DISPOSAL IN ARGILLITE R&D WORK PACKAGE: INTRODUCTION & KEY ACCOMPLISHMENTS

C. F. Jové Colón (SNL), C. Payne (SNL), A. Knight (SNL), H. Moffat (SNL), E. Coker (SNL), F. Caporuscio (LANL), K. Sauer (LANL), M. Cheshire (ORNL)

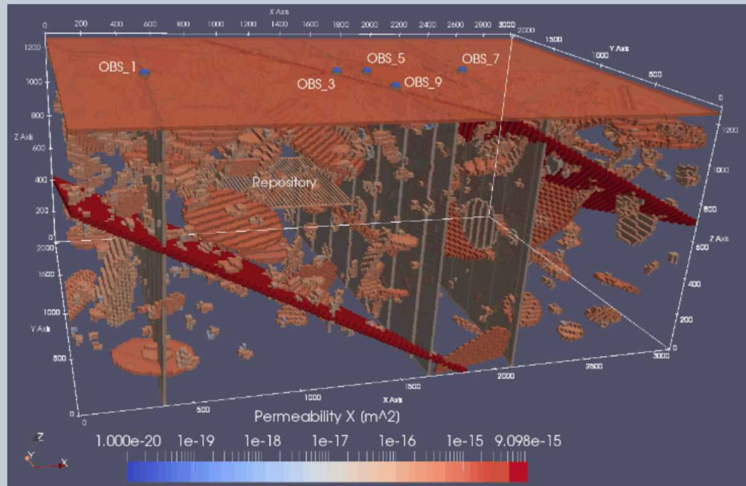
SFWD

SPENT FUEL & WASTE DISPOSITION

Annual Working Group Meeting
UNLV-SEB – *Las Vegas, Nevada*
May 21-23, 2019

Sandia National Laboratories

SAND2019-5596PE

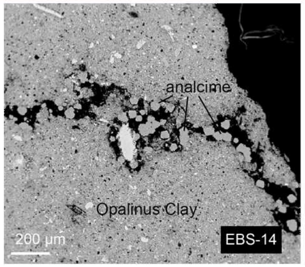


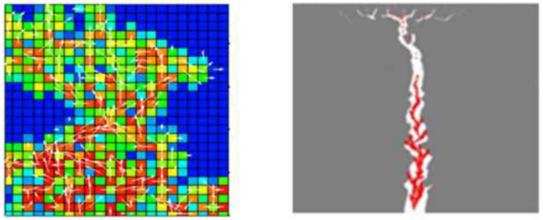
DISPOSAL IN ARGILLITE R&D: FY19 ACTIVITIES

- **Non-isothermal reactive-transport modeling (THC): 3D EBS for a single waste package under variably saturation conditions (SNL) (SC: 3.3.1 c, d; 4.2 d, e) (H: C-15; M-H: E-03, E-10, I-02, I-03)**
- **Engineered barrier system (EBS) model integration with performance assessment (PA) (LBNL, SNL) (SC: 3.3.1 c, d; 4.2 d, e) (M-H: P-01)**
- **Thermodynamic modeling of barrier material interactions (clay, cement, metal) and thermodynamic database (TDB) development (SNL, LLNL) (SC: 3.3.1 b-d; 4.2 d, e) (M-H: E-10)**
- **Bentonite clay interaction experiments (LANL, LBNL) (SC: 3.3.1 b-d; 4.2 d, e) (H: I-04, C-15, E-09, E-11; M-H: C-08, C-14, E-04, E-10, E-11, I-04)**
  - **High temperature mineral phase stability, clay – metal – cement – host rock interaction (LANL)**
  - **Low temperature RN sorption/diffusion in bentonite & modeling (LBNL)**
- **High temperature coupled thermal-hydrological-mechanical-chemical (THMC) modeling (LBNL) (SC: 3.3.1 b-d; 4.2 d, e) (H: I-04, E-11; M-H: E-03, E-10)**
- **Spent nuclear fuel (SNF) degradation model development – fuel matrix degradation model (FMDM) (with crystalline) & Cantera/Zuzax model (ANL, SNL) (SC: 3.3.1 b; 4.2 d, e) (H: D-05, E-14)**
- **First principles methods to study SNF corrosion product (schoepite) and thermodynamic data assessment (SNL) (SC: 3.3.1 b; 4.2 d, e) (H: E-14, D-05; M-H: P-15)**
- **International collaborations: FEBEX-DP, DECOVALEX19, SKB EBS Task Force, Mont Terri/Bure URLs (LBNL, SNL) (SC: 3.3.1 c, d; 4.2 c-g) (H: E-09, E-11, I-04; M-H: E-03, E-10 I-02, I-03, I-09)**

HIGHLIGHTS OF ACCOMPLISHMENTS

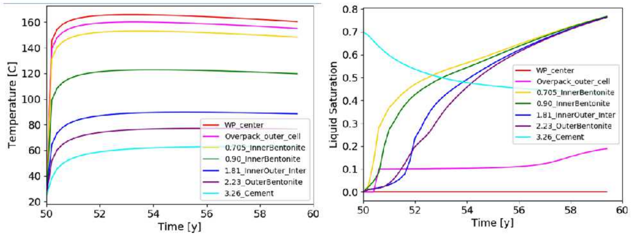
- High temperature experiments of bentonite interactions with barrier materials and host rocks: granodiorite & Opalinus Clay
- Thermodynamic modeling of bentonite – barrier material interactions & thermodynamic database development
- Advances in THMC modeling approaches of bentonite barrier, argillite rock, and excavated disturbed zone (EDZ fracture/damage behavior) & gas migration
- Development of (non)isothermal 1D-3D THC reactive transport model
- Refined and developed models for waste form degradation with electrochemical corrosion tests
- Generation thermodynamic data for UO_2 corrosion products using state-of-the-art 1^{st} principles methods
- Molecular dynamic studies of swelling clay behavior
- Development of a preliminary GDSA reference case for disposal in argillite media
- International collaborations:
  - FEBEX-DP: bentonite sorption/structural/compositional/thermal studies
  - DECOVALEX Task C: PFLOTRAN HC modeling of barrier interactions



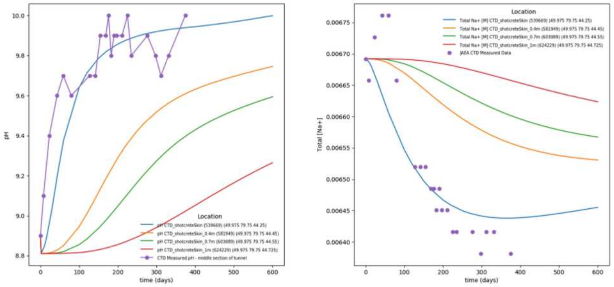

1) Continuum model approach using TOUGH-FLAC

2) Discrete fracture model approach using TOUGH-RBSN

FLOTRAN 3D Single Waste Package

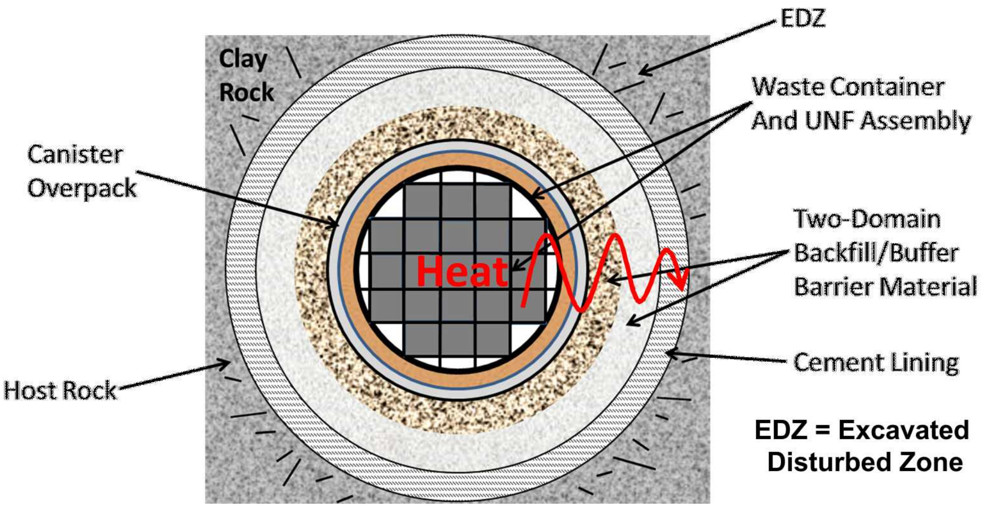


DECOVALEX19 Task C: FLOTRAN 3D HC model

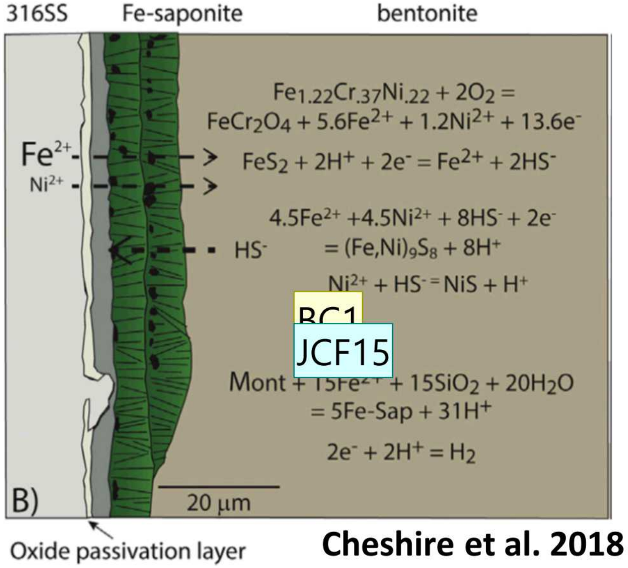


EBS INTERACTIONS & CANISTER HEATING

- **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 at elevated temperatures
- **Investigate effects of clay phase exposure to elevated temperatures** on sorption, diffusion, clay structure (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, reduce uncertainty



EDZ = Excavated Disturbed Zone



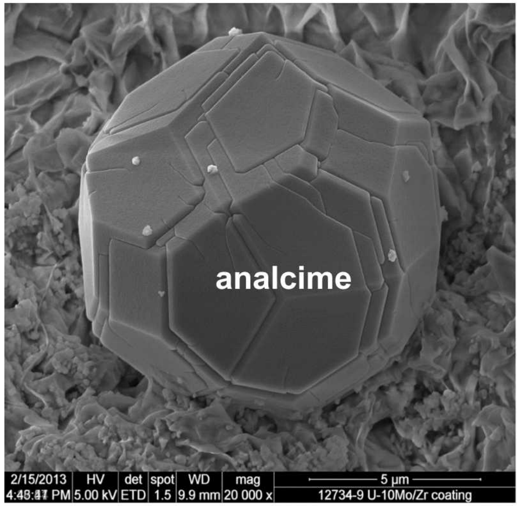
Cheshire et al. 2018

Slide 4

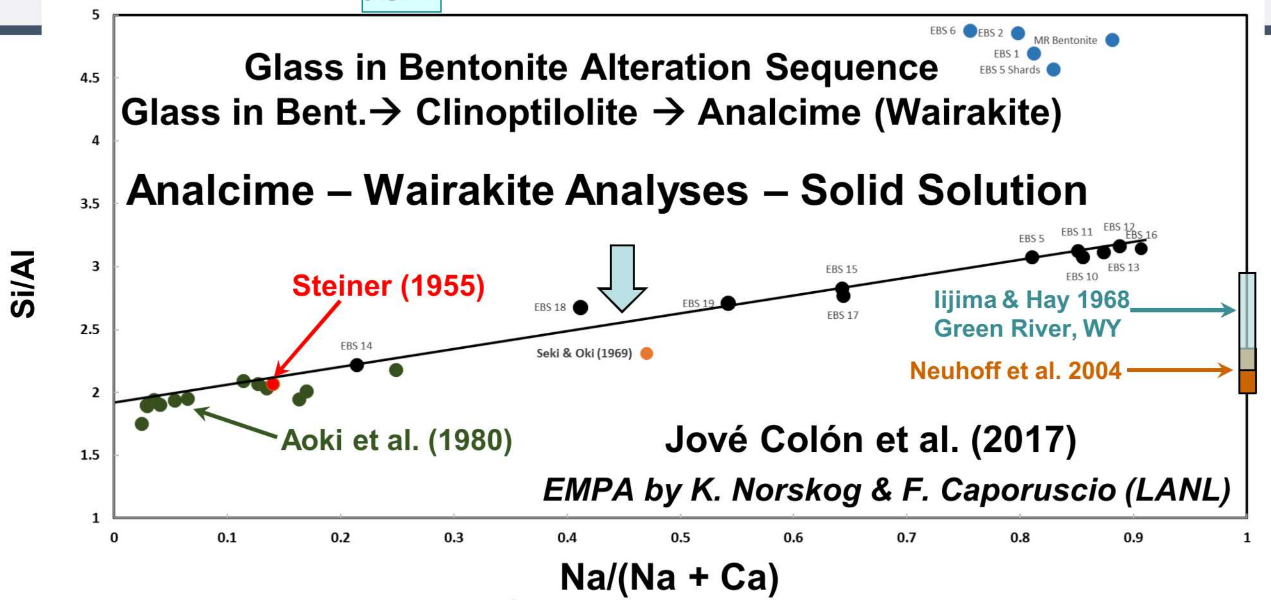
BC1	It is not clear what role the used fuel degradation model plays. Are you referring to decay and heat generation? Prior to canister penetration by corrosion, the used fule model can have no chemical effect; or are you discussing the potential chemical effects effects on the backfill after canister failure (radiolytic?). Bryan, Charles, 5/16/2019
JCF15	It refers to the Fuel Matrix Degradation Model (FMDM). It also refers to in-package chemistry model as well. It's mainly generic to represent used fuel interactions & radnuclide releases. Jove-colon, Carlos F, 5/16/2019

AUTHIGENIC ZEOLITE PRODUCED FROM CLINOPTILOLITE / GLASS IN BENTONITE

Analcime (Bentonite only)



Wairakite-rich zeolite (Opalinus clay + Bentonite)

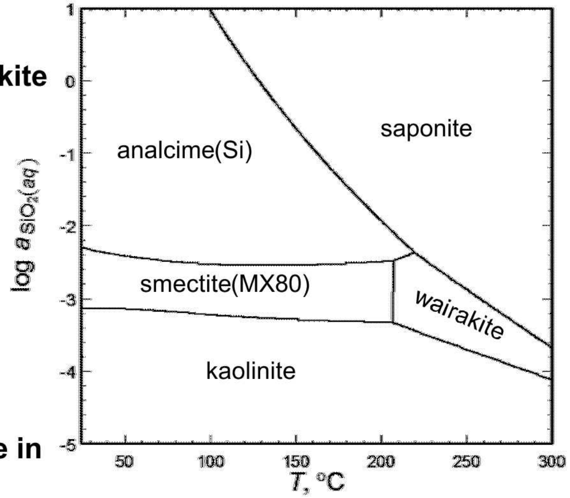


Bentonite Alteration and Zeolite Stability:

- Glass alteration in bentonite → high Si
- Formation of clinoptilolite, analcime – wairakite zeolites
- Analcime-wairakite solid solution
  - Expands zeolite stability?
- Little or no illite formation
  - Low K in solution
  - High Si in solution

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)

Slide 5

BC3 Is this

Bryan, Charles, 5/16/2019

BC4 Where is the glass coming from? Was this clay SWY-2? SWY-2 is, I think, from an ash or ash-rich unit, but it is Cretaceous. It is unlikely that there is any glass remaining in it. Have you seen glass in thin section?

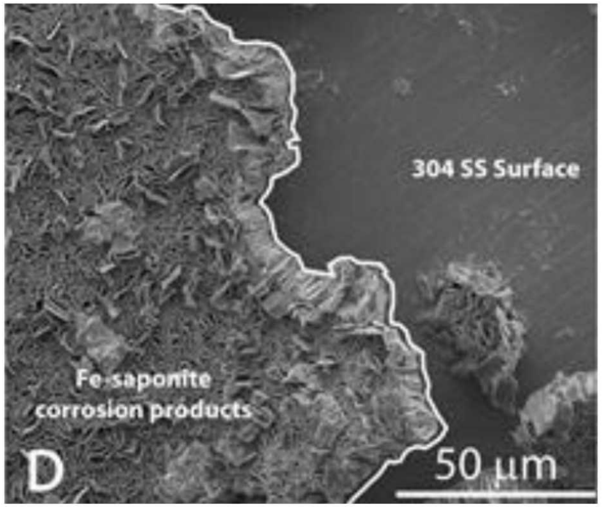
Bryan, Charles, 5/16/2019

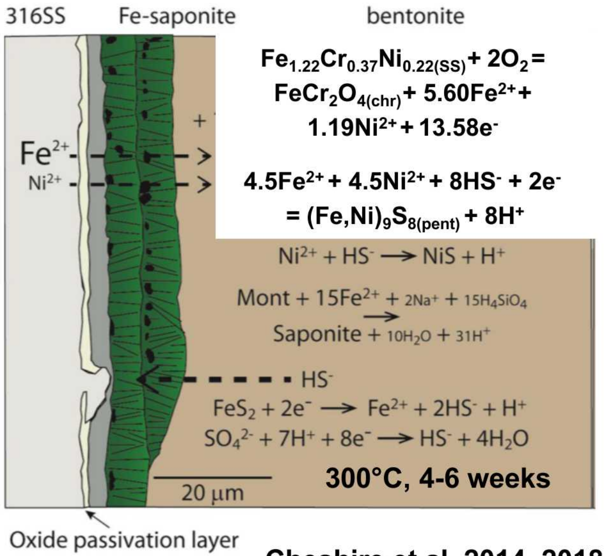
JCF1 The glass is relic from the volcanic ash unit. I don't know the volcanic unit pertaining the Coliny mine in WY from where the bentonite is from. Florie has seen the glass shards in the SEM but not sure if optically (thin section). According to the LANL team, the composition of the glass is close to that of clinoptilolite.

Jove-colon, Carlos F, 5/16/2019

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**





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

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

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

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

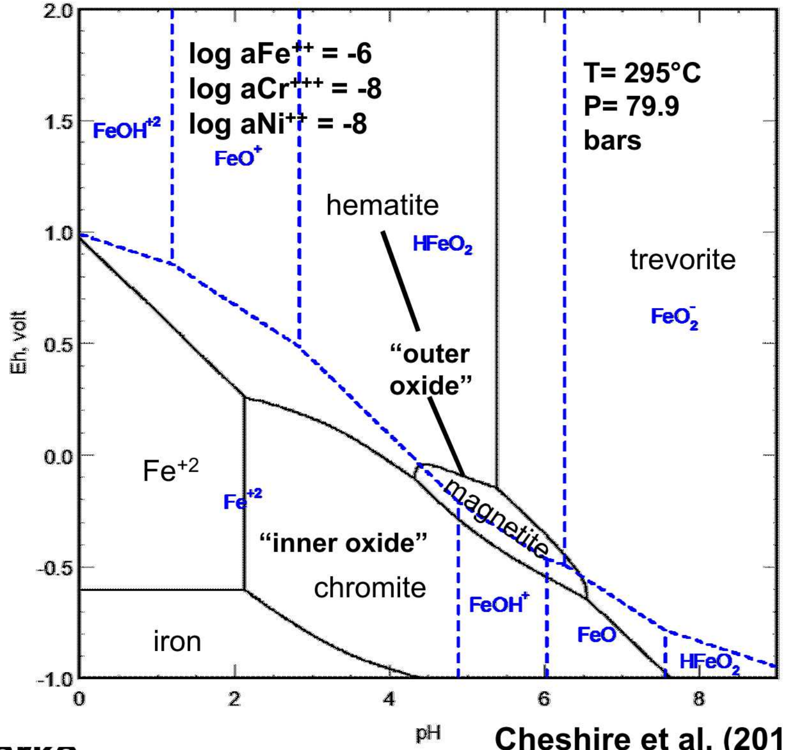
$FeS_2 + 2e^- \rightarrow Fe^{2+} + 2HS^- + H^+$

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

300°C, 4-6 weeks

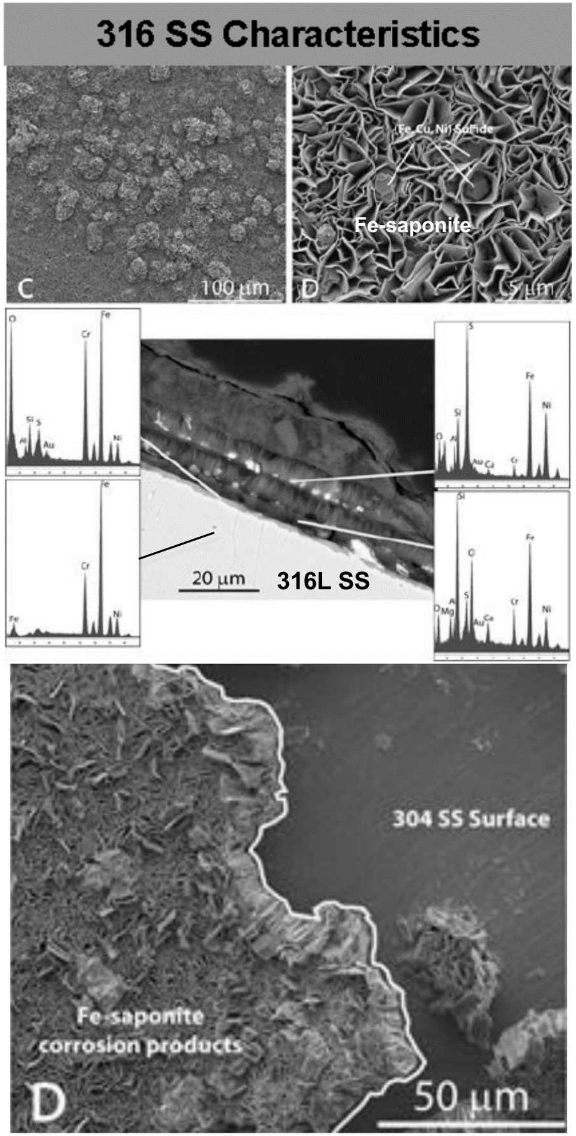
Cheshire et al. 2014, 2018

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



Cheshire et al. (2018)

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

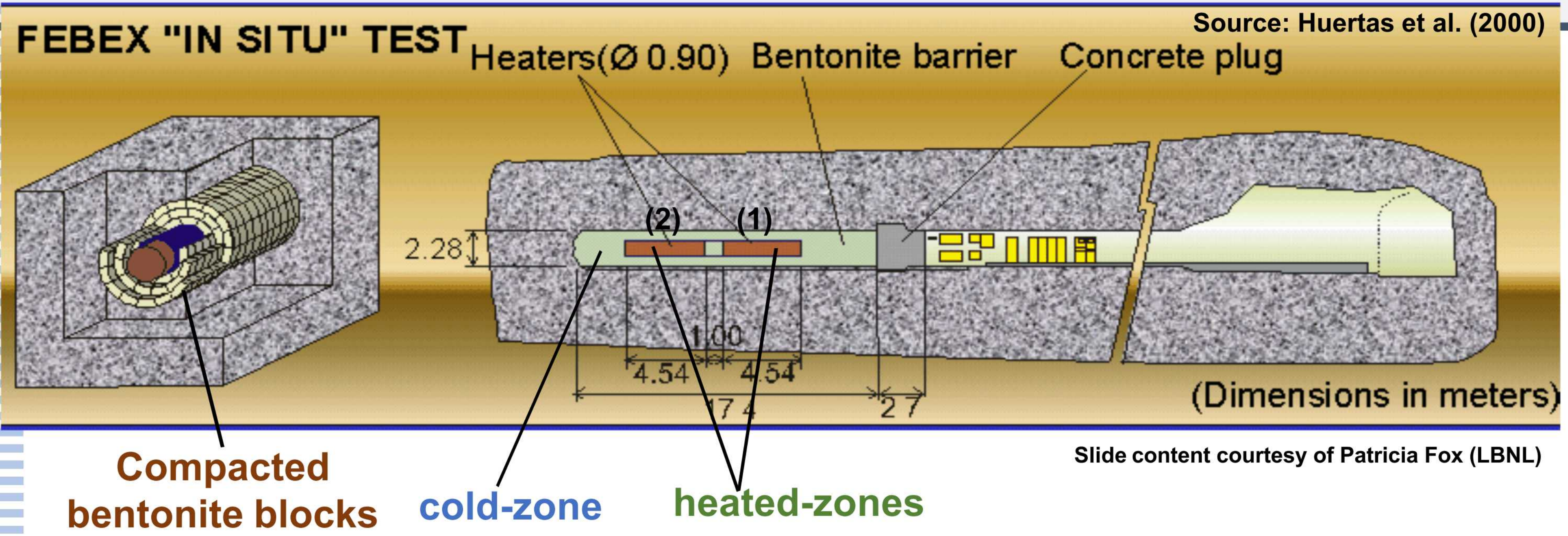


Cheshire et al. (2014, 2018)

Slide 7

BC5	Nice! The resolution of the analysis is on the order of cubic microns, because of the volume from which the X-rays are being generated. But the enrichment of the chrome next to the surface is clear, since it is even more enriched than the metal. What the really bright specks in the oxide layer are the sulfide? It is not clear in the image. An element may would have been nice. Bryan, Charles, 5/16/2019
JCF2	Good question. I need to ask Florie since they did the probe work. Maybe sulfides (not sure) since there's a pronounced S peak. Jove-colon, Carlos F, 5/16/2019

FEBEX FULL SCALE HEATER TEST EXPERIMENT

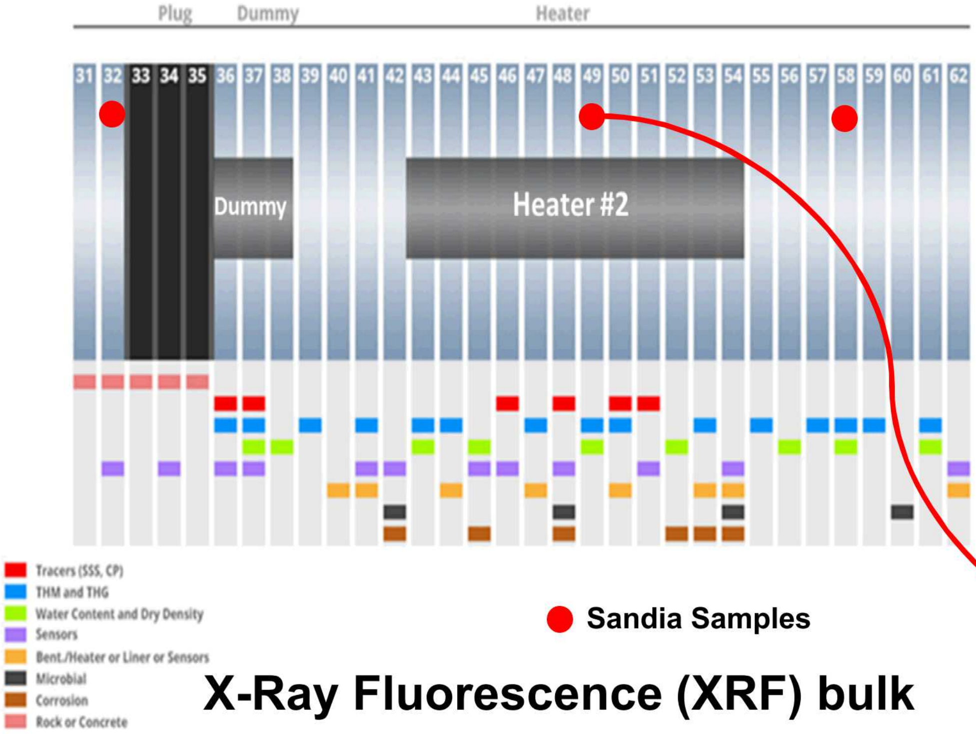


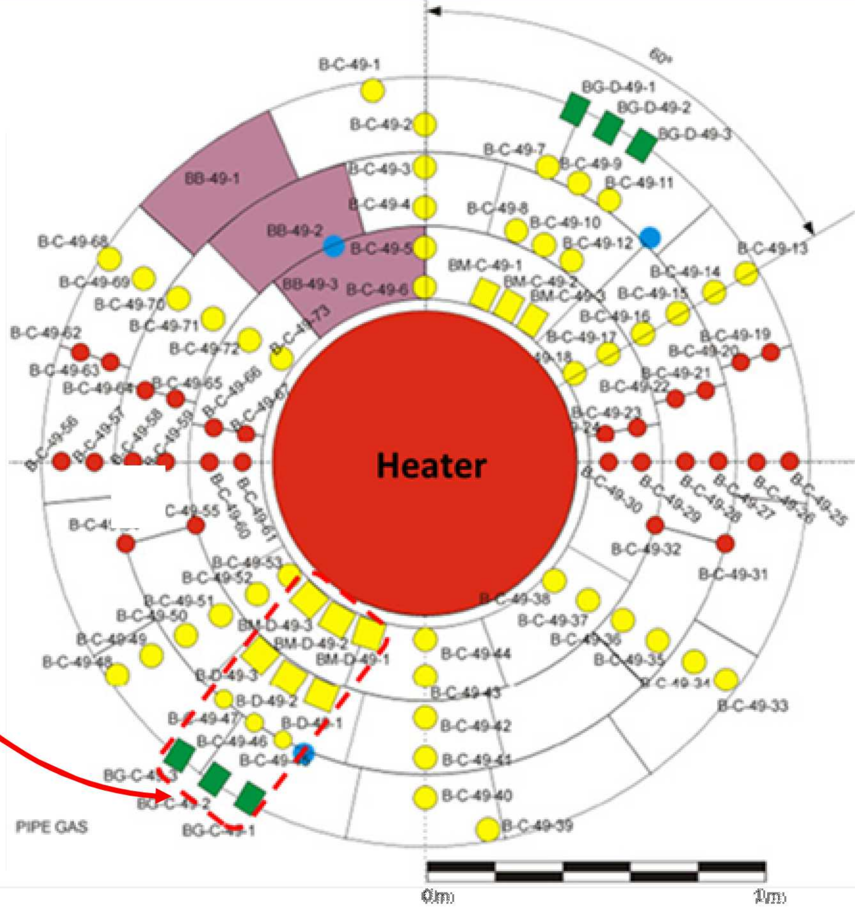
Source: Huertas et al. (2000)

Slide content courtesy of Patricia Fox (LBNL)

- **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

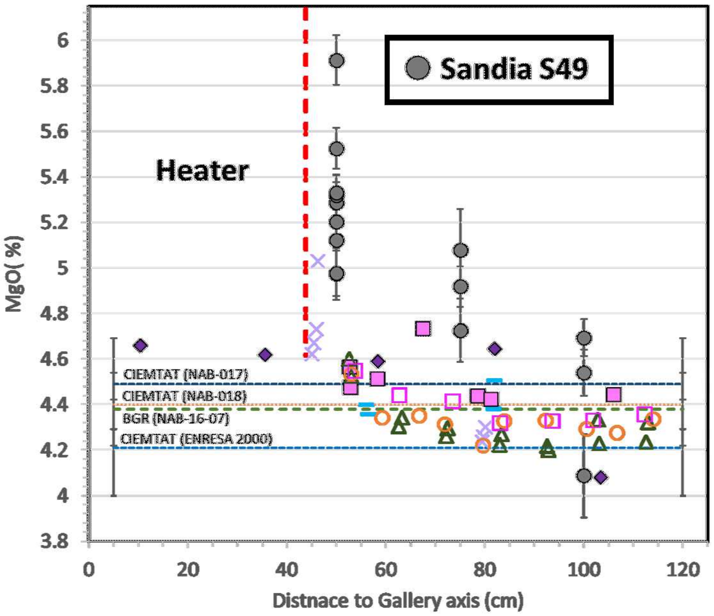


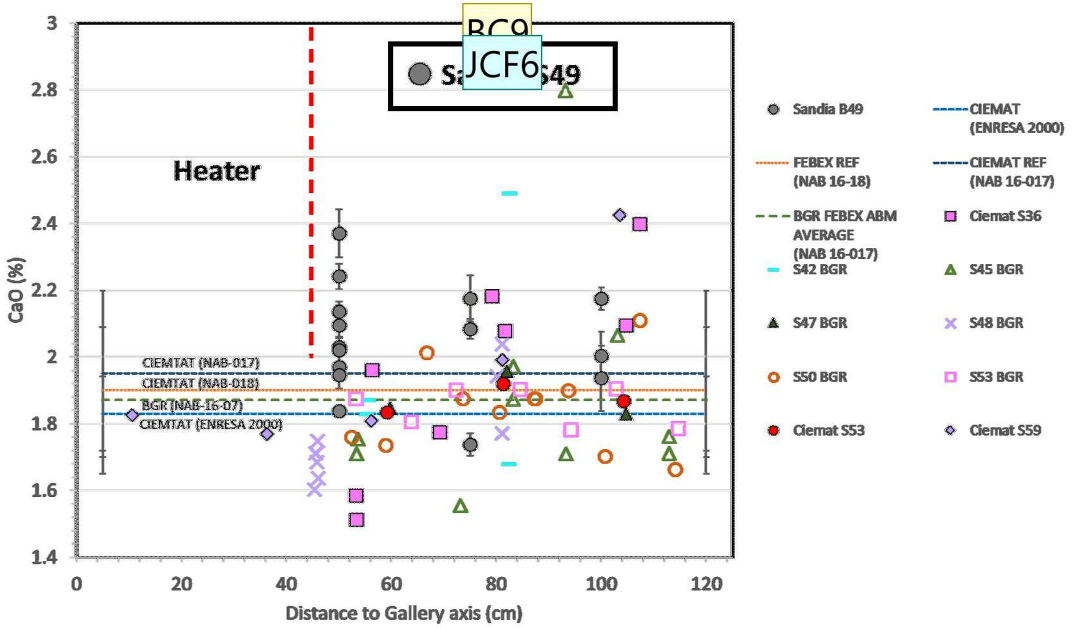


X-Ray Fluorescence (XRF) bulk composition, X-ray CT-scan, μ-XRF, SEM-EDS, X-Ray Diffraction (XRD), Thermogravimetric analysis (TGA)

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

Slide 10

BC8 Do higher temperatures favor Mg substitution into the clay? Were the sample all dried out to the same degree? Could the difference just be due to different water contents? No, that cant be right, or all elements would be affected.
Bryan, Charles, 5/16/2019

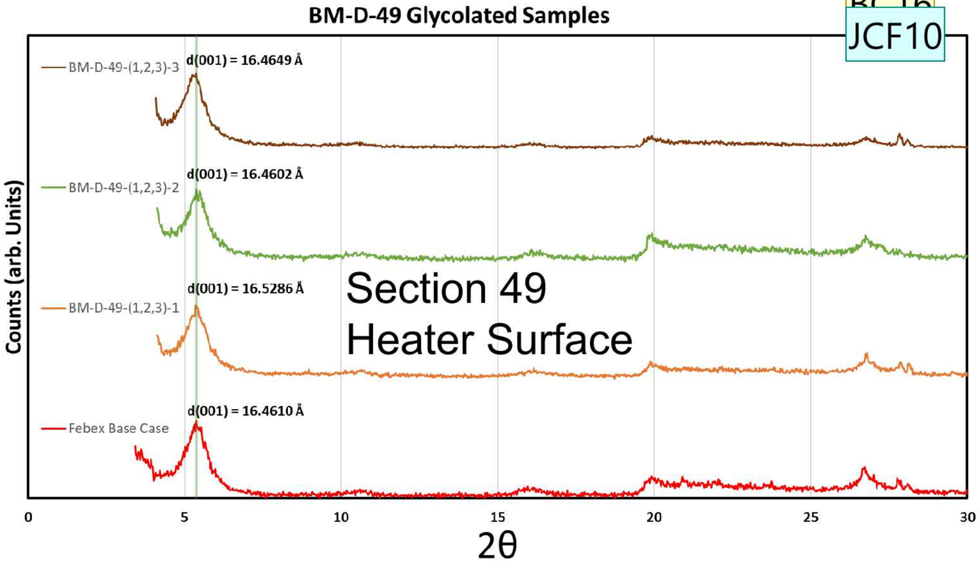
JCF5 Good question. I'll mention this saying that we're still trying to come up with a mechanism to explain this. The RH probe at a similar location shows an RH range of ~40% - ~60% close to the heater surface so it's dry to certain degree but not too dry.
Jove-colon, Carlos F, 5/16/2019

BC9 This is confusing. The legend says the gray circles are Sandia B49. Is this incorrectly labeled? If tis is just intended to be a second legend, you might put a box around it. Otherwise, given the eifferent label, it looks like some sort of specially plotted point.
Bryan, Charles, 5/16/2019

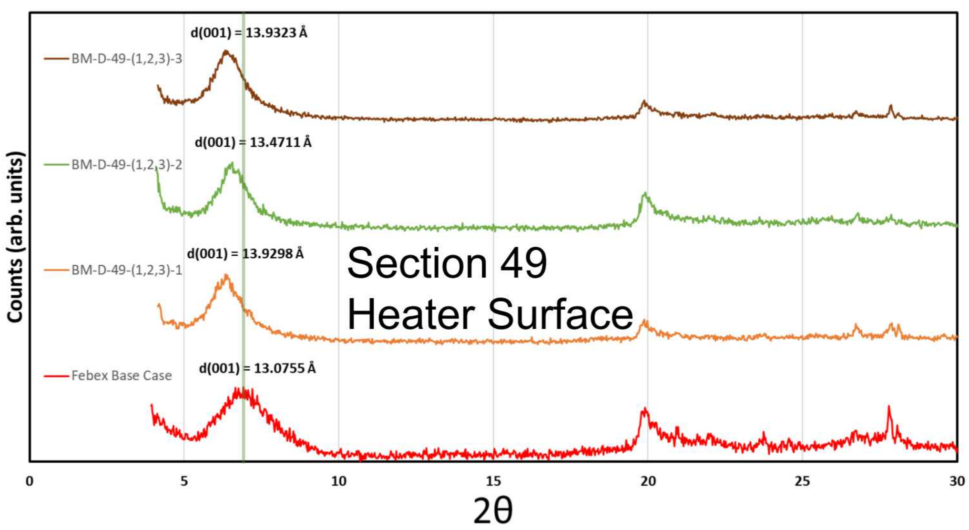
JCF6 The legend is correct. Gray circles are the samples for Section 49. No change.
Jove-colon, Carlos F, 5/16/2019

FEBEX-DP: BENTONITE X-RAY DIFFRACTION (XRD) CLOSE TO THE HEATER SURFACE

BM-D-49 Glycolated Samples



BM-D-49 - Dried at 60°C



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

RC1
JCF9

Slide 11

BC15 This is not obvious. the glycolated smaples all match. The for the unglycolated samples, the first and third patterns match in terms of d-spacings. Only the sample closest to the heatere shows significant changes. Could this be due to substitution of Fe (or maybe Mg, since it appears enriched near the heater) into the interlayer sites? This would affect the d-spacing.

Bryan, Charles, 5/16/2019

JCF9 All the samples pertain to blocks sampled near the heater surface. The Mg enrichment does correlate with the deviation from the FEBEX base case unheated sample. No changes.

Jove-colon, Carlos F, 5/16/2019

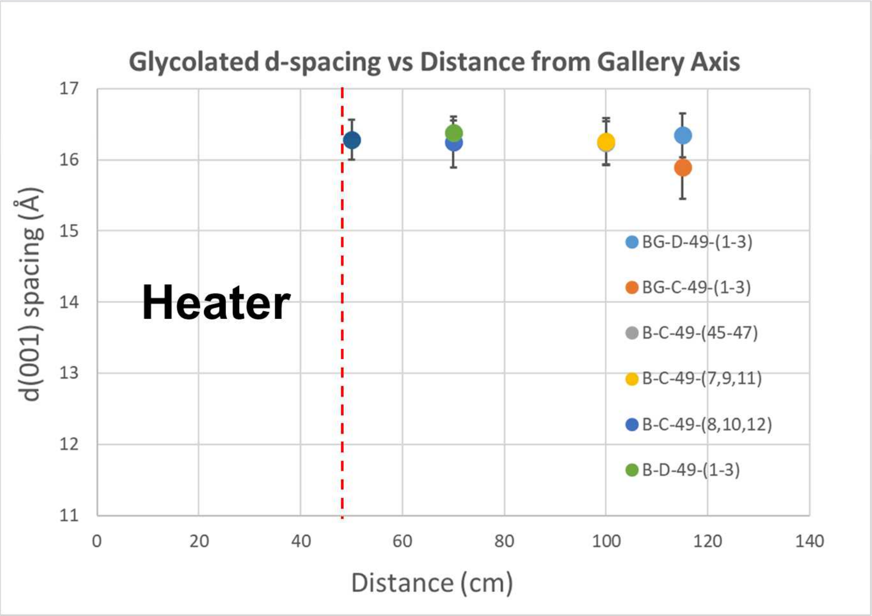
BC16 It would help to add a label to these graphs, indicating that distance from the heater surface increases from bottom to top.

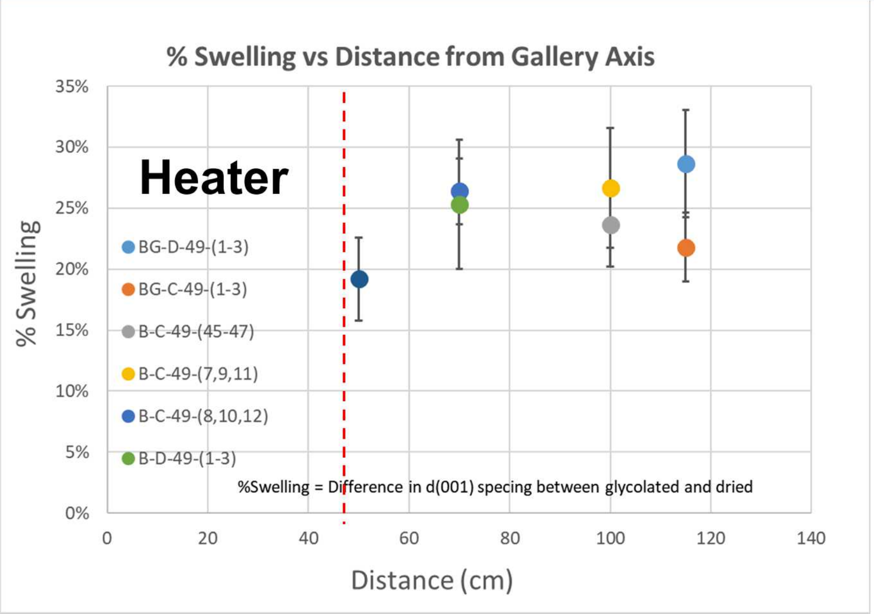
Bryan, Charles, 5/16/2019

JCF10 Since these are only for samples close to the heater surface (as labeled in the plot) I'll add text in the slide header.

Jove-colon, Carlos F, 5/16/2019

FEBEX-DP: BENTONITE X-RAY DIFFRACTION (XRD)



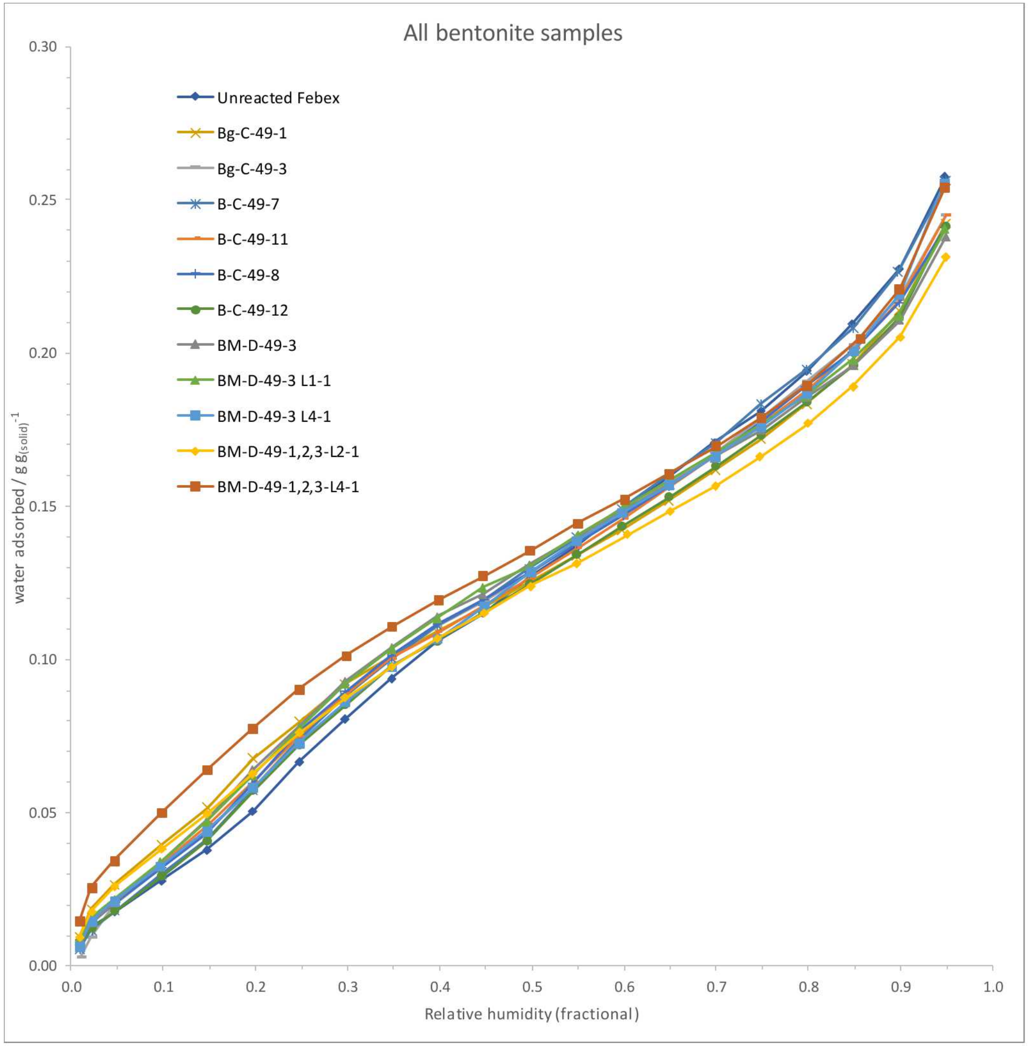


- No apparent effect of elevated temperatures on d(001) spacing for glycolated clay samples
- Slight decrease in swelling extent for samples in contact or close to the heater surface
- Prolonged exposure of bentonite to T = 95 – 100 ºC causes some changes in swelling
  - **Correlate with compositional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

HYDRATION/DEHYDRATION AND THERMAL ANALYSIS FEBEX-DP BENTONITE

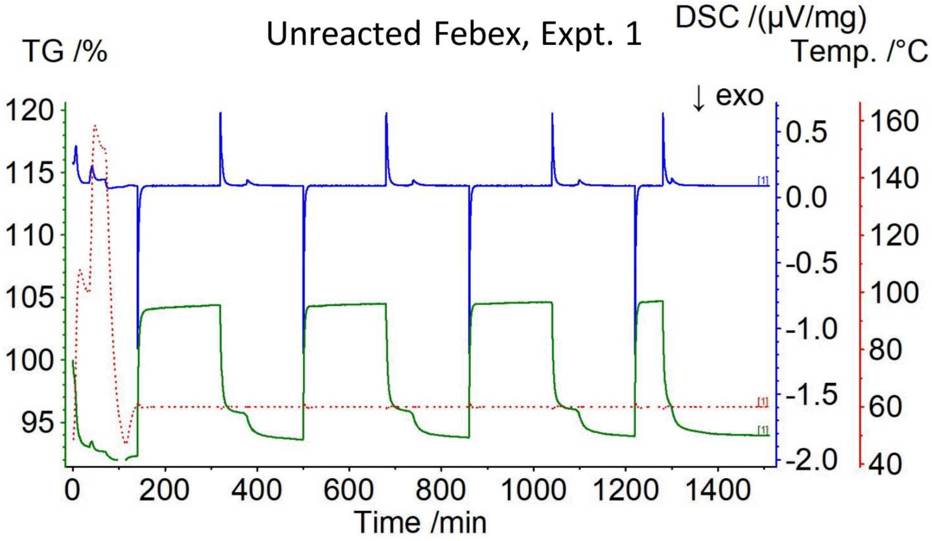
- Volumetric sorption
  - Samples were not sieved. Only mild grinding treatment
  - Samples degassed at 150 °C under vacuum for 20-40 hours
  - Sample tubes were immersed in a thermostatic bath maintained at 20 °C
  - Samples were fully evacuated and then exposed to volumetric doses of water vapor to determine their water adsorption isotherms at 20 °C
  - Instrumentation: Quantachrome Autosorb ASiQ2.
- Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)
  - Samples dehydrated under flowing dry nitrogen at 150 °C at the beginning
  - Samples were then cooled to 60 °C and exposed to a succession of dry and humid (60 % RH) flowing nitrogen atmospheres to cyclically hydrate and dehydrate the samples
  - This provides information about the rates of adsorption/desorption of water, as well as the quantity of water adsorbed and energetics of reaction
  - Instrumentation: Netzsch STA 449 F3 Jupiter with MHG humidity generator.

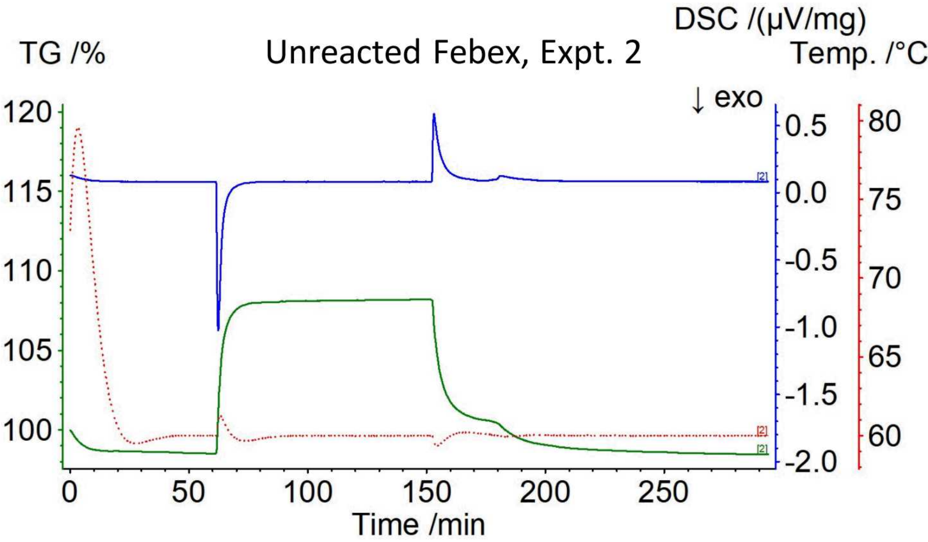
FEBEX-DP: VOLUMETRIC SORPTION



- All FEBEX-DP bentonite samples showed similar isotherms, except “BM-D-49-1,2,3 Location 4-1” which has slightly higher water uptake than others below 60% RH.
- H_2O capacity at 95% RH and 20 °C ranges from 0.23 to 0.26 $g_{(water)}\ g_{(solid)}^{-1}$

FEBEX-DP: THERMAL ANALYSIS (TGA/DSC)

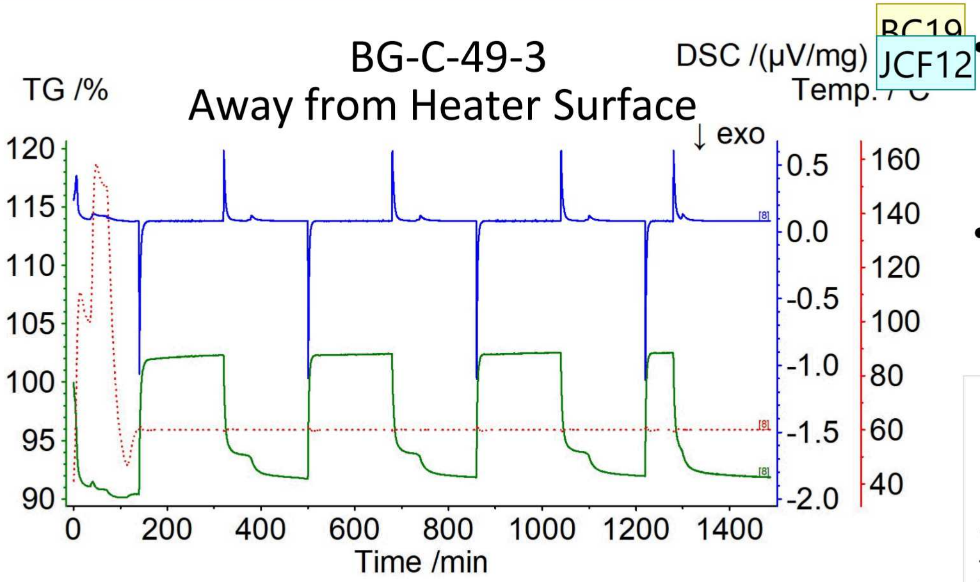


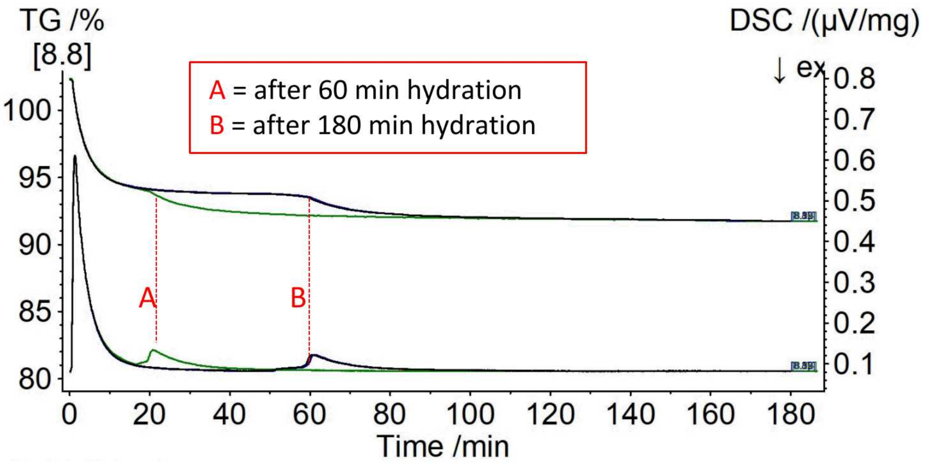


Expt. 1
1) Sample dehydrated under dry N_2 at 150 °C, then cooled to 60 °C.
2) 60 % RH N_2 for 180 min.
3) Dry N_2 for 180 min.
4) Steps 2 and 3 repeated twice.
5) 60 % RH N_2 for 60 min.
6) Dry N_2 for 240 min.

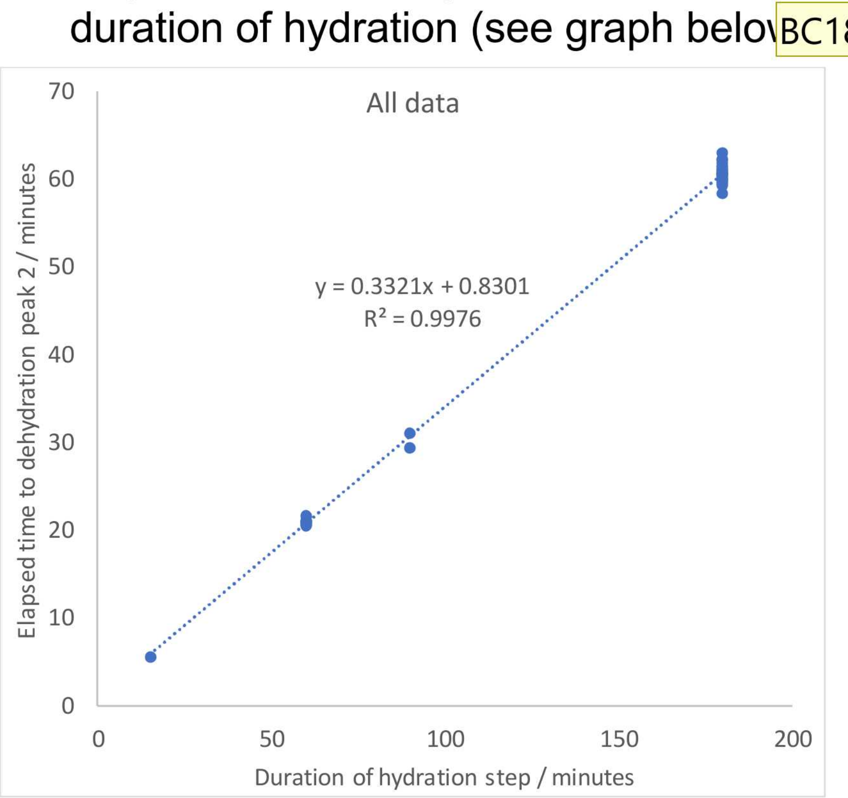
Expt. 2
Sample after expt. 1 subjected to:
1) Dry N_2, 60 °C, 60 min
2) 60% RH N_2, 60 °C, 90 min
3) Dry N_2, 60 °C, 150 min

FEBEX-DP: THERMAL ANALYSIS (TGA/DSC)





- All FEBEX-DP bentonite samples exhibit similar thermal behavior in hydration/dehydration cycles
- Good linear correlation between elapsed time of dehydration and duration of hydration (see graph belo



Slide 16

BC18 Very nice!

Bryan, Charles, 5/16/2019

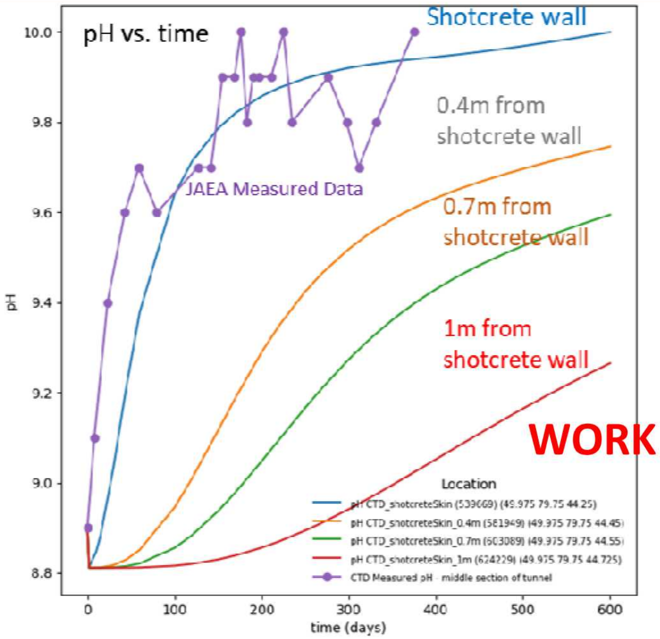
BC19 These graphs are the same as on the previous page, right? Is it necessary to show them again?

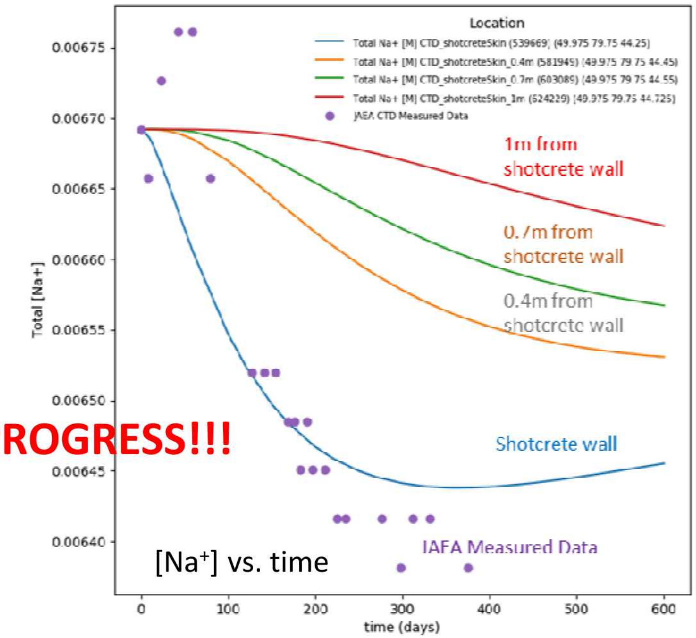
Bryan, Charles, 5/16/2019

JCF12 Actually, these are for different samples. No change.

Jove-colon, Carlos F, 5/16/2019

DECOVALEX19 TASK C: PFLOTRAN 3D REACTIVE TRANSPORT (RT) MODEL

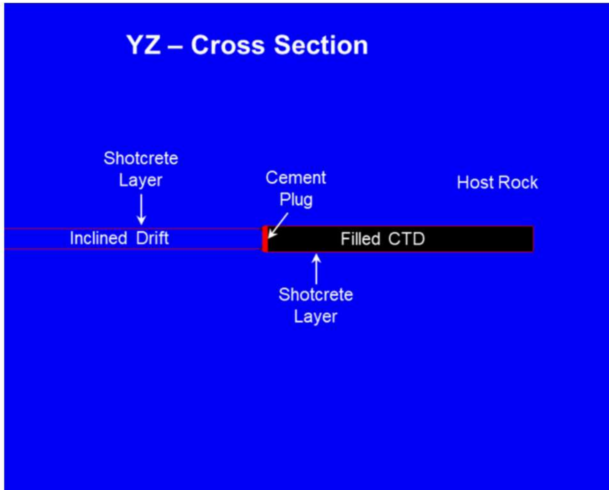




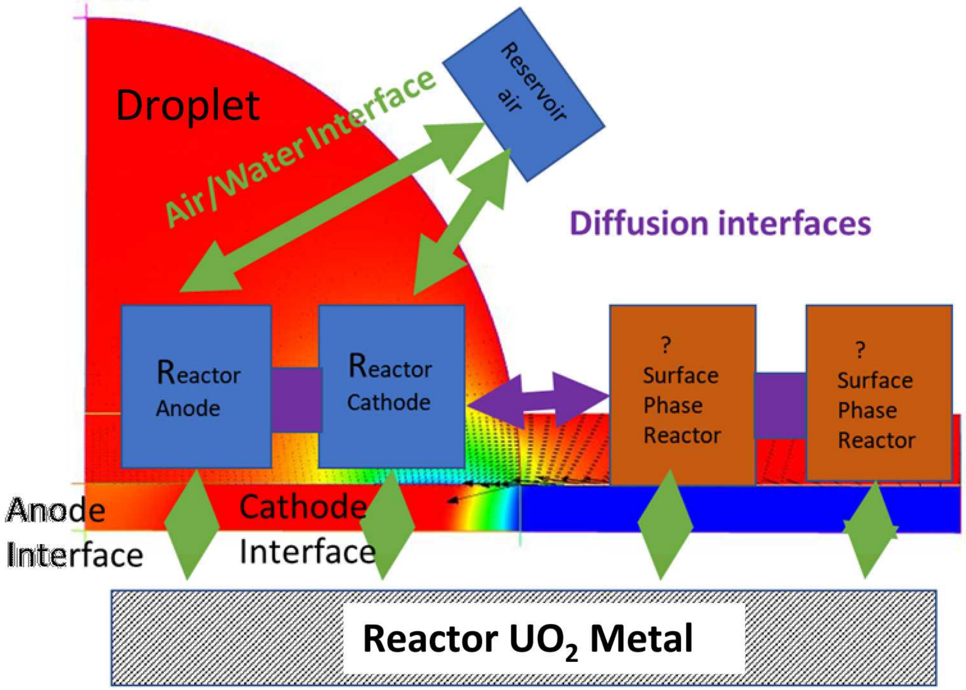
WORK IN PROGRESS!!!

Summary & Accomplishments

- Added brucite ($Mg(OH)_2$) and Friedel salt ($Ca_4Al_2Cl_2O_6{:}10H_2O$) to the cement phase assemblage – based on CTD shotcrete cement chemistry data
- Sensitivity analyses (SA) on TST rate law parameters for portlandite & brucite
- Some improvements on representing pH and [Na^+]. Still work to do on other solutes.



CANTERA/ZUZAX'S 0-D REACTOR NETWORK MODEL FOR UO2/METAL CORROSION



Cantera/Zuzax code development: Dr. H. Moffat (SNL)

- 0-D reactor model represents a series of interconnected reactors with inlets and outlets
- Expanded to be able to cover corrosion systems:
  - Porous flow charged fluid system volume
  - Metal electrode volume
  - Butler-Volmer charge transfer and general surface reaction mechanisms
  - Bidirectional Diffusion with Darcy's flow of electrolytes
  - Gas adsorption through an interface
  - Can have solid precipitates
  - Diffusion with respect to electrochemical potential treated with Stefan-Maxwell formulation
- **Goal: Model captures uranium speciation & solution chemistry feedbacks**

SUMMARY & ACCOMPLSHMENTS FY19 ACTIVITIES

- Bentonite-metal interactions & 3D THC modeling at elevated temperatures:
  - ➢ Produces zeolites (analcime) and sulfide phases with Fe-saponite growth perpendicular to metal substrate
  - ➢ Little or no illite forms in the experiments and URL heater tests
  - ➢ Thermodynamic analysis of clay-metal and clay-zeolite equilibria is consistent with experimental observations
  - ➢ Advances in non-isothermal 3D modeling of waste package & EBS
  - ➢ Future Work: Study effects of host rock composition & other barrier materials (e.g. cement); expand 3D non-isothermal model to various waste packages

- *Post mortem* FEBEX-DP bentonite studies & DECOVALEX Task C HC modeling:
  - ➢ Slight decrease in bentonite swelling correlates with Mg-enrichment in clay close to the heated surface
  - ➢ Thermal analyses under controlled hydration/dehydration show no significant differences between samples close to and far from the heater surface
  - ➢ Future Work: Exploit cyclic thermal analyses & XRD methods to evaluate high T effects;

- UO_2 / metal corrosion modeling & thermodynamic data generation for UO_2 corrosion products
  - ➢ Progress in FMDM & Cantera/Zuzax electrochemical model development for UO_2/metal corrosion
  - ➢ Future Work: Applications to wasteform interactions and in-package chemistry modeling; use 1st principle approaches in the generation of thermodynamic data of UO_2 corrosion products (metaschoepite)

1. Introduction, Purpose, and Context

2. Safety Strategy

2.1 Management Strategy

a. Organizational/mgmt. structure
b. Safety culture & QA
c. Planning and Work Control
d. Knowledge management
e. Oversight groups

2.2 Siting & Design Strategy

a. National laws
b. Site selection basis & robustness
c. Design requirements
d. Disposal concepts
e. Intergenerational equity

2.3 Assessment Strategy

a. Regulations and rules
b. Performance goals/safety criteria
c. Safety functions/multiple barriers
d. Uncertainty characterization
e. RD&D prioritization guidance

3. Technical Bases

3.1 Site Selection

a. Siting methodology
b. Repository concept selection
c. FEPs Identification
d. Technology development
e. Transportation considerations
f. Integration with storage facilities

3.2 Pre-closure Basis

a. Repository design & layout
b. Waste package design
c. Construction requirements & schedule
d. Operations & surface facility
e. Waste acceptance criteria
f. Impact of pre-closure activities on post-closure

3.3 Post-closure Bases (FEPs)

3.3.1 Waste & Engineered Barriers Technical Basis

a. Inventory characterization
b. WF/WP technical basis
c. Buffer/backfill technical basis
d. Shafts/seals technical basis
e. UQ (aleatory, epistemic)

3.3.2 Geosphere/ Natural Barriers Technical Basis

a. Site characterization
b. Host rock/DRZ technical basis
c. Aquifer/other geologic units technical basis
d. UQ (aleatory, epistemic)

3.3.3 Biosphere Technical Basis

a. Biosphere & surface environment:
  - Surface environment
  - Flora & fauna
  - Human behavior

4. Disposal System Safety Evaluation

4.1 Pre-closure Safety Analysis

a. Surface facilities and packaging
b. Mining and drilling
c. Underground transfer and handling
d. Emplacement operations
e. Design basis events & probabilities
f. Pre-closure model/software validation
g. Criticality analyses
h. Dose/consequence analyses

4.2 Post-closure Safety Assessment

a. FEPs analysis/screening
b. Scenario construction/screening
c. PA model/software validation
d. Barrier/safety function analyses and subsystem analyses
e. PA and Process Model Analyses/Results
f. Uncertainty characterization and analysis
g. Sensitivity analyses

4.3 Confidence Enhancement

a. R&D prioritization
b. Natural/anthropogenic analogues
c. URL & large-scale demonstrations
d. Monitoring and performance confirmation
e. International consensus & peer review
f. Verification, validation, transparency
g. Qualitative and robustness arguments

5. Synthesis & Conclusions

a. Key findings and statement(s) of confidence
b. Discussion/disposition of remaining uncertainties
c. Path forward

MAPPING TO SFWST R&D ROADMAP

High Impact R&D Topics	High-Priority R&D Activities	Medium-High-Priority R&D Activities
High temperature impacts	D-1, D-4, I-4, I-6, I-16, E-11, S-5	I-2, I-3, I-7, E-10
Buffer and seal studies	I-4, E-9, E-17, A-8, C-15	I-2, I-3, I-7, A-4, C-6, C-8, C-11
Generic PA Models	P-1, P-2, P-3, P-4	P-11, P-13, P-14
Coupled processes (Salt)	S-1, S-3, S-4, I-12, I-13	I-14, S-2, S-7, S-8, S-11
Gas flow in the EBS	I-6, I-8, I-18	I-9, P-17
Criticality	D-1, D-4, D-5	
Waste Package degradation	C-16, P-12	E-4, E-6
Radionuclide Transport	P-6	C-11, C-13, C-14. P-15, P-16
In-Package Chemistry	E-14	E-2, E-20, P-15, P-16
DFN issues		I-21, C-1, C-17
GDSA Geologic Modeling		O-2, O-3
THC Processes in EBS		E-3

Source: DOE SFWST Campaign R&D Roadmap Update, Sevougian et al. 2019, SAND2019-5179 R

QUESTIONS?

SFWD

SPENT FUEL &
WASTE DISPOSITION

Annual Working Group Meeting
May 21-23, 2019

UNLV-SEV – *Las Vegas, Nevada*

BC20

JCF13

BACKUP/EXTRA SLIDES

Slide 23

BC20 Correct the spelling.
Bryan, Charles, 5/16/2019

JCF13 Spelling corrected
Jove-colon, Carlos F, 5/16/2019

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 BC2 JCF14, weeks-months

Photo courtesy of F. Caporuscio (LANL)

Hydrothermal Apparatus

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)

Slide 24

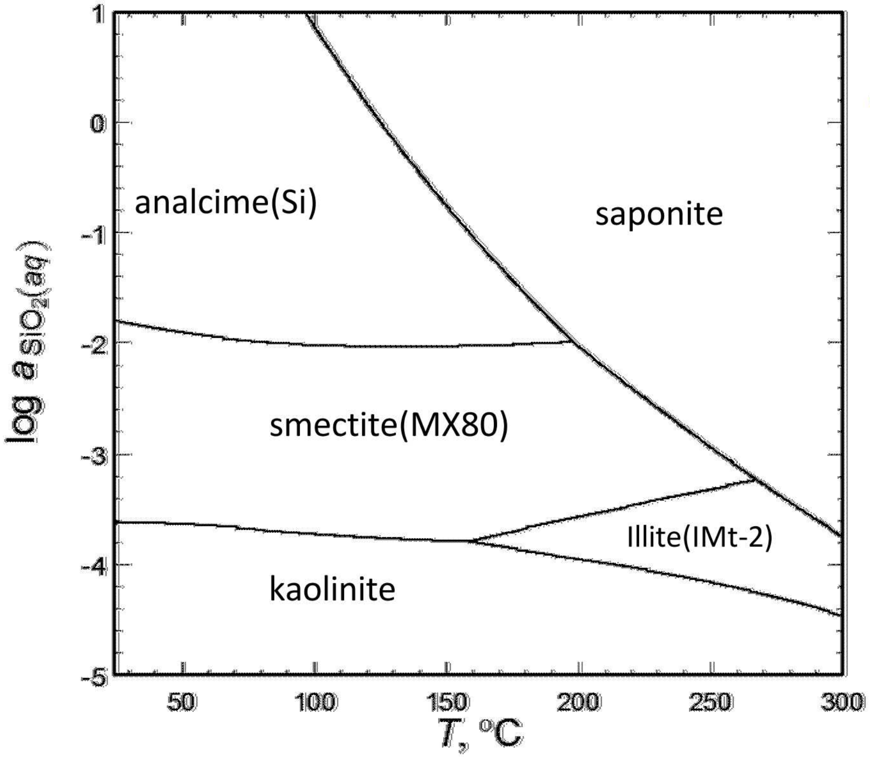
BC2 This is too deep for a mined repository if you assume hydrostatic pressure (1500 m) which would be relevant for a granite repository site. Is this aimed at deep borehole?

Bryan, Charles, 5/16/2019

JCF14 Florie assumed lithostatic/hydrostatic pressures around these values. Also, clay backfilling load plus swelling pressures may increase a bit. The use of pressures like this also ensures liquid stability in the experiments. It's assumed that these pressures (relatively low) will have little effect on the chemical reactions.

Jove-colon, Carlos F, 5/16/2019

ILLITE STABILITY



Activity Phase Diagram:

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

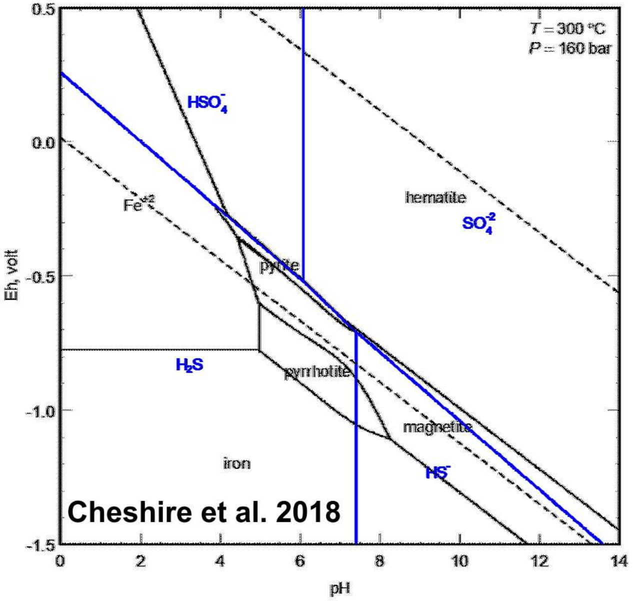
- **Activity phase diagrams constructed with CHNOSZ (Dick 2008). Aqueous activities constrained to represent experiments and to obtain stable phase topology**

- **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**

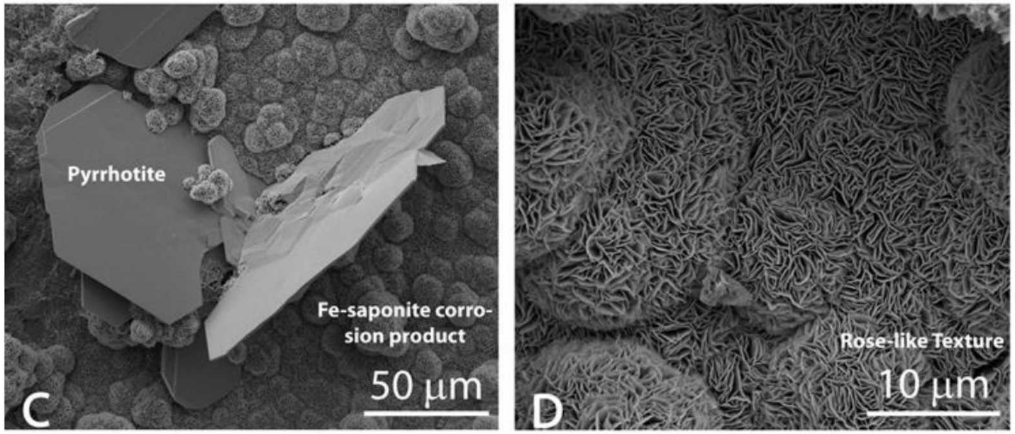
WASTE CANISTER DEGRADATION: LOW CARBON STEEL – CLAY

Results

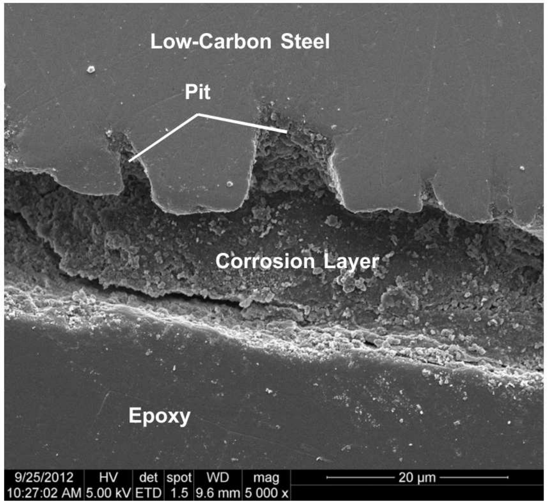
- **Corrosion Products:**
  - **Fe-smectites (Fe-saponite)**
  - **Pyrrhotite ($Fe_{1-x}S$)**
- **13 – 56 μm thick corrosion layer**
- **~20 μm pitting corrosion**
- **No passivation layer - corrosion exp[illegible]d to continue**
- **Extensive Fe_3O_4 layer develop**



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

Slide 26

BC6 You might discuss the effect of hydrogen build-up due to water reduciton. Anoxic iron corrosion is ot inhibited by hydrogen build-up until hydrpgen pressures get up to 300 bars. Was a pressure increase observed on the experiment due to hydrogen build-up? Note that in some experiments evaluating steel corrosion in WIPP brines, Westermann concluded that several tens of bars of hydrogen slowed the corrosion rate--but this is not consistent with the thermodynamics.

Bryan, Charles, 5/16/2019

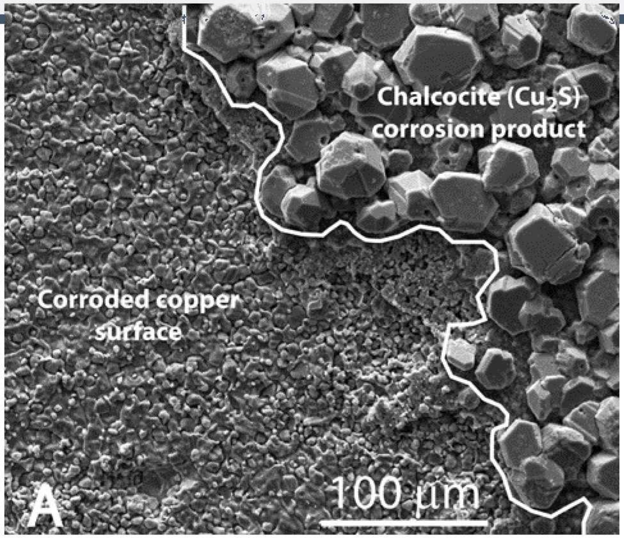
JCF3 I think the total P is ~160 bars. You're right that H build up will inhibit corrosion. I think there was H build up as it's expected but not to the point that it was excessive like the BORAL experiment. We can represent the phase equilibria fine by inferring a reduced environment at the interface. The corrosion in these experiments was rather agressive.

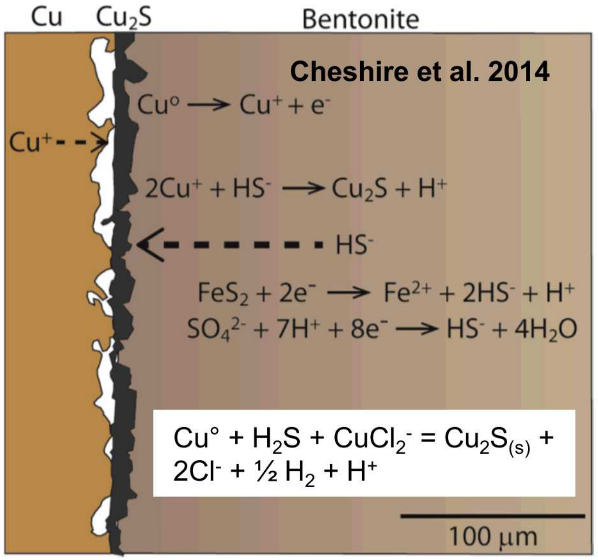
Jove-colon, Carlos F, 5/16/2019

WASTE CANISTER DEGRADATION: COPPER – CLAY INTERACTIONS

RC7 JCF4

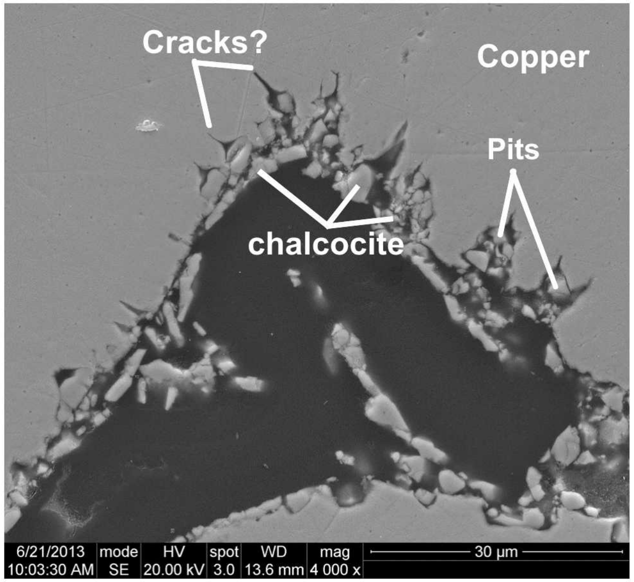
- Copper has been considered as canister and/or cladding/coating material
- Sulfide-induced corrosion (anoxic):
  - Pyrite (FeS_2) decomposition from bentonite
- Primary corrosion product → Chalcocite (Cu_2S):
  - $Cu^\circ + H_2S + CuCl_2^- = Cu_2S_{(s)} + 2Cl^- + \frac{1}{2} H_2 + H^+$
  - ~13 µm thick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





Cheshire et al. 2014

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



Slide 27

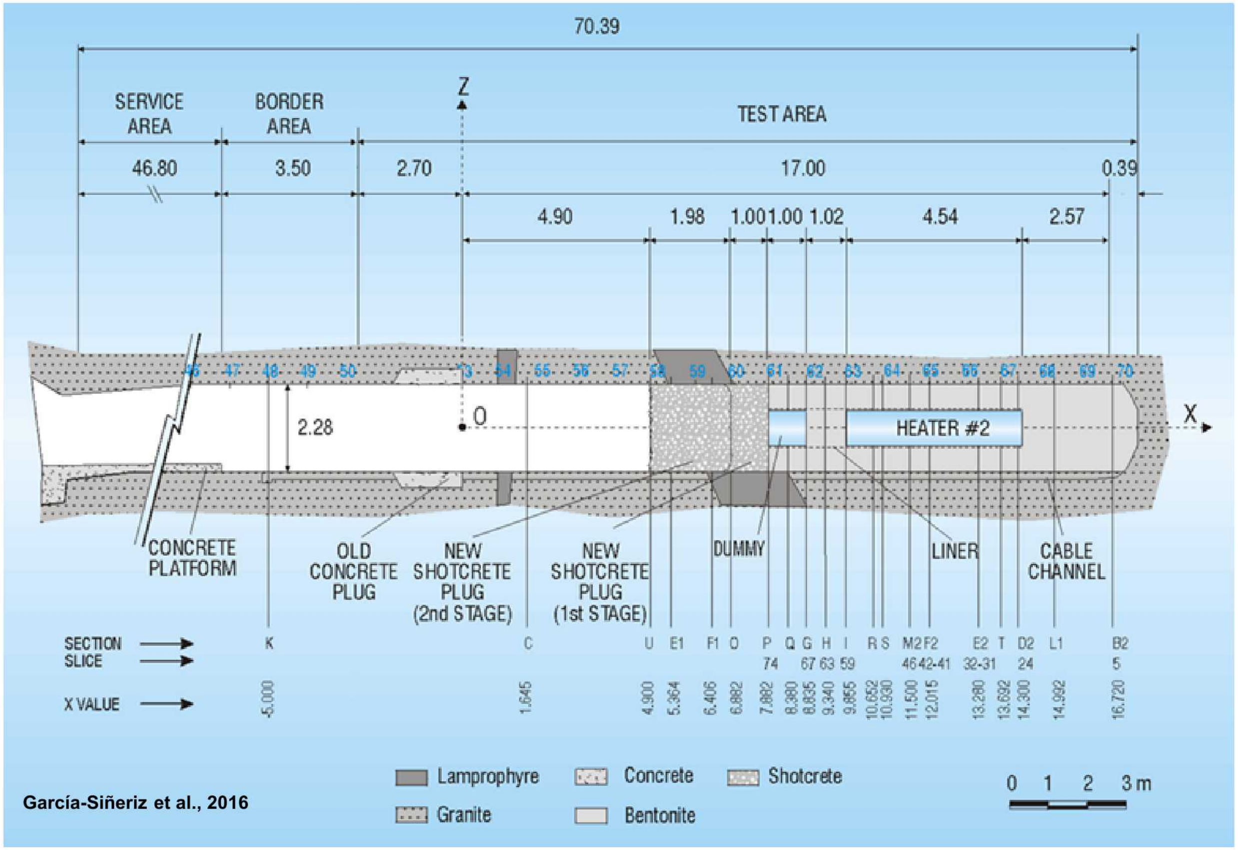
BC7 You should add a bullet discussing the source of the sulfide. Theere is sulfate in the water, and potentially trace pyrite in the bentonite (note that SWy-2 only contains 0.08% FeO). The pyrite won't break down down once the oxygen in the water is consumed. Did you use deoxygenated water? Is there sulfate in the bentonite? If not, then reduction of sulfate inthe water is the likely source.

Bryan, Charles, 5/16/2019

JCF4 Certainly, I'll explain these sources for S. According to the LANL team, the pyrite in the bentonite was consumed through the experiment (little or nothing left). A STRIPA brine was used in the exp. We believe the source of sulfate is pyrite and the abiotic reduction is something that has been observed. Maybe you were at the swedish talk at the IHLRWM meeting where the MINICAN exp (Cu canister buried in bentonite) showed chalcocite formation at 15 deg. C. I'll discuss this at the meeting if necessary.

Jove-colon, Carlos F, 5/16/2019

FEBEX-DP EXPERIMENT: SAMPLED SECTIONS

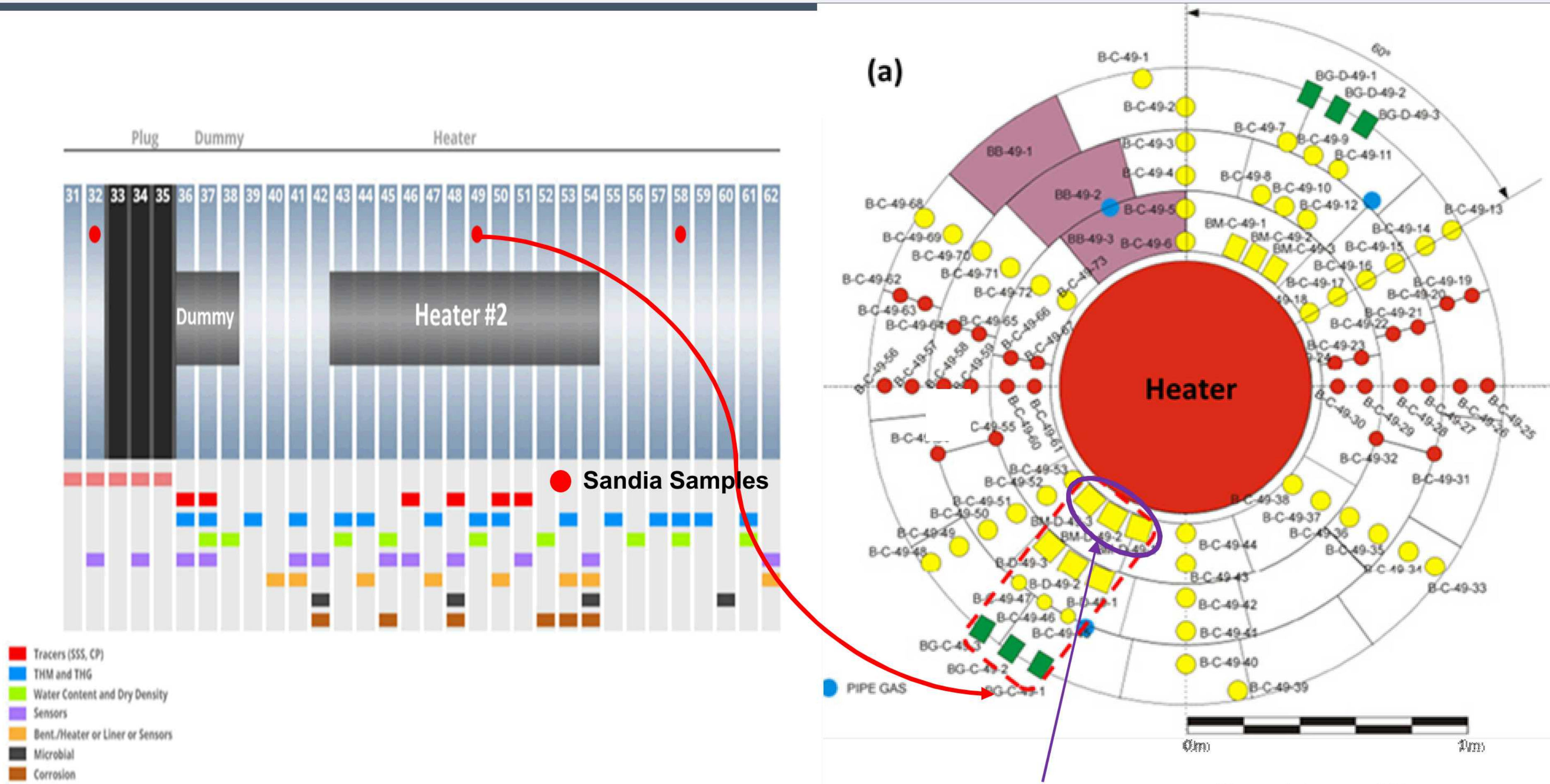


García-Siñeriz et al., 2016

FEBEX-DP Sampling

- **Section 49 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

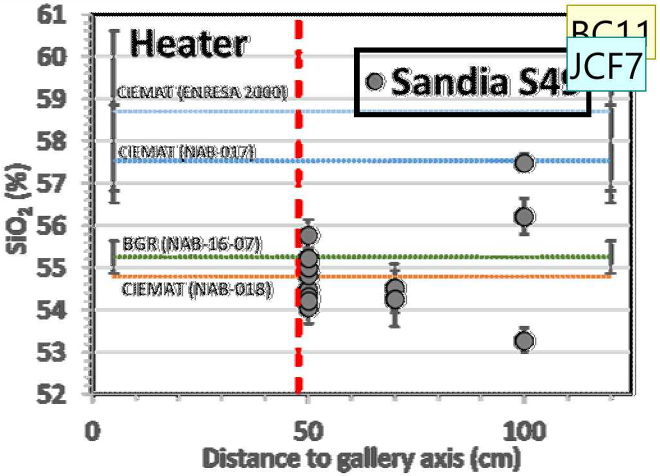


● Sandia Samples

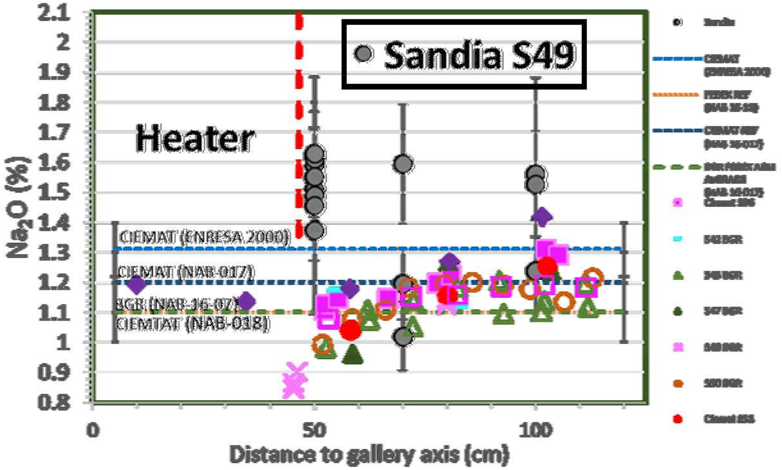
XRD Analyses samples close to heater surface

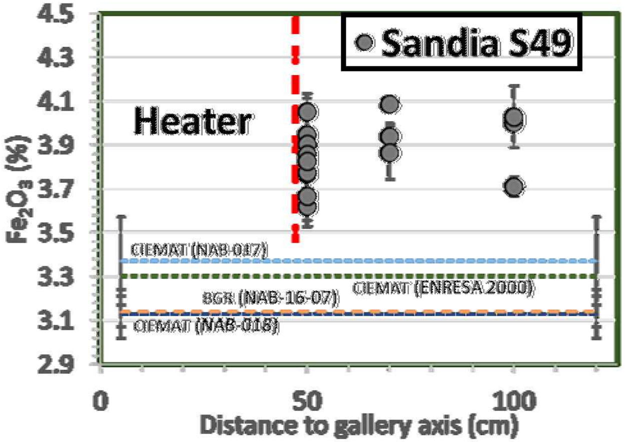
Section 49

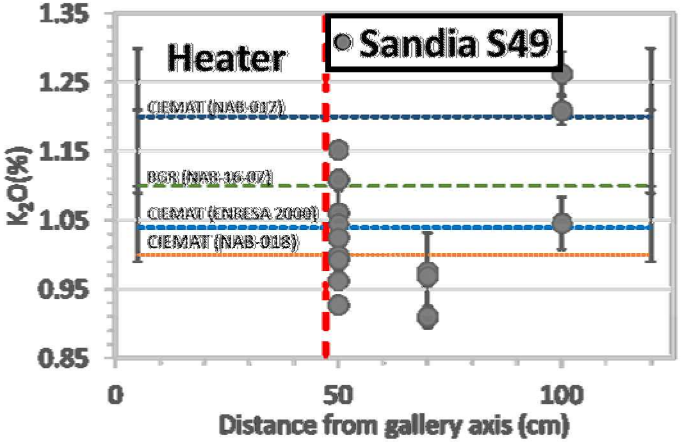
FEBEX-DP BULK BENTONITE SAMPLES: X-RAY FLUORESCENCE (XRF)



RC11
JCF7







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

RC14
JCF8

Slide 30

BC11 Same comment as previously, It owuld help to box this if it is an legend, especially since the point is the same size as the plotted ones.   Doing this by XRF should work, but I would want to run lots of standards to assess uncertainties. Suggest doing digestion and wet chemical analysis.

Bryan, Charles, 5/16/2019

JCF7 Ok. I'll consider that. Wet chamical analysis using AA is something we're considering.

Jove-colon, Carlos F, 5/16/2019

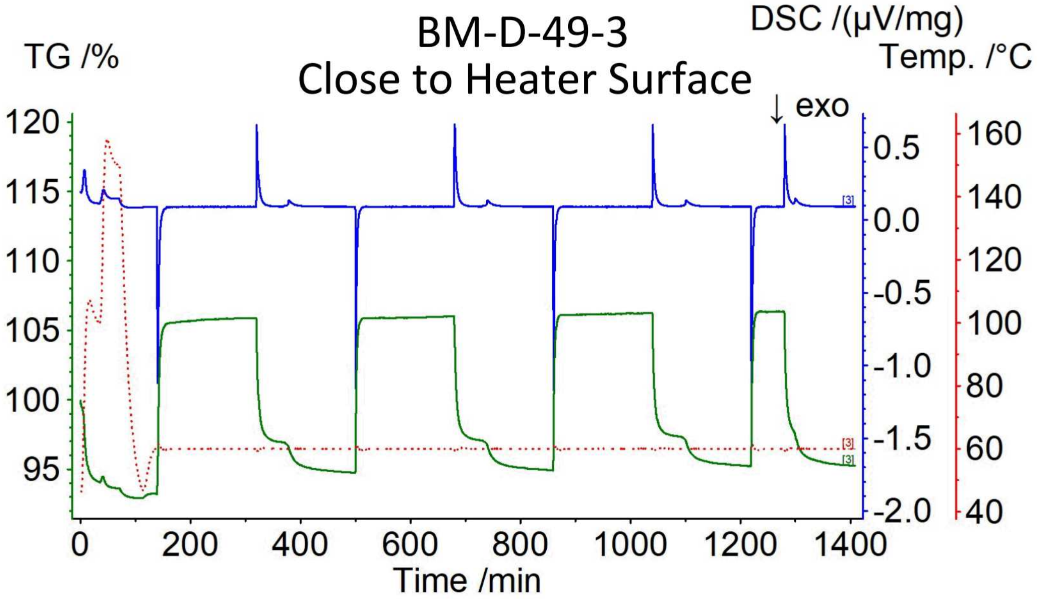
BC14 The bullet above says Fe2O3 is slightly enriched. Which is correct?

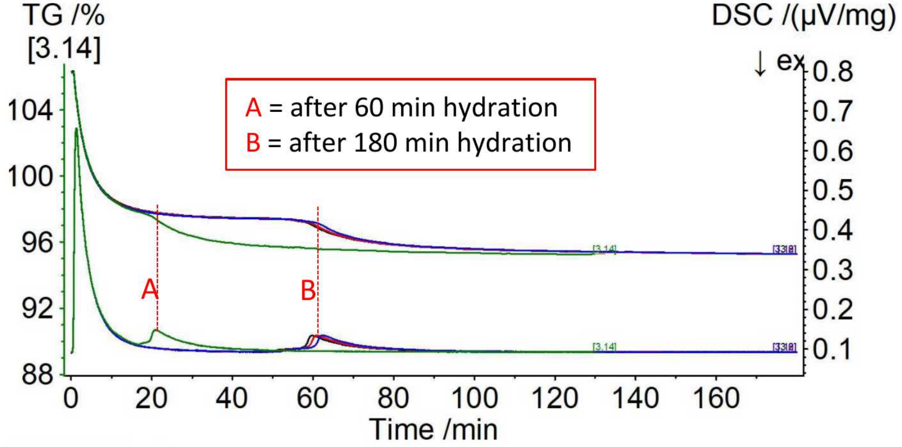
Bryan, Charles, 5/16/2019

JCF8 Fe2O3 is slightly enriched but not too much within the scatter of the data. I'll remove Fe2O3 from thst bullet.

Jove-colon, Carlos F, 5/16/2019

THERMAL ANALYSIS (TGA/DSC)


BM-D-49-3
Close to Heater Surface



Observations:

- **Water adsorption is rapid (steady state after ~ 15 min exposure).**
- **After first adsorption/desorption cycle, adsorption curves are identical.**
- **Dehydration occurs in two distinct steps:**
  1. **Major mass loss and endotherm after 1.3 min. under dry conditions.**
  2. **Minor mass loss later, depending on duration of adsorption step.**
- **Results similar for all samples examined**
- **Dependence of 2nd desorption peak on adsorption time (even though mass is ~ constant after 15 min of adsorption) suggests rearrangement of adsorbed water in the clay layers after saturation.**
- **Due to undefined mass loss occurring between loading sample into instrument and beginning of run, quantification of mass loss and energetics is only approximate.**

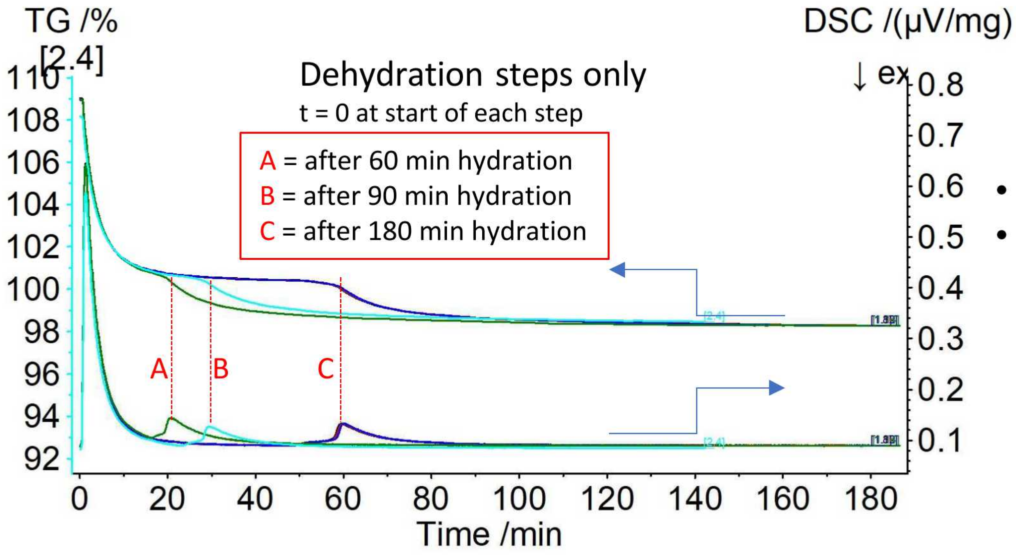
RC17
JCF11

Slide 31

BC17 This lside is a little bit hard to follow, but I worked it out. Very nice data!!
Bryan, Charles, 5/16/2019

JCF11 I'll try to decrease the text and I'll explain it in the presentation.
Jove-colon, Carlos F, 5/16/2019

THERMAL ANALYSIS (TGA/DSC)


Dehydration steps only
t = 0 at start of each step

A = after 60 min hydration
B = after 90 min hydration
C = after 180 min hydration

Observations:

- **Water adsorption is rapid (steady state after ~ 15 min exposure).**
- **After first adsorption/desorption cycle, adsorption curves are identical.**
- **Dehydration occurs in two distinct steps:**
  1. **Major mass loss and endotherm after 1.3 min. under dry conditions.**
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