

# Used Fuel Disposition Campaign

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

*Carlos F. Jové Colón (SNL)*

*UFD Working Group Meeting  
Las Vegas, Nevada – June 9 – 11, 2015*

SAND 2015-?????



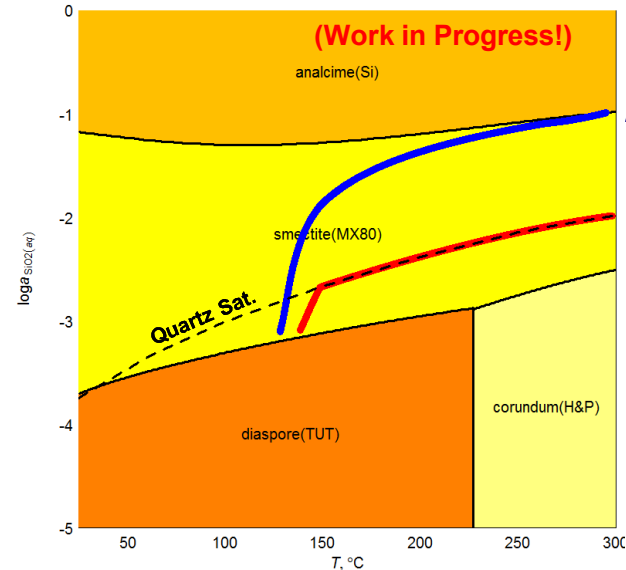
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- **Work Package #: FT-15SN080607**
- **Engineered barrier system model integration with performance assessment**
- **Thermodynamic and sorption modeling of barrier materials**
- **Clay interaction experiments: U transport, mineral phase stability and thermal limits**
- **High temperature mechanical (TM) modeling**
- **International Collaborations (e.g., THM, FEBEX-DP, SKB TF)**

- Evaluation of clay and zeolite thermodynamic data at elevated pressures and temperatures
- Key thermodynamic data (G, H, S, and Cp) for relevant clay phases: smectite (MX80), illite (IMt-2), illite-smectite (ISCz1), saponite (SapCa-1)
- Updated thermodynamic databases:
  - PFLOTRAN (reactive transport)
  - EQ3/6 (reaction path modeling)
  - CHNOSZ (activity phase diagrams)
  - Cantera (clay hydration)
- Reaction path modeling (EQ3/6) of metal-clay-solution interactions:
  - Bounded cases for SiO<sub>2</sub>(qtz) solubility
  - Bounded case for zeolite solubility
- Stability relations of clays at elevated pressures and temperatures
- Rest of FY15 and FY16:
  - Evaluate sensitivities:
    - *redox*
    - *Aqueous component activities*
  - Compare modeling with LANL experimental results
  - Links and key thermodynamic data

Simplified activity phase diagram with EQ3/6 reaction path results

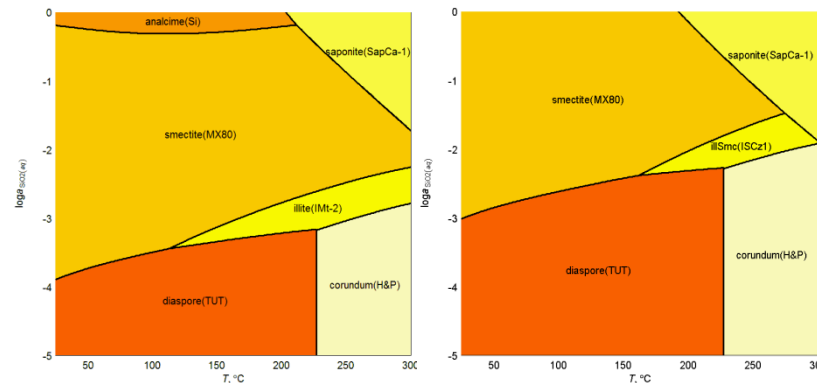


Reaction path calculation ramping up temperature with reaction progress

Analcime-Si solubility bound

Qtz solubility bound

Reactant Phases:  
 Smectite(MX80)  
 Pyrite  
 SiO<sub>2</sub>(am)  
 Na Clinoptilolite  
 Fe(metal)



- 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

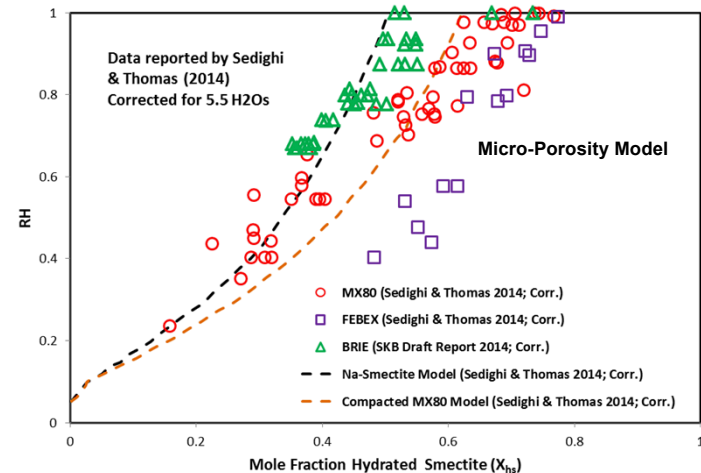
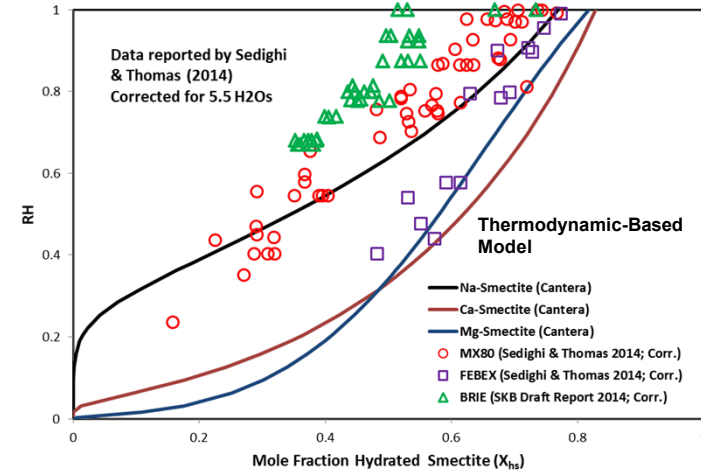
Sedighi and Thomas (2014)

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

$X_{hs}$  = mole fraction of hydrated smectite  
 $FW_{sm}$  = Formula weight of anhydrous smectite  
 $n_c$  = Number of H2Os in the interlayer  
 $\nu_{il}$  = Molar volume of H2O (interlayer)  
 $\rho_{dry}^{sm}$  = 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

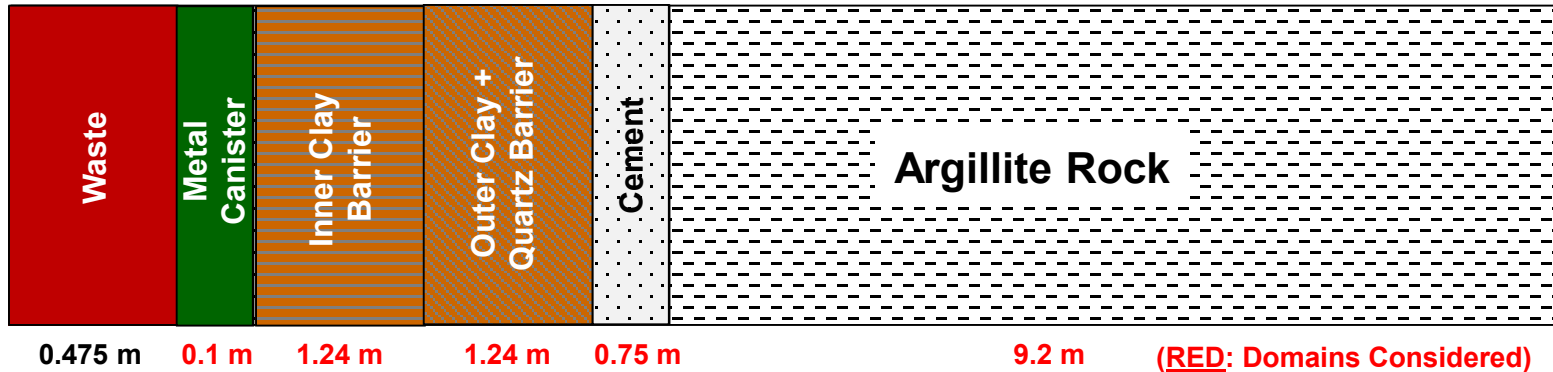
(Work in Progress!)



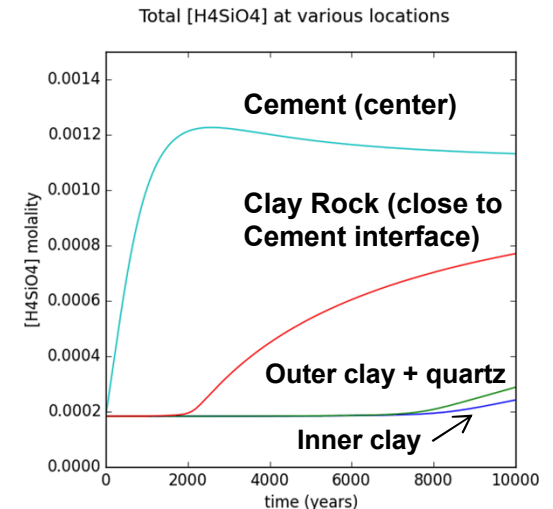
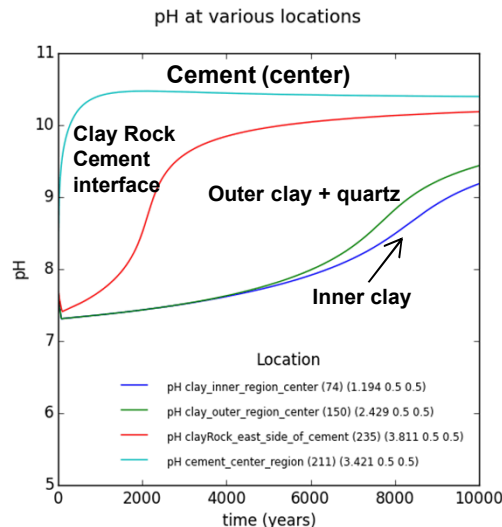
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# 1D Reactive Transport of Layered EBS – Argillite Disposal Media

## PFLOTRAN 1D Reactive Transport Modeling (Work in Progress!)

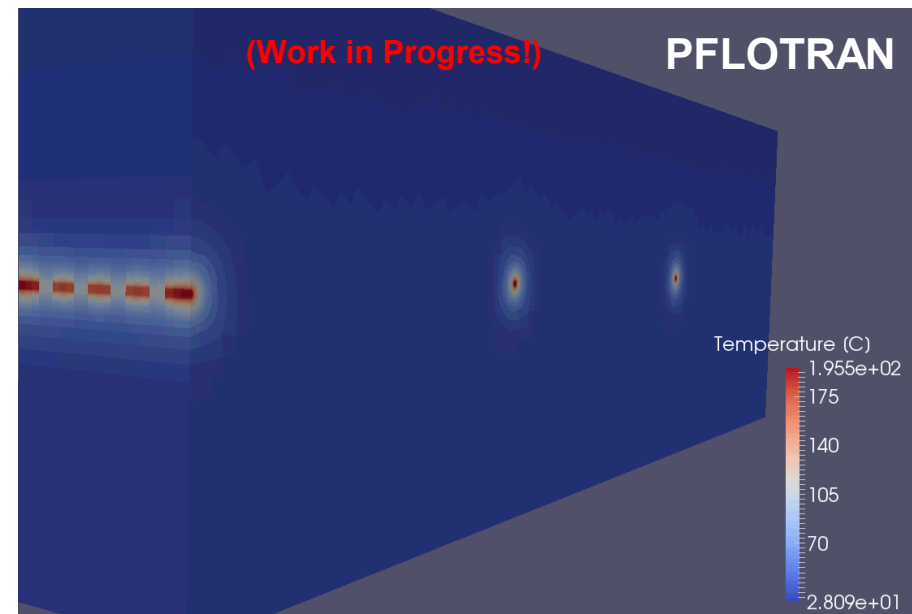
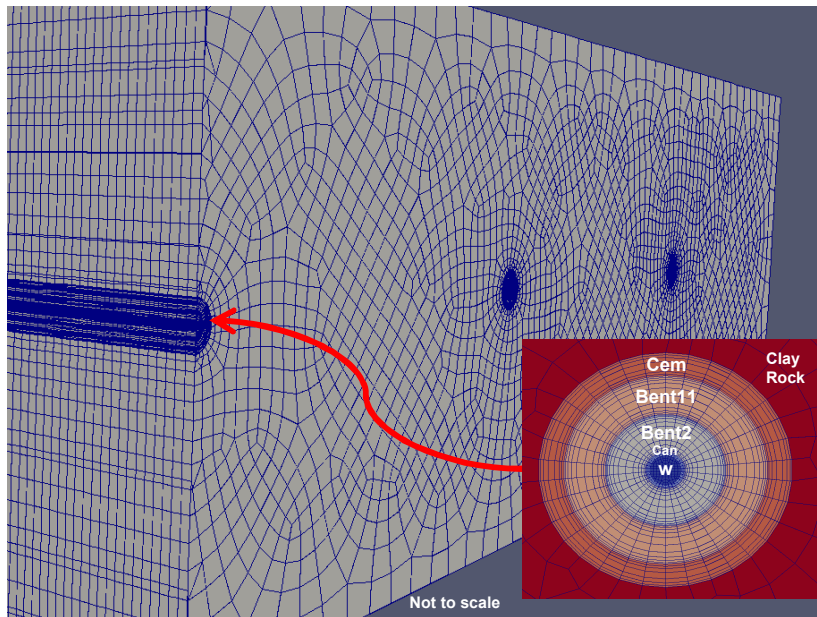


- 1D reactive transport PFLOTRAN calculations – efficient scoping
- Evaluation of species concentration and solid volume fraction profiles with time
- Evaluation of aqueous and solid phase inclusion/suppression (e.g. cement composition)
- Next stage:
  - Temperature effects
  - 2D multilayered EBS geometry
  - Variations in clay barrier phase compositions



# PFLOTRAN: 3D Repository Scale TH Model

- 3D Unstructured mesh (SNL Cubit) ported to PFLOTRAN
- Envisioned THC modeling:
  - Near- and far-field scale process model integration
  - Reactive transport modeling using HPC resources:
    - *Currently 1D for multicomponent EBS*
    - *Geochemical interactions at EBS interfaces: phase dissolution/precipitation*



## ■ Integration of process models with GDSA PA

- Near- and far-field processes for disposal in argillite

## ■ Evaluation of clay phase stability at elevated temperatures

- Secondary phase mineral assemblage: corrosion products (silicates, carbonates, sulfides, oxides)
- Evaluation of redox and aqueous composition feedbacks on clay stability and related phases
- Reactive transport ( RT) modeling at elevated temperatures
  - *Exploit HPC resources for RT modeling of multicomponent systems*
  - *Examine effects on porosity reduction*

## ■ Thermodynamic data analysis and applications to geochemical modeling

- Inputs to various geochemical modeling efforts: EBS interactions, reactive transport modeling
- Concept of links to chemical elements and key thermodynamic data (mentored by Tom Wolery)
- Maintain data consistency and alignment with international efforts (e.g., NEA TDB)

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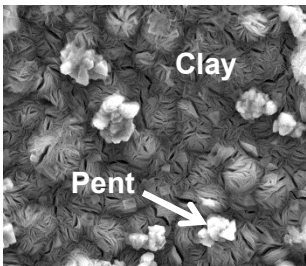
# **Backup Slides**

# Used Fuel Disposition

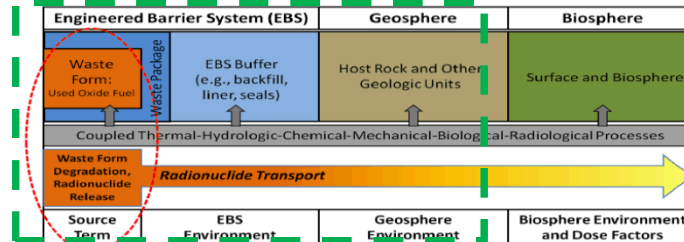
# Overview UFD EBS: DR Argillite Disposal R&D

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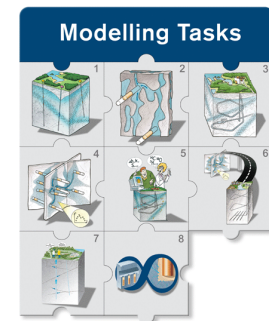
Clay-Metal Interactions



GDSA PA Level Of Integration



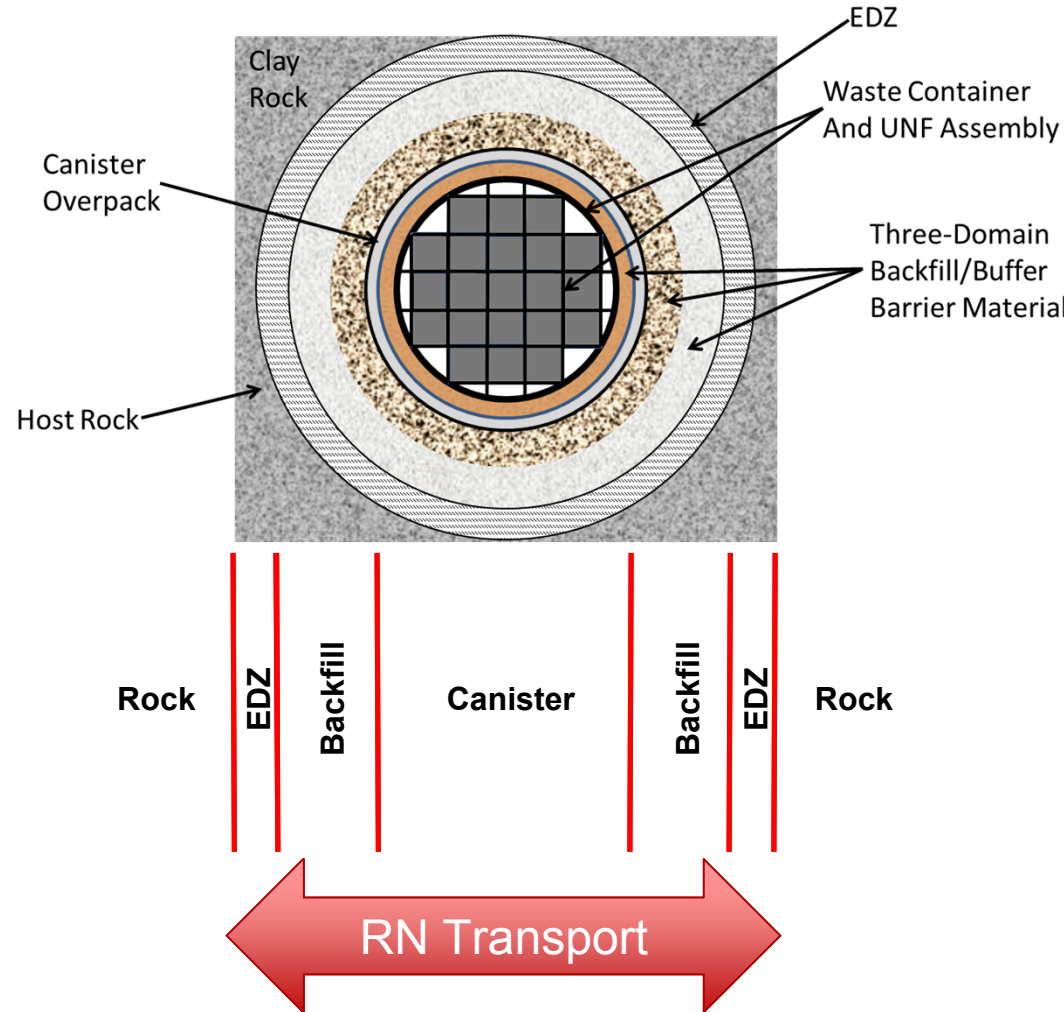
SKB TF



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## 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



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## Idea Proposal: Reactive-Transport Modeling of the Near- and Field with PFLOTRAN (Cont.)

### Reactive transport modeling base case scenario(s):

- Interaction with EBS components gauged by hydrothermal experiments (e.g., corrosion of steel and copper with clay)
- Backfill/buffer composition, secondary phases (e.g., pyrite) to constraints for metal corrosion reactions (e.g., copper):
  - i.  $\text{FeS}_2(\text{s}) + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \frac{1}{4}\text{H}^+ + \frac{1}{4}\text{SO}_4^{--} + \frac{7}{4}\text{HS}^-$
  - ii.  $\text{H}_2\text{S}(\text{aq}) = \text{H}^+ + \text{HS}^-$
  - iii.  $\text{H}_2\text{S}(\text{g}) = \text{H}^+ + \text{HS}^-$
  - iv.  $\text{Fe} + 2\text{H}^+ + \frac{1}{2}\text{O}_2 = \text{Fe}^{++} + \text{H}_2\text{O}$
  - v.  $\text{Fe}^{++} + \text{HS}^- = \text{FeS} + \text{H}^+$
  - vi.  $2\text{Cu} + \text{HS}^- + \text{H}_2\text{O} = \text{Cu}_2\text{S} + \text{H}_2(\text{g}) + \text{OH}^-$
- Evaluate geochemical feedbacks (e.g., redox zones) and U transport and concentration profiles

