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INVESTIGATING THE SORPTION CAPACITY OF CLAY MINERALS FOR APPLICATIONS IN NUCLEAR WASTE REPOSITORY DESIGN

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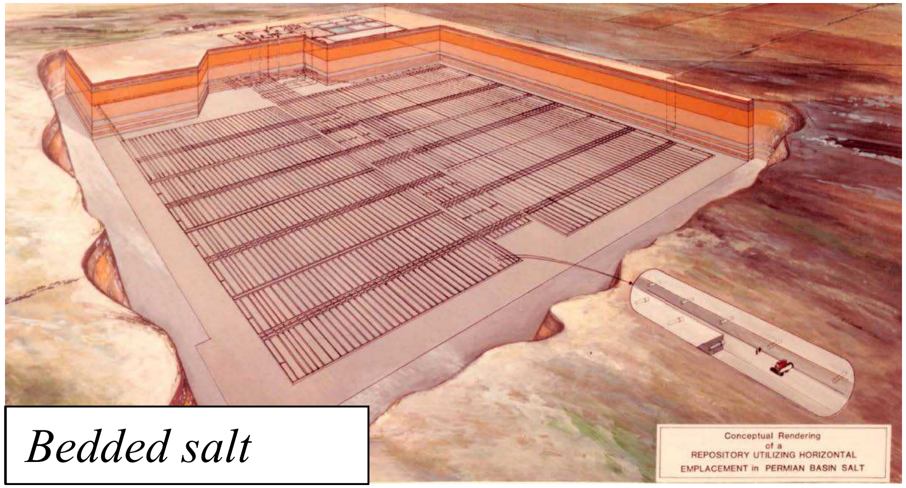
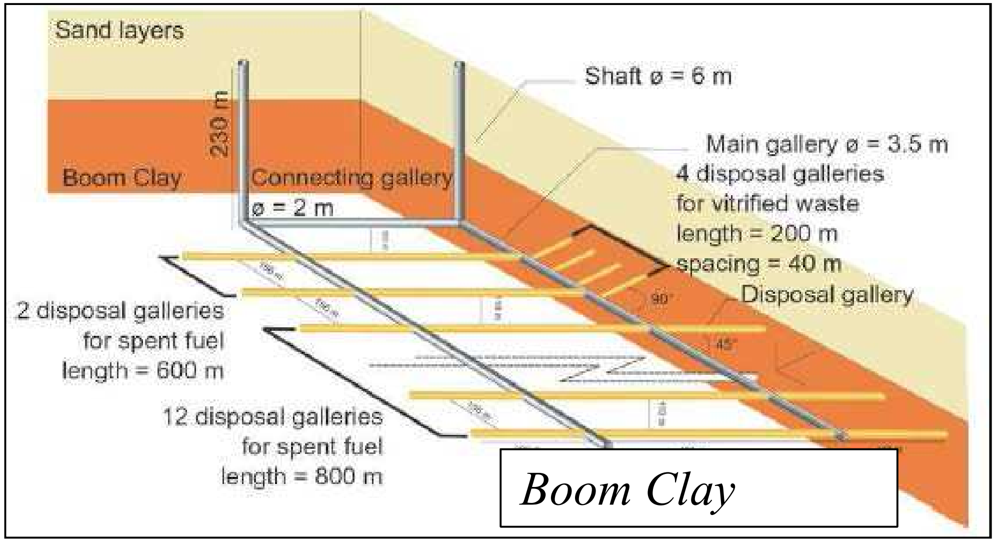
Generic Repository Designs contain clay minerals either as the host formation or in Engineered Barriers and Seals

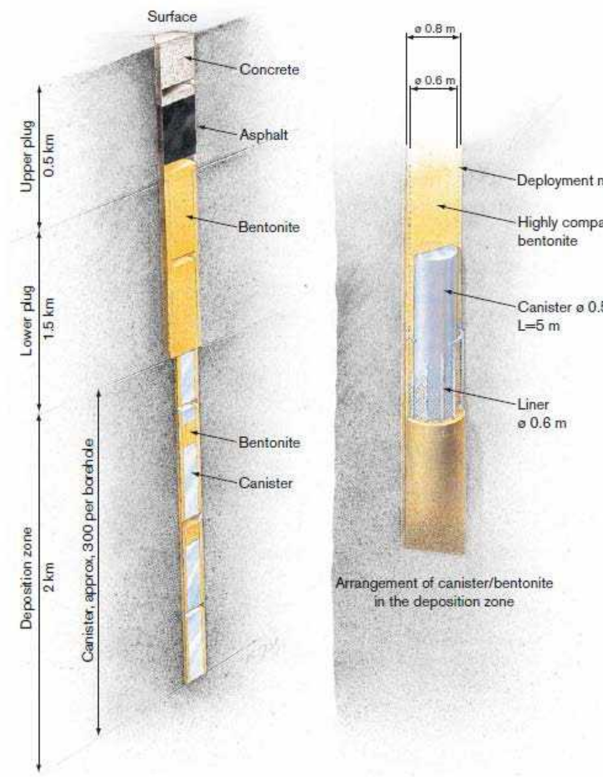


Bedded salt



Boom Clay

(image courtesy of E. Hardin)



Deep Borehole in Crystalline Basement

Overview

Clay minerals are likely candidates to aid in ***nuclear waste isolation*** due to their *low permeability*, *favorable swelling properties*, and *high cation sorption capacities*

- Understanding the *chemical* and *physical changes* that occur in clay minerals at various temperatures above the current thermal limit (of 100 °C) can enable decision-makers with information critical to evaluating the potential trade-offs of increasing the thermal limit within the repository.

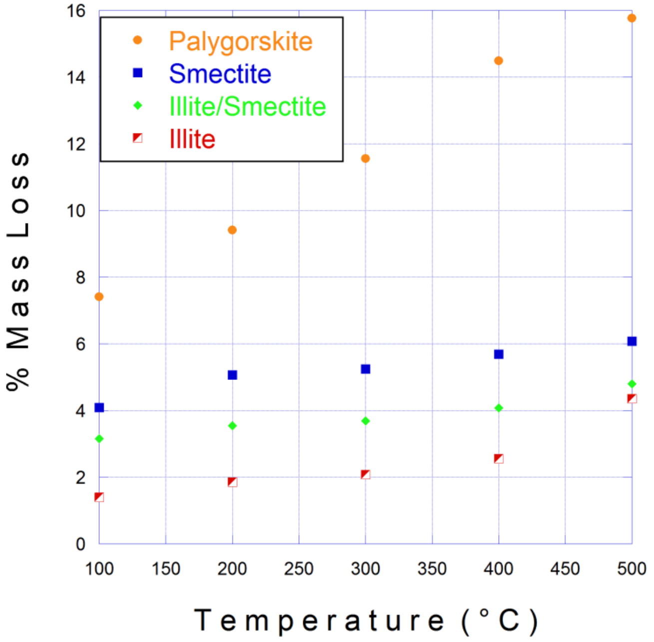
- Understanding of how varying conditions (e.g., thermal, level of compaction) in the repository will impact *radionuclide sorption* and *transport* in clay materials either as engineered barriers or as disposal media.

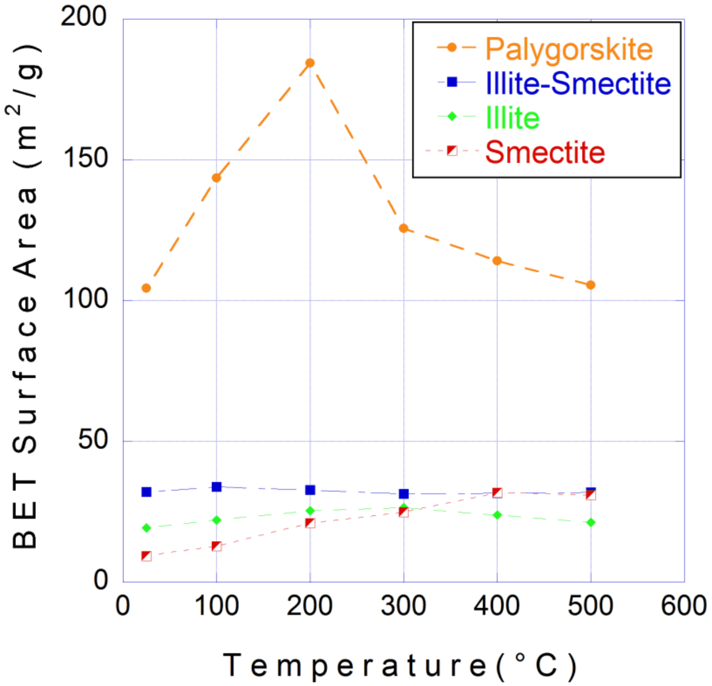
Overview

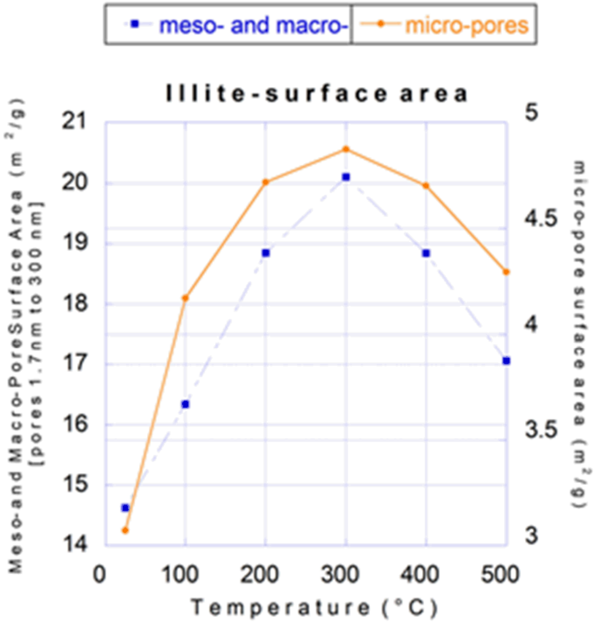
This talk is composed of 2 sections:

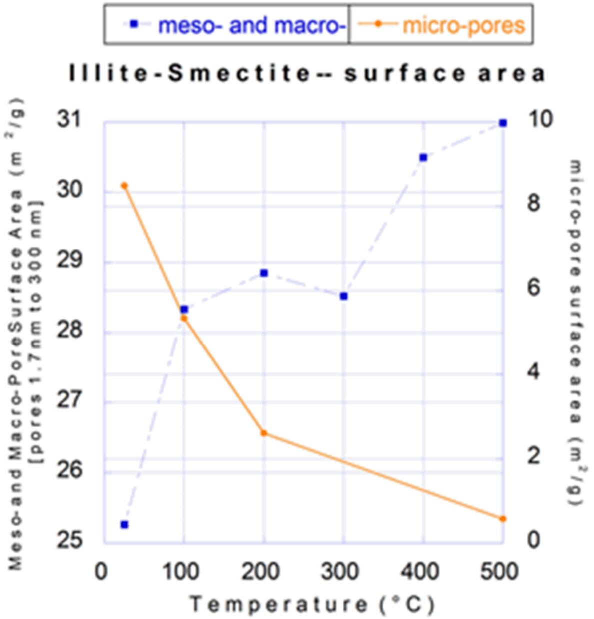
1) ***Sorption*** *(CEC) of clay minerals is altered by thermal effects*

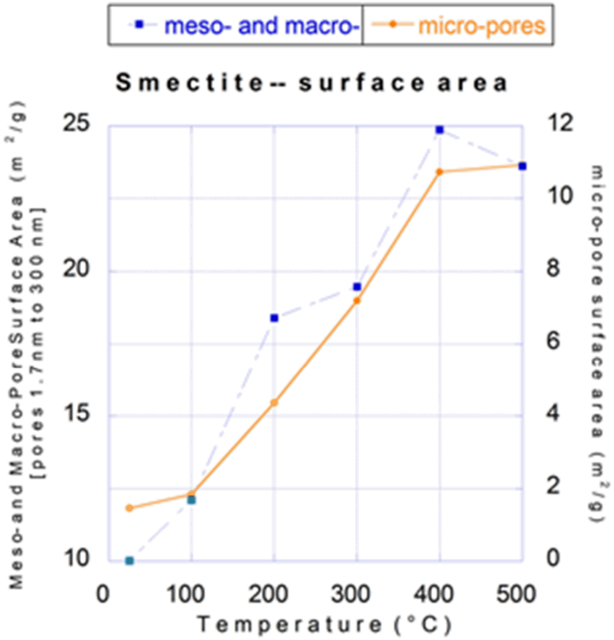
2) ***Interactions and Transport*** *of anionic species with clay minerals*

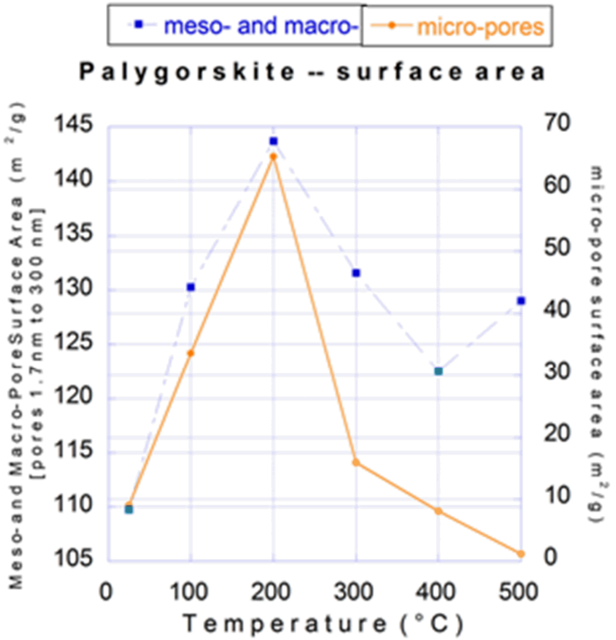

% Mass Loss
Temperature (°C)
0
2
4
6
8
10
12
14
16
100
150
200
250
300
350
400
450
500
● Palygorskite
■ Smectite
◆ Illite/Smectite
▨ Illite

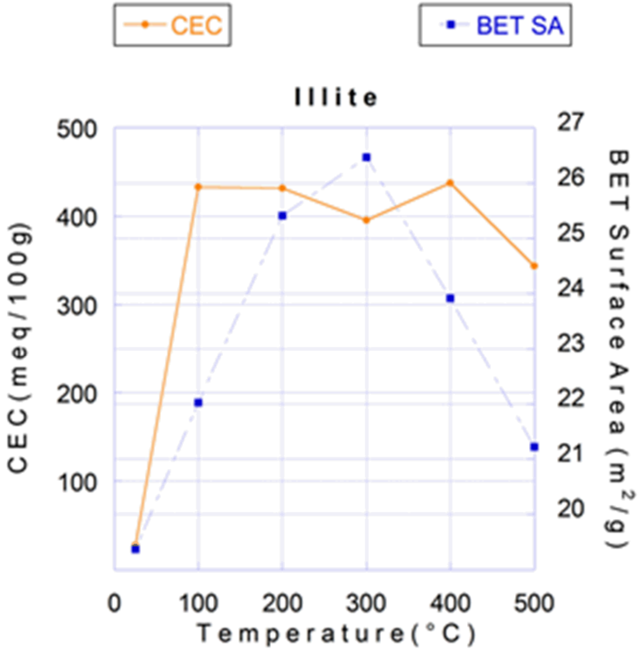

BET Surface Area (m^2/g)
Temperature(°C)
0
50
100
150
200
0
100
200
300
400
500
600
Palygorskite
Illite-Smectite
Illite
Smectite

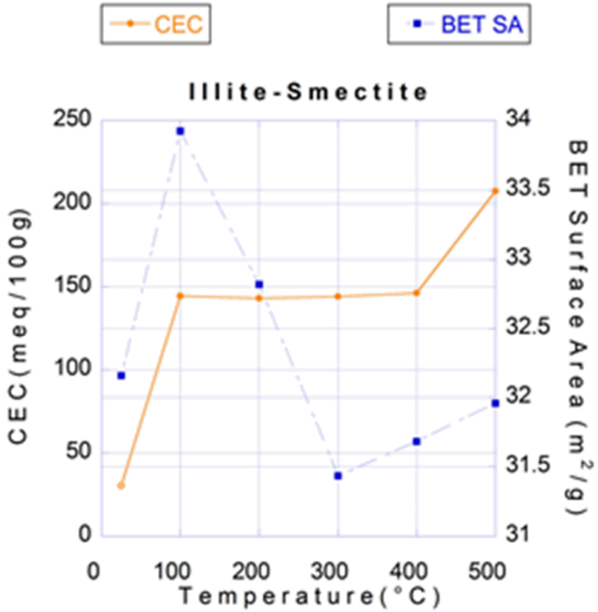

meso- and macro-
micro-pores
Illite-surface area
Meso-and Macro-PoreSurface Area (m²/g) [pores 1.7nm to 300 nm]
21
20
19
18
17
16
15
14
micro-pore surface area (m²/g)
5
4.5
4
3.5
3
0
100
200
300
400
500
Temperature (°C)

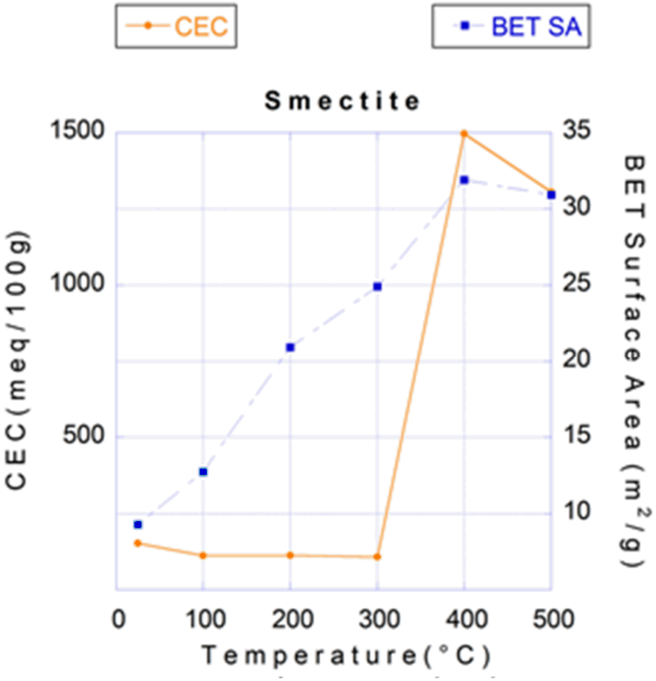

meso- and macro-
micro-pores
Illite-Smectite-- surface area
Meso-and Macro-PoreSurface Area (m²/g) [pores 1.7nm to 300 nm]
31
30
29
28
27
26
25
micro-pore surface area (m²/g)
10
8
6
4
2
0
0
100
200
300
400
500
Temperature (°C)

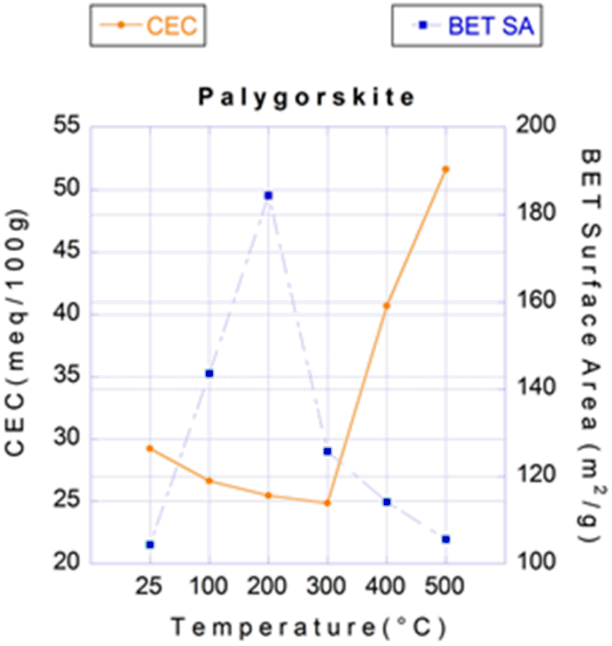

meso- and macro-
micro-pores
Smectite-- surface area
Meso-and Macro-PoreSurface Area (m²/g) [pores 1.7nm to 300 nm]
25
20
15
10
micro-pore surface area (m²/g)
12
10
8
6
4
2
0
0
100
200
300
400
500
Temperature (°C)


meso- and macro-
micro-pores
Palygorskite -- surface area
Meso-and Macro-PoreSurface Area (m²/g) [pores 1.7nm to 300 nm]
145
140
135
130
125
120
115
110
105
micro-pore surface area (m²/g)
70
60
50
40
30
20
10
0
0
100
200
300
400
500
Temperature (°C)


CEC
BET SA
Illite
CEC (meq/100g)
500
400
300
200
100
BET Surface Area (m^2/g)
27
26
25
24
23
22
21
20
0
100
200
300
400
500
Temperature (°C)


CEC
BET SA
Illite-Smectite
CEC (meq/100g)
250
200
150
100
50
0
BET Surface Area (m^2/g)
34
33.5
33
32.5
32
31.5
31
0
100
200
300
400
500
Temperature (°C)


CEC
BET SA
Smectite
CEC (meq/100g)
1500
1000
500
BET Surface Area (m^2/g)
35
30
25
20
15
10
0
100
200
300
400
500
Temperature (°C)


CEC
BET SA
Palygorskite
CEC (meq/100g)
55
50
45
40
35
30
25
20
BET Surface Area (m^2/g)
200
180
160
140
120
100
25
100
200
300
400
500
Temperature (°C)

Conclusions and Next Steps

Part 1. Thermal Treatments and CEC

- *Thermal treatments show significant effects on CEC for all four clays studied.*

- *For Illite and Illite-Smectite, an order of magnitude increase in CEC is seen even at 100 °C.* Given the ubiquity of illite in sealing formations, e.g. shale caprocks, ***this result could have an important effect on transport and fate in the far-field, or near field in the case where the repository is in a clay rich host formation.***

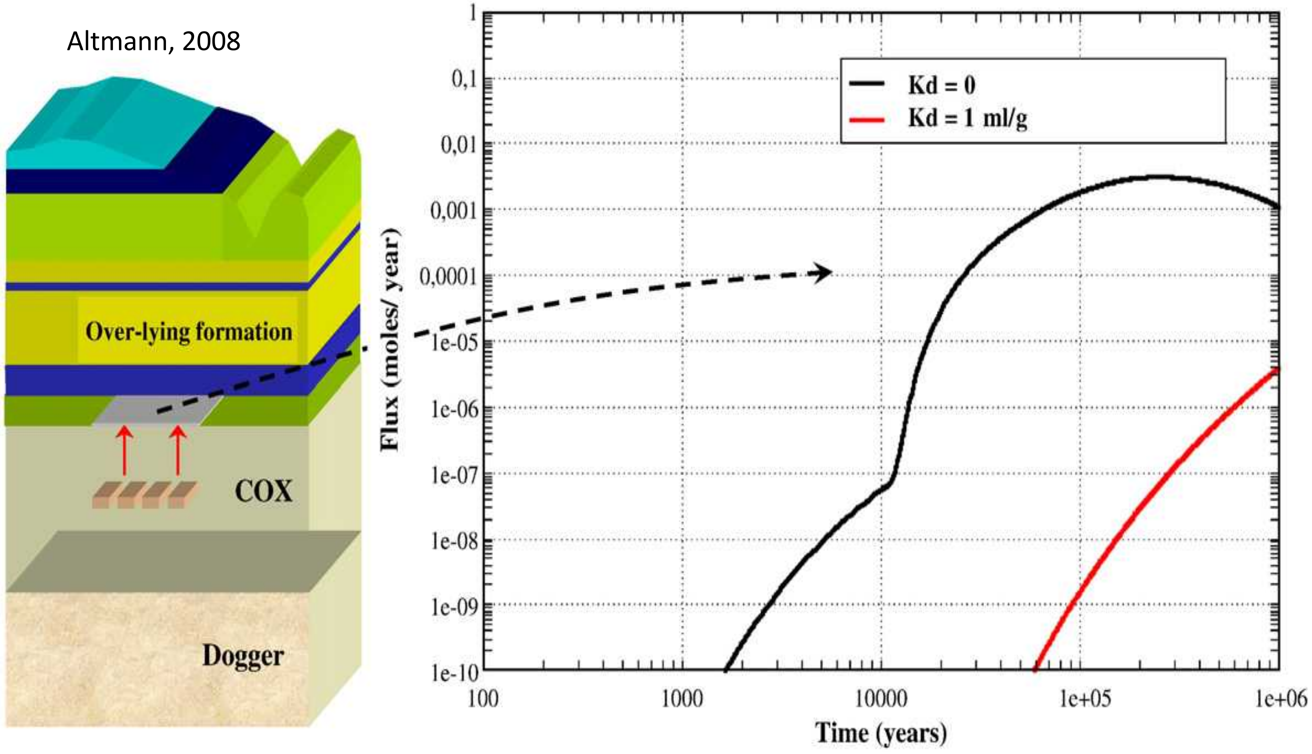
- For montmorillonite, the significant increase in CEC at 400 °C is perhaps of only of marginal importance, as this range of temperatures is likely well beyond any future allowance for the thermal limit in a repository environment.

- Taken together, all of these results warrant a case for further study. *It remains to be seen what role time duration of thermal treatment may play in alteration of the clay minerals in this study*. For example, will longer exposure at a lower temperature, say 200 °C result in a change in CEC equivalent to a shorter duration exposure at 500 °C?

- X-ray diffraction (XRD), thermogravimetric (TGA) analysis, and differential scanning calorimetry (DSC) can be used to gain insight into the mechanisms and alterations that have resulted in changes in the CEC. Heated samples will be analyzed by XRD to ascertain if d_{001}-spacings are changed during heat treatments. TGA will be used to identify mass loss for longer durations of heat treatments, while DSC will be used to identify mineralogical phases that development during eat treatment.

- In addition to investigating the effect of duration for temperatures closer to reasonable thermal limits, i.e., 200-300°C, experimental understanding of how compacted clay respond to thermal treatment is a potential topic for future research.

Part 2. Iodide interactions with negatively charged interlayers? Q: Who cares? A: PA.

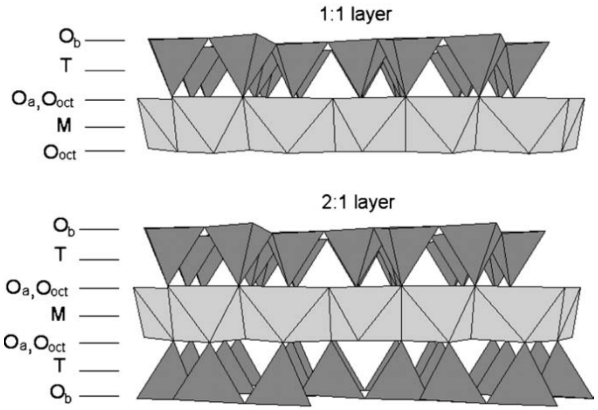


Altmann, 2008

Clay Mineral	Column K_D Value (mL/g)	Batch K_D Value (mL/g)	Ref.
Opalinus (Illite)	0.008-0.02		Van Loon et al., 2003
Montmorillonite	0.57		Sato et al., 1992
Callovo-Oxfordian (Interstratified illite/smectite)		0.15-0.37	Bazer-Bachi et al., 2006
Illite		27.7	Kaplan et al., 2000
Montmorillonite		-0.33	Kaplan et al., 2000

Physical/chemical relationships that may lead to disparate iodide sorption behavior

Clay mineralogy

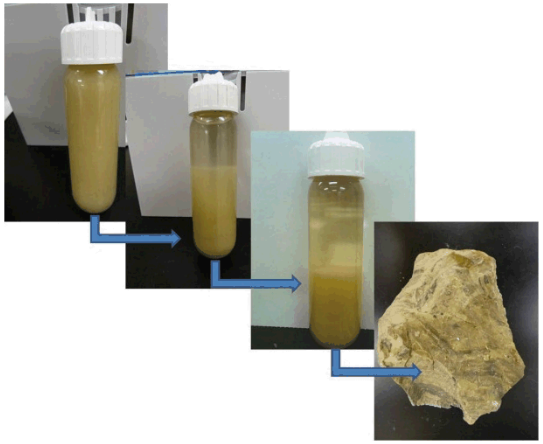


Handbook of Clay Science, Eds.: Bergaya, F., Theng, B.K.G., Lagaly, G.; Elsevier, 2006.

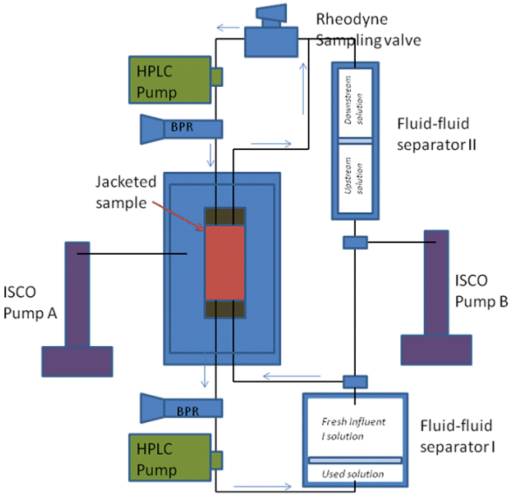
Potential reasons for anion interactions

1. They aren’t
2. Iodine redox reactions
3. Clays are not pure
4. Nano-environments

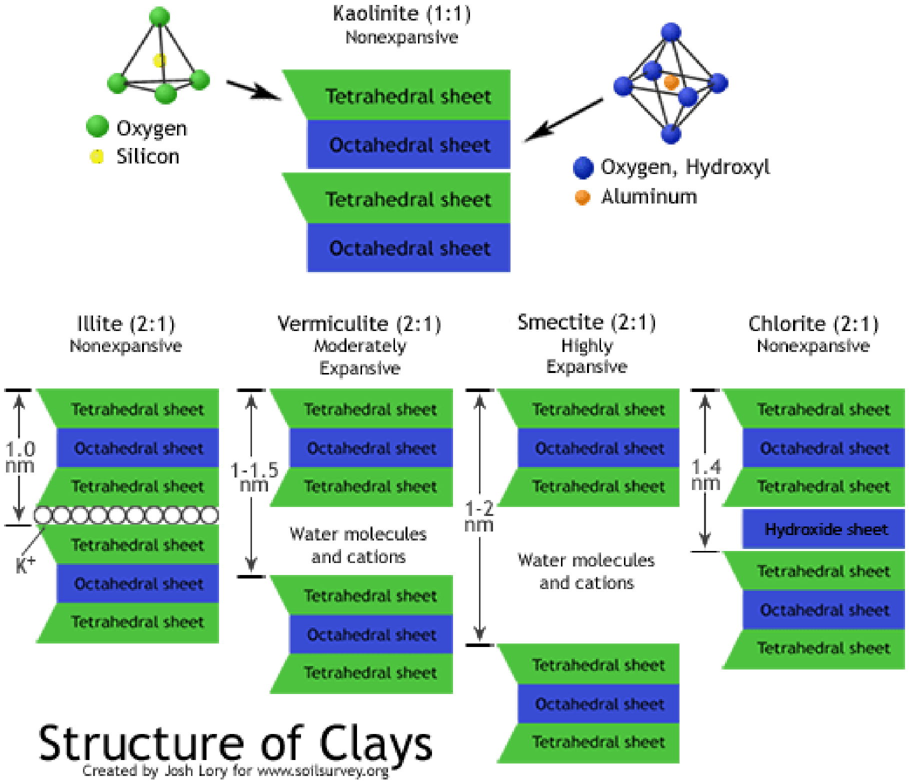
Experimental conditions/results



Future Work



Clays are (Mg, Al)-silicates with sheets, layers, edges and interlayers. Layered and fibrous clays are used here.



Structure of Clays
Created by Josh Lory for www.soilsurvey.org

http://soils.missouri.edu/tutorial/page8.asp

http://backreaction.blogspot.com/2008/03/cookies-palygorskite-and-maya-blue.html

Clays have a fixed negative charge, how can an anion (iodide) interact with a clay particle?

1. **They aren't.**
   - Impure radiotracers
   - Isotopic exchange with natural iodine
   - Uptake into carbonate minerals
   - K_D value too small to accurately measure

2. **Iodine redox reactions**
   - Iodide/iodate/iodine all possible
   - Iodate generally more surface reactive
   - Redox transformations are enhanced by COx clay
   - Clay oxic state is important

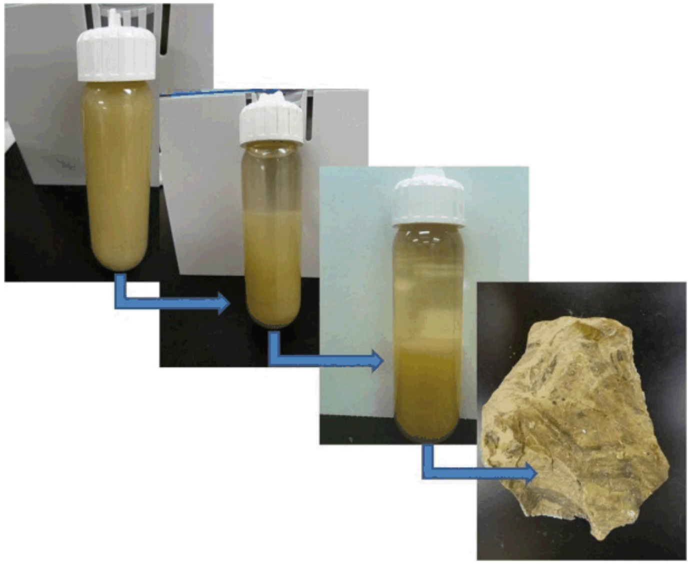
3. **Clays are not pure**
   - Organic matter
   - Reduced iron in clay structure
   - Presence of other reduced minerals (e.g., pyrite)

4. **Nano-environments**
   - Heterogeneous charge environments
   - Forced overlap in compacted systems

Several types of batch sorption experiments were completed to characterize the clay surface environment

7 clays under consideration: All clays obtained from the clay bank repository (Purdue Univ.)

- Kaolinite
- Ripidolite
- Illite
- Illite/Smectite
- Montmorillonite
- Palygorskite
- Sepiolite



Sorption experiments:

- **N_2 BET**
- **Methylene Blue (MB)**
  - Na-exchanged clays
  - Variable amounts of MB were added until clay surface was saturated
- **$BaCl_2$ Exchange**
  - Excess of barium displaces native cations
  - Measure native cation release
- **Iodide**
  - Solid:Liquid ratio: 100g/L
  - No specific pH control; 'natural' pH of clay
  - Seven day reaction time

Concentration (M)	NaCl	NaBr	KCl
1.0	X		
0.1	X	X	X
0.01	X		

Surface area was separated between total, interior, and exterior surface areas.

	MB CEC (meq/100 g)	$BaCl_2$ CEC (meq/100 g)	BET S.A. (m^2/g)	MB S.A. (m^2/g)	Internal S.A. (m^2/g)
Kaolinite	1.50	4.61	11.31	11.76	0.45
Ripidolite	3.00	6.03	8.02	23.49	15.47
Illite	14.98	27.61	31.46	117.21	85.76
Illite.Smectite	24.69	30.39	29.82	193.23	163.41
Montmorillonite	109.53	151.92	28.29	857.17	828.88
Sepiolite	17.41	8.98	201.43	136.27	-65.16
Palygorskite	39.96	29.22	141.52	625.45	483.93

Iodide uptake is dependent on ionic composition of swamping electrolyte.

		CEC meq/100g	K_D [mL/g] (Std. Dev.)		
			NaCl	NaBr	KCl
Layered	**Kaolinite**	4.61	1.61 (0.28)	0.02 (0.63)	-0.01 (0.22)
	Ripidolite	6.03	1.13 (0.38)	-0.16 (0.72)	-0.31 (0.17)
	Illite	27.61	0.54 (0.12)	0.13 (0.002)	-0.50 (0.24)
	Illite.Smectite	30.39	0.38 (0.08)	-0.01 (0.11)	-0.49 (0.11)
	Montmorillonite	151.92	-0.32 (0.35)	-0.58 (0.07)	-1.69 (0.90)
Fibrous	**Sepiolite**	8.98	0.01 (0.28)	0.79 (0.14)	0.11 (0.30)
	Palygorskite	29.22	0.24 (0.30)	1.26 (0.05)	0.99 (0.17)

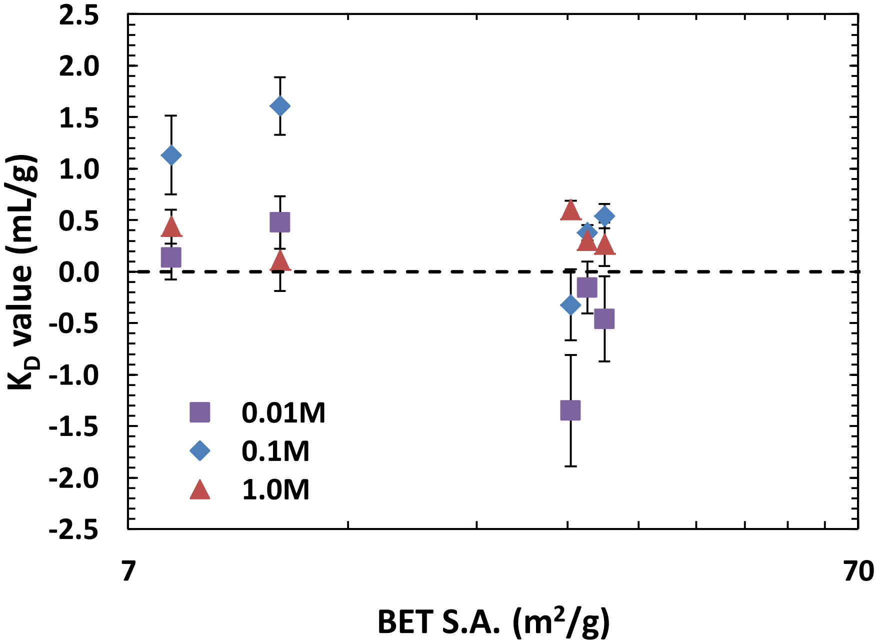
All electrolytes at 0.1M

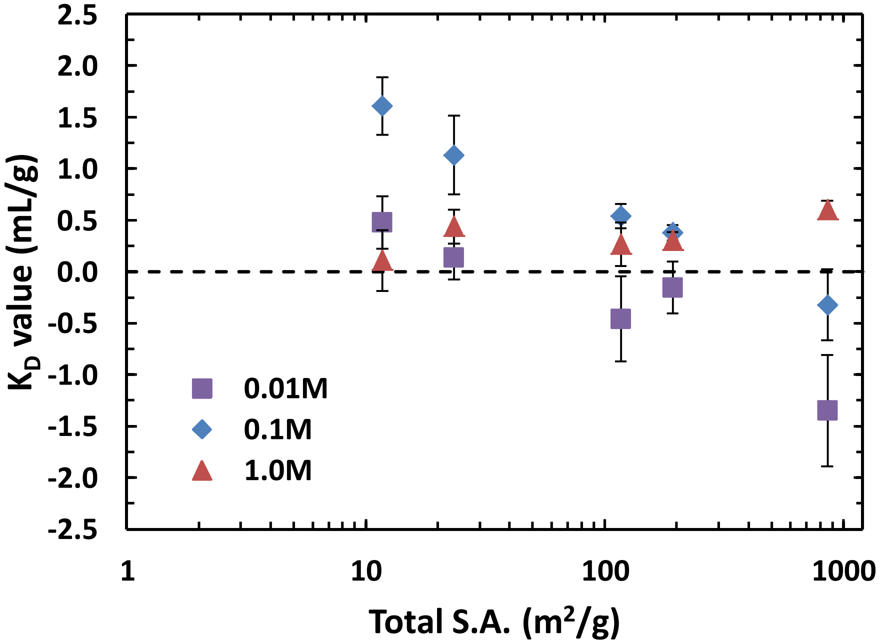
Iodide uptake is dependent on ionic composition of swamping electrolyte.

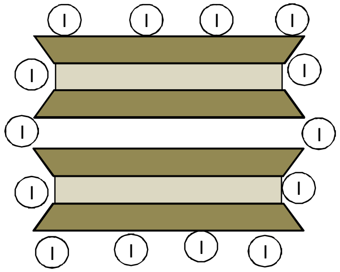
		CEC meq/100g	K_D [mL/g] (Std. Dev.)		
			$CaCl_2$	$CaBr_2$	$MgCl_2$
Layered	**Kaolinite**	4.61	0.34 (0.35)	-0.34 (0.28)	0.09 (0.43)
	Ripidolite	6.03	0.16 (0.33)	-0.05 (0.01)	0.22 (0.66)
	Illite	27.61	1.02 (0.22)	-0.48 (0.32)	0.37 (0.01)
	Illite.Smectite	30.39	0.87 (0.16)	-0.30 (0.09)	0.90 (0.34)
	Montmorillonite	151.92	0.56 (0.18)	-2.16 (0.53)	-1.70 (0.47)
Fibrous	**Sepiolite**	8.98	-0.43 (0.12)	0.52 (0.25)	-0.35 (0.37)
	Palygorskite	29.22	0.41 (0.78)	0.80 (0.41)	0.48 (0.10)

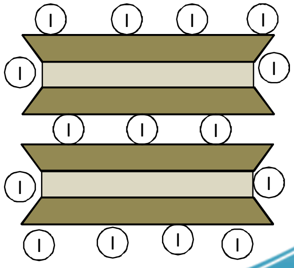
All electrolytes at 0.05M

K_D values trend with total surface area, suggesting interactions with negatively charged surfaces.

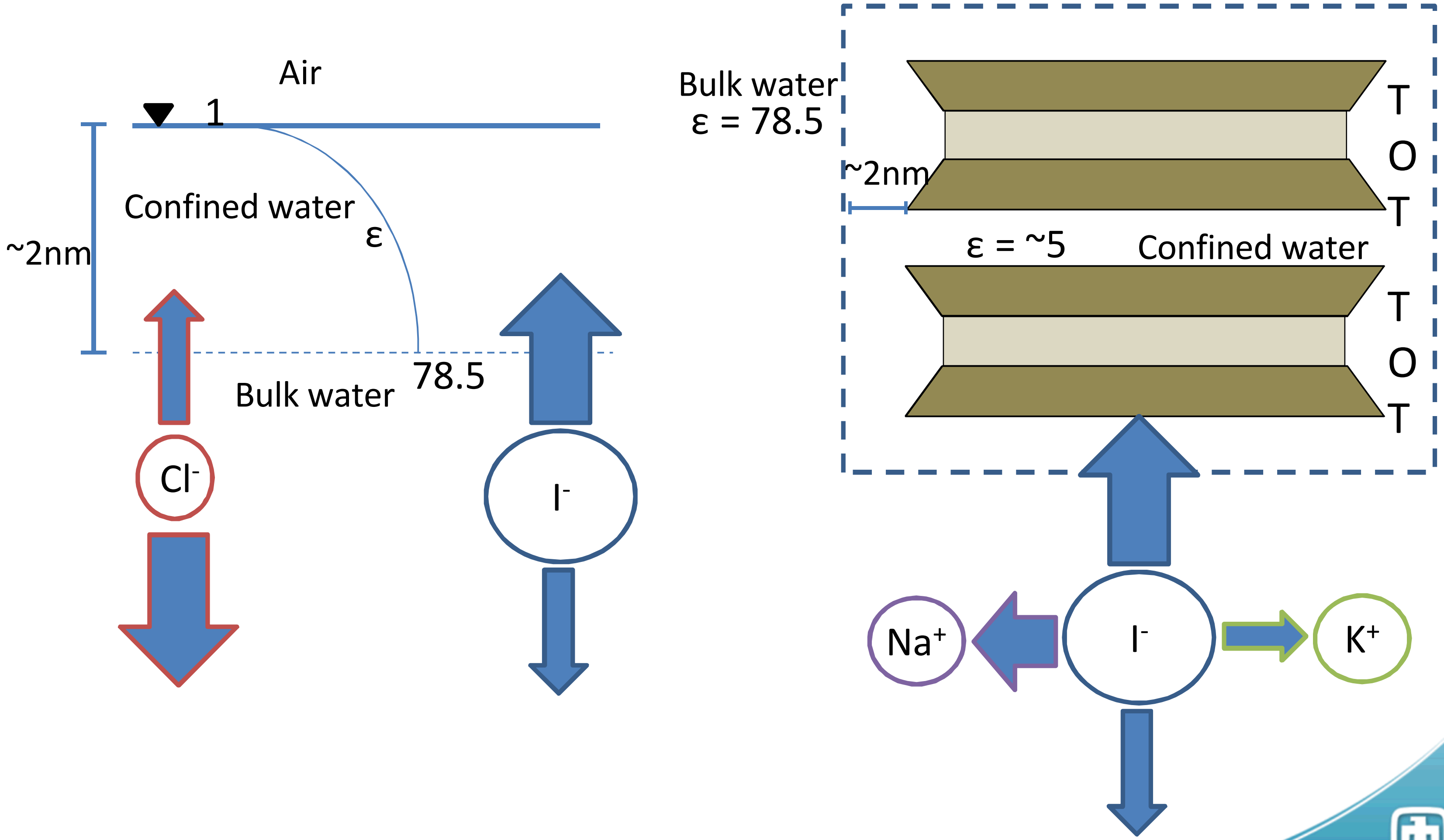




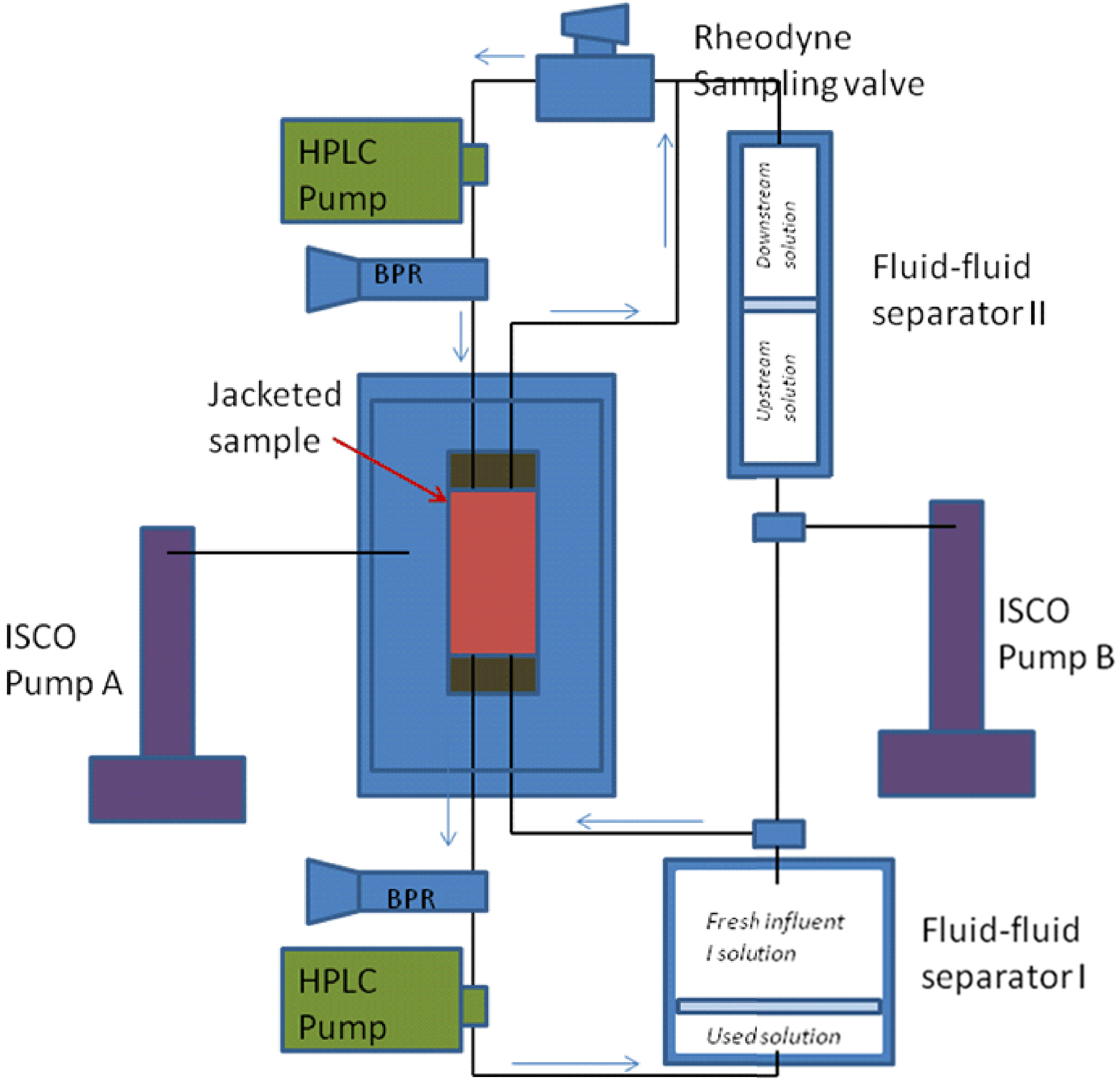




Data is consistent with ion pair formation caused by surface induced changes to water structure.



Diffusion studies will be completed in a constant pressure system.



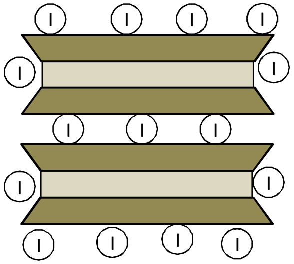
Schematic courtesy of Tom Dewers

Conclusions and Next Steps

Part 2. Anionic Interactions with Clay Minerals

In summary, iodide interactions are heavily influenced by CEC, ionic strength and ionic identity.

- The data suggests unexpected iodide uptake trends with CEC.
- Iodide uptake is dependent on clay textures and structures.
- Thermodynamic interpretation of iodide uptake as a function of ionic composition.
  - Needs to consider: pore size/dimensions, dielectric shifts, ion polarizability, ion pair formation constant
- Diffusion experiments with varied clay minerals, compactions and ionic strengths/compositions.



The Big Picture:

- ‘Inert’ anionic tracers may not be the best choice in clay dominated systems.
- Broader instead of deeper ‘sorption’ studies can give information about ion behavior and its relationship to mineral structure.

Back-Up Slides

	0.1M Electrolyte								
	NaCl			NaBr			KCl		
	Before spike	Before Centrifuging	After Centrifuging	Before spike	Before Centrifuging	After Centrifuging	Before spike	Before Centrifuging	After Centrifuging
Kaolinite	4.23	4.21	4.39	4.43	4.47	4.28	4.18	4.12	4.07
Ripidolite	8.73	8.51	8.10	8.76	8.63	8.20	8.79	8.59	7.81
Illite	8.45	8.27	8.16	8.48	8.31	7.95	8.28	8.08	8.01
Illite/Smectite	4.00	4.06	4.24	4.22	4.26	4.03	3.91	3.85	3.82
Montmorillonite	8.15	8.05	8.05	8.19	8.14	8.05	8.09	8.03	7.90
Sepiolite	7.89	7.66	7.83	7.98	7.63	7.75	7.92	7.64	7.80
Palygorskite	7.98	7.76	7.90	8.05	7.84	7.82	7.84	7.63	7.87

	NaCl Electrolyte								
	0.01M			0.1M			1.0M		
	Before spike	Before Centrifuging	After Centrifuging	Before spike	Before Centrifuging	After Centrifuging	Before spike	Before Centrifuging	After Centrifuging
Kaolinite	4.70	4.83	4.73	4.23	4.21	4.39	4.04	4.27	4.19
Ripidolite	8.79	8.57	8.15	8.73	8.51	8.10	8.74	8.59	8.37
Illite	8.68	8.46	8.30	8.45	8.27	8.16	8.37	8.22	7.87
Illite/Smectite	4.38	4.57	4.40	4.00	4.06	4.24	3.57	3.65	3.74
Montmorillonite	8.65	8.55	8.50	8.15	8.05	8.05	7.78	7.77	7.73
Sepiolite	7.92	7.64	7.83	7.89	7.66	7.83	7.78	7.50	7.71
Palygorskite	8.17	7.93	7.99	7.98	7.76	7.90	7.83	7.75	7.75

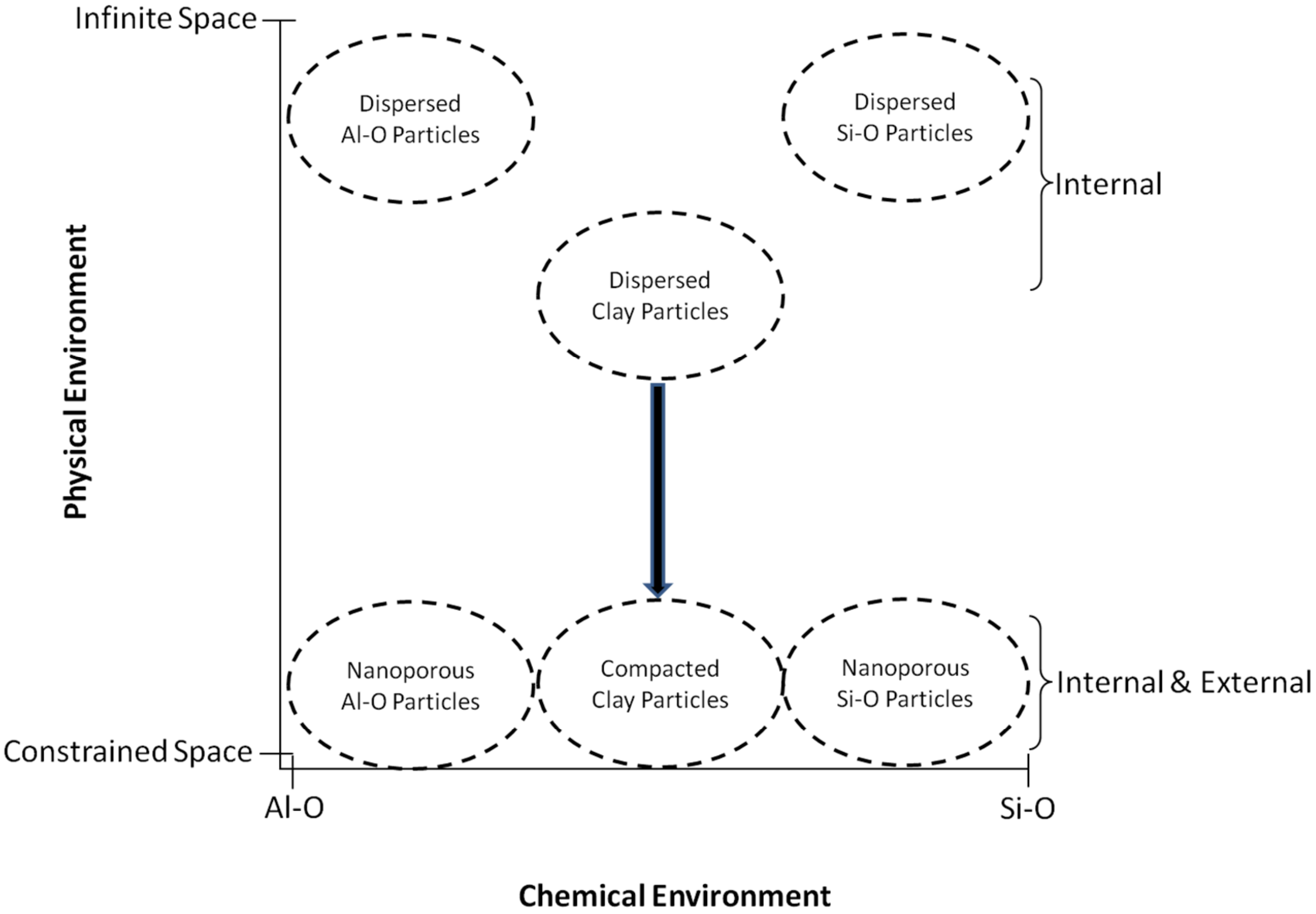
Iodide uptake depends on swamping electrolyte concentration.

		CEC meq/100g	K_D [mL/g] (Std. Dev.)		
			0.01M NaCl	0.1M NaCl	1.0M NaCl
Layered	**Kaolinite**	4.61	0.48 (0.26)	1.61 (0.28)	0.11 (0.29)
	Ripidolite	6.03	0.14 (0.21)	1.13 (0.38)	0.44 (0.17)
	Illite	27.61	-0.46 (0.41)	0.54 (0.12)	0.27 (0.21)
	Illite.Smectite	30.39	-0.16 (0.25)	0.38 (0.08)	0.30 (0.08)
	Montmorillonite	151.92	-1.35 (0.54)	-0.32 (0.35)	0.60 (0.09)
Fibrous	**Sepiolite**	8.98	1.38 (4.03)	0.01 (0.28)	-0.01 (0.30)
	Palygorskite	29.22	-0.23 (0.54)	0.24 (0.30)	0.70 (0.26)

Iodide uptake depends on swamping electrolyte concentration.

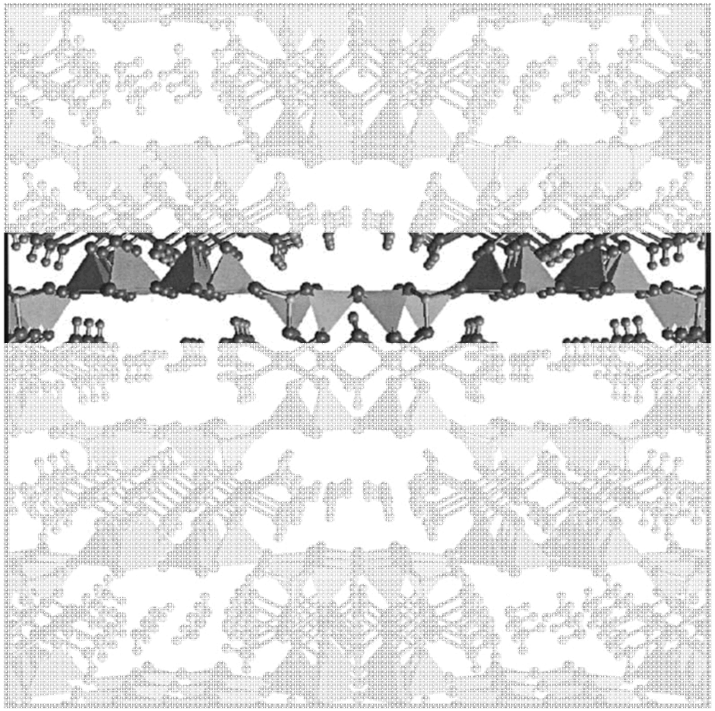
			K_D [mL/g] (Std. Dev.)		
		CEC meq/100g	0.005M $CaCl_2$	0.05M $CaCl_2$	0.1M $CaCl_2$
Layered	**Kaolinite**	4.61	0.08 (0.28)	0.34 (0.35)	0.14 (0.23)
	Ripidolite	6.03	0.54 (0.10)	0.16 (0.33)	0.34 (0.21)
	Illite	27.61	0.21 (0.32)	1.02 (0.22)	0.22 (0.35)
	Illite.Smectite	30.39	0.40 (0.07)	0.87 (0.16)	0.43 (0.02)
	Montmorillonite	151.92	-0.92 (0.26)	0.56 (0.18)	-0.13 (0.31)
Fibrous	**Sepiolite**	8.98		-0.43 (0.78)	-0.04 (0.26)
	Palygorskite	29.22	0.28 (0.07)	0.41 (0.12)	0.18 (0.03)

Clay particle proximity has the potential to change observed reactivity



Miller, A.W., Wang, Y. (2012). *Environ.Sci. Technol.* **DOI:** 10.1021/es203025q.

Fibrous clays have columnar voids for water inclusion



Fois et al., 2003. **Microporous and Mesoporous Materials**. 57, 263-272.

http://backreaction.blogspot.com/2008/03/cookies-palygorskite-and-maya-blue.html