Hydrothermal-Bentonite Investigations Under Repository Conditions

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U.S. DEPARTMENT OF ENERGY

FY'13-FY'14 Objectives

EBS Program

- Experiment characterizations (CEC, cation exchanges, expandability).
- Quantify alkali, alkaline earth cation effects on montmorillonite reactivity.
- Provide information on complete repository thermal pulse event, using long-term (6 month) experiments.
- Investigate the Fe-saponite, chalcocite growth at metal interface with bentonite.
- Further investigation of SiO_2 precipitation and aluminosilicate formation.

International Program

- Characterize the bentonite-20% H_2O reaction products (Collaboration with LBNL).
- Investigate bentonite-Opalinus Clay-metal interaction.

Experimental Conditions

Experimental Reactants

- Unprocessed, Wyoming bentonite
  - K-Na-Ca-Cl solution -- Stripa V2
- Opalinus Clay, Mont Terri, Switzerland
  - Na-Ca-K-Cl-CO_3-SO_4 solution -- Opalinus

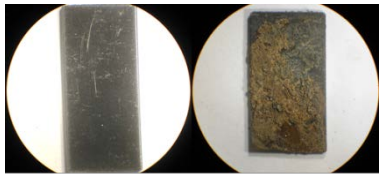
Heating Conditions

- ~160 bar; 120 to 300ºC; 5 weeks
- ~160 bar; isothermal 300ºC; 6 weeks
- ~160 bar; 300 to 120ºC; 24 weeks

316L SS

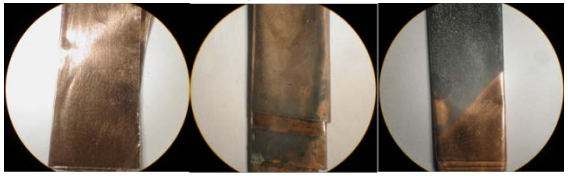
Ramped, 5 weeks 300ºC, 6 weeks Cooled, 24 weeks

Low-C Steel



Ramped, 5 weeks

Copper



Ramped, 5 weeks 300ºC, 6 weeks

300 ºC; 6 weeks

EBS14: Opalinus Clay
EBS15: Bent+Opalinus+316SS
EBS17: Bent+Opalinus+Cu

20 capsule experiments
differing solution chemistry
various rock types
corrensite, gypsum

300 ºC; 6 months

EBS13: 316SS
EBS16: Cu

12 capsule experiments
differing solution chemistry

66 weeks experimentation

- ✓ K, Ca, Li Cation Exchange
- ✓ NH_4 – CEC Determination
- ✓ Electron Microscopy
- ✓ Microprobe Chemical
- ✓ Solution Chemistry
- ✓ 150+ XRD analyses

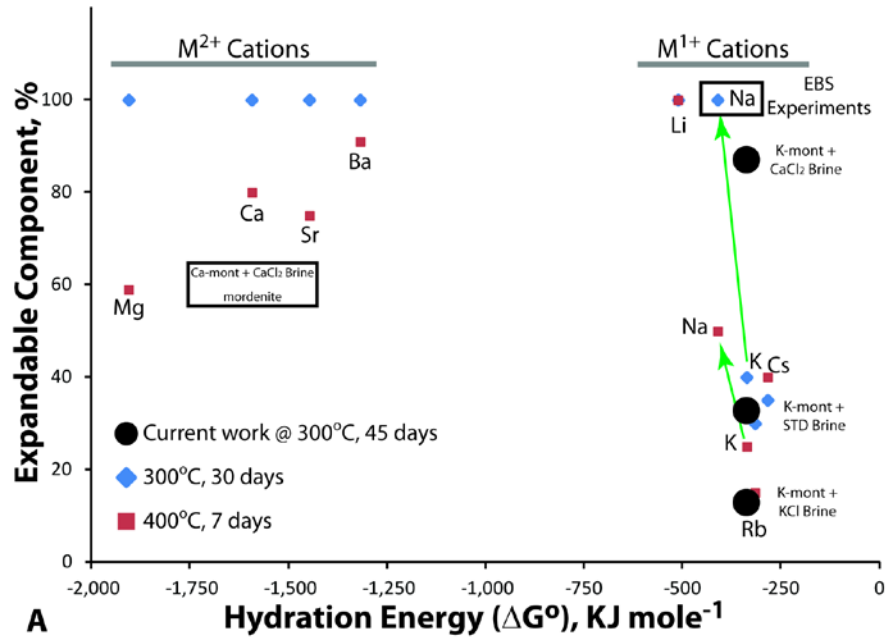
Used Fuel Disposition

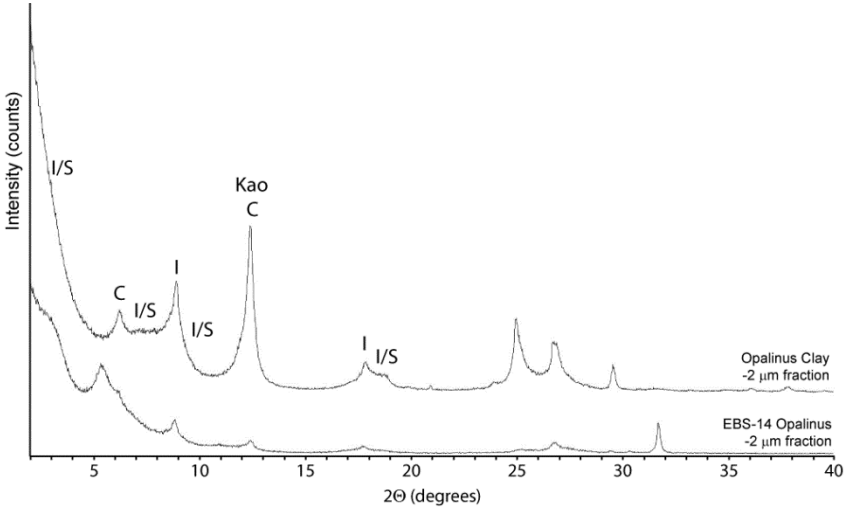
Bentonite-Host Rock Reactivity

Bentonite evolution at elevated pressures and temperatures: An experimental study for generic nuclear repository designs, *In Press, American Mineralogist* (2014).

Opalinus Clay
- Kaolinite altering to analcime
- Breaking down pyrite yielding Fe_2O_3
- CO_2 and H_2S generated

Bentonite
- No illitization during 6 month test
- Analcime formation
- Silica precipitation





Interlayer	$\Delta G_{hydration}$	% Expandable			
Cation	kJ mol^{-1}	Bentonite	Ramped	Isothermal	"Dry"
K^+	-337	93	94	96	~*93*
Na^+	-411	100	100	100	100
Li^+	-511	n.d.	98	100	100
Ca^{2+}	-1593	98	96	98	n.d.
CEC	meq/100 g	73*(5)*	69*(5)*	71*(3)*	n.d.

Bentonite-Metal Interaction

Corrosion Products

Fe-smectite and chlorite-steels
Early stage
- pentlandite ($(Fe,Ni)_9S_8$),
- millerite (NiS)
- pyrrhotite ($Fe_{1-x}S$)

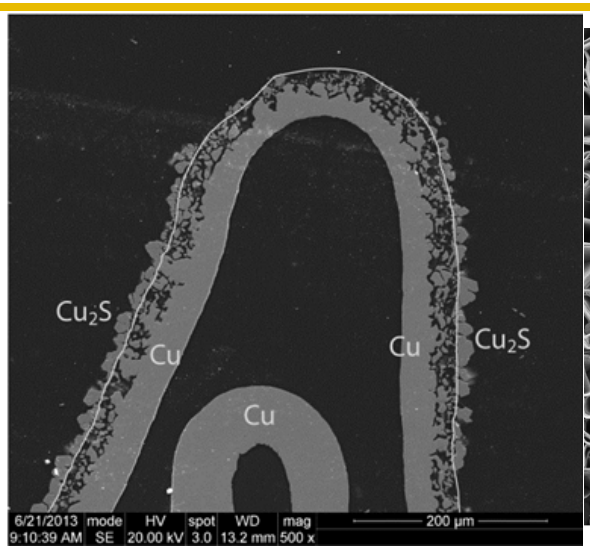
Chalcocite (Cu_2S)-Cu

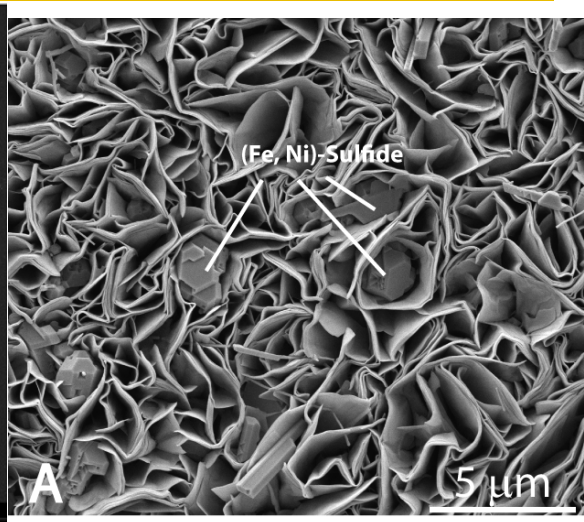
Corrosion rates: 42 days @ 300°C

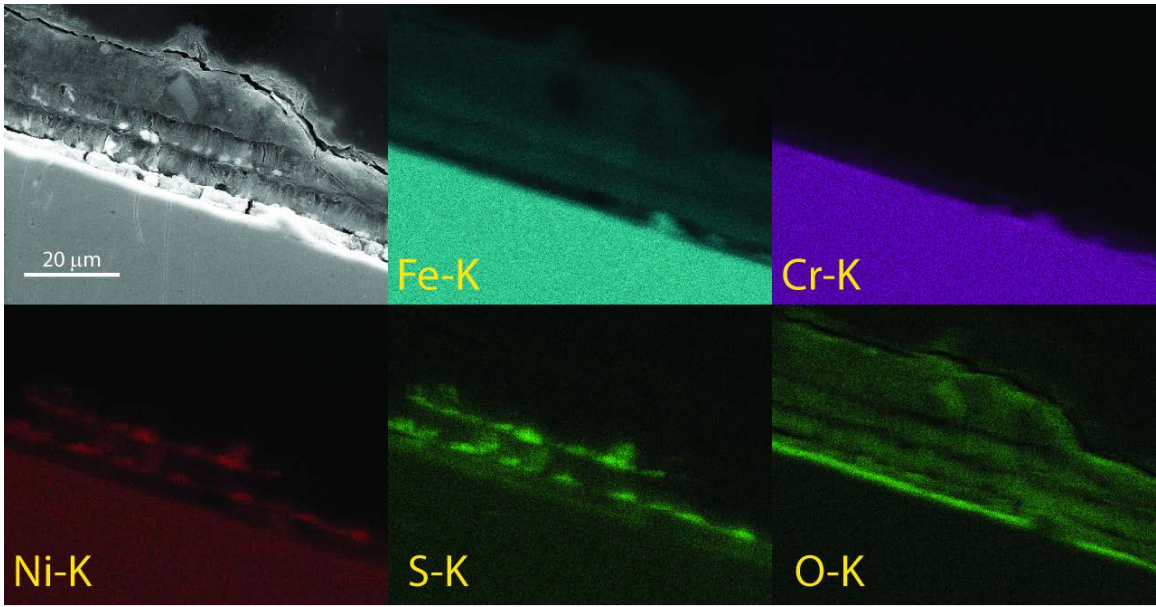
0.1 μm d^{-1} (43 μm a^{-1}) SS
0.6 μm d^{-1} (214 μm a^{-1}) LCS
0.8 μm d^{-1} (292 μm a^{-1}) Cu

Corrosion Types

- Uniform corrosion → SS
- Pitting corrosion → LCS & Cu







Future Work

- Continue with host rock-bentonite experiments and analyses.
- Continue with post-maximum temperature cooling effects.
- Quantify the thermodynamic properties of reaction products.
- Model the chemical dynamics of corrosion processes.
- Investigate radionuclide ‘getters’ for engineered bentonite buffers.
- Develop a radiogeochemical-hydrothermal laboratory.

Thermochemistry Capabilities

Solution Calorimetry

Chemical reactions enthalpies

Reactions of interest
phase transformation, dehydration
Steps in a thermodynamic cycle
enthalpy of formation

Differential Scanning Calorimetry

Determination of:

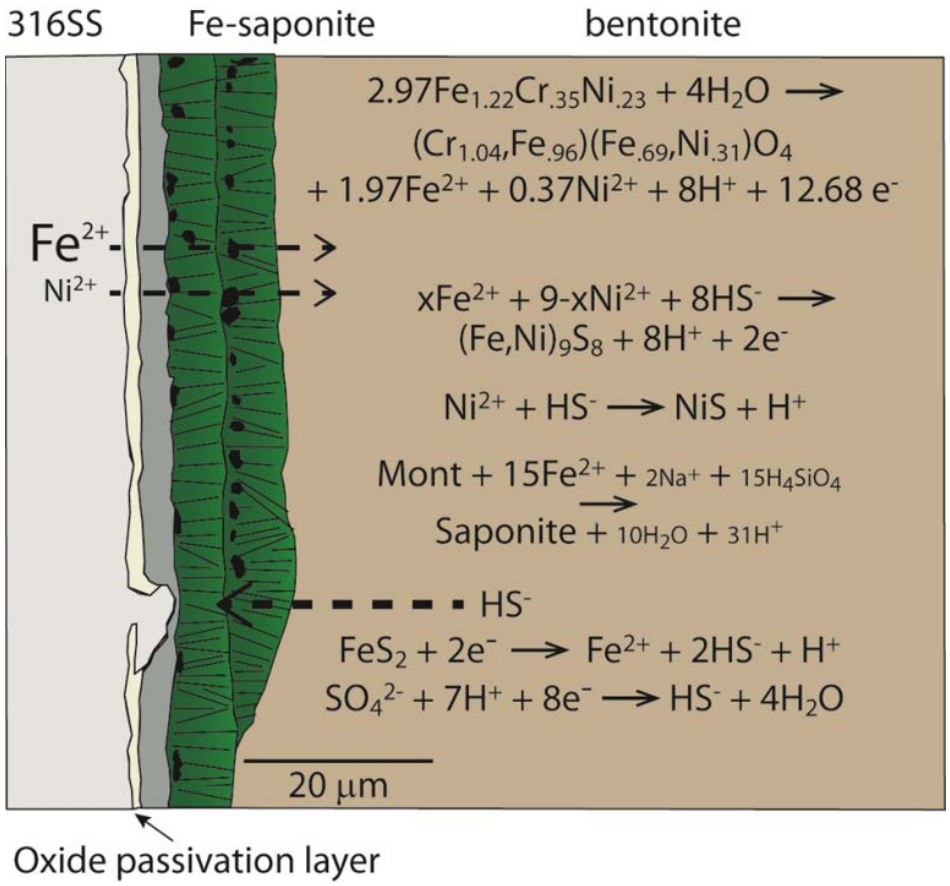
1. Decomposition/transition temperature
2. Heat released or absorbed
3. Mass changes
4. Mineral heat capacities

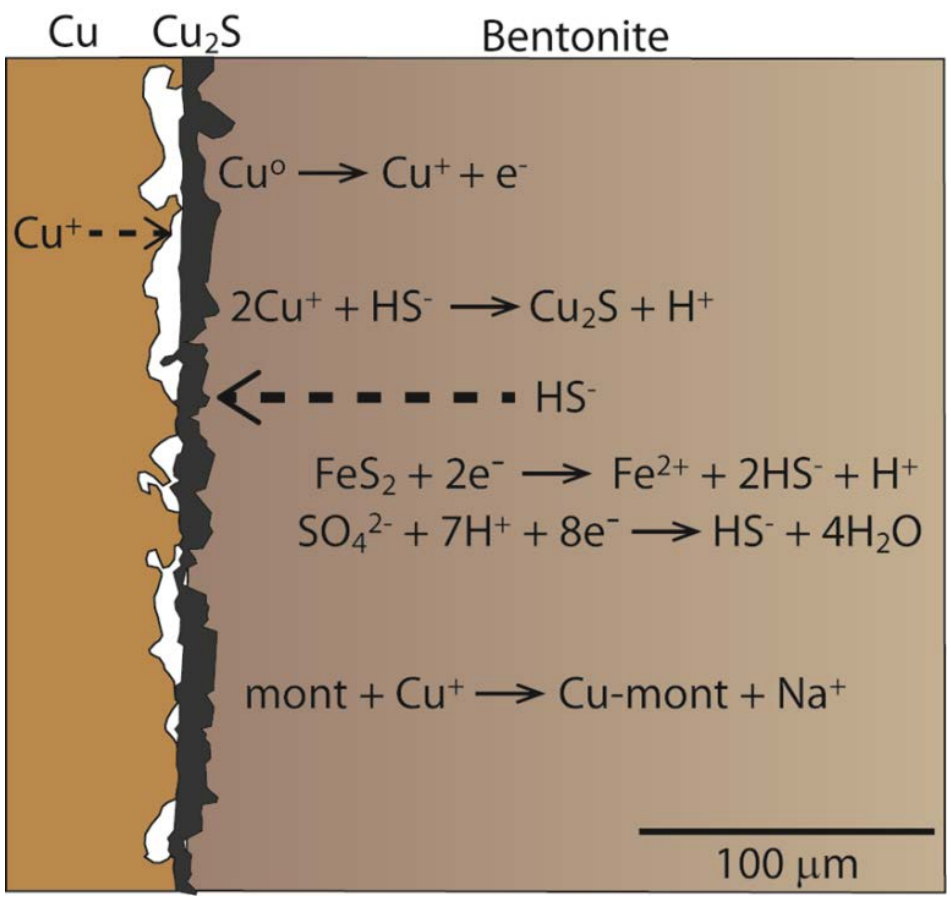
Future Work

Thank You!

Questions?

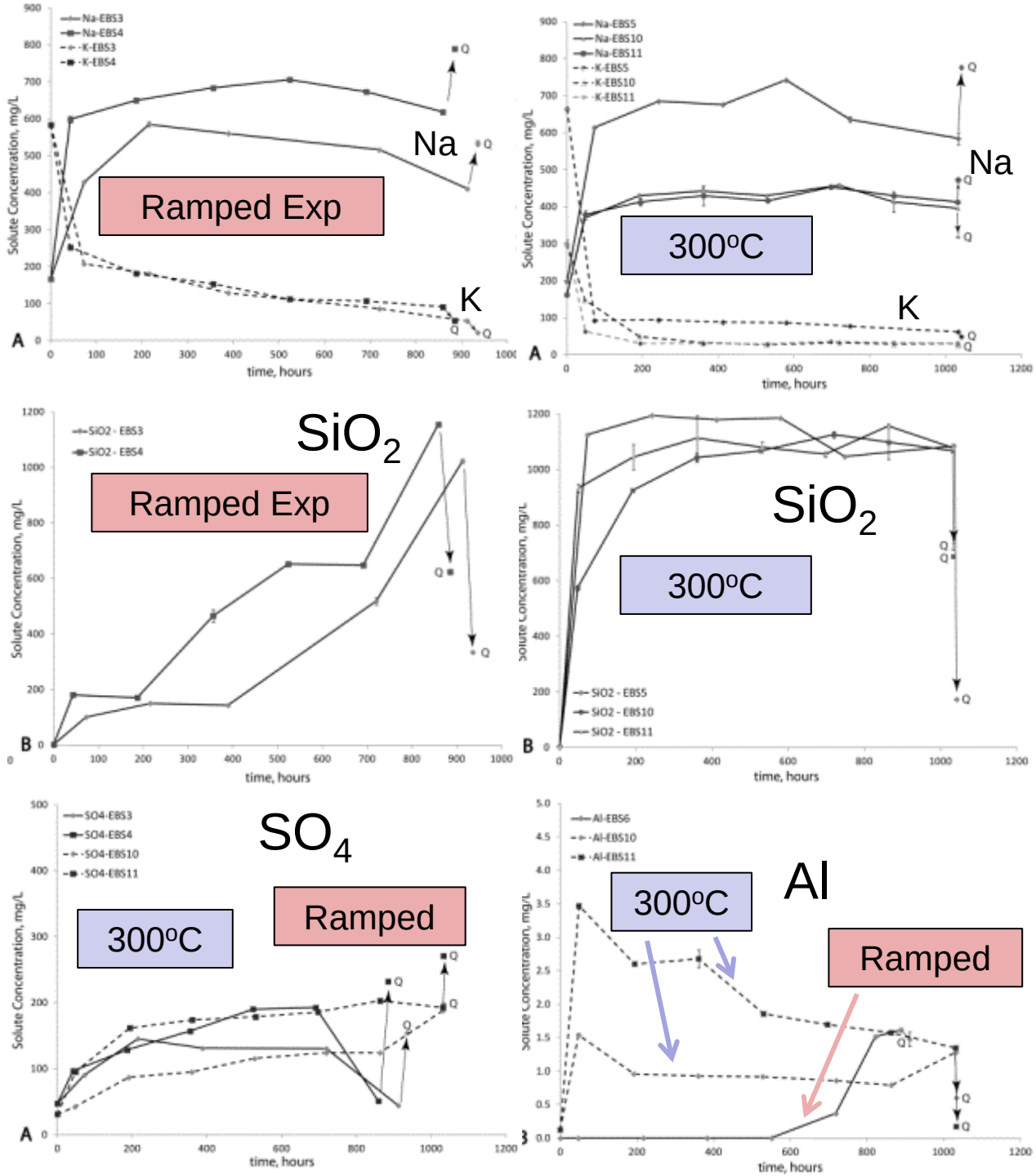
Used Fuel Disposition





Used Fuel Disposition

Aqueous geochemistry



Na-K is exchanged.
- Na-rich solution

Si increases incrementally with temperature.
- Cristobalite saturated

Al increases at 300ºC.
- Mineral dissolution

Sulfur increases.
- Primarily H_2S form
- Sulfide mineral