SAND2016-5371PE

Used Fuel Disposition Campaign

UFD – Disposal in Argillite R&D: Geochemical Modeling Activities of Barrier Material Interactions

Carlos F. Jové Colón
Sandia National Laboratories

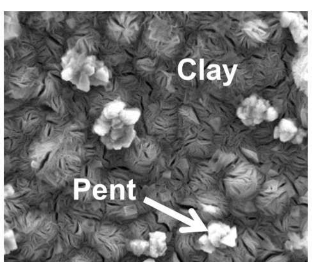
Las Vegas, Nevada – June 7 – 9, 2016

SAND2016-######

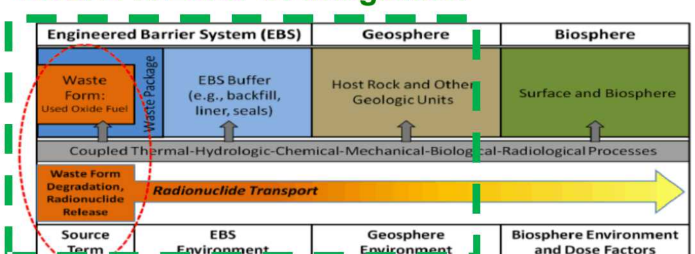
Overview UFD EBS: DR Argillite Disposal R&D

- Work Package #: FT-16SN08030207
- 1D reactive-transport modeling with decay heat effects
- Engineered barrier system model integration with performance assessment (PA)
- Thermodynamic and sorption assessment of barrier materials
- Clay interaction experiments: High temperature mineral phase stability, thermal limits, clay – metal interactions, RN transport
- High temperature mechanical (TM) modeling
- International Collaborations (e.g., FEBEX-DP, DECOVALEX, SKB TF)

Clay-Metal Interactions



GDSA PA Level Of Integration

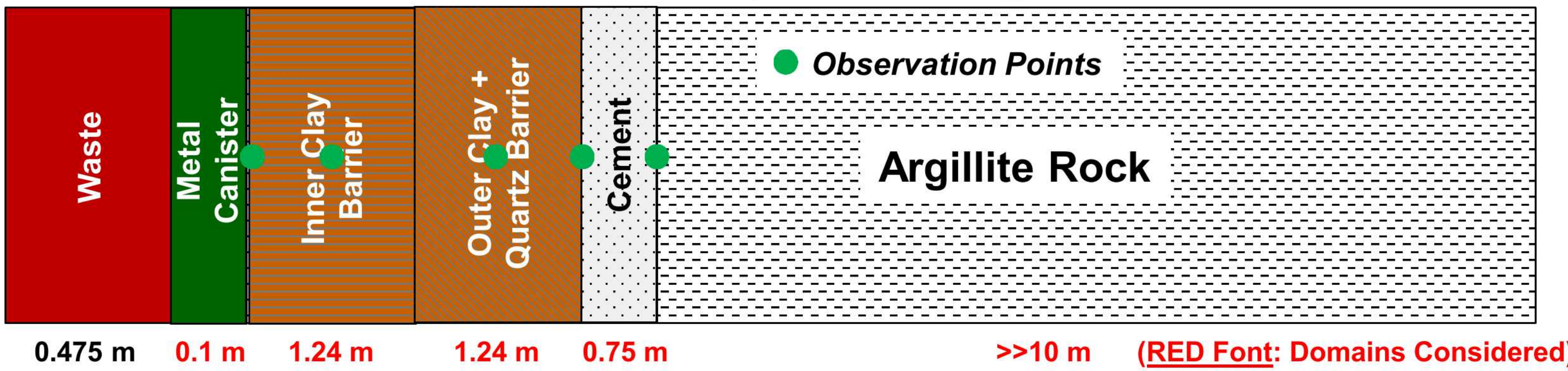


FEBEX-DP

Used
Fuel
Disposition

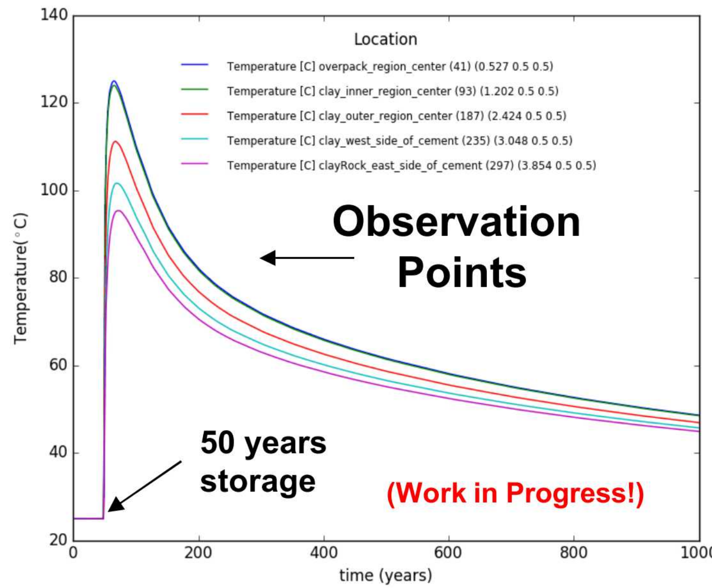
1D Reactive Transport of Layered EBS – Argillite Disposal Media

PFLOTRAN 1D Reactive Transport Modeling



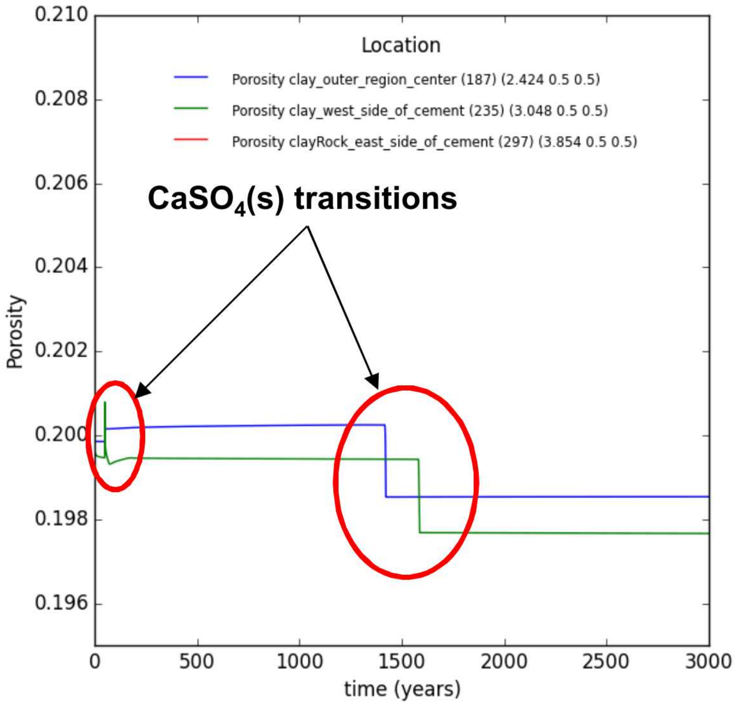
- **1D reactive transport (RT) PFLOTRAN calculations:**
  - 24 minerals, 4 initial pore solution chemistries
  - Efficient model scoping in High Performance Computing (HPC) platforms
  - Evolution of mineral volume fraction and aqueous speciation with time: equilibrium & kinetics
- **Temperature effects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

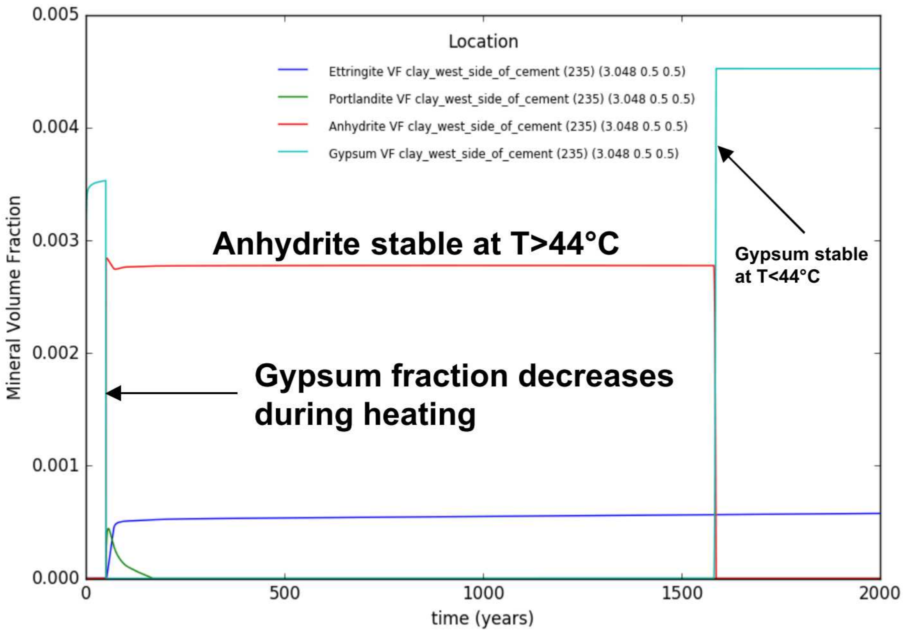
gypsum → anhydrite + 2 H_2O



Used Fuel Disposition

1D Reactive Transport of Layered EBS – Argillite Disposal Media (Cont.)



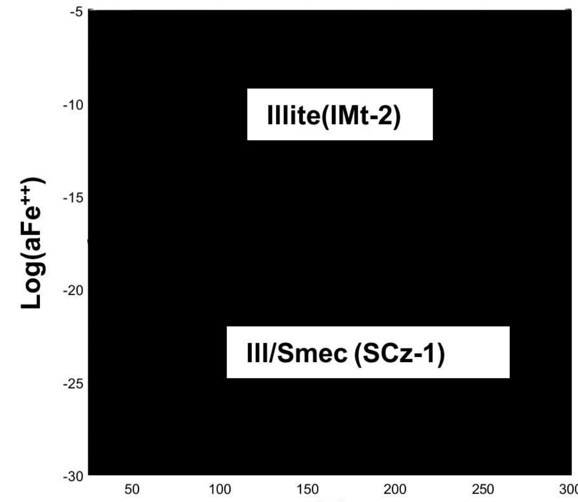


- **1D reactive transport modeling in PFLOTRAN:**
  - **Decay heat effects capture $CaSO_4$(s) phase transitions (T≈44°C)**
  - **Porosity changes**

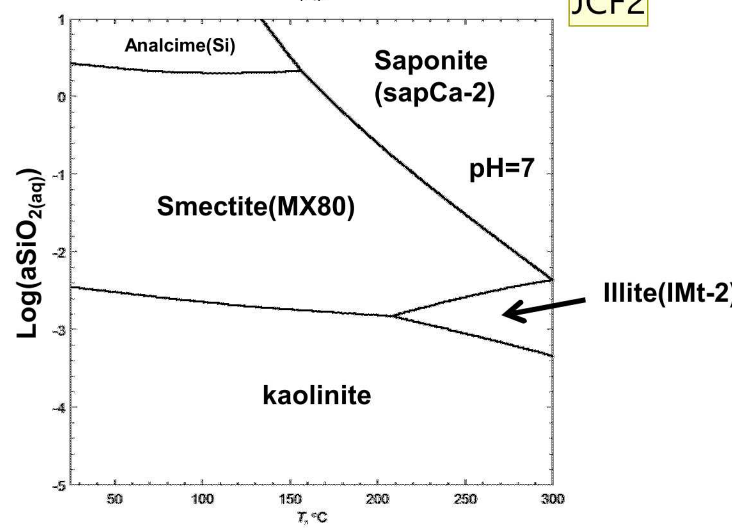
(Work in Progress!)

Thermodynamic Assessments: Solid – Fluid Data Evaluations

- **Evaluation of clay and zeolite thermodynamic data at elevated pressures and temperatures**
- **Sensitivity evaluations:**
  - **Clay stability relations**
  - **Redox: Fe++-- Fe+++ activities**
  - **Silica analcime(Si) stability**
  - **Temperature**
- **Thermodynamic Database Development**
  - **Chemical Thermodynamic Data. I: Links to the chemical elements. Paper revised for resubmission to Geochim. Cosmo. Acta**
  - **Chemical Thermodynamic Data. II: Water in SUPCRT92 & similar codes. Paper to be submitted soon!**
- **Rest of FY16 and FY17:**
  - **Focus on compositional & redox sensitivities on clay stability relations**
    - **e.g., illite, smectite, & Fe**
  - **Chemical Thermodynamic Data. III: revising the Helgeson et al. (1978) mineral dataset**
  - **Corrosion reactions and relations to Fe-smectite**



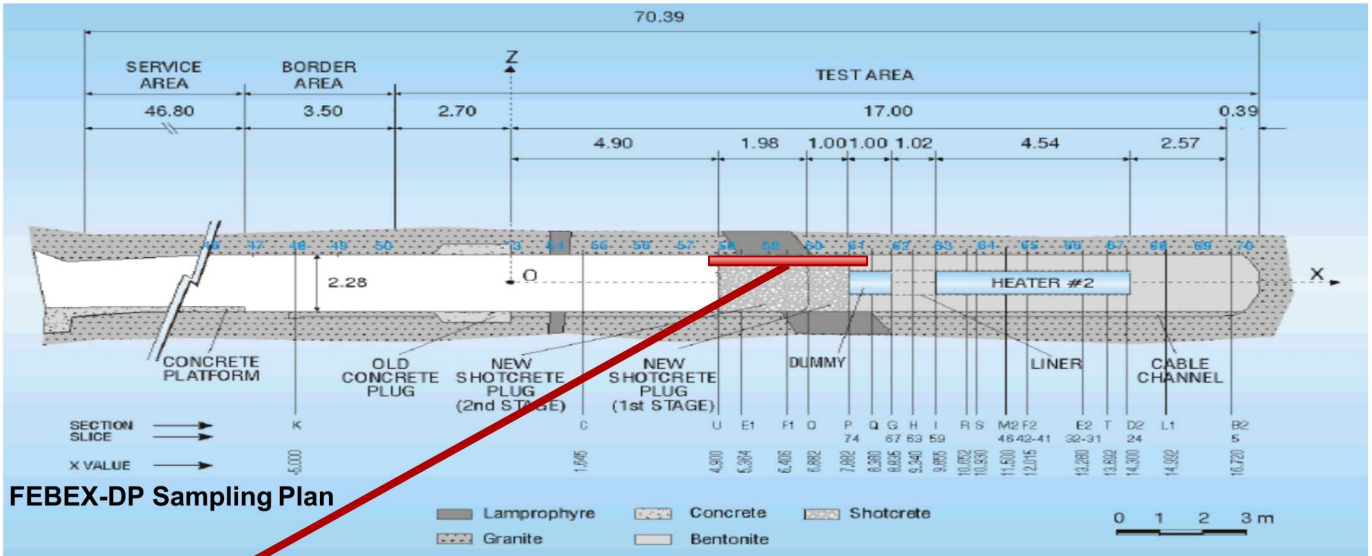
JCF2

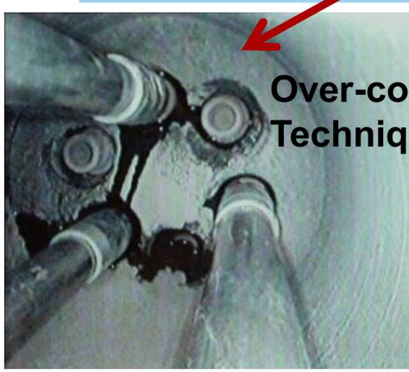


Slide 5

JCF2	Conisder illite only with MX80 or another Fe+2 diagram vs. T with more phases....but maybe not to make it simple Jove-colon, Carlos F, 6/5/2016

FEBEX-DP (Grimsel URL)



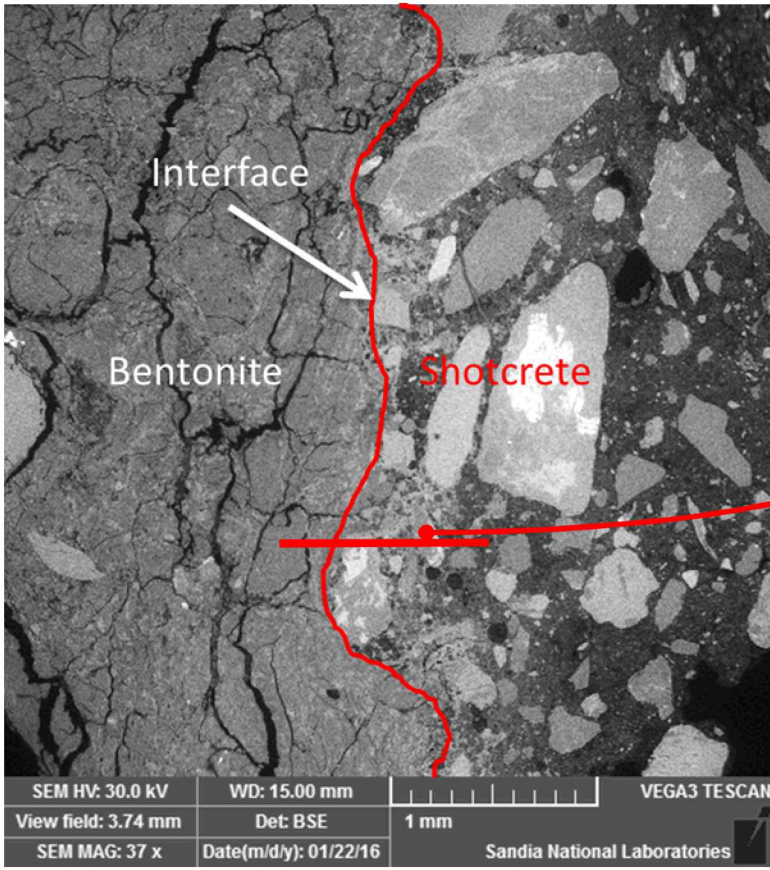


Mäder (2014)

CFJC (SNL)

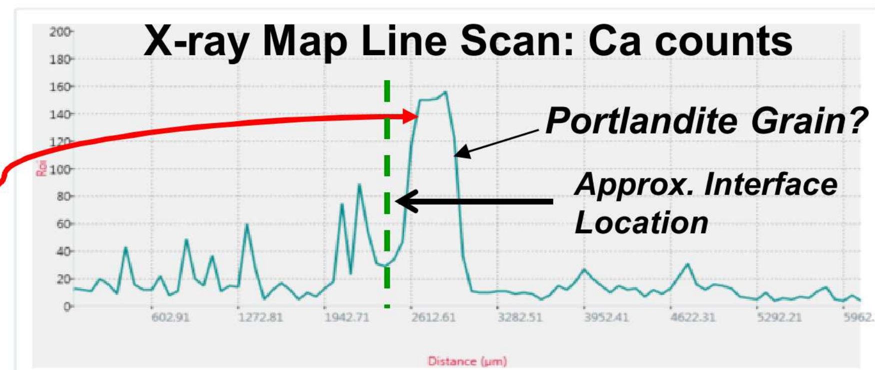
- Shotcrete/bentonite interface sampling
- Characterization studies cement/bentonite interactions
  - Phase identification (SEM-EDS, XRD)
  - X-ray CT Scan: micron-scale structures

FEBEX-DP: Bentonite – Concrete Interface Characterization (SEM – EDS – BSEI)



Back-Scattered Electron Image (BSEI) of Bentonite – Cement Interface

- **So far – no indication of strong elemental gradients beyond the interface region**
- **Cracks (desiccation?) tend to be abundant at the interface**



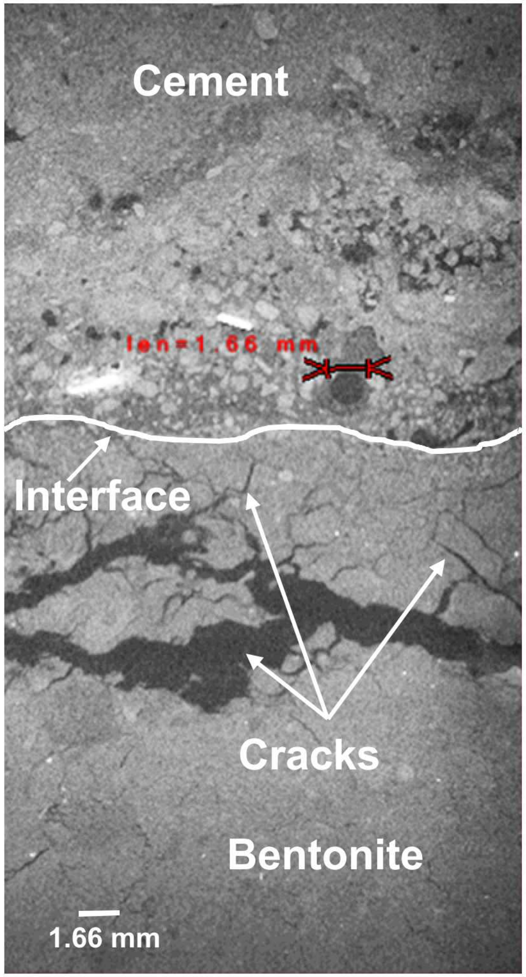
- **Portlandite ($Ca(OH)_2$) mineralization at the interface?**
- **More elemental line-scans needed to resolve compositional gradients**

Used
Fuel
Disposition

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

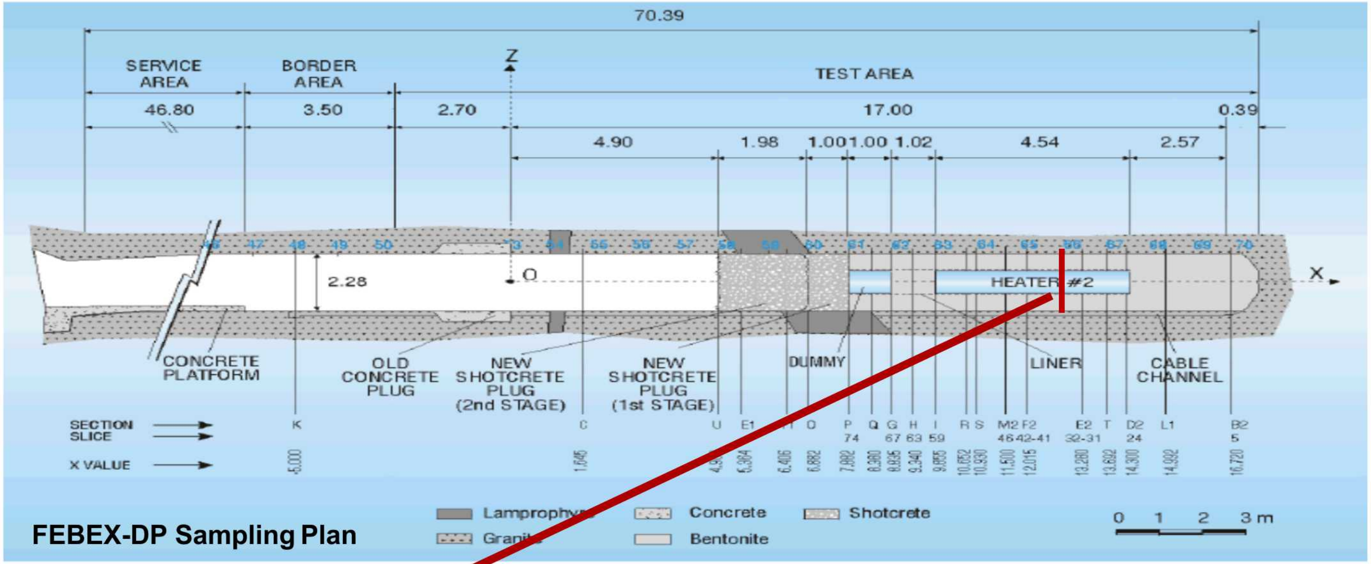
- **X-ray CT Scan:**
  - **Non destructive**
  - **Can manage hand-size samples**
  - **Scan resolution: 10.5 microns**
- **Can resolve important features:**
  - Cracks
  - Large pores
- **3D image analysis**
  - Continuous pores and cracks
  - "Heavy" minerals: oxides, sulfides

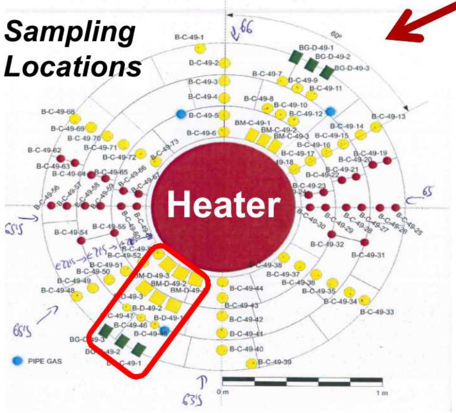
Core Specimen



Imaging by J. Eric Bower (SNL)

FEBEX-DP: Sampling Close to Heater





Bentonite Block (Close to Heater)

Carbon Steel Liner (Surrounding Heater)

FY17 Outlook

- **1D reactive-transport (RT) modeling of EBS in PFLOTRAN**
  - Leveraging High Performance Computing (HPC)
  - Decay heat effects – assess code stability at T>125°C
  - Applications to disposal in argillite/crystalline media
  - Implementation of metal corrosion model conceptualizations (Fe, Cu)
  - Capture temperature effects: dehydration, phase transformations (gypsum → anhydrite)
- **Integration of process models with GDSA PA**
- **Evaluation of clay phase stability at elevated temperatures**
  - Redox effects on Fe-bearing clay stability and related phases
  - Comparison with other studies on smectite alteration in the presence of Fe
- **Thermodynamic data analysis and applications to geochemical modeling**
  - Paper/Report: “Chemical Thermodynamic Data. II”: Water in SUPCRT92 and similar computer codes (mentored by Tom Wolery (LLNL)) – Submittal in 2016
  - Work on “Chemical Thermodynamic Data. III”: Revising the Helgeson et al. (1968) mineral dataset
- **International Collaborations**
  - Continue SKB TF, FEBEX-DP,
  - DECOVALEX: Groundwater Recovery experiment (GREET) at Mizunami URL, Japan

ACKNOWLEDGMENTS

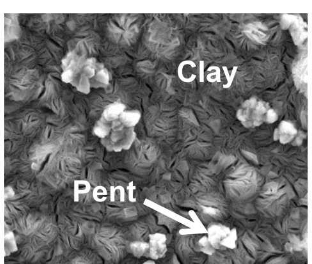
- Dr. Michael C. Cheshire (currently at ORNL) conducted the experimental and characterization work on clay steel-interactions presented here.
- Discussions with Charles R. Bryan (SNL) on steel corrosion are greatly appreciated.
- This work supported by the DOE-NE Used Fuel Disposition Campaign Fuel Cycle Technologies R&D program.

Backup Slides

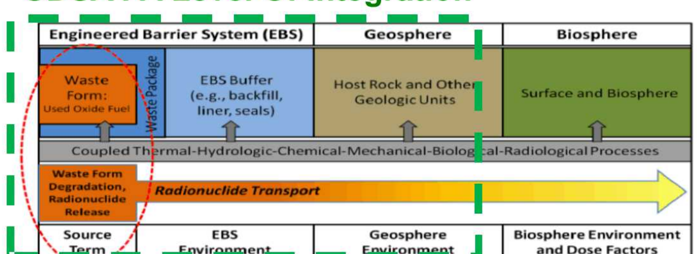
Overview UFD EBS: DR Argillite Disposal R&D

- **Work Package #: FT-16SN08030207**
- **Engineered barrier system model integration with performance assessment**
- **Thermodynamic and sorption modeling of barrier materials**
- **Clay interaction experiments: U transport, mineral phase stability and thermal limits**
- **High temperature mechanical (TM) modeling**
- **International Collaborations (e.g., THM, FEBEX-DP, SKB TF)**

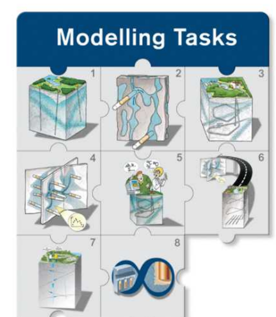
Clay-Metal Interactions



GDSA PA Level Of Integration



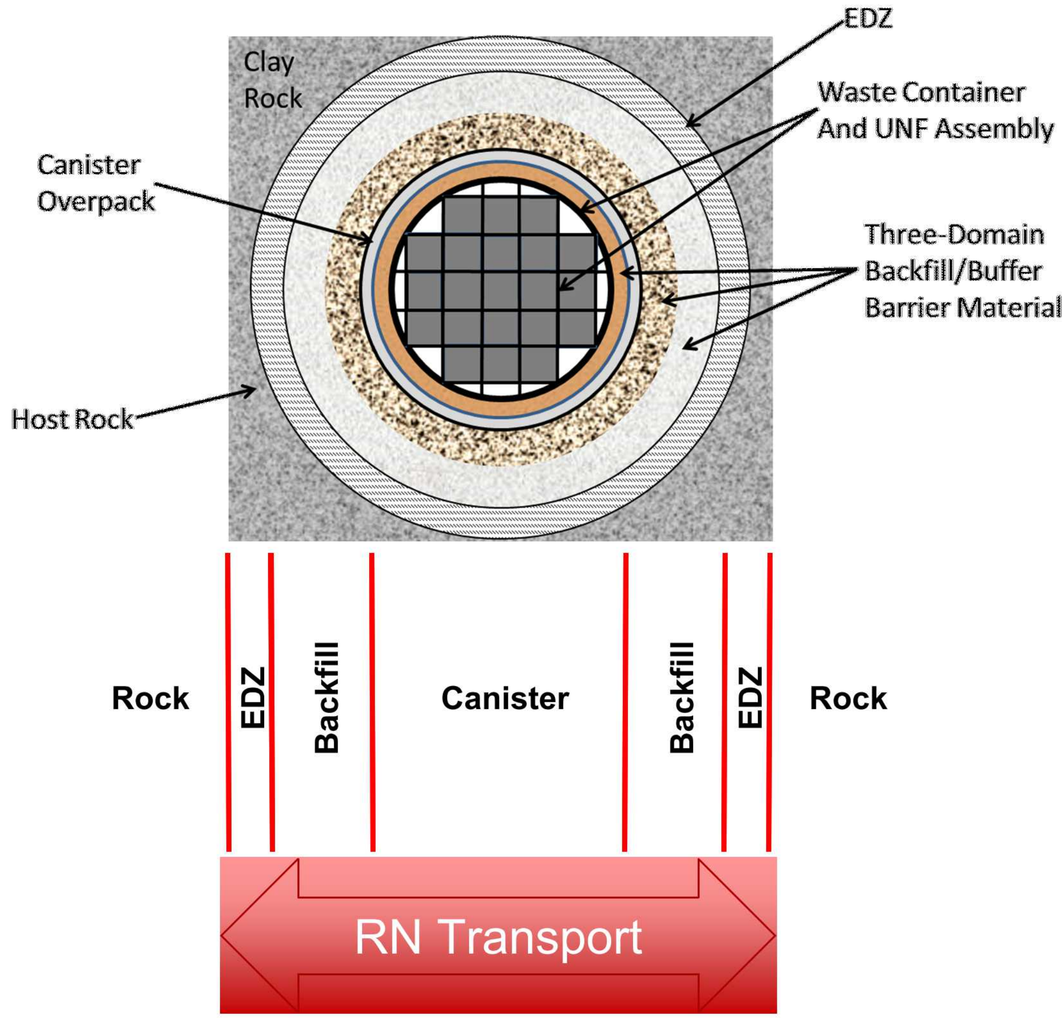
SKB TF



Used Fuel Disposition

Reactive-Transport Modeling of the Near- and Field with PFLOTRAN

- **Reactive-transport simulations of base-case scenarios on the near- and far-field domains**
- **1D or 2D scoping model representation for a single canister**
- **Coupled processes (THC):**
  - Solute transport
  - Fluid-rock-canister interactions (solution-mineral equilibria, dissolution/ precipitation, sorption)
  - Heat load according to waste type
  - Variable backfill saturation(?)
- **Evaluate U transport from wasteform source to the EBS / host-rock interface**
- **Evaluate changes in mineral volume fractions and porosity**



Clay Hydration Modeling and Micro-Porosity Evolution

- Relationships between swelling clay micro-porosity and clay hydration (Sedighi and Thomas 2014)
- Thermodynamic relations based on H2O adsorption by swelling clays
- Connections with clay water content and relative humidity (RH): Data retrieval from URL and laboratory experiments
- Comparisons between theoretical models and field/lab data:
  - Predicted trends are in agreement with data
  - Data scattering can be significant
- Rest of FY15 and FY16:
  - Calibrate hydration model to montmorillonite clay compositions
  - Continue analysis of data generated by international programs (e.g., SKB Task Force on EBS)
  - If possible, comparison with parameters used in THM models

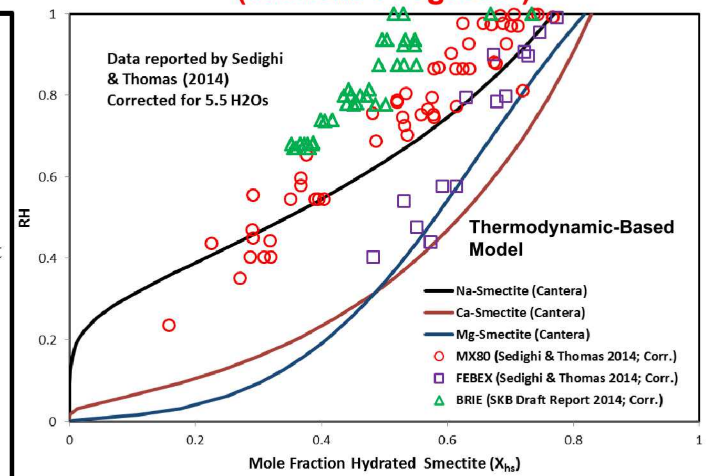
Sedighi and Thomas (2014)

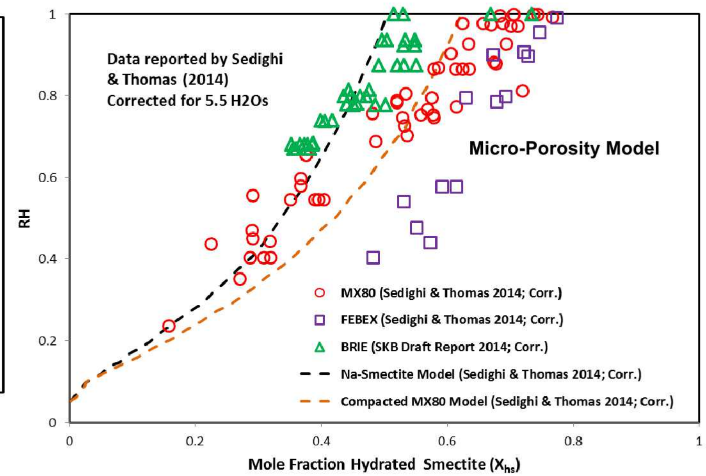
$$n_{micro} = X_{hs} \frac{n_c \upsilon_{il}}{Fw_{sm}} \rho_{dry}^{sm}$$

n_{micro} = Clay micro-porosity = θ_{wc}^{il} = water content
X_{hs} = Mole fraction of hydrated smectit
Fw_{sm} = Formula weight of anhydrous smectite
n_c = Number of H2Os in the interlayer
υ_{il} = Molar volume of H2O (interlayer)
ρ_{dry}^{sm} = Clay dry density

- Thermodynamic-based model calibrated by H2O adsorption data
- Micro-porosity model calibrated by water content and RH data
- Effect of clay chemistry on hydration / swelling

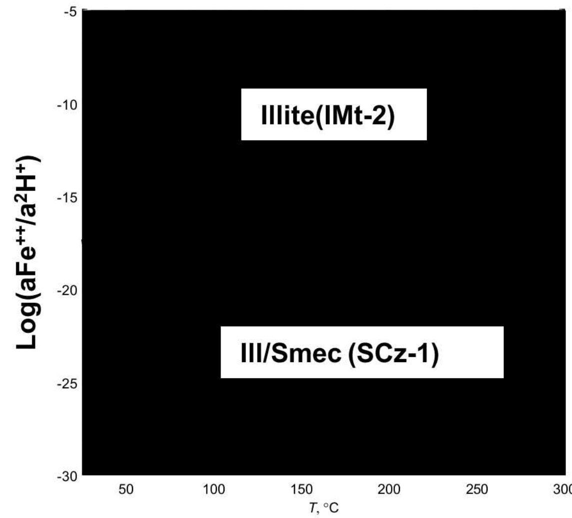
(Work in Progress!)



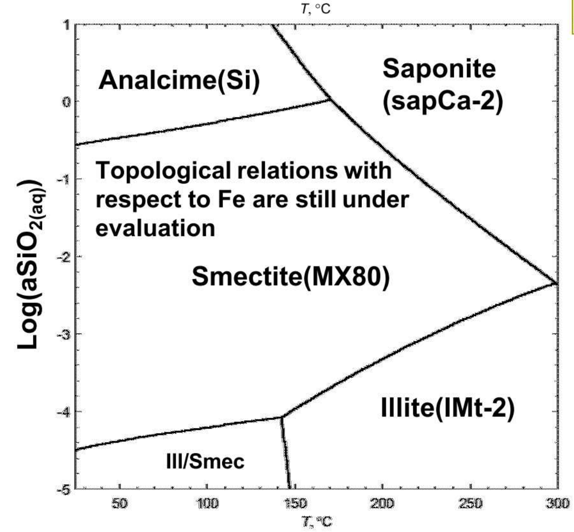


Thermodynamic Assessments: Solid – Fluid Data Evaluations

- Evaluation of clay and zeolite thermodynamic data at elevated pressures and temperatures
- Sensitivity evaluations:
  - Clay stability relations
  - Redox: Fe++-- Fe+++ activities
  - Silica analcime(Si) stability
  - Temperature
- Thermodynamic Database Development
  - Chemical Thermodynamic Data. I: Links to the chemical elements. Paper revised for resubmission to Geochim. Cosmo. Acta
  - Chemical Thermodynamic Data. II: Water in SUPCRT92 & similar codes. Paper to be submitted soon!
- Rest of FY16 and FY17:
  - Focus on compositional & redox sensitivities on clay stability
  - Chemical Thermodynamic Data. III: revising the Helgeson et al. (1978) mineral dataset



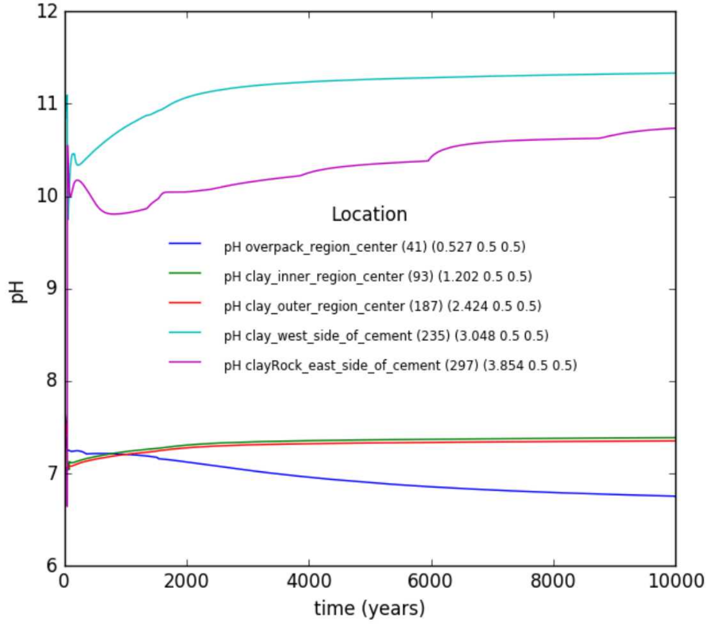
JCF2

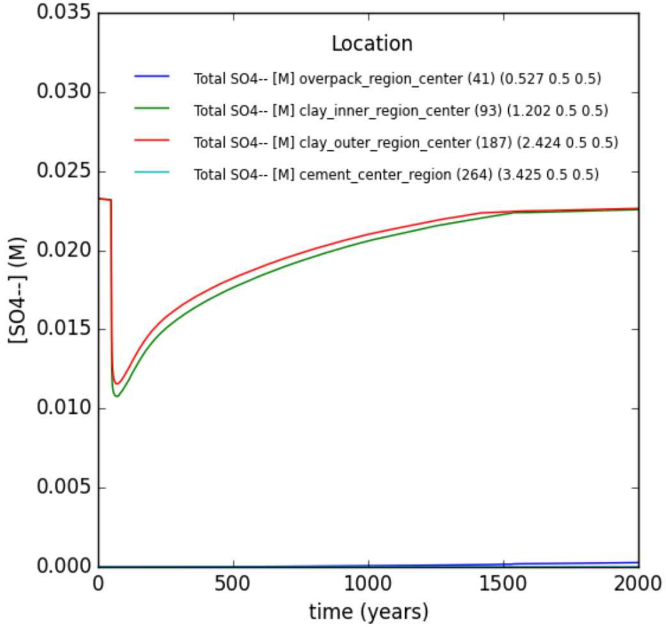


Slide 16

JCF2 Conisder illite only with MX80 or another Fe+2 diagram vs. T with more phases....but maybe not to make it simple
Jove-colon, Carlos F, 6/5/2016

1D Reactive Transport of Layered EBS – Argillite Disposal Media (Cont.)





- **1D reactive transport modeling in PFLOTRAN:**
  - **Changes in pore solution chemistry: FEBEX bentonite porewaters**
  - **pH effects during peak heating at EBS interfaces**