SAND2012-4385C

Used Fuel Disposition Campaign

Thermodynamic Modeling of Clay Hydration and C-S-H Cement Leaching

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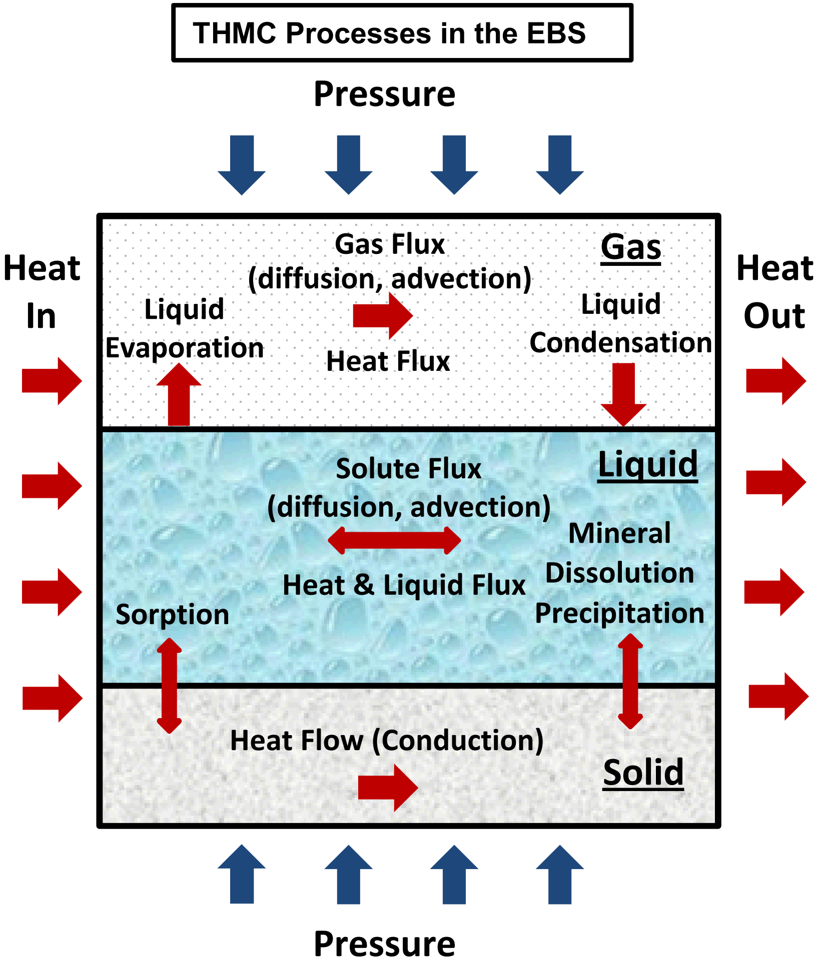
Interactions at EBS Interfaces

- **Knowledge gaps and R&D prioritization in EBS (based on the UFDC Disposal R&D Roadmap, Nutt et al. 2011) :**
- **Highest ranked issues:**
  - *Waste Form*
  - *THM Processes*
  - *Waste Container*
  - *Radionuclide speciation and solubility*
  - ***Buffer/Backfill and Seals Barrier Materials - (Chemical Processes)***
    - **Seals: Cementitious Phases**
    - **Buffer/Backfill: Clay**
- **High rank of THMC processes is relevant to interactions at EBS interfaces:**
  - ***Shares a boundary with far-field region***
  - ***Loci for important degradation processes in the near-field***
    - ***Fluid interactions with EBS materials***
    - ***Effects on barrier material stability***



Modified After Olivella et al. (2011)

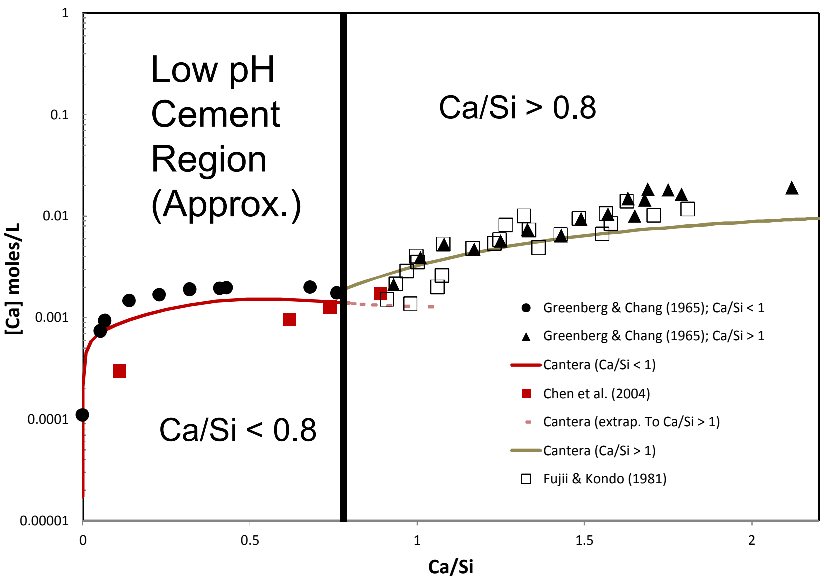
C-S-H Leaching Model Using Cantera

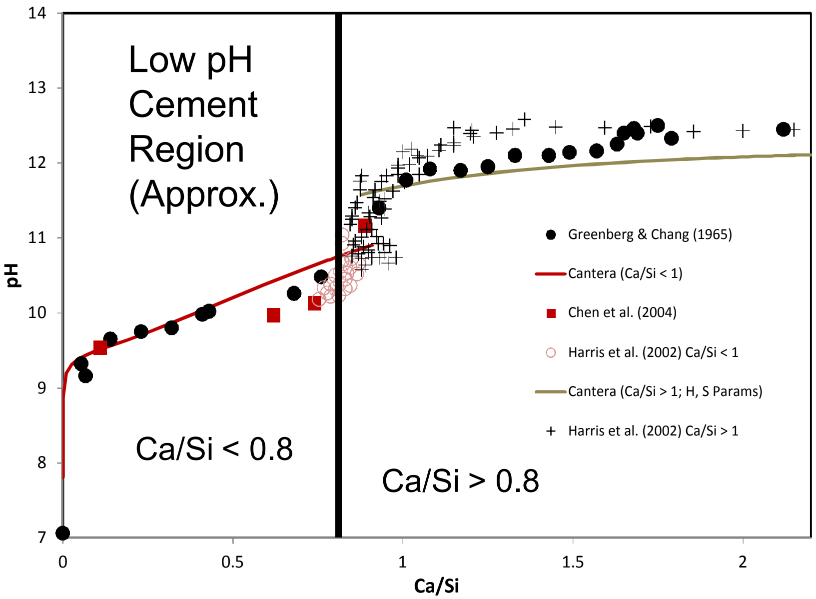
- **Cantera code implementation with the Margules class to represent the sub-regular solid solution behavior**

$$\boxed{\begin{gathered} H^{EX} = X_{SiO_{2(am)}} X_{Ca(OH)_2} (W_{H1} + W_{H1} X_{SiO_{2(am)}}) \\ S^{EX} = X_{SiO_{2(am)}} X_{Ca(OH)_2} (W_{S1} + W_{S1} X_{SiO_{2(am)}}) \\ G^{EX} = H^{EX} - TS^{EX} \end{gathered}}$$

- **Pitzer model class to represent the aqueous phase**
- **Solid solution model implementation:**
  - Consists of two separate C-S-H solid solution domains on the basis of two ranges of Ca/Si ratios in the solid: Ca/Si < 0.8 and Ca/Si > 0.8
  - Based on two end member solids: $SiO_{2(am)}$ and $Ca(OH)_2$
  - The model is consistent with the binary non-ideal solid solution model advanced by Sugiyama and Fujita (2006)
- **Retrieval and evaluation of Margules parameters was conducted using the code coupling of Cantera with the DAKOTA optimization code**
- **Results show solute leaching curves as a function of Ca/Si ratio in the solid are in very good agreement with experimental data trends for aqueous Ca, Si, and pH**
- **International Collaboration: Initiated communication with Dr. Urs Maeder (Univ. of Bern) on the participation in the CI experiment on cement-clay interaction at Mont Terri**

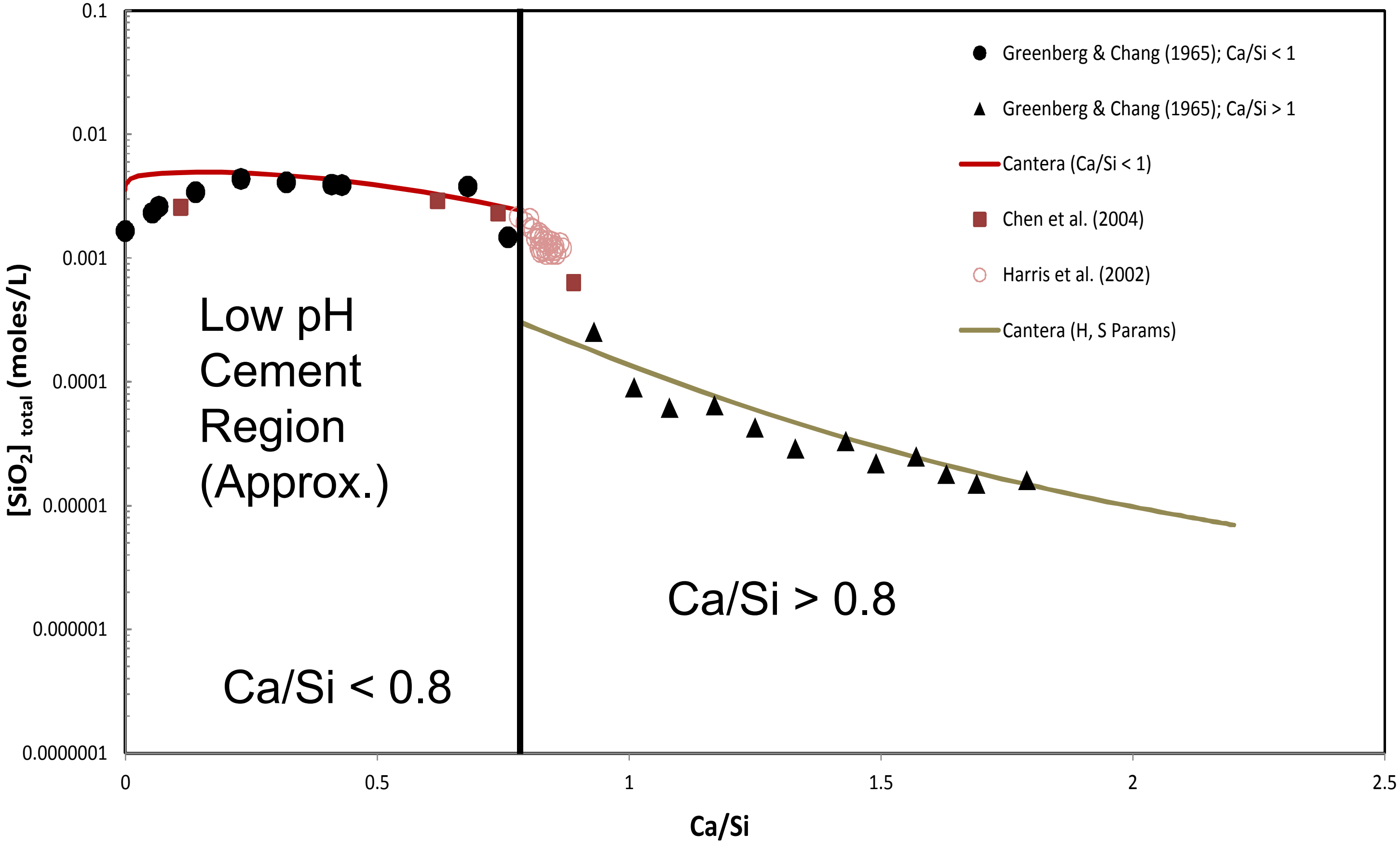
Cantera C-S-H Cement Leaching Modeling Results: Ca and pH





DRAFT Version

Cantera C-S-H Leaching Modeling Results (Cont.): $SiO_{2(aq)}$



DRAFT Version

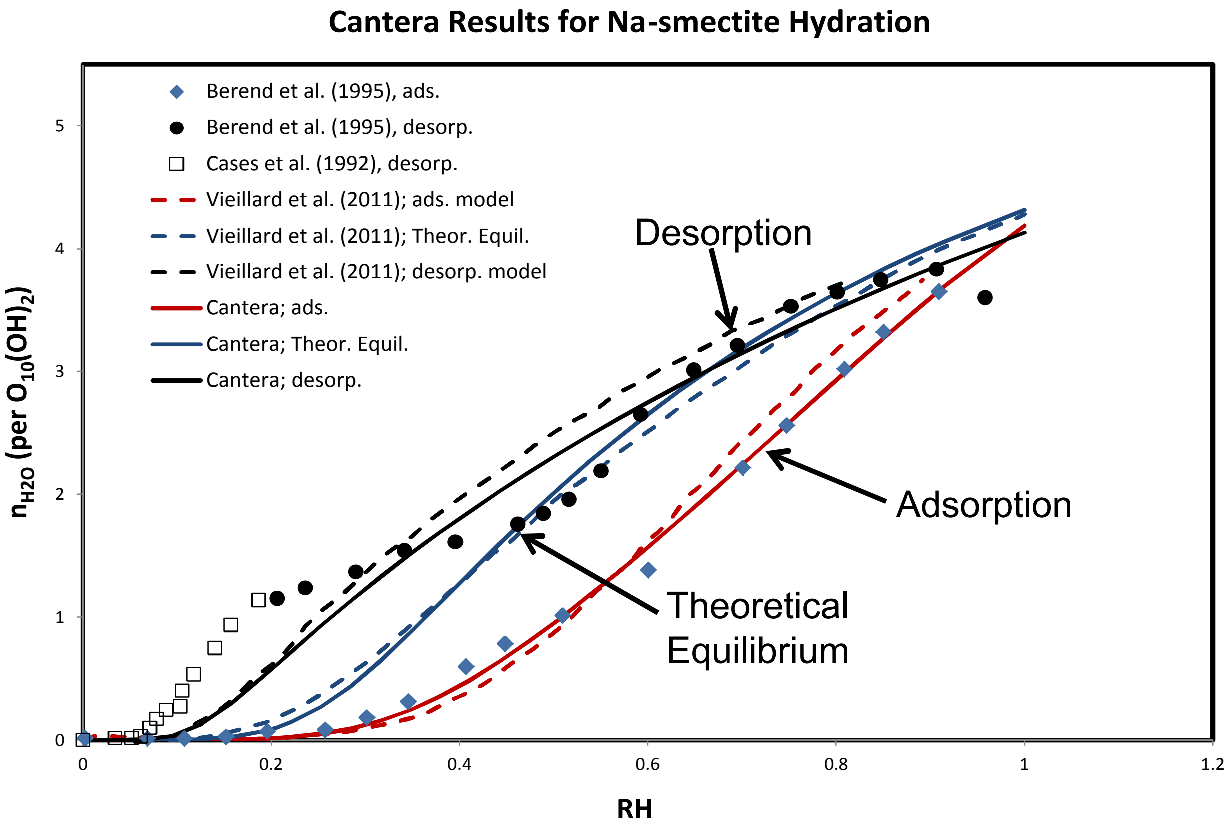
Cantera Clay Hydration Model

- **Clay Hydration Model:**
  - **Cantera** code implementation with the Margules parameterization to represent the non-ideal solid solution:
    - *Margules parameterization based on sub-regular solid solution for two clay end-members following the approaches advanced by Ransom and Helgeson (1994) and Vieillard et al. (2011):*

$$\boxed{\begin{gathered} Smectite\ (dehyd.) + nH_2O = Smectite\ (hyd., nH_2O) \\ H^{EX} = X_{smect.\,hyd.} X_{smect.\,dehyd.} (W_{H1} + W_{H1} X_{smect.\,dehyd.}) \\ S^{EX} = X_{smect.\,hyd.} X_{smect.\,dehyd.} (W_{S1} + W_{S1} X_{smect.\,dehyd.}) \\ G^{EX} = H^{EX} - TS^{EX} \end{gathered}}$$

  - Each clay phase has its own set of thermodynamic data:
    - *Dehydrated smectite data from LLNL clay thermodynamic work (Thomas Wolery)*
    - *Hydrated smectite data retrieved from Vieillard et al. (2011) model assuming 5.5 H_2O's for the fully hydrated clay*
    - *Thermodynamic data for H_2O vapor from the EoS of Wagner and Pruß (2002)*

Cantera Clay Hydration Model: Na Montmorillonite Hydration


Cantera Results for Na-smectite Hydration

FY12 Accomplishments

- **Thermodynamic data compilation for cementitious solids**
  - YMP and CEMDATA07 → input formatted for use with the Cantera thermodynamic modeling code
- **C-S-H leaching model implementation in Cantera using the Margules solid solution class**
  - Implementation of the binary non-ideal solid solution model advanced by Sugiyama and Fujita (2006)
- **Clay hydration model implementation using the Margules solid solution class**
  - Thermodynamic description and Margules parameterization based on sub-regular solid solution between dehydrated and hydrated clay end-members
- **Thermal analysis of multilayered EBS (with Harris Greenberg – LLNL)**

Rest of FY12 and FY13

FY12

- Expand and continue DSEF thermal analysis for multi-layered EBS on the evaluation of thermal profiles.
  - Examination of the effects of mixed buffer material and their thermal conductivities
- Expansion and further testing of the clay hydration model to more clay compositions
- Further testing of the C-S-H cement leaching model and cement phase solubilities

FY13

- Continue thermal analysis for multi-layered EBS (with Harris Greenberg at LLNL)
- Continue assessment of thermodynamic data for clays and cementitious materials at elevated temperatures (in conjunction with LLNL)
- Thermodynamic description of clay interactions at high temperatures and pressures (with LANL experimental work on barrier material interactions)
- Explore the use of Gibbs energy minimization models for sorption and ion exchange – Implementation with the Cantera code
- Establish collaboration with the CI experimental (cement-clay interaction) program at Mont Terri

Used Fuel Disposition Campaign

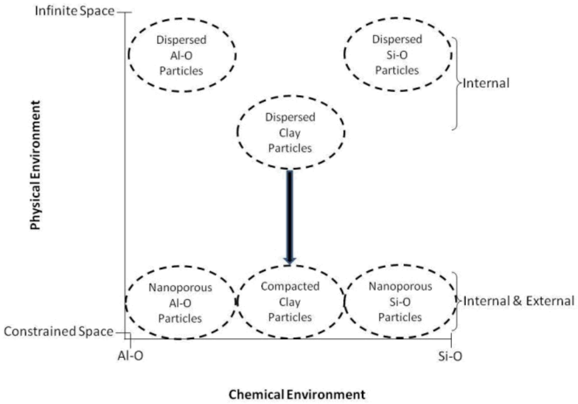
Quantifying weak interactions between iodide and clay minerals

Andrew Miller
Yifeng Wang
Jessica Kruichak
Melissa Mills
Hernesto Tellez

Sandia National Laboratory

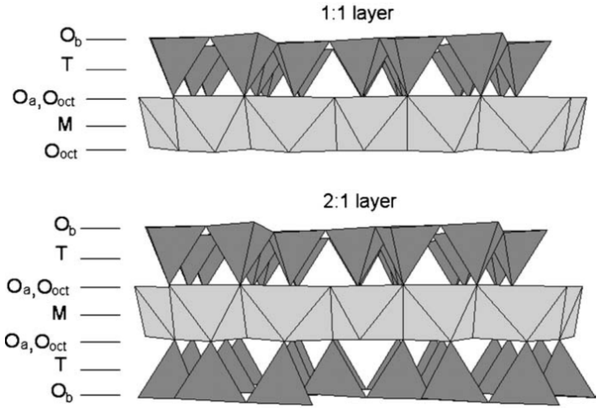
This talk relates clay physical/chemical relationships with iodine uptake behavior.

Review Article



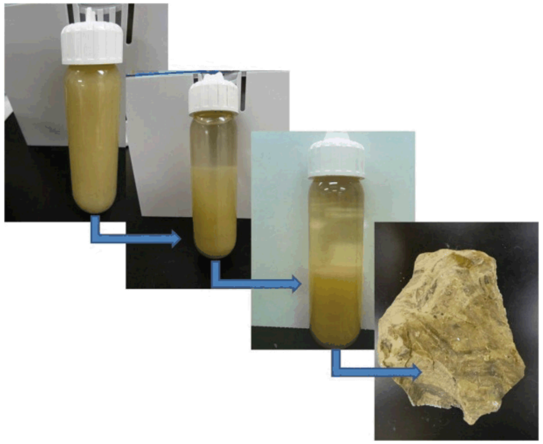
Miller, A.W., Wang, Y. (2012). *Environ.Sci. Technol.* **DOI:** 10.1021/es203025q.

Clay mineralogy

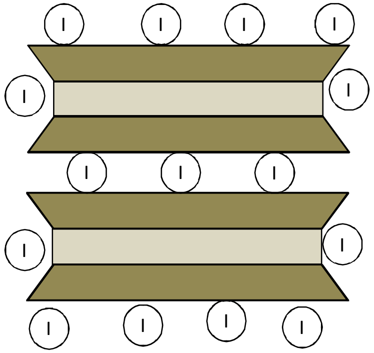


Handbook of Clay Science, Eds.: Bergaya, F., Theng, B.K.G., Lagaly, G.; Elsevier, 2006.

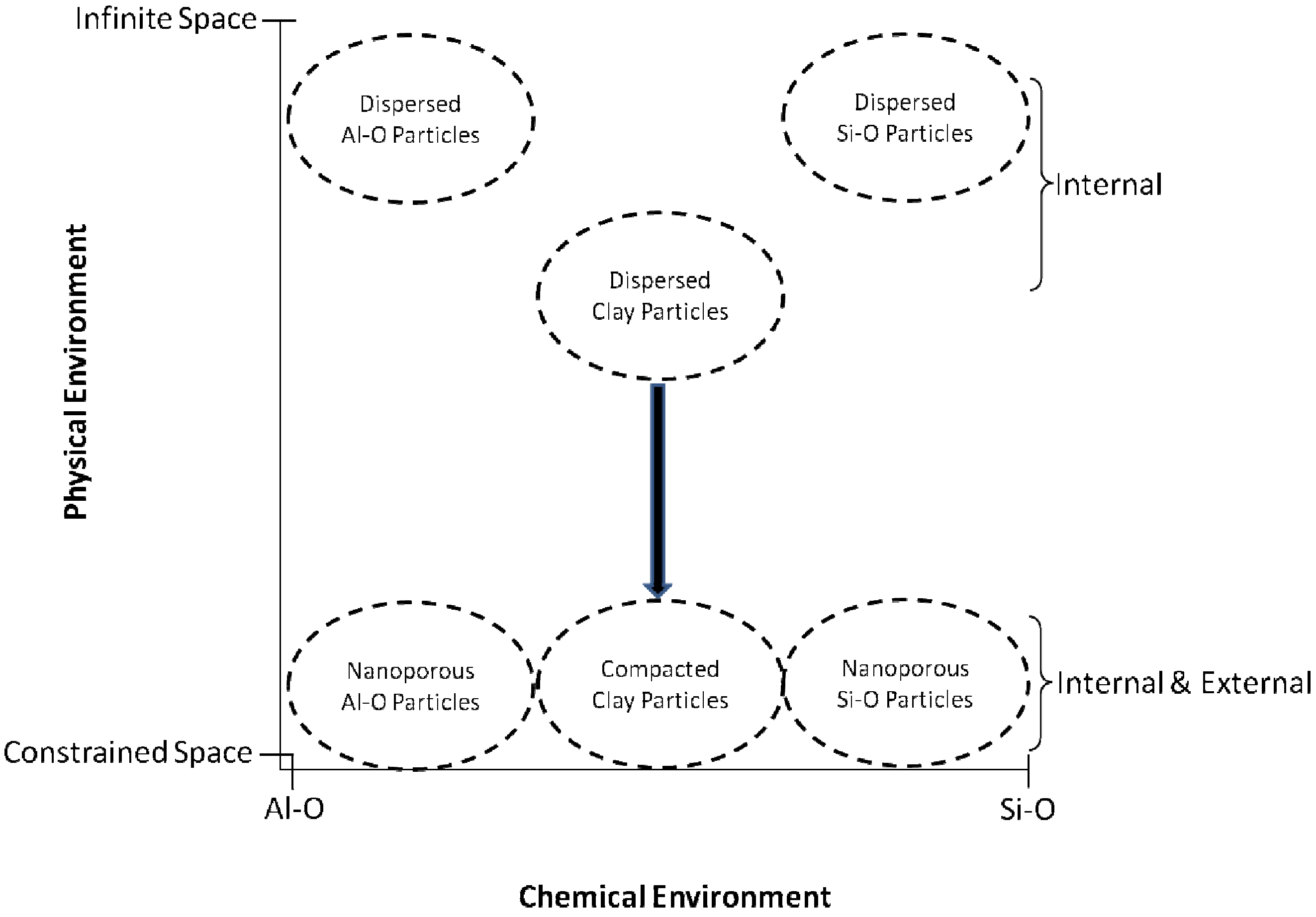
Experimental conditions/results



Path forward



Clay particle proximity has the potential to change observed reactivity.



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

Large tables of batch determined reactivity are in the review article.

Ref. #	Clay	Major Clay mineral (%)	Other Minerals	Ions studied	K_d (mL/g)	IX/SCM ?	Notes
[67]	Callovo-Oxfordian #1	Illite/Smectite (30-35)	Illite, kaolinite, chlorite, quartz, calcite, pyrite	I	1.50E-01	N	Concentration dependant I retention, values for [I]=5E-6, sample 1 and 8e-6, sample 2; max value for each
	Callovo-Oxfordian #2				3.70E-01		
[62]	Bentonite	Montmorillonite	Quartz	Cs	1.50E+02	N	
				Sr	2.50E+01		
				I	0-1		
[51]	Illite Du Puy	Illite		Am	3.16E+05	Y	Paper performs sorption envelope experiments for the ions given Kd values reported here are approximated from the envelope at pH 7
				Th	3.16E+05		
				Pa	1.00E+05		
				U	1.00E+05		
				Np	1.00E+01		
[57]	FEBEX Bentonite	Smectite	quartz, plagioclase, cristobalite, feldspar, calcite, tridymite	Sr	1.78E+04	Y	Sorption envelopes created values given for pH 7; I = 0.01M
					1.58E+02		I = 0.1M
	Silver Hill Illite	Illite		Sr	1.41E+02		I = 0.1M
					8.91E+01		I = 0.2M
[74]	Boom Clay	Illite (10-45), Illite/Smectite (10-30), Kaolinite (5-20), Chlorite (0-10), chlorite/smectite (0-5)	Quartz, K-Feldspar, Albite, carbonates, pyrite	Cs	4.10E+03	N	Replication experiments
				Cs	1.50E+03		
		Na-Illite (100)		Se	6.00E+01		Sorption envelopes created, value estimated for pH = 7, I = 0.1M
		Na-Smectite (100)		Se	1.55E+02		Sorption envelopes created, value estimated for pH = 7, I = 0.1M
		Na-Illite (30)/Na					Sorption envelopes created, value estimated for pH

Large tables of diffusion behaviors are also available in the review article.

Ref. #	Clay	Major Clay mineral (%)	Ions involved	K_d (mL/g)	Diffusion coefficient (m^2/sec)	Compaction	Compaction units	Ion porosity	Notes
[1]	Bentonite	Montmorillonite	Cl		1.60E-11	1.3	g/cm^3	2.3	All D and porosity values at 0.1M ionic strength, others in reference
					2.30E-12	1.6	g/cm^3	2.1	
					2.40E-13	1.9	g/cm^3	0.7	
[90]	Opalinus	Illite (23)/Kaolinite (22)	Cl		5.54E-12	1	MPa		
					3.99E-12	5	MPa		
			I	0.008-0.02	4.57E-12	1	MPa		
					3.22E-12	5	MPa		
[102]	Bentonite MX 80	Montmorillonite	Na	2.80E+00	3.80E-07	1.8	g/cm^3	0.32	Wider range of ionic strength and packing densities in reference. Porosity determined not for each individual ion but for a given amount of compaction
			Sr	1.50E+02	3.50E-07	0.8	g/cm^3	0.7	
				8.00E+01	9.00E-08	1.8	g/cm^3	0.32	
			Cs	2.65E+02	6.40E-08	0.8	g/cm^3	0.7	
				5.80E+02	3.30E-08	1.8	g/cm^3	0.32	
			Co	2.40E+03	1.00E-09	0.8	g/cm^3	0.7	
				2.40E+03	1.00E-10	1.8	g/cm^3	0.32	
[104]	Kunipia-F	Montmorillonite (95)	Tc	3.00E+00	6.90E-10	0.2	g/cm^3		More elements and compaction data in reference
			I	5.70E-01	8.40E-10	0.2	g/cm^3		
			Np	4.20E+02	1.20E-11	0.2	g/cm^3		
			Tc	1.30E+00	3.20E-11	1.4	g/cm^3		
			I	1.30E-01	8.50E-11	1.4	g/cm^3		
			Np	1.80E+02	3.00E-13	1.4	g/cm^3		
			Tc	9.40E-01	1.00E-11	2.0	g/cm^3		
			I	6.00E-02	2.40E-11	2.0	g/cm^3		
			Np	2.70E+02	3.00E-14	2.0	g/cm^3		

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

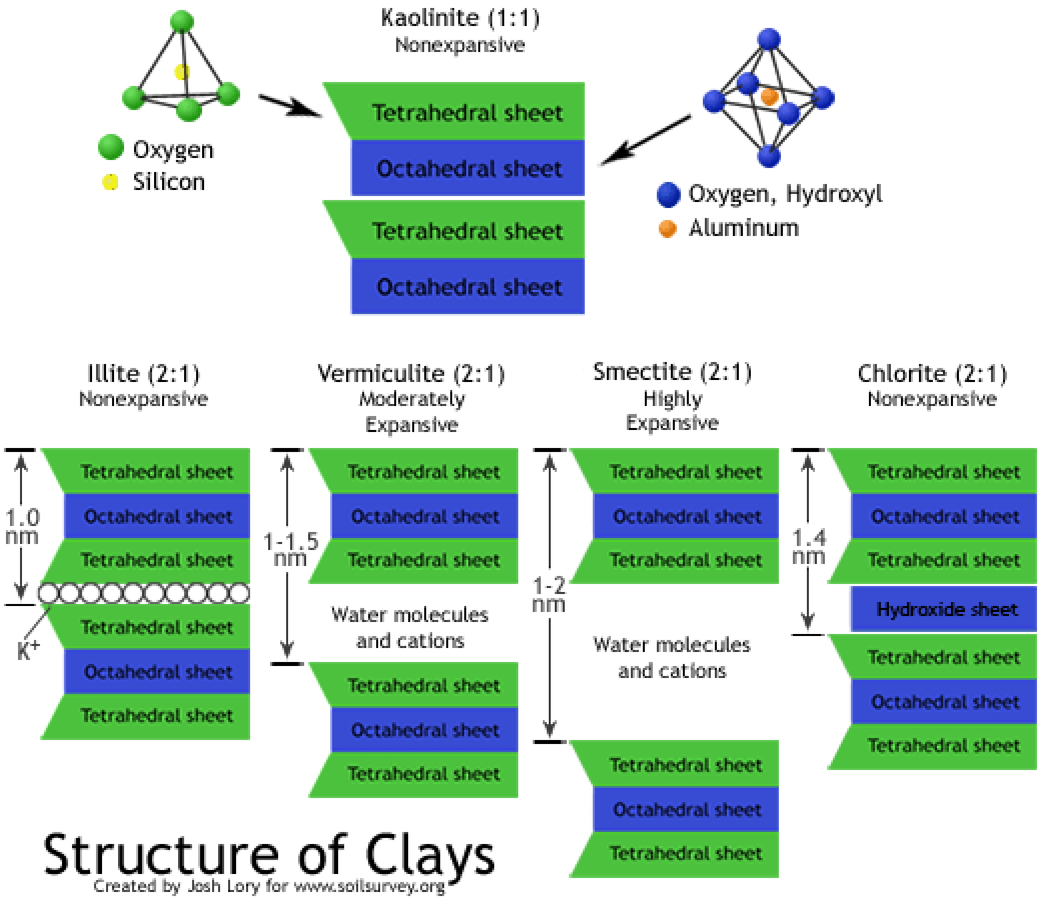
1. **They aren't.**
   - Impure radiotracers
   - Isotopic exchange with natural iodine
   - Uptake into carbonate minerals

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

Clays are (Mg, Al)-silicates with sheets, layers, edges and interlayers.



Structure of Clays

Created by Josh Lory for www.soilsurvey.org

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

Surface Charge Separation

Cation Exchange Capacity

$$\equiv X - Na^+ + K^+ \leftrightarrow \equiv X - K^+ + Na^+$$

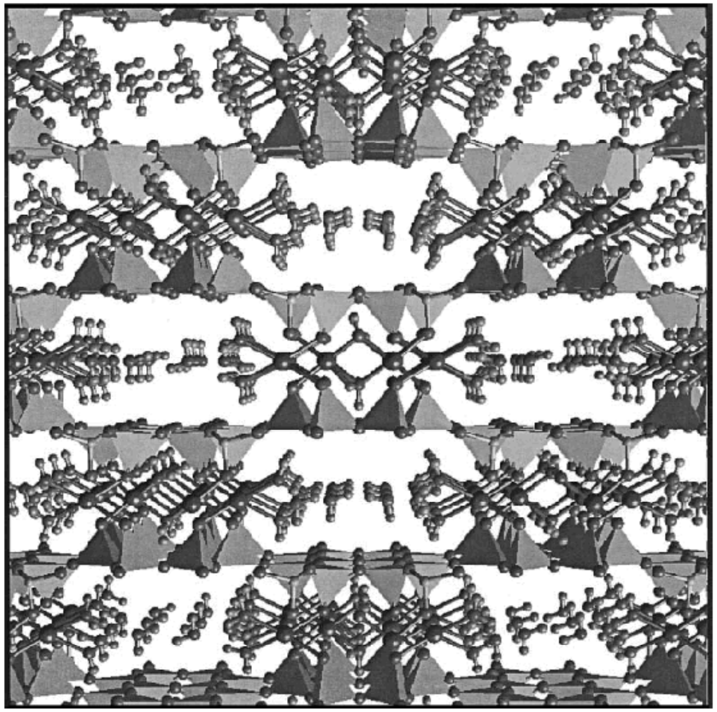
Edge Exchange

$$\equiv AlO^- + H^+ \leftrightarrow \equiv AlOH$$

$$\equiv AlOH + H^+ \leftrightarrow \equiv AlOH_2^+$$

$$\equiv SiO^- + H^+ \leftrightarrow \equiv SiOH$$

Fibrous clays have columnar voids for water inclusion.



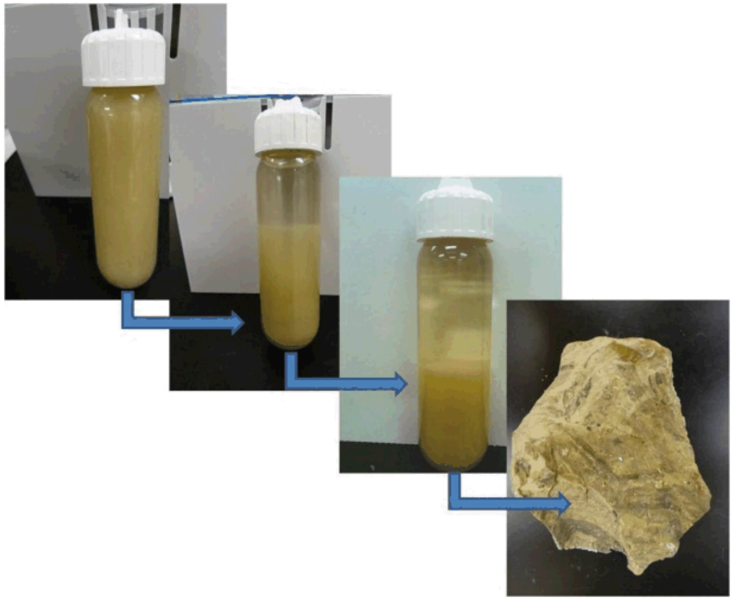
Fois et al., 2003. **Microporous and Mesoporous Materials**. 57, 263-272.

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

Surface titrations and batch uptake experiments characterize the clay surface.

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

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



Uptake experiments:

- **Methylene Blue (MB)**
  - Na-exchanged clays
  - Variable amounts of MB were added until clay surface was saturated
- **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		

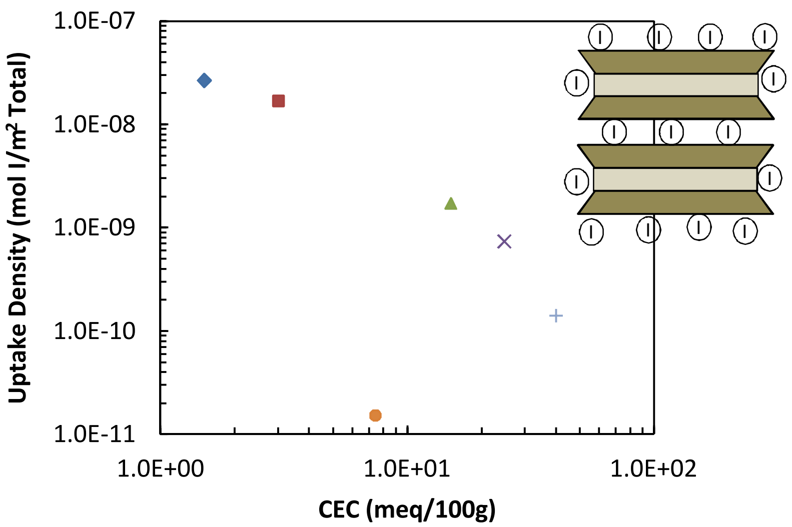
Iodide uptake is dependent on ionic composition of swamping electrolyte.

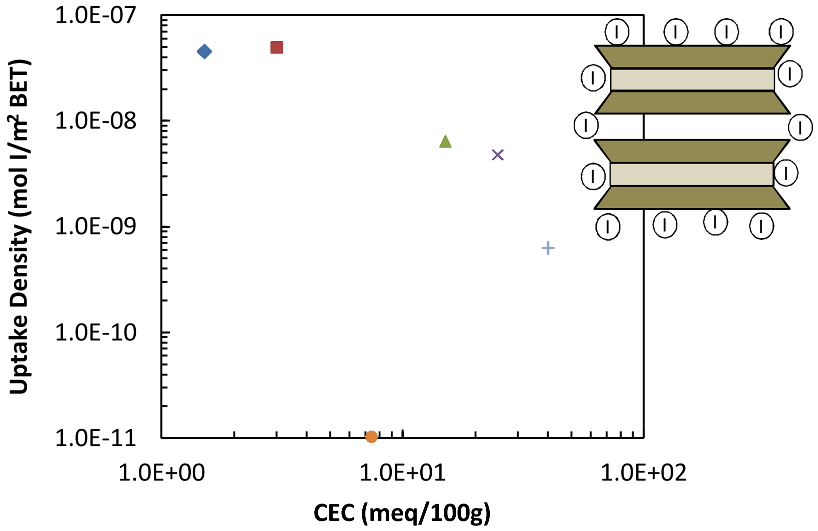
		CEC meq/100g	% removal			% RSD		
			NaCl	NaBr	KCl	NaCl	NaBr	KCl
Layered	**Kaolinite**	1.50	13.8	3.7	-0.1	2.4	6.5	2.2
	Ripidolite	3.00	10.1	2.4	-3.2	3.4	7.6	1.8
	Illite	14.98	5.1	1.3	-5.3	1.1	0.0	2.5
	Illite.Smectite	24.69	3.6	-0.1	-5.1	0.7	1.1	1.1
	Montmorillonite	109.53	-3.4	-6.1	-21.4	3.5	0.7	11.4
Fibrous	**Sepiolite**	17.41	0.1	7.3	1.0	2.8	1.3	2.9
	Palygorskite	39.96	2.3	11.2	9.0	3.0	0.5	1.6

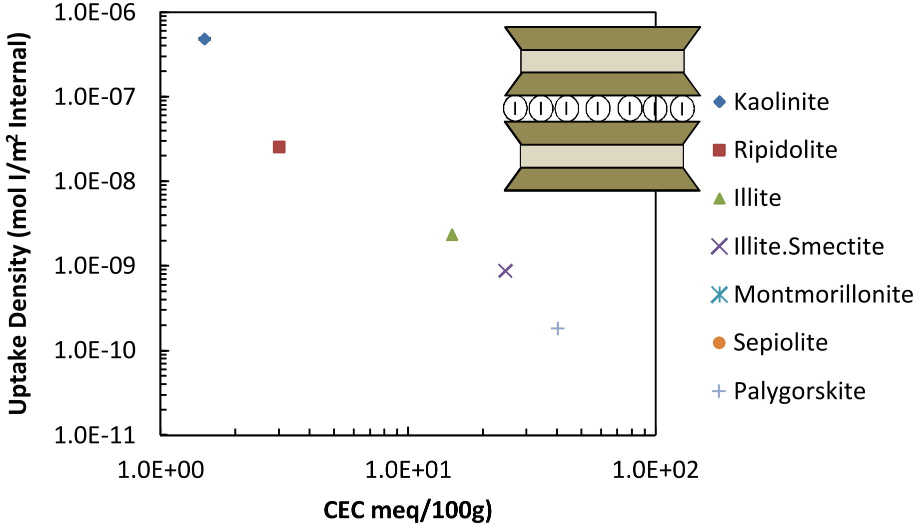
Iodide uptake depends on swamping electrolyte concentration.

		CEC meq/100g	% removal			% RSD		
			NaCl 0.01M	NaCl 0.1M	NaCl 1.0M	NaCl 0.01M	NaCl 0.1M	NaCl 1.0M
Layered	**Kaolinite**	1.50	4.5	13.8	1.0	2.5	2.4	2.9
	Ripidolite	3.00	1.3	10.1	4.2	2.1	3.4	1.6
	Illite	14.98	-4.9	4.6	2.6	4.4	5.9	2.1
	Illite.Smectite	24.69	-1.6	3.6	2.9	2.6	0.7	0.8
	Montmorillonite	109.53	-15.9	-3.4	5.7	6.2	3.5	0.8
Fibrous	**Sepiolite**	17.41	5.6	0.1	-0.2	29.5	2.8	3.1
	Palygorskite	39.96	-2.6	2.3	6.5	5.4	3.0	2.4

Iodide uptake normalized to interior surface area suggests interlayer interactions.







$$\equiv X + I^- \leftrightarrow \equiv XI^-$$

$$\equiv X - Cl^- + I^- \leftrightarrow \equiv X - I^- + Cl^-$$

Ion pair formation in the interlayer may be able to describe interactions.

log K	NaCl	NaBr	KCl
Ion pair of electrolyte	0.82	0.73	0.53
Ion pair I with cation	0.6	0.6	0.4

Element	Ionic Radii	Hyd Energy (kJ/mol)
Na	1.16	-406
K	1.52	-322
Cs	1.81	-287
Ca	1.14	-1577
Cl	1.81	-363
Br	1.96	-336
I	2.2	-295

	CEC meq/100g	% removal		
		NaCl	NaBr	KCl
Kaolinite	1.50	13.8	3.7	-0.1
Ripidolite	3.00	10.1	2.4	-3.2
Illite	14.98	4.6	1.3	-5.3
Illite.Smectite	24.69	3.6	-0.1	-5.1
Montmorillonite	109.53	-3.4	-6.1	-21.4
Sepiolite	17.41	0.1	7.3	1.0
Palygorskite	39.96	2.3	11.2	9.0

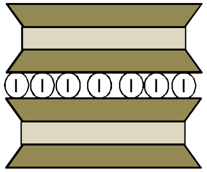
$$K^{eff} = f(\ldots \Delta F_h \ldots)$$

$$\Delta F_h = f(\ldots \epsilon, D \ldots)$$

$$\epsilon, D = f(\ldots \sigma_{fixed} \ldots)$$

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

The data suggests unexpected interlayer concentrations of iodide.



Little to no conversion to iodate was observed.

Iodide uptake is heavily related to CEC.

Iodide uptake is heavily related to ionic composition of electrolyte.

Iodide uptake is dependent on clay textures and structures

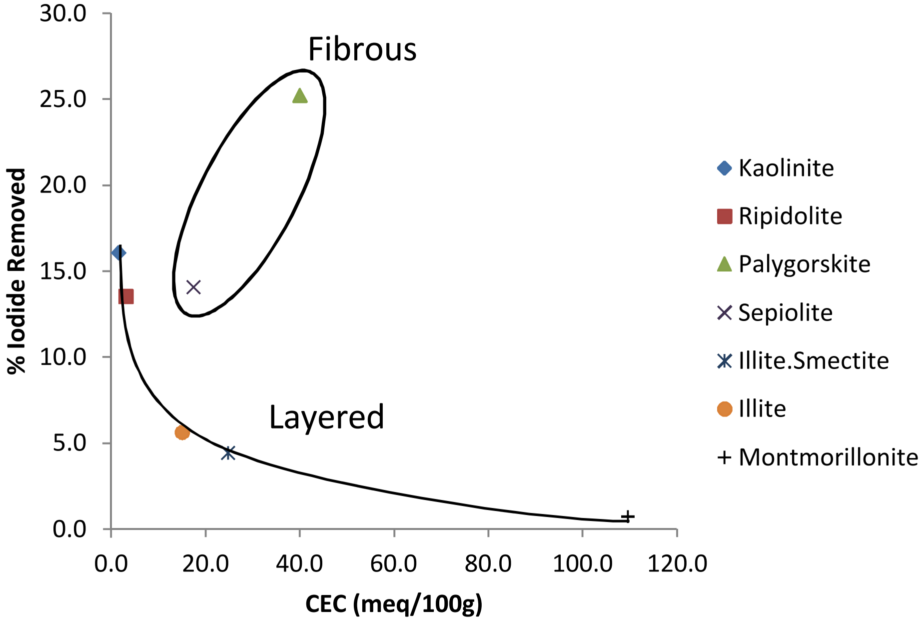
Future Work:

- Mathematical interpretation of iodide uptake as a function of ionic strength and fixed charge
- Diffusion experiments with varied clay minerals, compactions and ionic strengths/compositions

	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 removal trends vs. CEC are different for layered and fibrous clays.



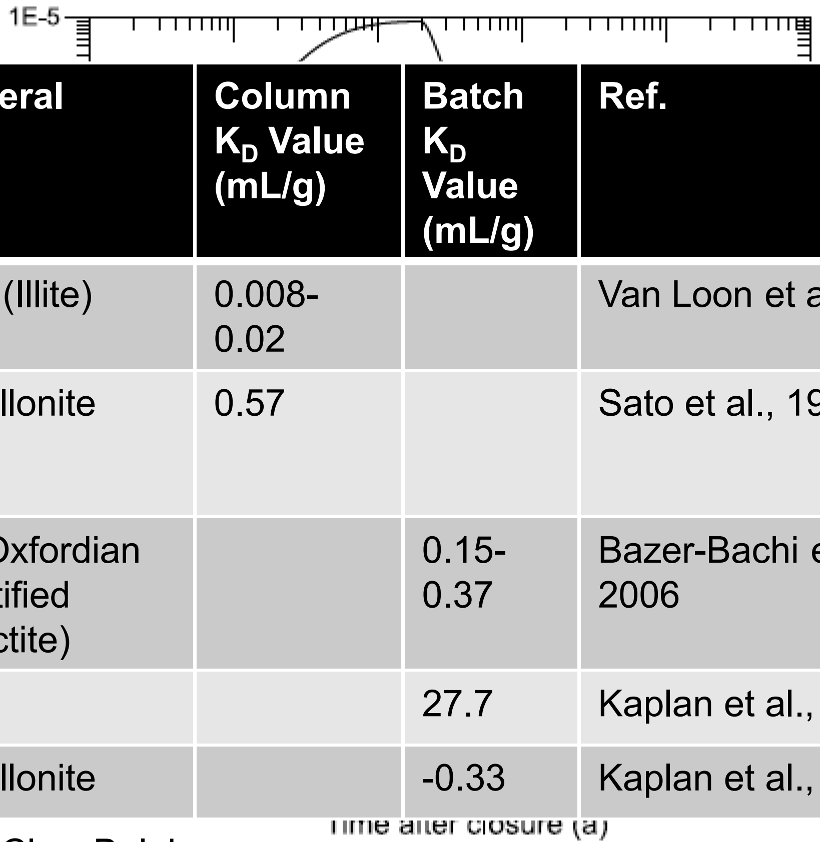
$$K^{eff} = K^0 \exp[-(k_B T)^{-1} \Sigma \upsilon_i (\Delta F_e + \Delta F_h)$$

$$\Delta F_h = \frac{z^2 e^2}{8\pi\epsilon_0 r_i}(\frac{1}{D} - \frac{1}{D_\infty})$$

Clay Mineral	Solid:Solution (g/L)	K_D values (mL/g)	
		Initial Spike Concentration	
		10.152mg/L	50mg/L
Illite	100	0.68	0.60
	66	0.54	0.42
Illite/Smectite	100	0.40	0.46
	66	0.37	0.50
Montmorillonite	100	-0.49	0.08
	66	-0.32	-0.19
Palygorskite	100	3.83	3.38
	66	3.35	3.71
Sepiolite	100	1.44	1.64
	66	0.39	1.47
Kaolinite	100	1.49	1.92
	66	2.40	2.61
Ripidolite	100	1.10	1.57
	66	1.37	1.67

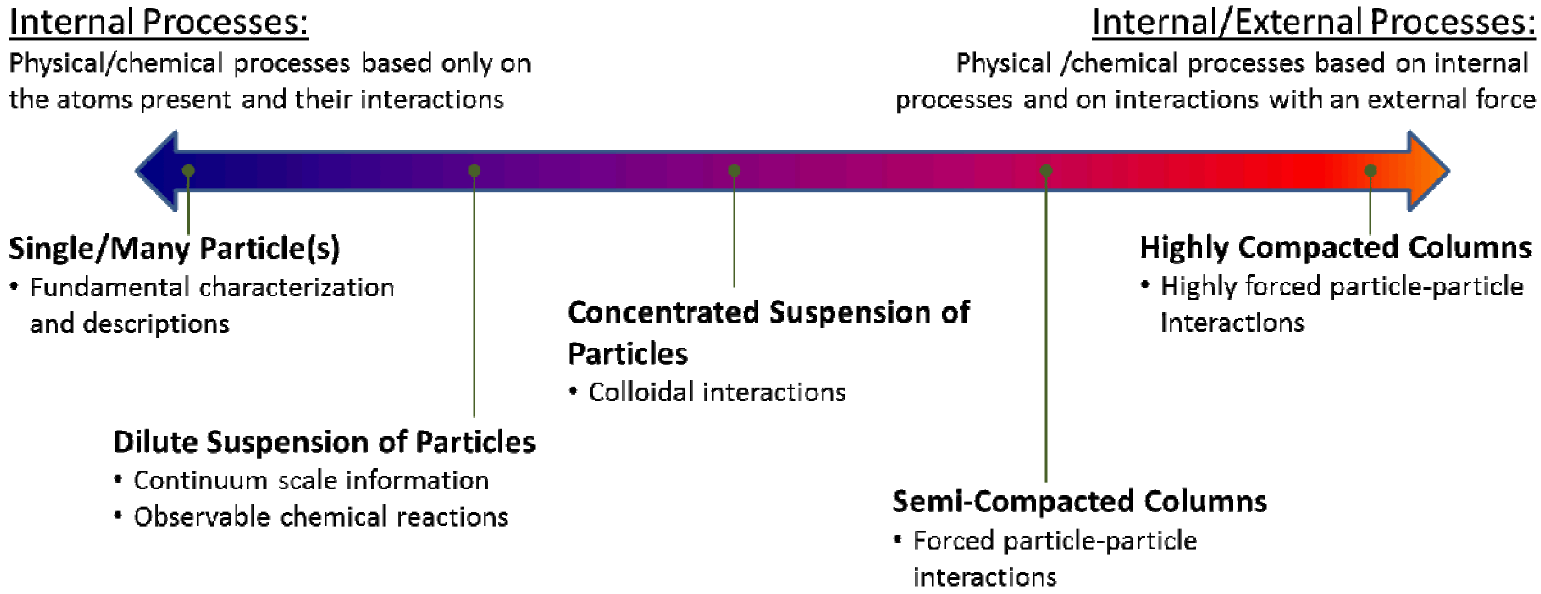
Iodine behavior in clays is uncertain.

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



Boom Clay, Belgium
Mallants et al., 2001. Journal of Nuclear Materials, 298, 125-135.

Particle-particle interactions create nano-environments



Internal Processes:
Physical/chemical processes based only on the atoms present and their interactions

Internal/External Processes:
Physical /chemical processes based on internal processes and on interactions with an external force

Single/Many Particle(s)
- Fundamental characterization and descriptions

Dilute Suspension of Particles
- Continuum scale information
- Observable chemical reactions

Concentrated Suspension of Particles
- Colloidal interactions

Semi-Compacted Columns
- Forced particle-particle interactions

Highly Compacted Columns
- Highly forced particle-particle interactions

- As solids concentration increases chemical (and charge) environment changes
  - Single/Many Particles: No particle-particle interactions (by definition)
  - Dilute Suspensions: No particle-particle interactions (by assumption)
  - Concentrated Suspensions: DLVO type interactions, possible polymerization of clay particles
  - Semi-Compacted Column: Overlapping double layers
  - Highly-Compacted Columns: Overlapping double layers and compression of the interparticle space

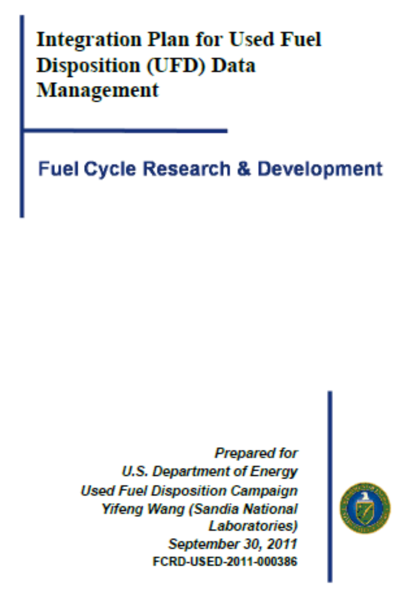
Miller, A.W., Wang, Y. (2012). *Environ.Sci. Technol.* **DOI:** 10.1021/es203025q.

Used Fuel Disposition Campaign

UFD Data Management and Integration

Yifeng Wang & Carlos Jove-Colon

US-ROK Joint Fuel Cycle Studies
SNL, June 6, 2012

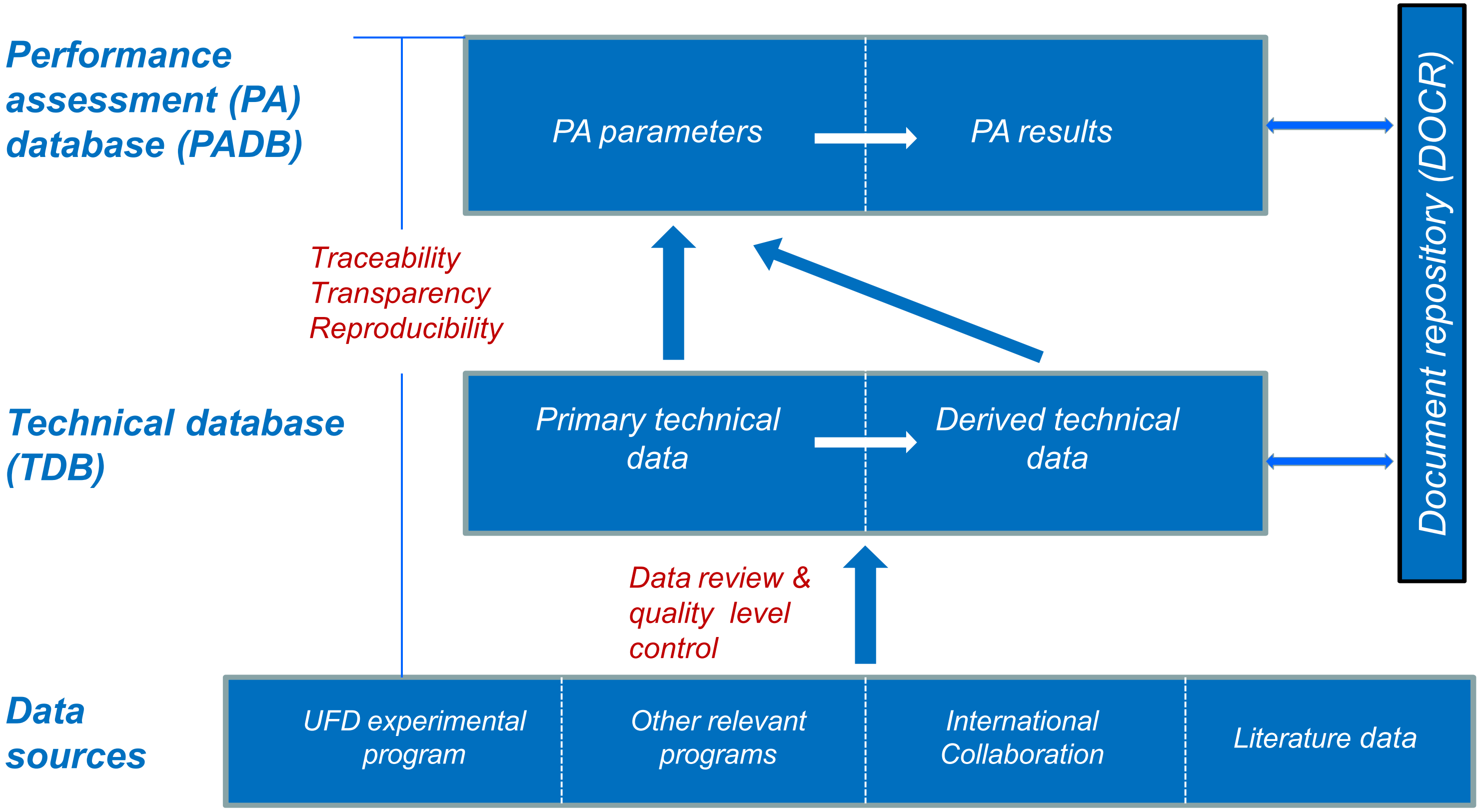


Integration Plan for Used Fuel Disposition (UFD) Data Management

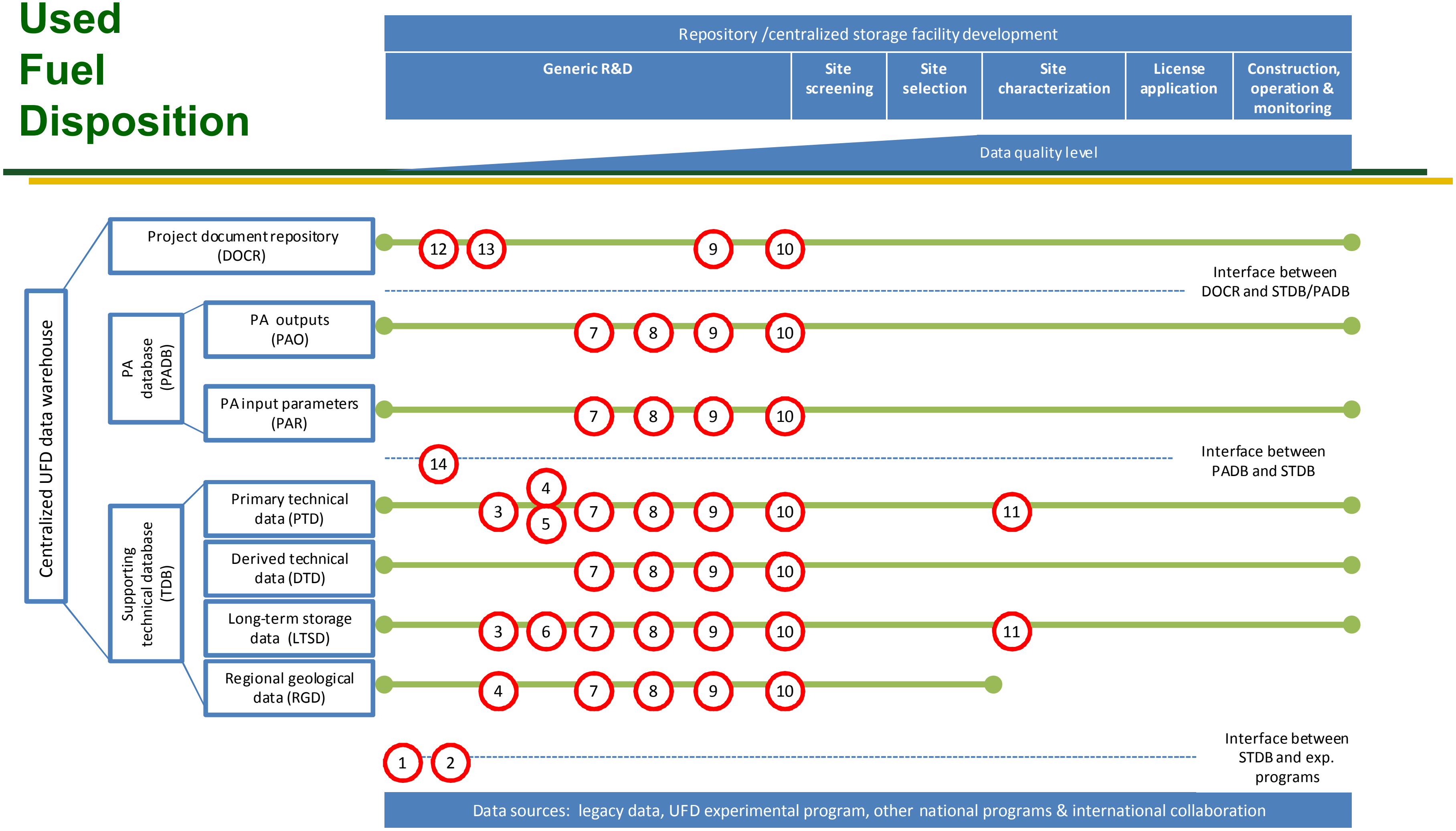
Fuel Cycle Research & Development

Prepared for
U.S. Department of Energy
Used Fuel Disposition Campaign
Yifeng Wang (Sandia National Laboratories)
September 30, 2011
FCRD-USED-2011-000386

General Architecture of UFD Data Management

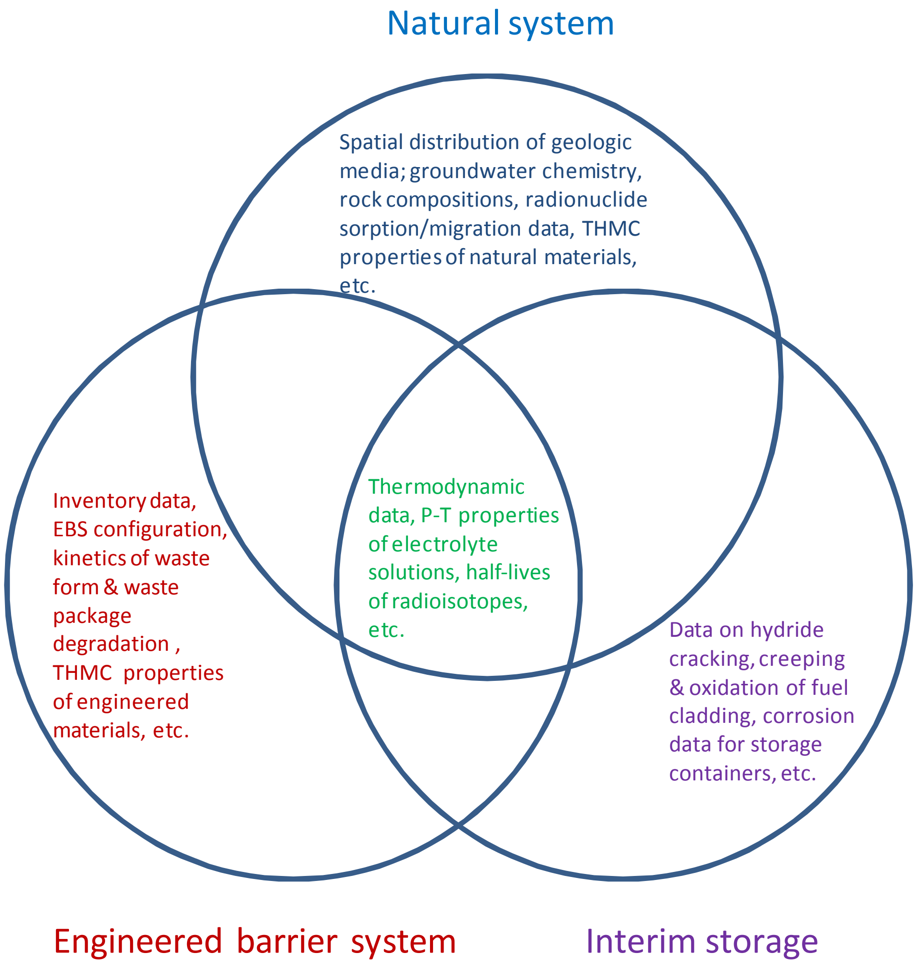


Used Fuel Disposition



1. Establishing consistent testing conditions
2. Quality control for technical data entry
3. Collection of common data blocks
4. Collection of natural system data
5. Collection of EBS data
6. Collection of long-term storage data
7. Data model development & DB design
8. Infrastructure setup
9. Configuration management
10. Data migration
11. Collecting & archiving site-specific data
12. Establishing a document repository
13. Archiving UFD docs
14. Development of PADB-STDB interface

Common Data



Natural system

Spatial distribution of geologic media; groundwater chemistry, rock compositions, radionuclide sorption/migration data, THMC properties of natural materials, etc.

Inventory data, EBS configuration, kinetics of waste form & waste package degradation , THMC properties of engineered materials, etc.

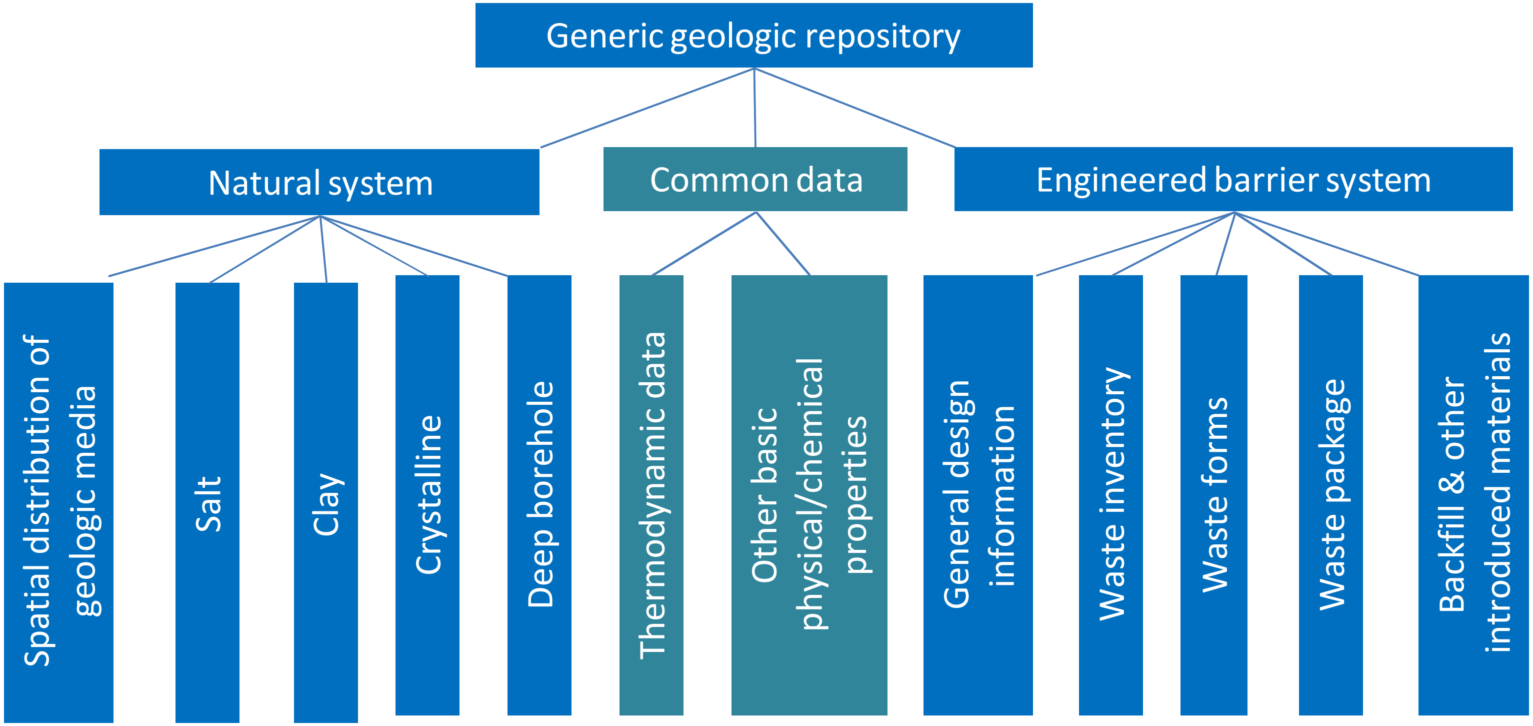
Thermodynamic data, P-T properties of electrolyte solutions, half-lives of radioisotopes, etc.

Data on hydride cracking, creeping & oxidation of fuel cladding, corrosion data for storage containers, etc.

Engineered barrier system

Interim storage

Data Arrangement



Generic geologic repository

- Natural system
  - Spatial distribution of geologic media
  - Salt
  - Clay
  - Crystalline
  - Deep borehole
- Common data
  - Thermodynamic data
  - Other basic physical/chemical properties
- Engineered barrier system
  - General design information
  - Waste inventory
  - Waste forms
  - Waste package
  - Backfill & other introduced materials

Current Status: Data Collection, Archiving & Synthesis

- Collection & synthesis of key technical data
  - Comprehensive literature review of radionuclide interactions with clays (Miller & Wang, 2012, ES&T)
  - Key parameter values for THMC modeling of the near field of a clay repository (LBNL)
  - Sorption data
    - JAEA-SDB/DDB Sorption and Diffusion Database Compilation (Tachi et al. 2009, 2011)
      - 28,540 Kd values; 350 reference sources
      - Materials: Clay and other minerals, Rock (granite, mudstone, etc.), cementitious
      - QA Evaluation Criteria: (I) Completeness - documentation, (II) Quality, (III) Consistency
      - Web-based
    - KAERI Sorption Database (Int. Collaboration with South Korea)
    - RES^{3}T - Rossendorf Expert System for Sorption Thermodynamics
  - Thermodynamic data for clay & cementitious mineral phases
    - Part of the EBS work package activity:
      - Clay: Data, methods, and approaches used in the YMP thermodynamic DB development
      - Cement: Synthesis of YMP and CEMDATA07 (Europe) cement thermodynamic data
      - Implementation of solid solution model for cement leaching and clay hydration
- Initial establishment of a sharepoint site as a repository
- Integration & communications among work packages
- Initiating US-ROK JFCS on thermodynamic database development