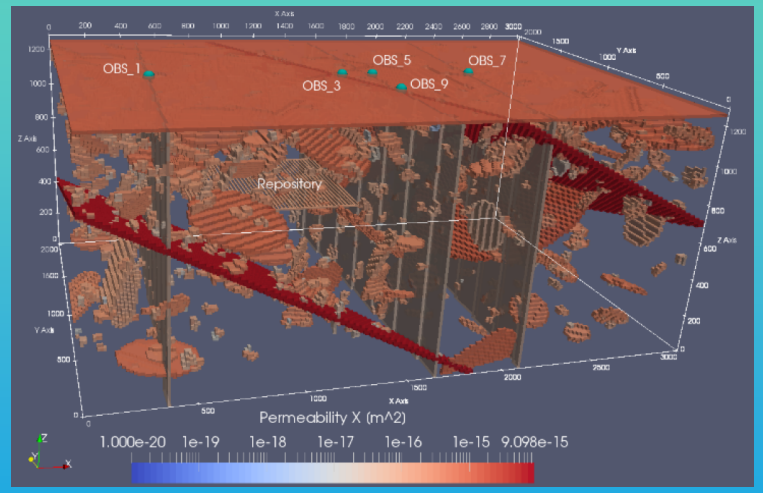
SAND2021-6008PE



Experimental/characterization studies: bentonite hydration/dehydration: TGA/DSC/*in situ* XRD

SAND ####

Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

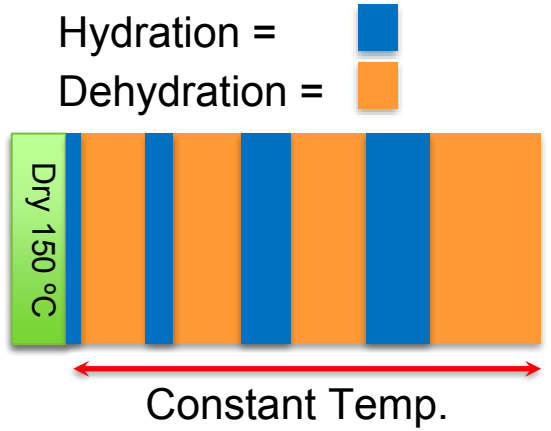
Eric N. Coker
Sandia National Laboratories
Albuquerque, NM

Outline

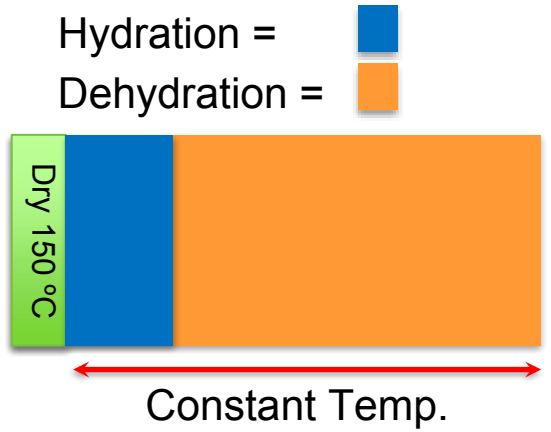
- Introduction
- Experimental details
  - Thermogravimetric Analysis – Differential Scanning Calorimetry
  - High-temperature X-Ray Diffraction
- Results
  - Bentonite hydration-dehydration cycling
- Summary
- Future work

Experimental details

- Thermogravimetric Analysis and Differential Scanning Calorimetry (TGA/DSC)
  - Netzsch STA 449 F3 Jupiter with ProUmid MHG humidity generator
  - 20 mg bentonite or Febex dehydrated *in situ* at 150 ºC under dry N_2 prior to test
  - Alternating humid – dry cycles to follow adsorption and desorption of water at 60 or 85 ºC

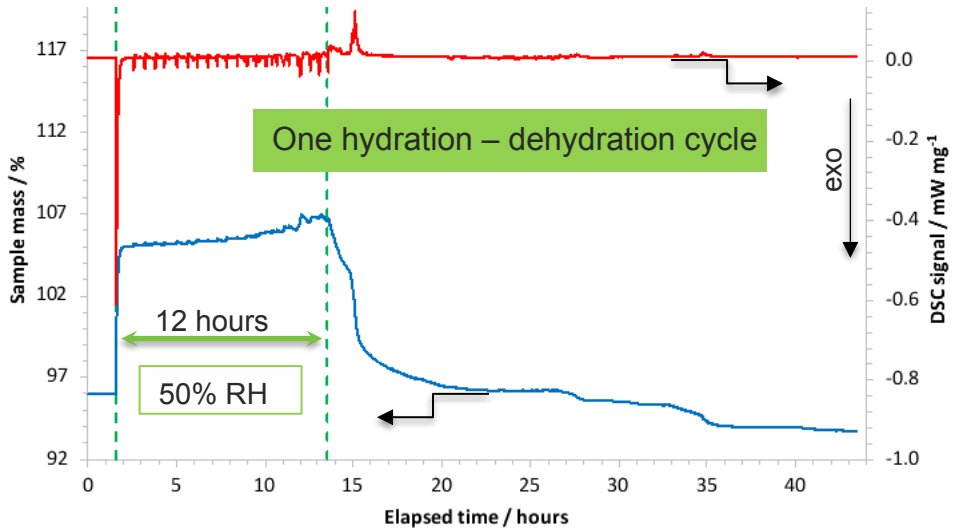


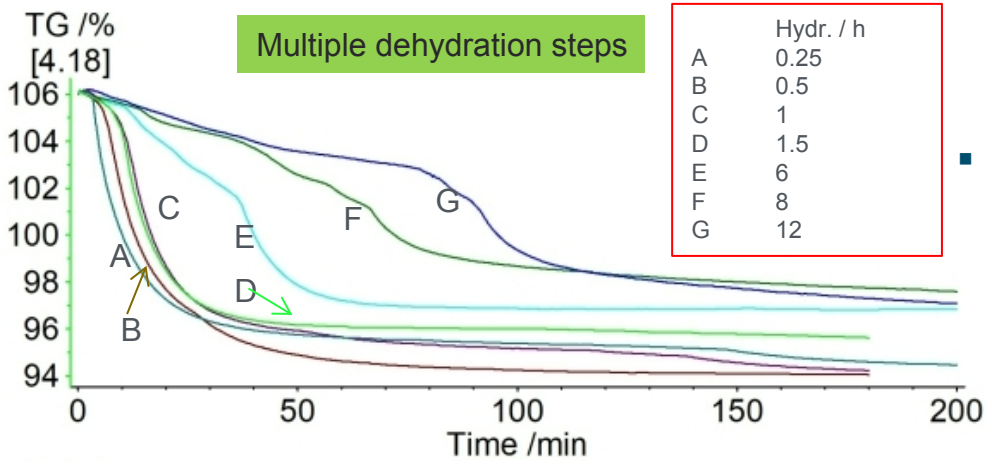
- *In situ* X-ray Diffraction
  - Scintag Pad-X diffractometer with Buehler environmental chamber
  - 30 mg bentonite powder dispersed loosely on Si wafer
  - Sample heated to 150 ºC under dry He to dehydrate *in situ*
  - Chamber flushed with humid He, then dry He to hydrate and dehydrate the sample at 60 or 85 ºC



Results: bentonite 60 ºC

Hydration/dehydration at 60 ºC, 50%RH (dewpoint 46 ºC)

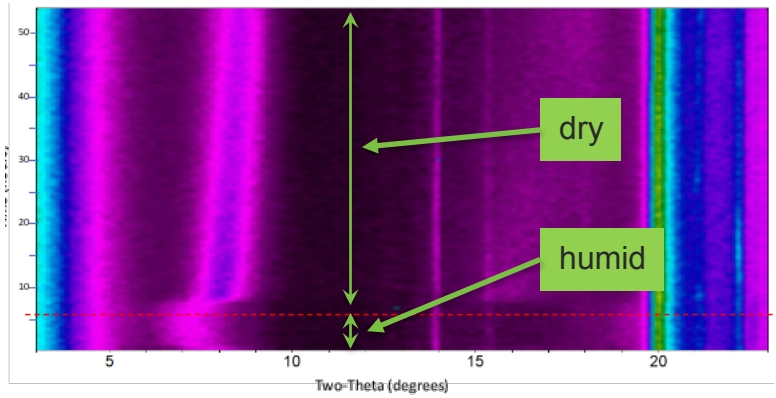


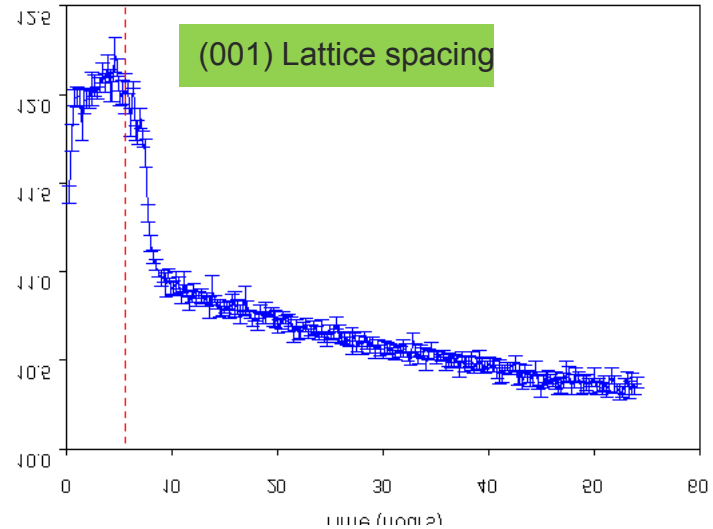


	Hydr. / h
A	0.25
B	0.5
C	1
D	1.5
E	6
F	8
G	12

- Fast initial adsorption (plateau in 20 min)
- Slower subsequent adsorption over several hours
- Various desorption steps
  - Advection; Δm ~ t, during 1st hour
  - Diffusion; Δm ~ $t^{1/2}$, from 1 to 12 hours
  - Discrete desorption steps thereafter
- Shape of mass loss curve during dehydration is dependent on duration of preceding hydration
  - After hydration for 1.5 h or less – mostly diffusion controlled
  - After hydration for 6 h or more – advection and diffusion
- In situ XRD under similar conditions
  - Lattice spacing mirrors mass loss profile
  - $[001]_{hydrated}$ ~ 12.2 Å, consistent with 1w state
  - $[001]_{dehydrated}$ ~ 10.3 Å, consistent with 0w state
  - Other diffraction peaks barely affected by changing hydration state

In situ XRD



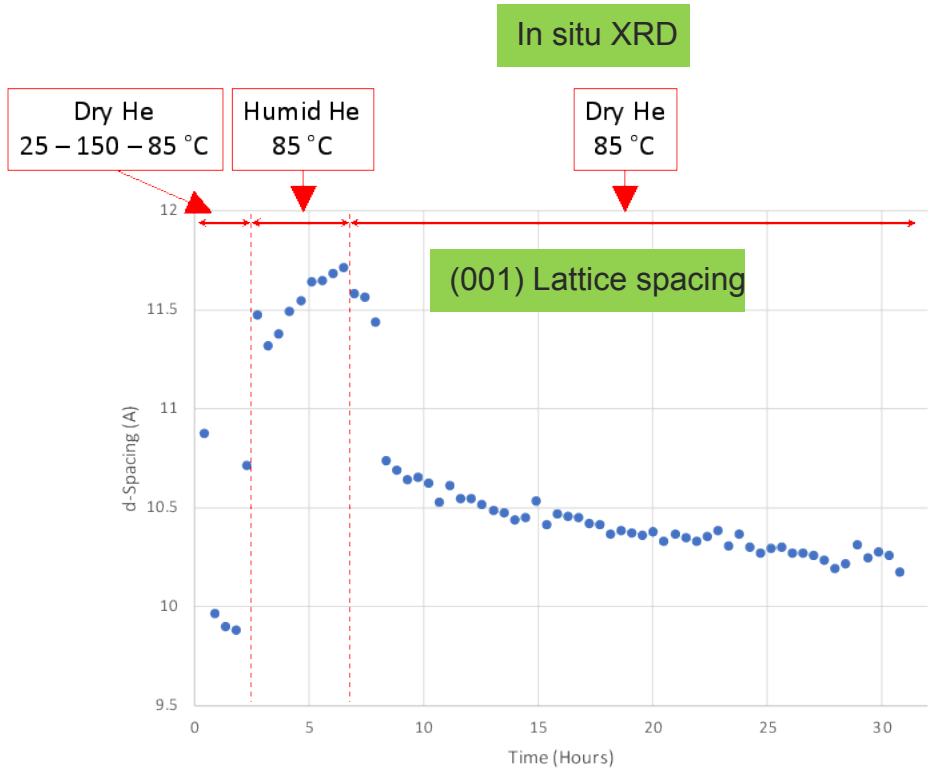


Results: bentonite 85 ºC

Hydration/dehydration at 85 ºC, 31%RH (dewpoint 58 ºC)

- Similar trends as at 60 ºC
  - Advection at short times after long adsorption
  - Diffusion after longer time, and after short hydration
- Overall dehydration rate faster

- In situ XRD under similar conditions
  - Lattice spacing mirrors mass loss profile
  - $[001]_{hydrated}$ ~ 11.7 Å, consistent with 1w state
  - $[001]_{dehydrated}$ ~ 10.3 Å, consistent with 0w state



Summary

- Water adsorption into/onto dried bentonite is initially rapid
  - plateau reached after ~ 20 min exposure
- Extended adsorption duration (hours) gives gradual increase in mass
- Dehydration observed to occur through both advection and diffusion mechanisms
- Dependence of desorption profile on preceding duration of adsorption suggests rearrangement of adsorbed water in the clay layers after saturation.
- Lattice spacing (001) during hydration/dehydration cycle shows similar trend to that seen by TGA.

Future work

- Modify humidity-delivery system to enable TGA/DSC measurements under higher RH
- Utilize in situ XRD system with fast scan ability to follow initial changes in d-spacing with more fidelity
- Determine hydration enthalpies through isothermal microcalorimetry (in-situ mixing of dry bentonite with H_2O)