Used Fuel Disposition Campaign

Waste package degradation: Clay – Metal Interactions

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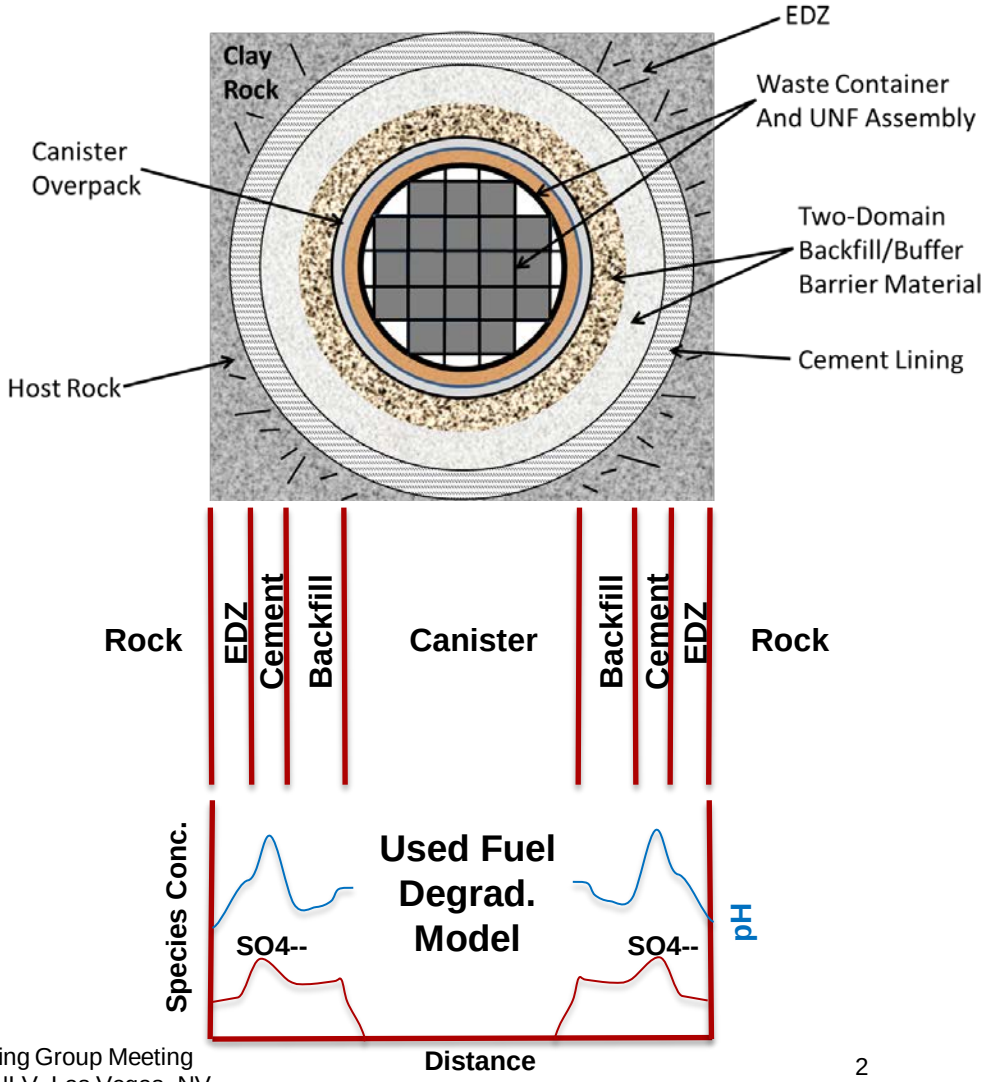
National Nuclear Security Administration

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

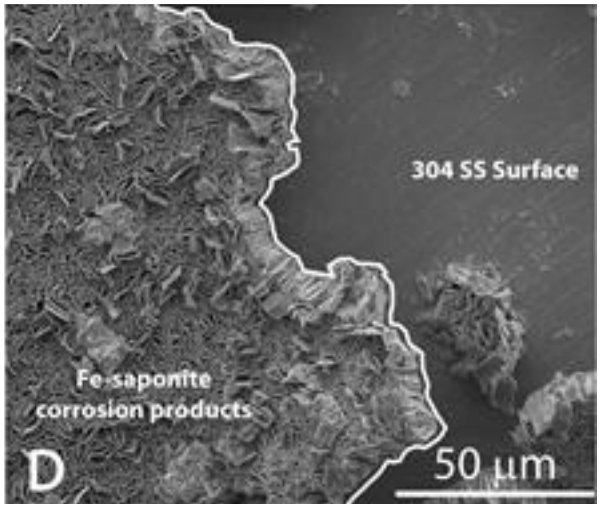
- Reactive transport modeling base case scenario(s):
  - Interaction with EBS components gauged by anoxic hydrothermal experiments (e.g., Steel/copper corrosion in the presence of clay)
  - Backfill/buffer composition, secondary phases (e.g., pyrite) influencing metal corrosion reactions (e.g., copper):
  - Evaluate geochemical feedbacks (e.g., redox zones) and U transport and concentration profiles

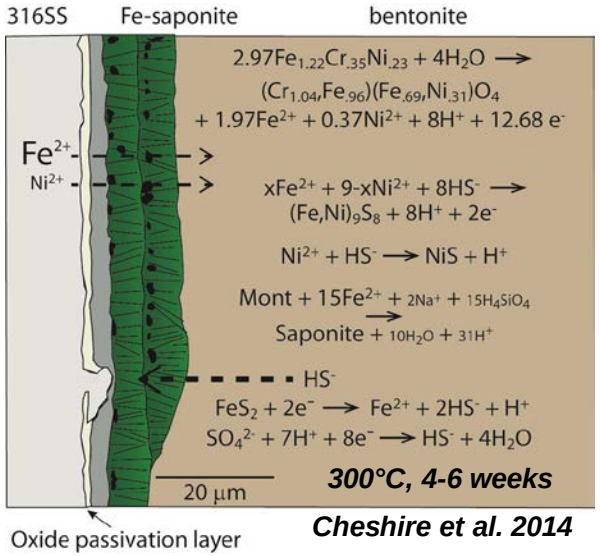


Used Fuel Disposition

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

- **Uniform corrosion – no pitting:**
  - $2.97Fe_{1.22}Cr_{0.35}Ni_{0.23} + 4H_2O \rightarrow (Cr_{1.04},Fe_{0.96})(Fe_{0.69},Ni_{0.31})O_4 + 1.97Fe^{2+} + 0.37Ni^{2+} + 8H^+ + 12.68e^-$
- **Corrosion products:**
  - **Chromite passivation layer**
  - **Fe-rich smectite**
  - **Chlorite**
  - **Pentlandite $(Fe,Ni)_9S_8$ (early)**
  - **Millerite (NiS)**
- **5 µm corrosion layer.**
  - 43 µm/year corrosion rate
- **316SS more extensive passive layer**

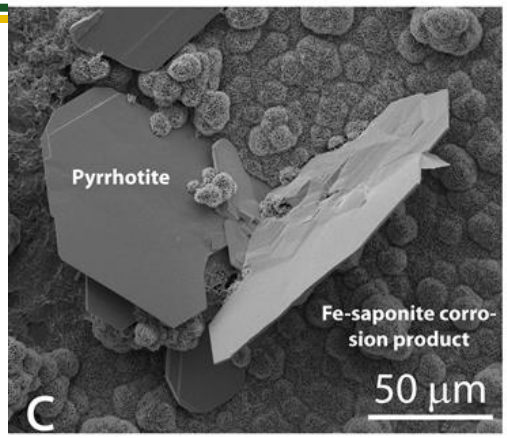


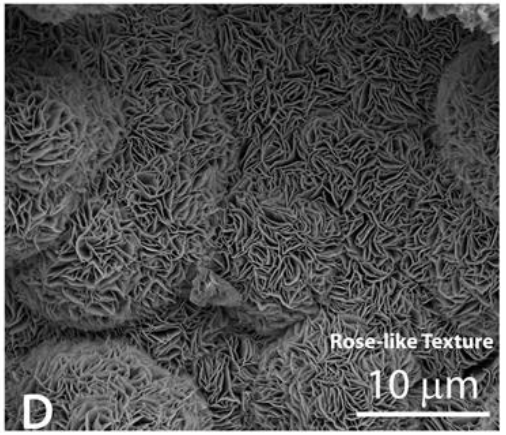


Cheshire et al. 2014

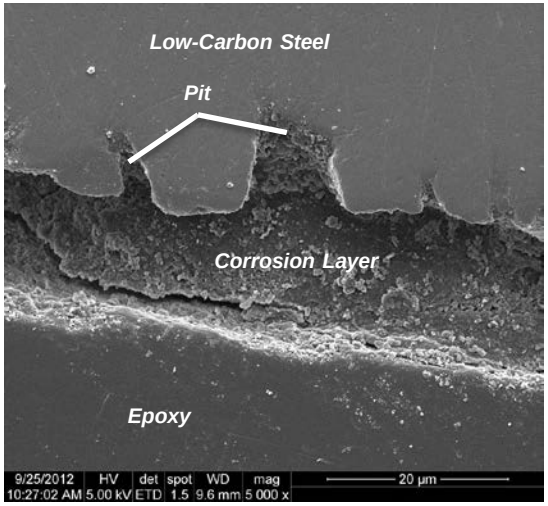
Waste Canister Degradation: Low Carbon Steel – Clay Interactions

- **Corrosion Products:**
  - **Fe-smectites (Fe-saponite)**
  - **Pyrrhotite ($Fe_{1-x}S$)**
- 13 to 56 µm thick 'corrosion-product' layer.
- ~20 µm corrosion pitting
  - 214 µm/year corrosion rate
- No passivation layer → corrosion expected to continue
- Extensive Fe_3O_4 layers develops





Cheshire et al. 2014

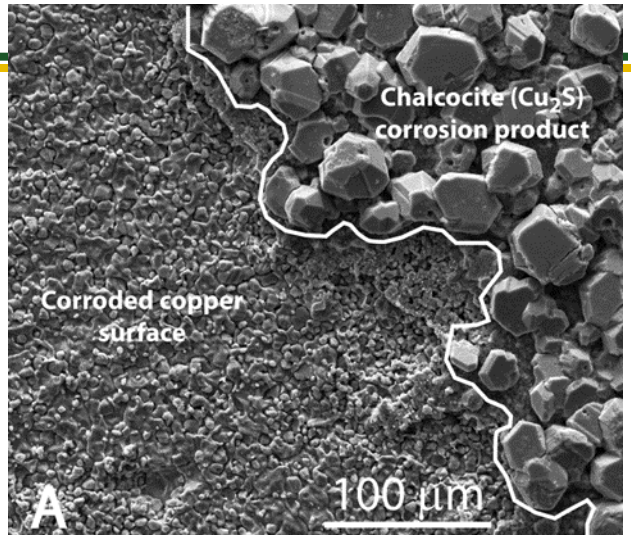


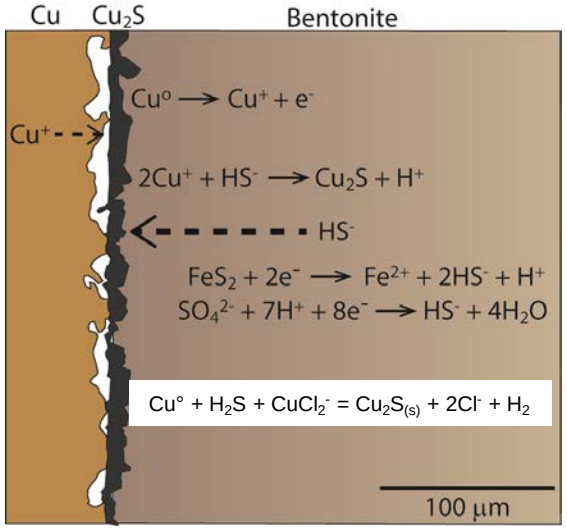
Ramped-up exp's:
- ***T = 25/100/200/300/25°C,***
- ***5 weeks***

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

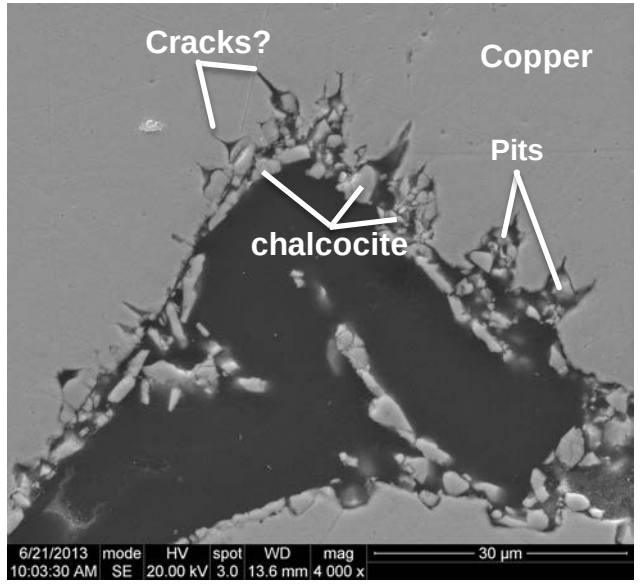
Waste Canister Degradation: Copper – Clay Interactions

- Sulfide-induced corrosion (anoxic):
  - Pyrite (FeS_2) decomposition
- Primary corrosion product → Chalcocite (Cu_2S):
  - $Cu^{\circ} + H_2S + CuCl_2^- = Cu_2S_{(s)} + 2Cl^- + H_2$
- 13 µm thick chalcocite layer
- Appears as pitting corrosion





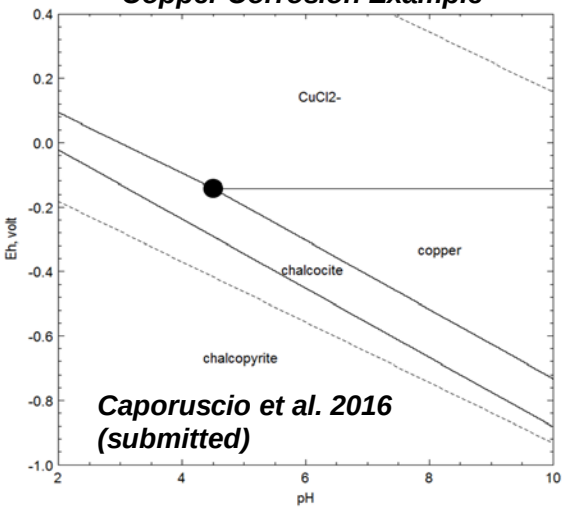
Cheshire et al. 2014



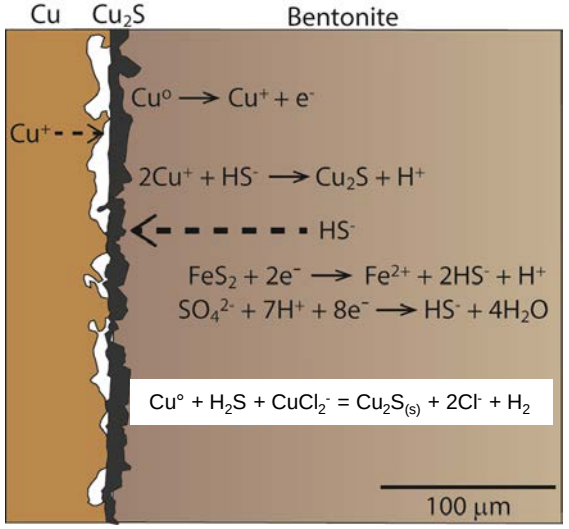
Geochemical and Reactive-Transport Model Implementation

- **Waste package degradation based on clay – metal interactions:**
  - **Fe-rich clay parageneses**
  - **Corrosion products**
  - **Aqueous-Solid Equilibria**
  - **Sulfide effects (e.g., pyrite decomposition)**
- **Implementation within a reactive transport model:**
  - **PFLOTRAN**
  - **Model Conceptualization (BC's, transport-limited)**

Copper Corrosion Example



Caporuscio et al. 2016 (submitted)



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BACKUP SLIDES

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