SAND2015-1996C

Understanding Radionuclide Interactions with Layered Materials: The Effect of Nanopore Confinement

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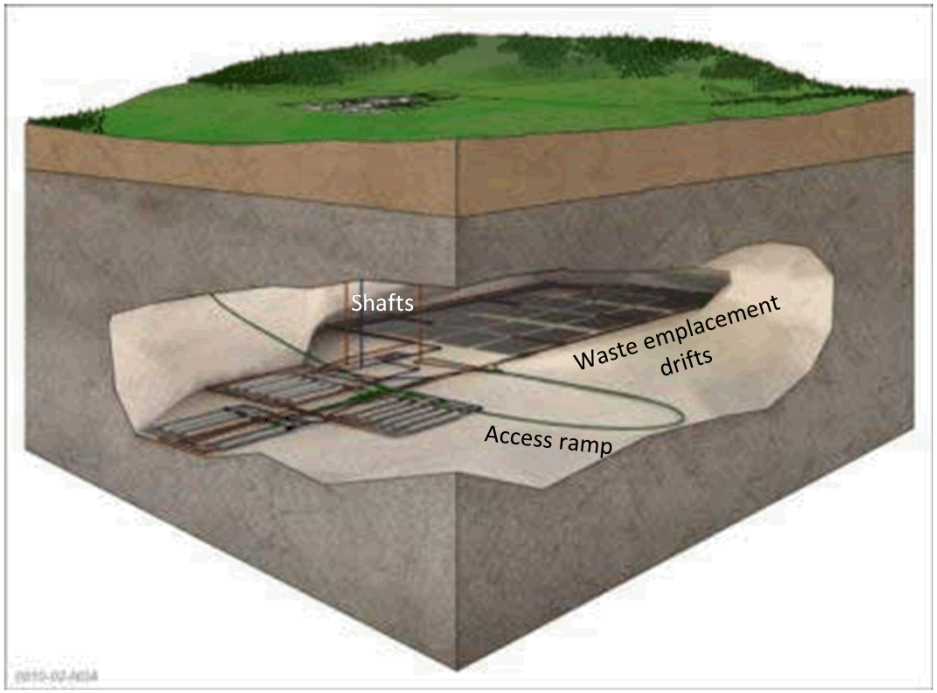
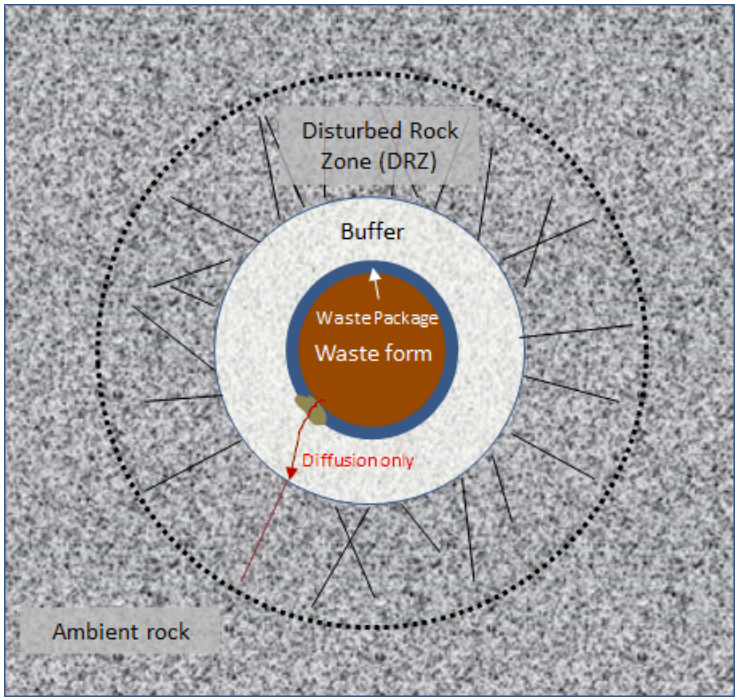
Deep Geologic Nuclear Waste Disposal





http://www.bbc.com/news/uk-england-cumbria-21253673

Key radionuclides:
Pu-239, Th-230, Am-241 – Strong interaction (colloids)
U-238, Np-237 – Moderate interaction
I-129, Tc-99 – Weak interaction (anions)

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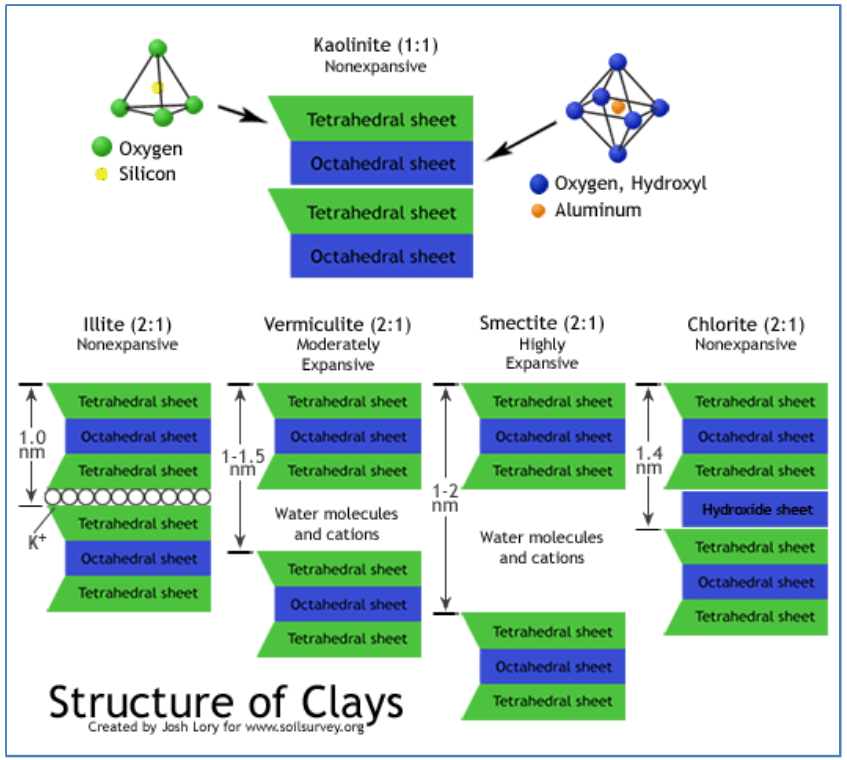
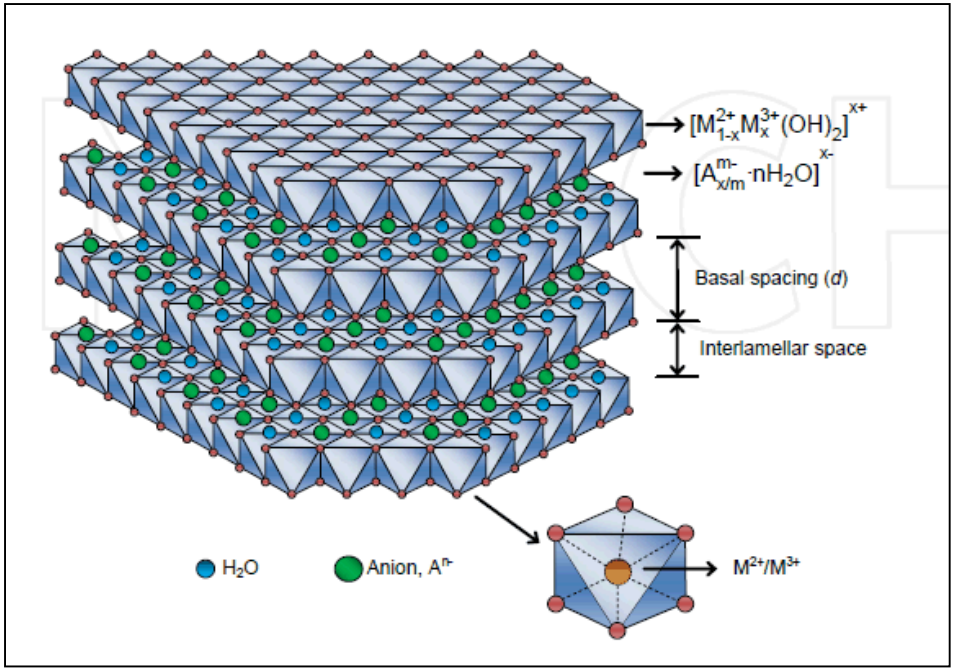
Layered Materials Used in Nuclear Waste Disposal



Clays (cationic clays)



Tronto et al. (2013)

Layered double hydroxide (anionic clays)

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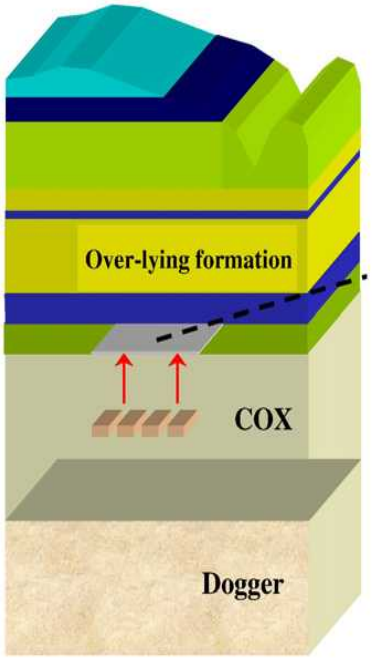
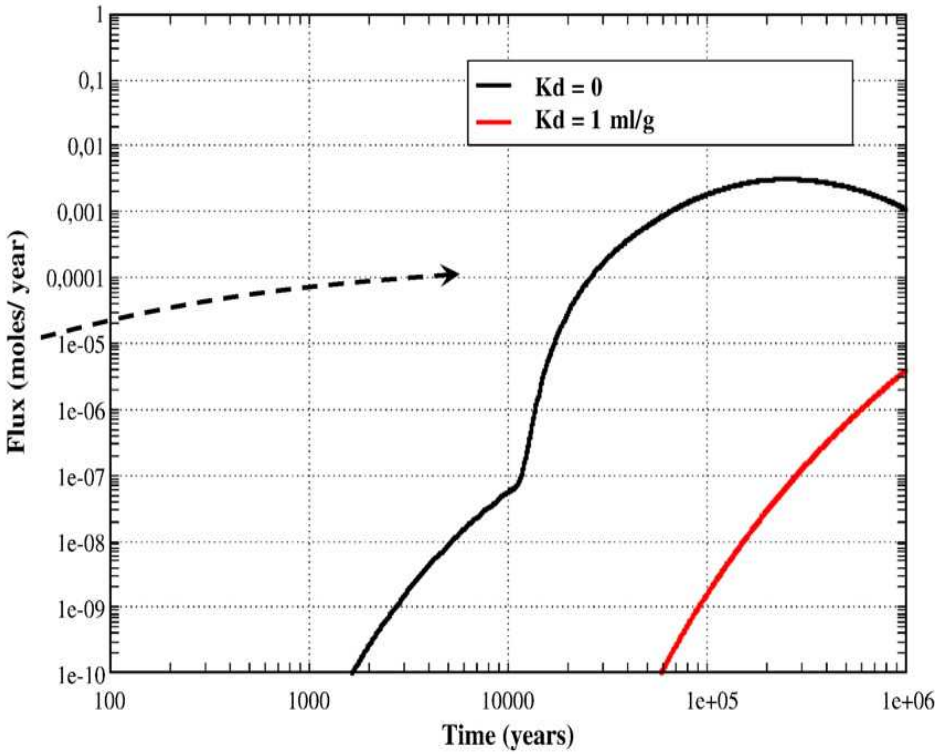
Iodide Interaction with Clays

Altmann, 2008





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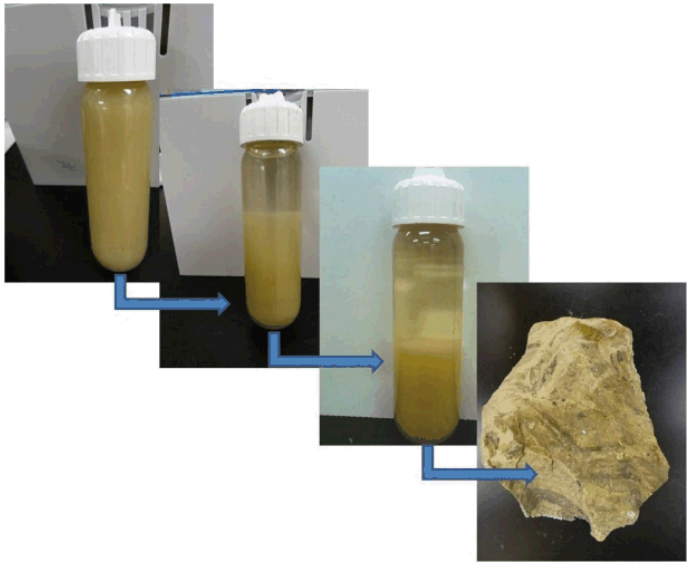
Retention of Iodide by Clays

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

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		

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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

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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

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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

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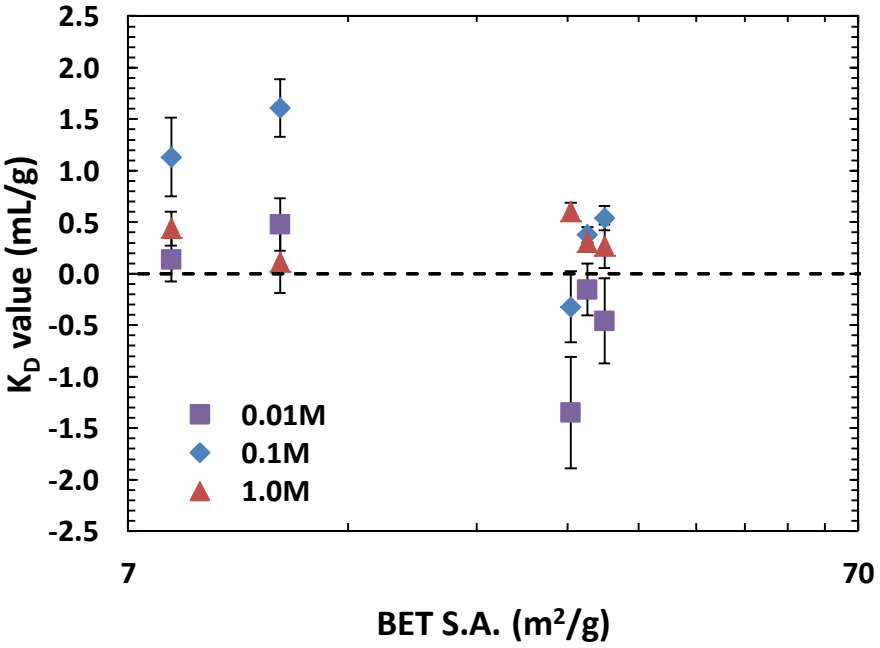
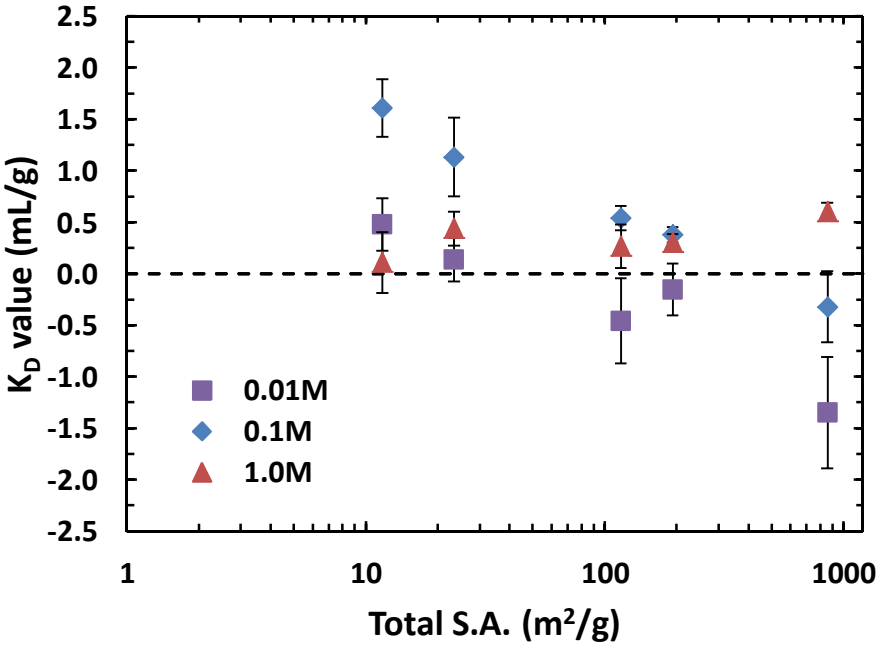
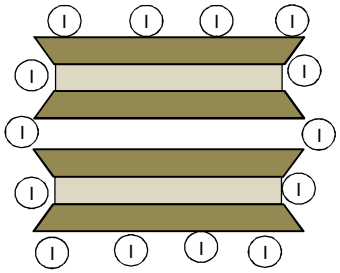
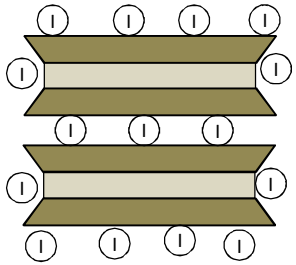
K_D values trend with total surface area, suggesting interactions with negatively charged surfaces.









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Nanogeochemistry: Nanostructures, emergent properties and their control on geochemical reactions and mass transfers

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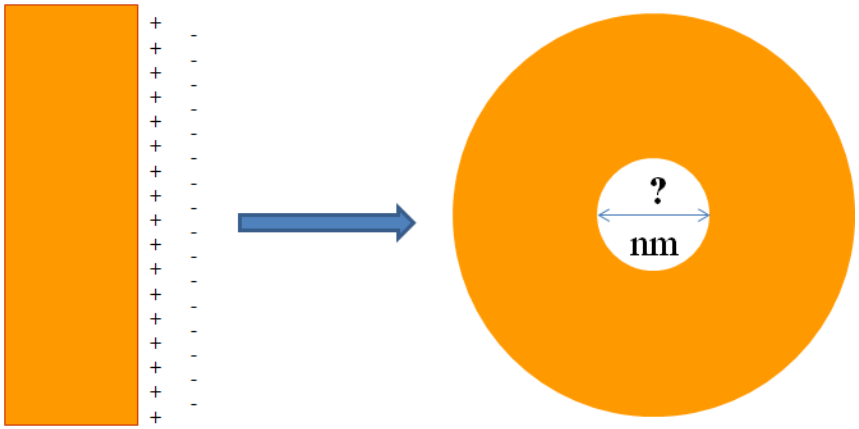
ARTICLE INFO ABSTRACT



Unconfined Confined

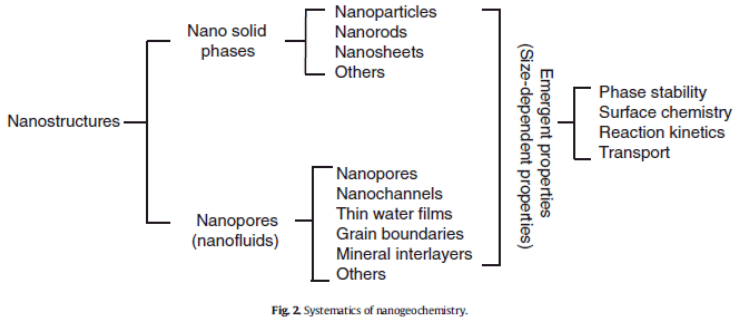


Fig. 2. Systematics of nanogeochemistry.

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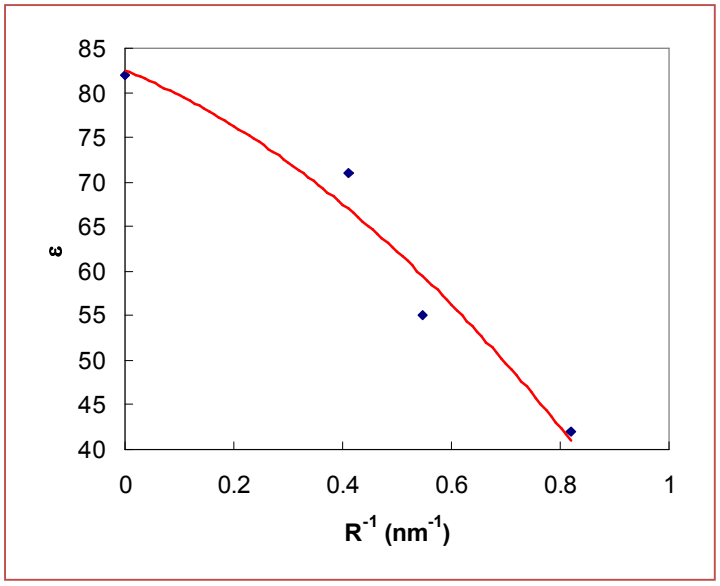
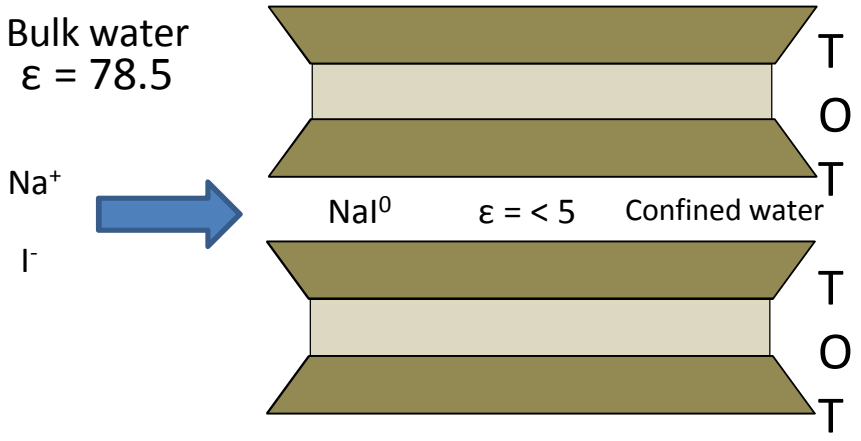
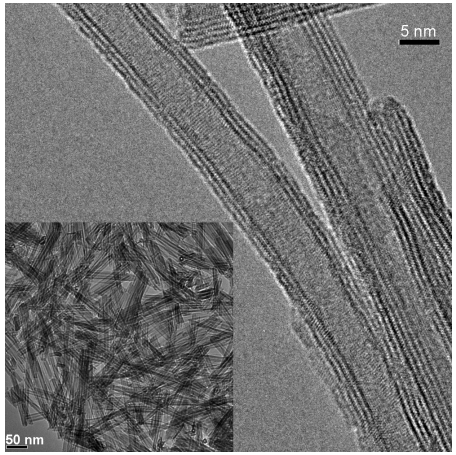
Data is consistent with ion pair formation caused by reduced dielectric constant of confined water

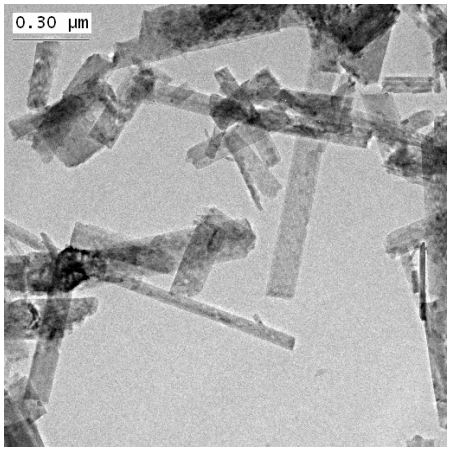


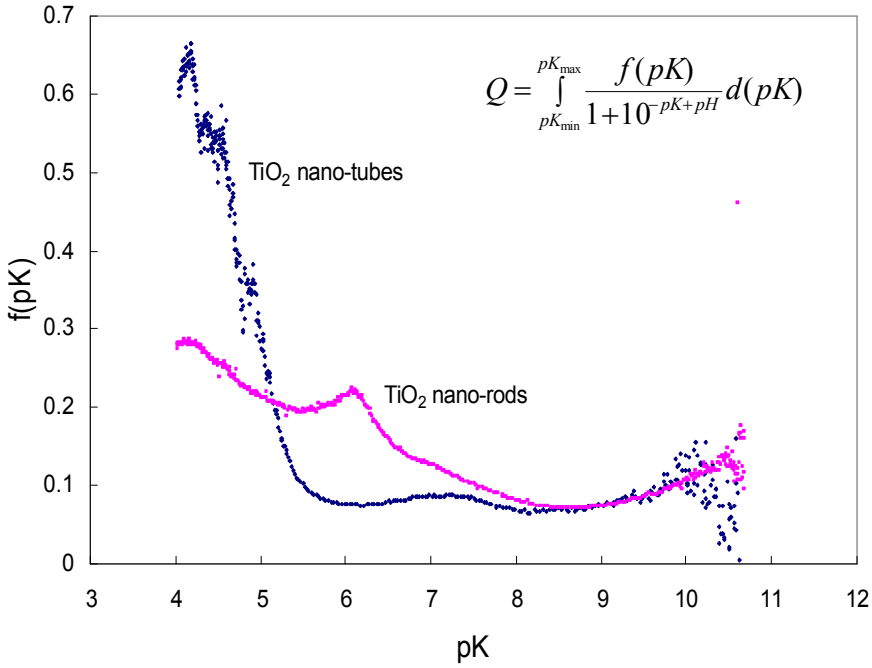


Senapati & Chandra, 2001, J. Phys. Chem.

Confined surface vs. unconfined surface







Wang et al. (2008)

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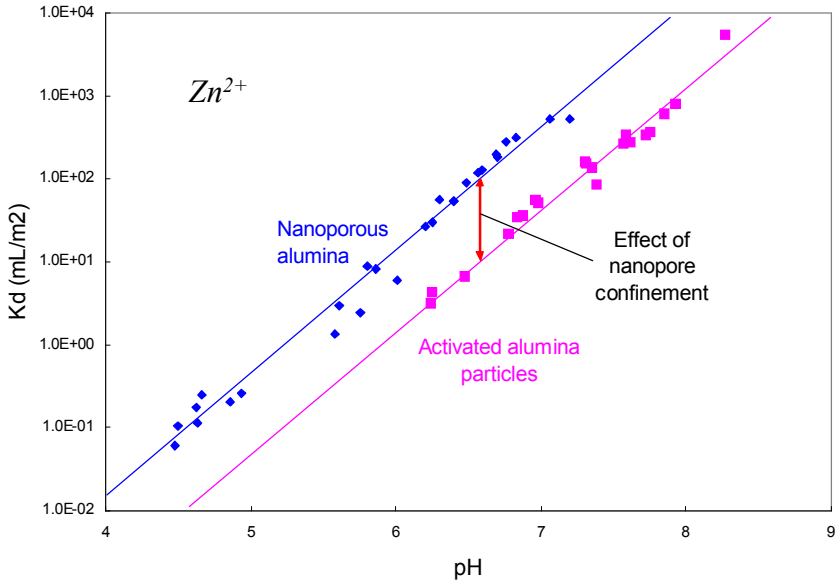
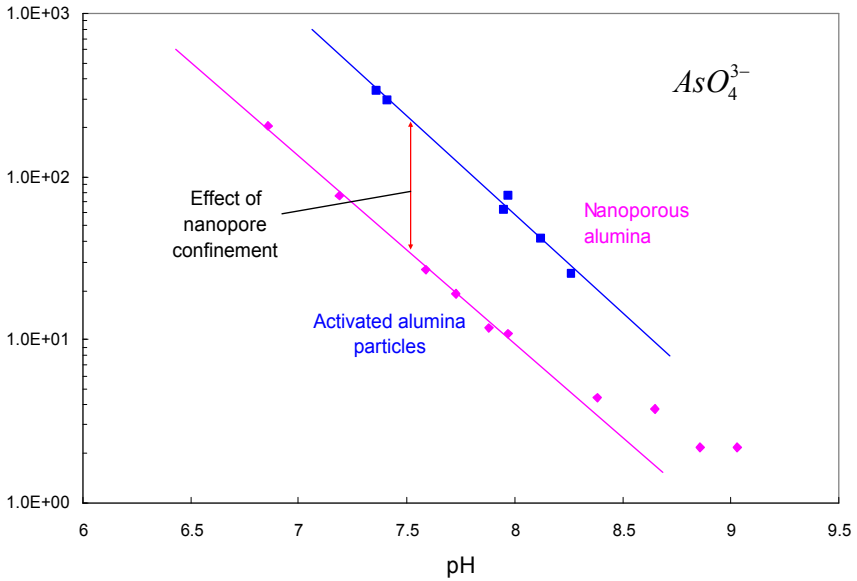
Nanopore Confinement and Ion Sorption





Nanopore confinement enhances ion sorption onto a solid-water interface for both cations and anions.

Wang et al., 2003, Mat. Res. Soc. Symp. Proc.; 2003, Geology

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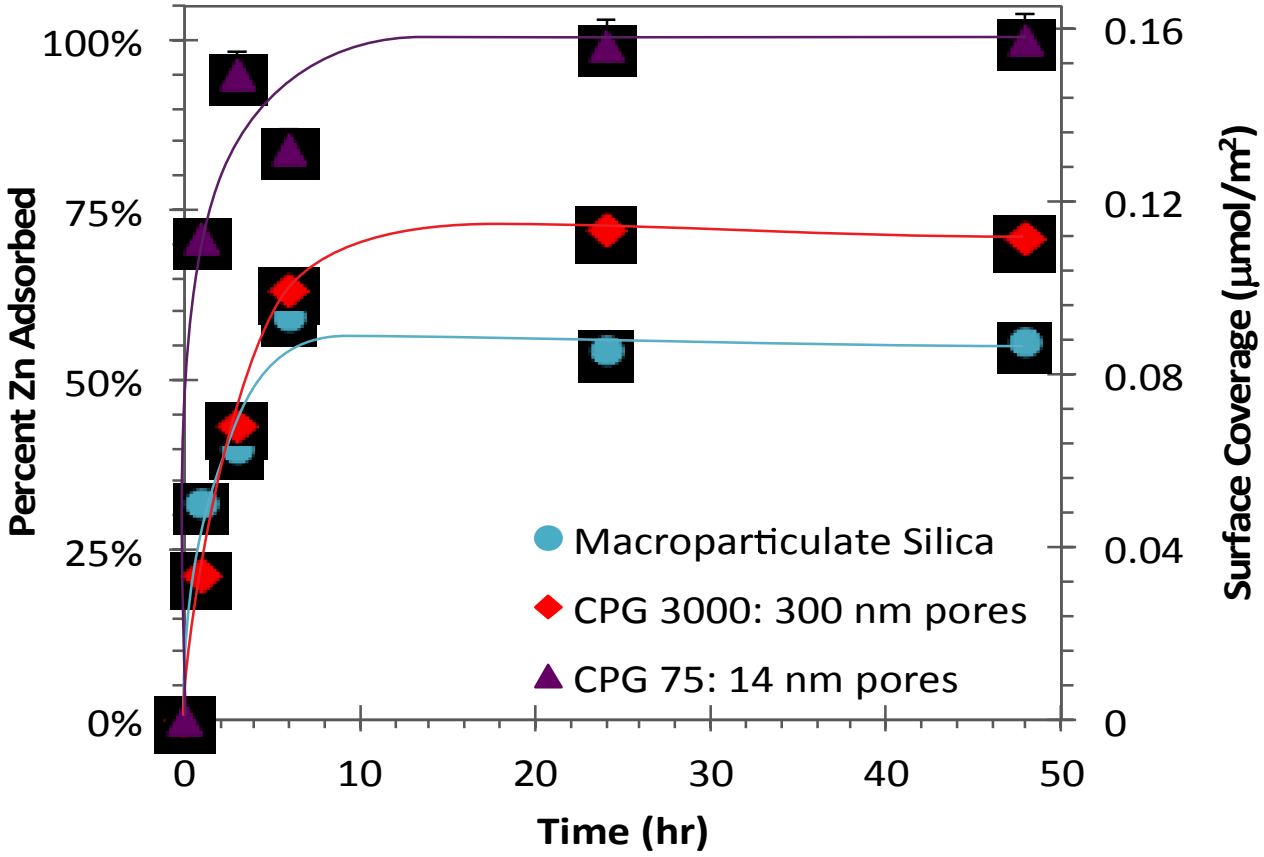
Zn Adsorption Capacity



Nelson et al. (2014)

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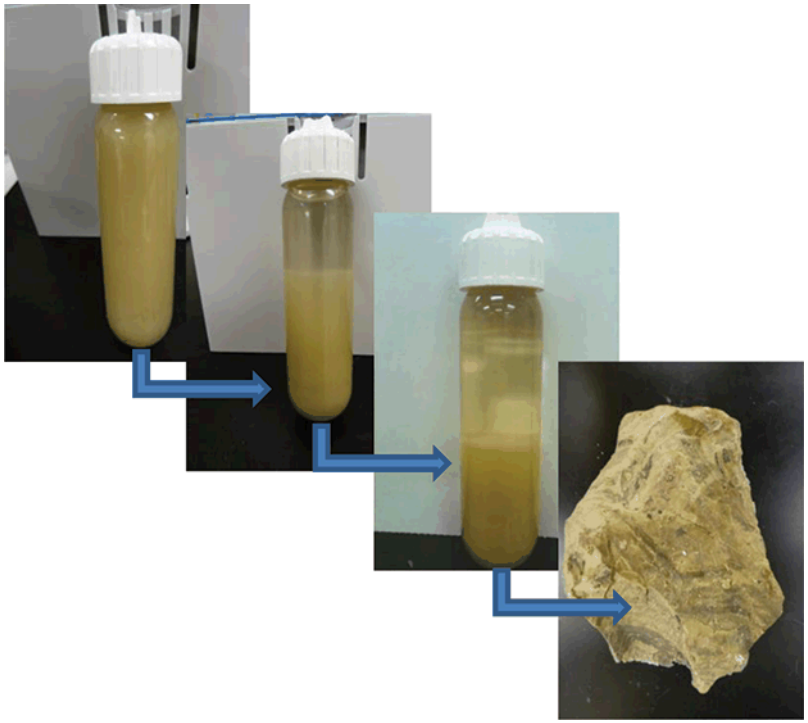
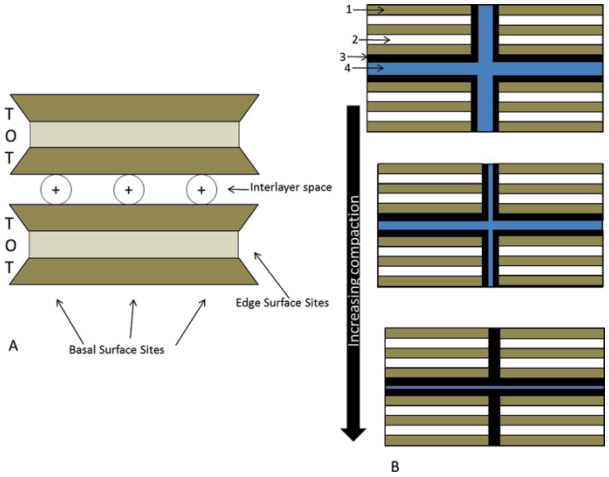
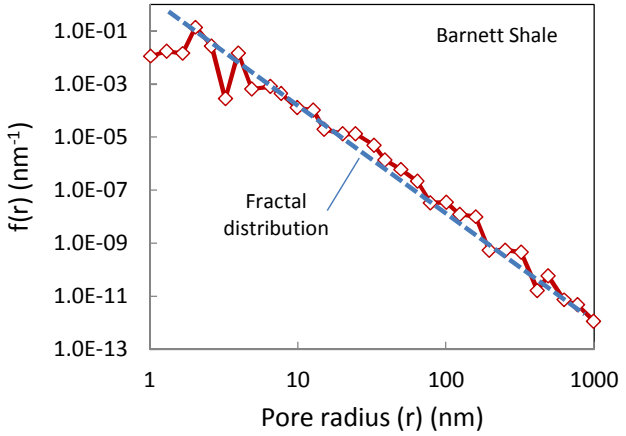
Understanding Radionuclide Uptake in Compacted Clay Materials



Miller and Wang (2012)





Wang (2014)

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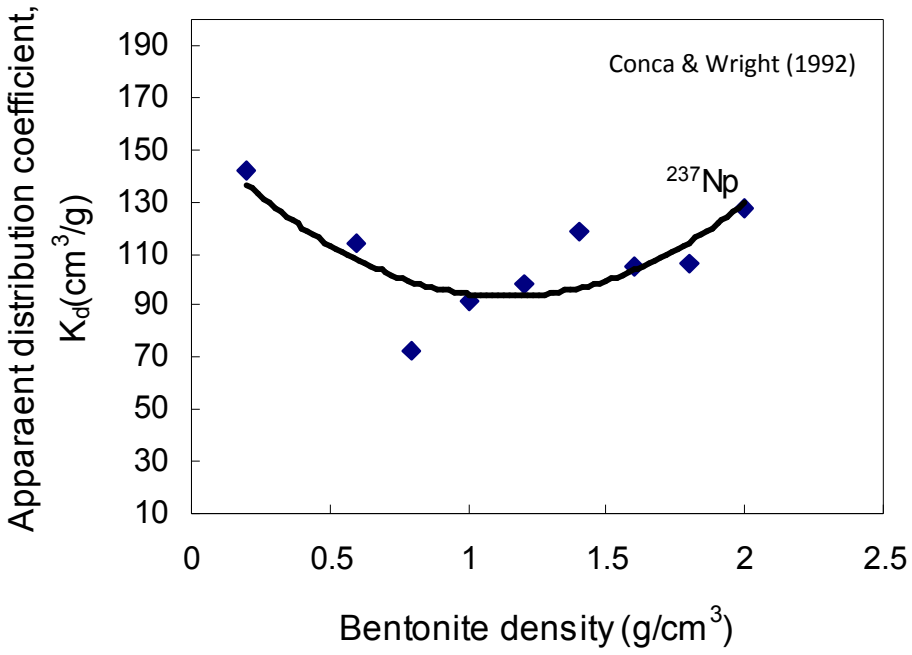
Compaction does affect Radionuclide uptake



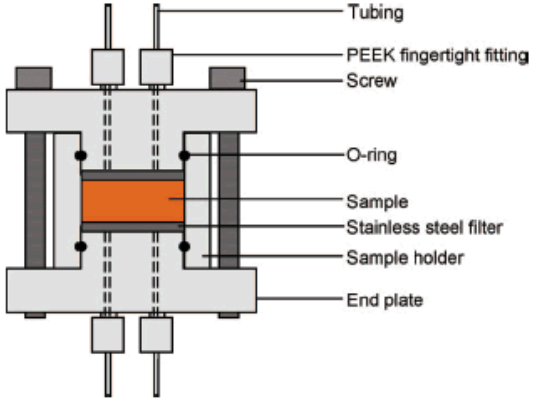


FIGURE 1. Cross-section picture of the diffusion cell used for the sorption measurements on compacted bentonite.

TABLE 4. R_d, K_e and ΔG_{ex} Values for Sorption of Cs^+ on Compacted Bentonite for Different Bulk Dry Densities (ρ_b)[a]

ρ_b [kg m^{-3}]	1300	1600	1900
[Na^+] [M]	0.183	0.207	0.254
R_d [dm^3 kg^{-1}]	69.0 ± 2.0	109 ± 4	620 ± 4
K_e	21.6	38.6	269
ΔG_{ex} [kJ mol^{-1}]	−7.6	−9.1	−13.9

[a] R_d was calculated by eq (1), K_e was calculated by eq (5) and ΔG_{ex} is defined by eq (6).

$$K_e = \frac{[X-Cs][Na^+]}{[X-Na][Cs^+]}$$

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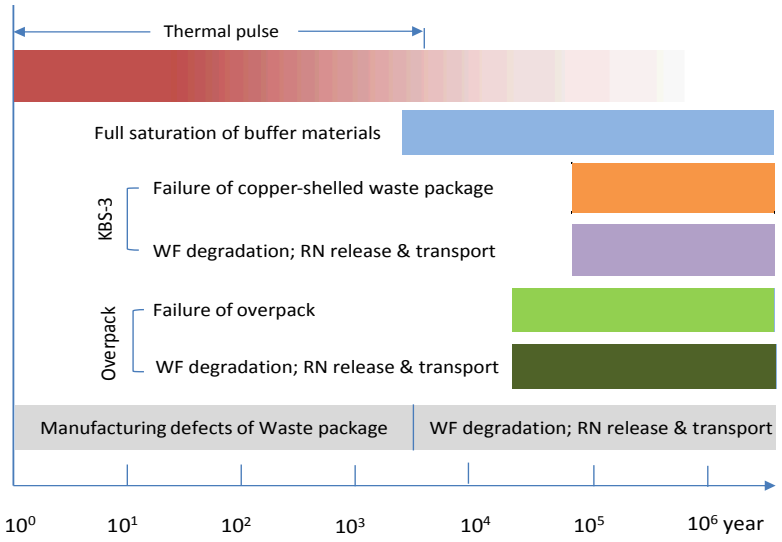
Future Perspectives

- Nanogeochemistry may allow us to develop a consistent theoretical frame work for bridging surface sorption and ion exchange in layered materials.
- Knowledge gained from materials science research will help develop a new generation of buffer materials for nuclear waste isolation.
- One important issue related to nuclear waste disposal is how the decay heat will affect the performance of buffer materials.



Acknowledgment

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