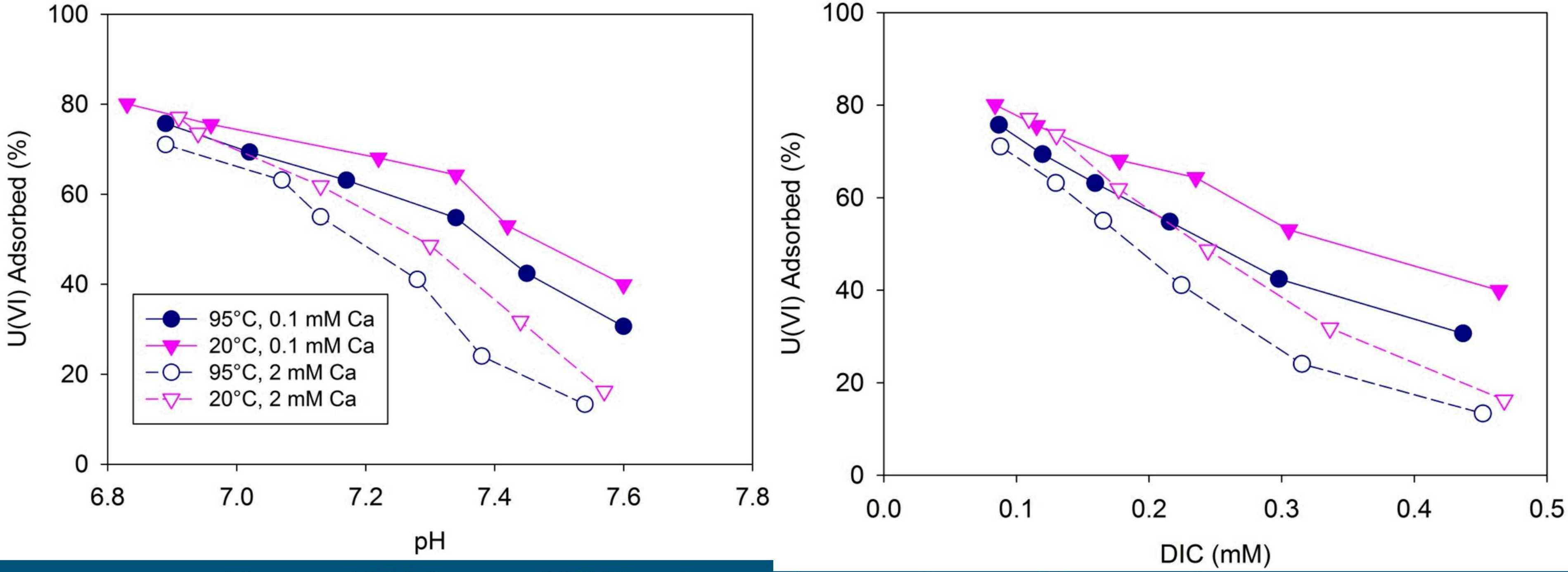
*Fernández et al. (2004)

Composite samples were created from 3 replicate blocks from each location, air-dried and sieved to < 63 mm.

Moisture content and temperature from Villar et al. (2018)

Lower U(VI) Sorption onto Heated Bentonite

< 63 mm fraction, bentonite composite samples, 0.5 g/L bentonite



Up to 10% lower U(VI) adsorption on heated bentonite.

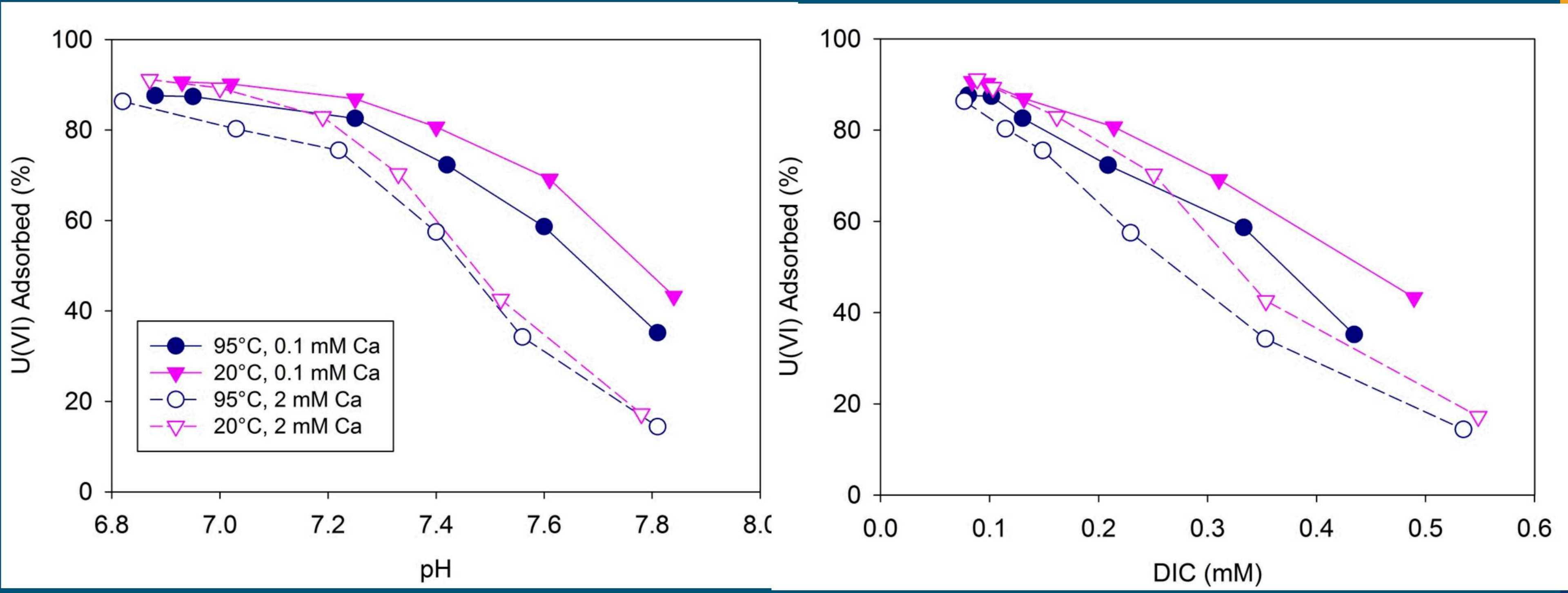
- Adsorption is lower in presence of 2 mM Ca compared to 0.1 mM Ca.
- Adsorption decreases as pH and DIC increase.

Possible reasons for lower U(VI) adsorption:

- aqueous U(VI) speciation
- relative fraction of clay (montmorillonite) mineral phase
- structure/composition of clay mineral fraction
- structure/composition of accessory mineral fraction (e.g., Fe-oxides)

U(VI) adsorption onto **purified** bentonite

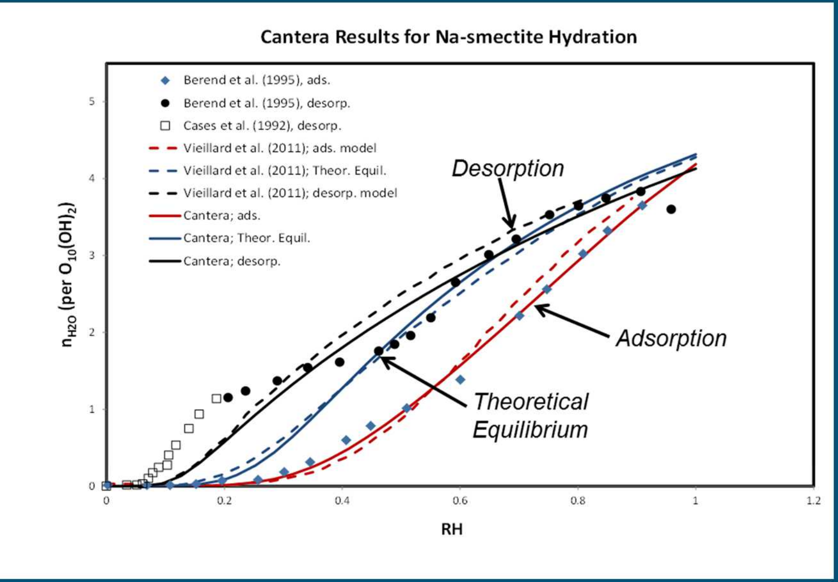
< 2 µm fraction, carbonate minerals removed



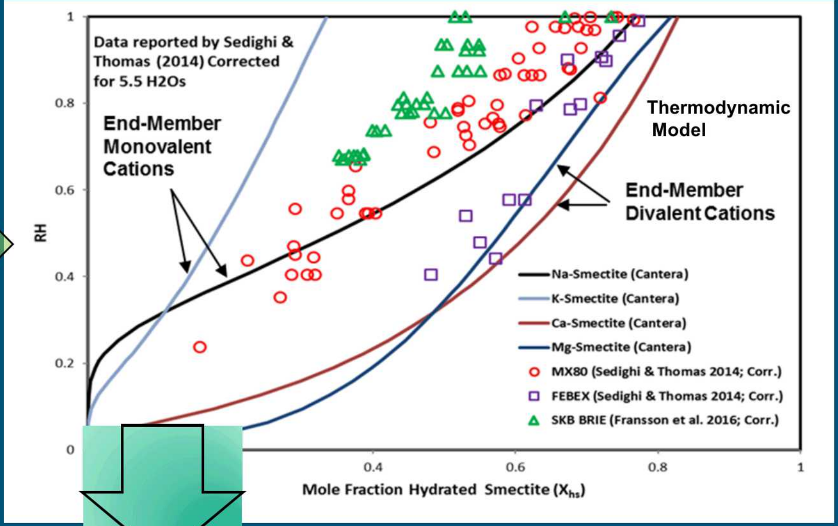
Lower U(VI) adsorption on 95°C heated bentonite persists after purification.

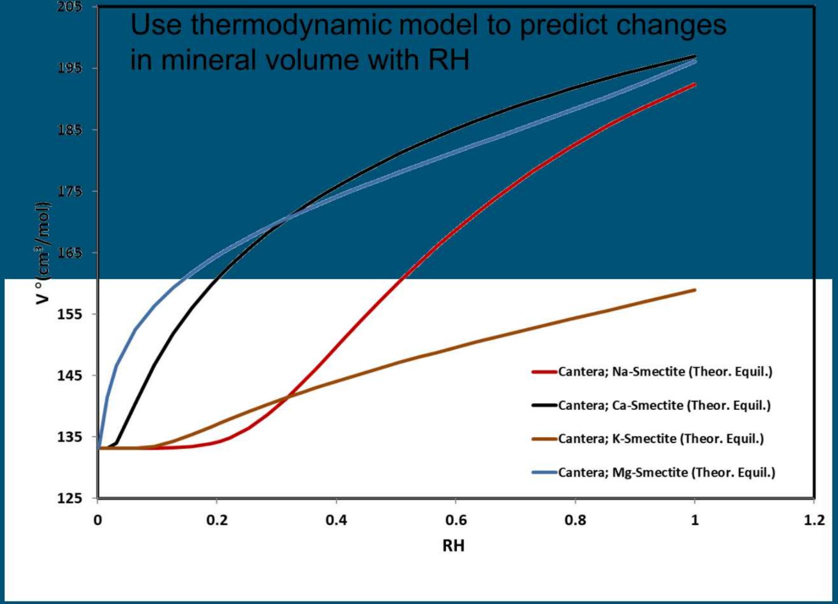
- Consistently lower U(VI) adsorption onto 95°C heated sample in presence of 0.1 mM Ca
- Smaller difference in presence of 2 mM Ca
- As with bulk samples, U(VI) adsorption is lower at higher Ca concentration

Clay Hydration Modeling: Comparison with BRIE Water Retention Data + MX80 Bentonite



Fitting H_2O adsorption data for various smectite clay compositions

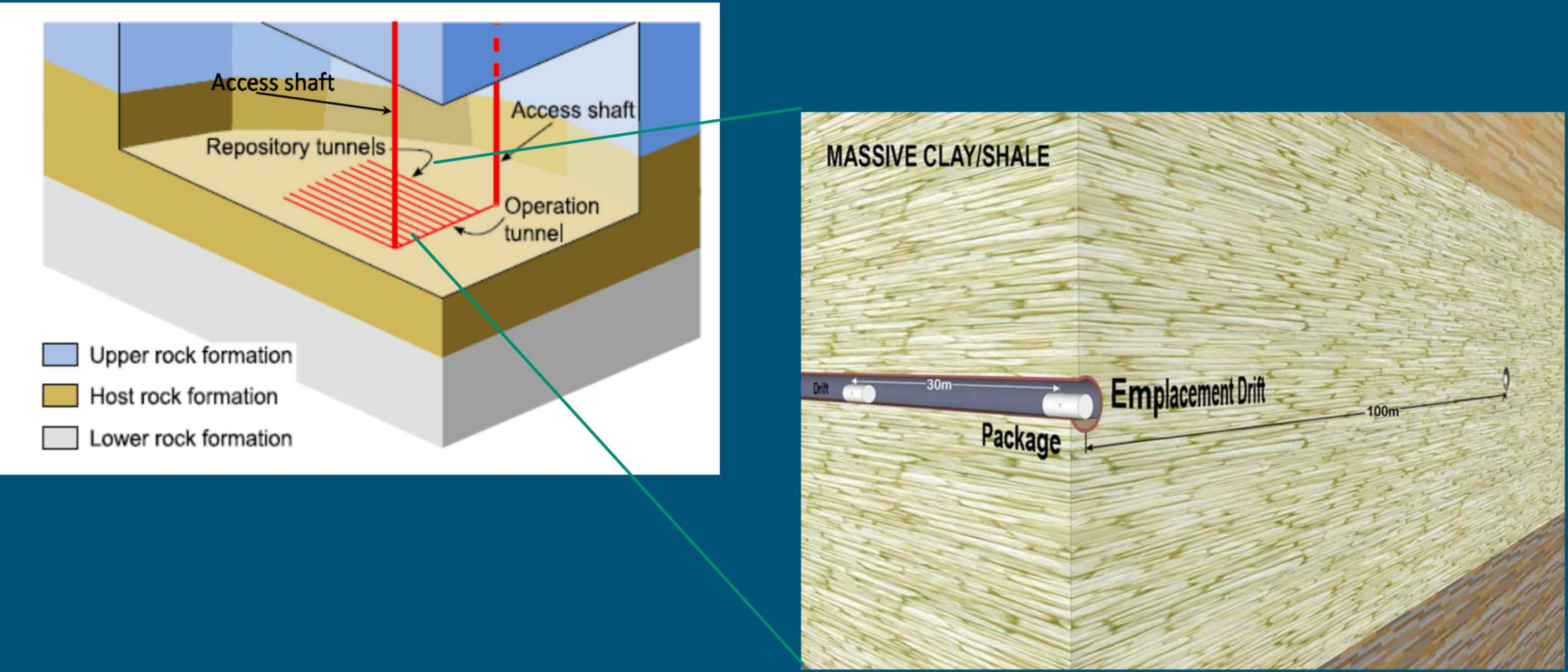




Use thermodynamic model to predict changes in mineral volume with RH

- **Relationships between clay composition and swelling behavior**
- **Data retrieval from URL and laboratory experiments**
  - **FEBEX**
  - **Bentonite MX80**
- **Trends for monovalent and divalent cationic composition consistent with thermodynamic model predictions for clay hydration**

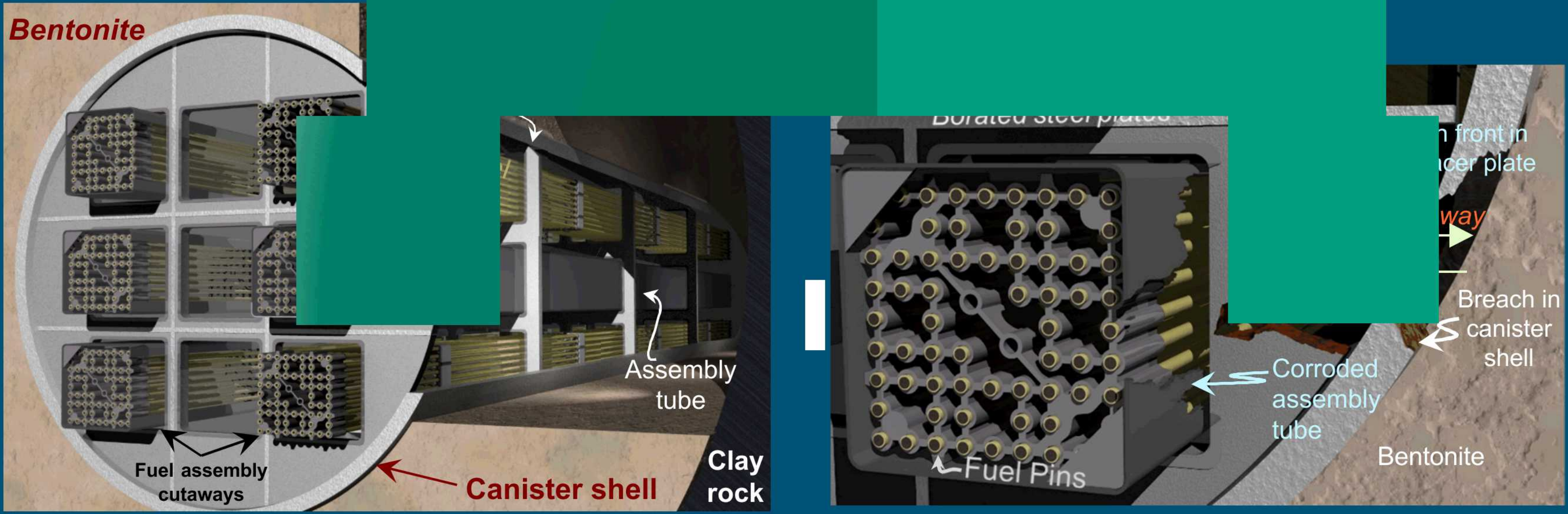
Spent Fuel Waste Science Technology (SFWST) Campaign: Disposal in Argillaceous Clay Rock



- Coupled process modeling of Thermal-Hydrological-Chemical-Mechanical (THCM) 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) corrosion)**
  - **Low temperature radionuclide (RN) sorption/diffusion in bentonite & modeling**

Conceptual Model for Transport in Bentonite

Slide content: Jim Jerden (ANL) and Ruth Tinnacher (CSU)



- **Bentonite (montmorillonite)** is the proposed backfill material in the EBS.
- **Diffusion –** dominant transport mechanism in the EBS
- **Temperature and chemical gradients (e.g., solution chemistry)** are expected over time and across the EBS.