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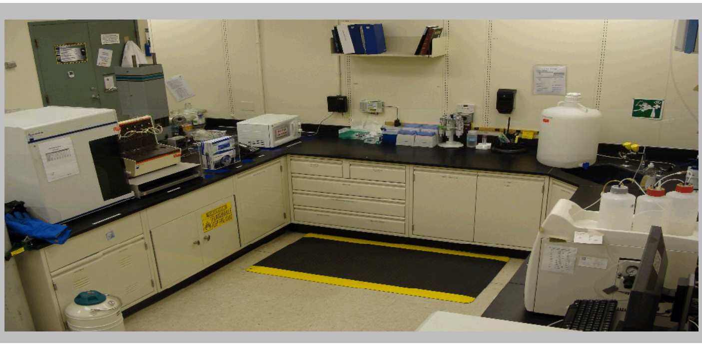
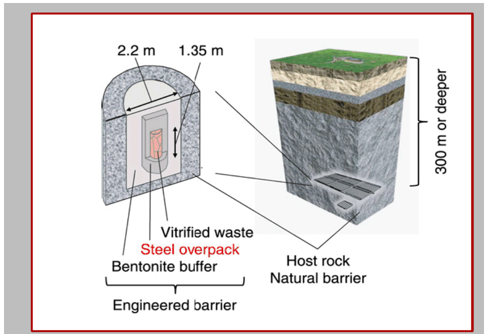
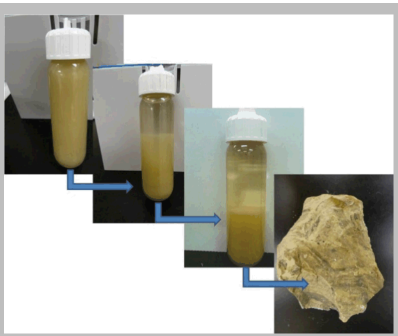






Capturing and Immobilizing Radioactive Nuclei Using Organic Materials

J. Kruichak, A. Miller, M. Mills, and Y. Wang

Agenda

- About me
- Lab capabilities
- Iodine uptake by negatively charged clay interlayers? Publication
- Methods for capturing and immobilizing radioactive nuclei with metal fluorite inorganic material. Patent

About me

- I have been working at Sandia National Labs for 7 years
- I have been in the department- Nuclear waste disposal research and analysis throughout my 7 years
- I started as an undergraduate student
- B.S in chemistry and biology from UNM
- M.S in chemistry (concentration in biological chemistry) from UNM
- Continued working at Sandia as a graduate student
- I have been a staff member for 2.5 years

Publications/Patents

- Cowden Dahl, K., Dahl, R., **Kruichak, J**., Hudson, L. 2009. Neoplasia. 11(1208-1215).
- Miller, A., **Kruichak, J**., Mills, M., Wang, Y. 2015. Journal of Environmental Radioactivity. 147(108-114)
- Wang, Y. et al. September 2010. Development of a new generation of waste form for entrapment and immobilization of highly volatile soluble radionuclides.
- Bryan, C. Kr**uichak, J.** January 2016. NMSBA white paper. Evaluation of New Mexico lignites as a source for humic and fulvic acids.
- Wang, Y., Miller, A., Bryan, C., **Kruichak, J**., Methods of capturing and immobilizing radioactive nuclei with metal fluorite-based inorganic materials. April 2015. Patent number: US9,000,250 B1
- Wang, Y., Miller, A., Bryan, C., **Kruichak, J**., Methods of capturing and immobilizing radioactive nuclei with metal fluorite-based inorganic materials. November 2015. Patent number: US9,180,428 B1

Conference presentations

- American Chemical Society Fall 2016 national meeting. August 2016. Philadelphia, PA. **Co-author**. Reactivity of Fe(III) in the octahedral sheet of natural and synthetic Fe-phyllosilicates: XAS study.
- American Chemical Society Fall 2016 national meeting. August 2016. Philadelphia, PA. **Author.** Mineralogical alteration of Mancos shale under conditions relevant to unconventional gas reservoirs.
- Used Fuel Disposition (UFD) working group meeting. June 2016. Las Vegas, NV. **Co-author**. Thermal treatment of clay minerals.
- Used Fuel Disposition (UFD) working group meeting. June 2016. Las Vegas, NV. **Author**. Investigation of the thermal effects on the settling behavior of clay mineral particles.
- American Geophysical Union (AGU) Fall meeting. December 2015. San Francisco, CA**. Co-author.** Characterization of heat-treated clay minerals in the context of nuclear waste disposal.
- American Geophysical Union (AGU) Fall meeting. December 2015. San Francisco, CA. **Author.** Alteration of Mancos shales by synthetic hydrofracturing fluid.
- Goldschmidt conference. August 2015. Prague, Czech Republic. **Co-author**. ?Switching of? Fe(III) in the octahedral sheet of Fe-phyllosilicate.
- American Chemical Society Spring 2015 national meeting. March 2015. Denver, CO. **Co-author.** Controls of the reactivity of clay structure Fe(II)/Fe(III) redox couple.
- Shales at all scales workshop. June 2015. Santa Fe, NM. **Co-author**. Fundamental study of disposition and release of methane in shale gas reservoir: experimental studies.
- BES geosciences research PI meeting. May 2014. Gaithersburg, MD. **Co-author.** Reactivity of structural iron in natural nontronite and synthetic Fe-phyllosilicate.
- Used Fuel Disposition (UFD) working group meeting. June 2014. Las Vegas, NV. **Co-author.** Sorption capacity in clay minerals for UFD applications.
- Clay mineral society 51st annual meeting. May 2014. College Station, TX. **Co-author**. Investigation the SORPTION CAPACITY of clay minerals for applications in nuclear waste repository design.
- Goldschmidt conference. June 2014. Sacramento, CA. **Co-author**. Reactivity of structural iron in natural nontronite Nau-1 and synthetic Fe phyllosilicate.
- International high level radioactive waste meeting. April 2013. Albuquerque, NM. **Co-author.** Iodide interaction with negatively charged interlayers?
- American nuclear society international high-level radioactive waste management meeting. May 2013. Albuquerque, NM. **Co-author.** Iodide uptake onto clay minerals and the relationship to fixed charge.
- American Chemical Society Fall 2012 national meeting. March 2012. San Diego, CA. **Author**. New generation of adsorbent materials for entrapping and immobilizing highly mobile radionuclides.
- Waste management meeting. March 2012. Phoenix, AZ. **Co-author**. Iodine interactions with clay and the relationship to surface charge and clay structure.
- American Geophysical Union (AGU) Fall meeting. December 2012. San Francisco, CA**. Co-author.** Iodide interaction with clay minerals: a novel uptake mechanism.
- Goldschmidt conference. June 2012. Montreal, Canada. **Co-author.** Iodide and Iodate interactions with clay minerals.

Lab operations coordinator

- Aside from R&D I manage wet chemistry and geochemistry laboratories

Provide a safe environment for students and other staff members to conduct their research

Lab operations coordinator

Radioactive materials laboratory management as well

ELSEVIER

Journal of Environmental Radioactivity

Volume 147, September 2015, Pages 108–114

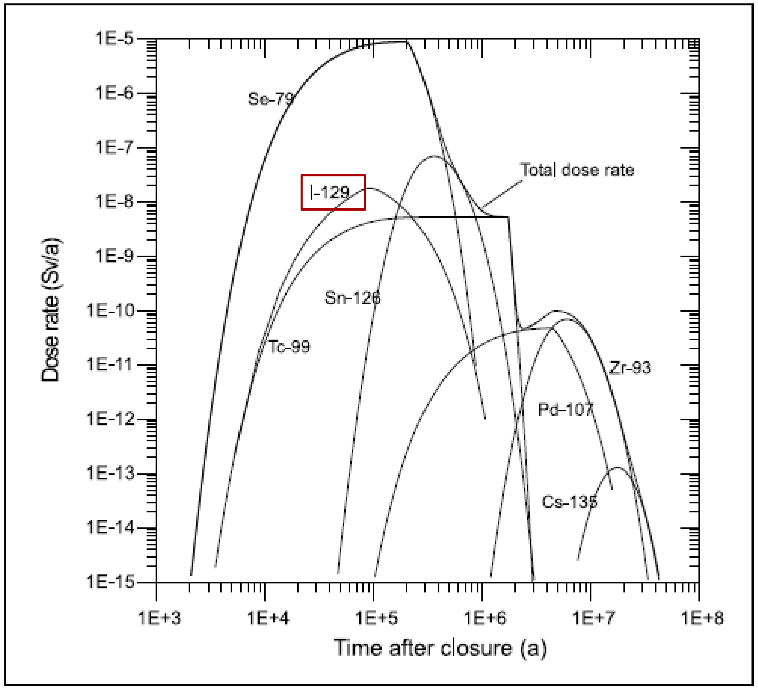
Iodide uptake by negatively charged clay interlayers?

Andrew Miller[a], Jessica Kruichak[b], Melissa Mills[b], Yifeng Wang[b]

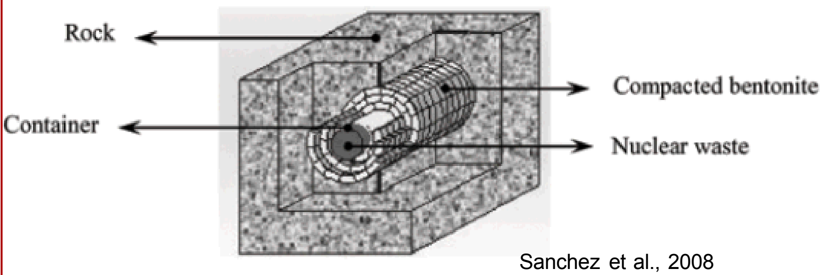
Why focus on iodide interactions with clays?

- Subsurface clay formations are the major rock types being considered by several countries for geological disposal of nuclear waste as disposal media or engineered barriers

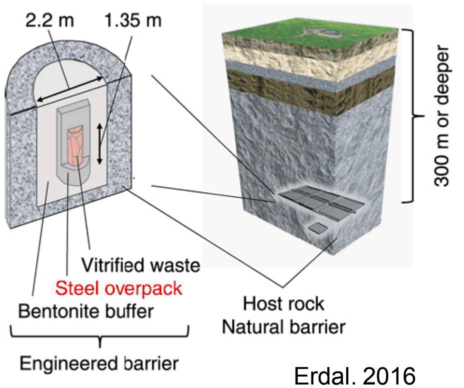
- Clays are ideal materials as they possess low permeabilities and high cation sorption/exchange capacity



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



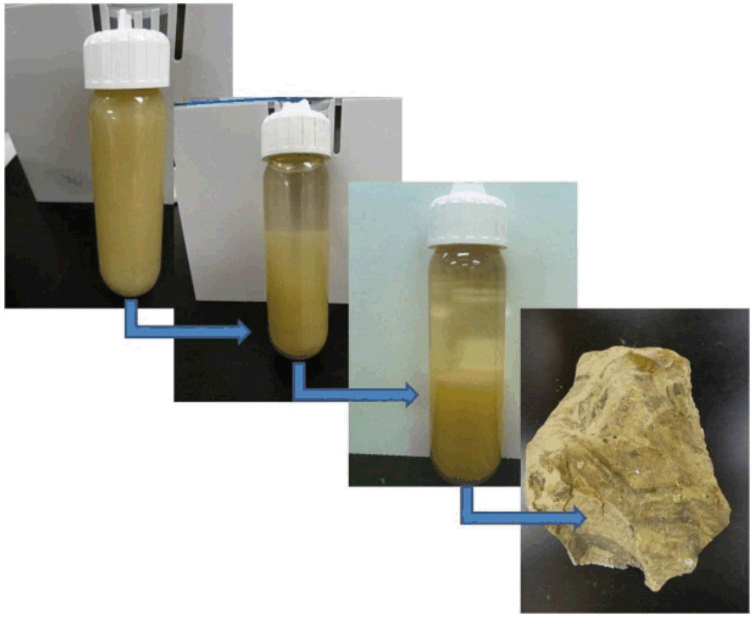
Sanchez et al., 2008



Erdal. 2016

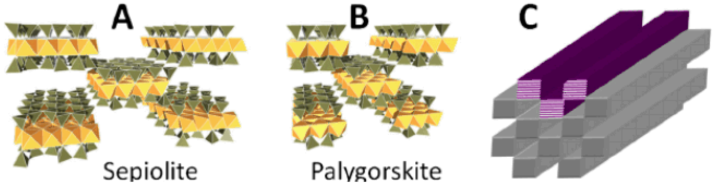
Goal

- In this study we focus on a series of clay minerals and measure iodine uptake under several swamping electrolyte strengths and compositions
- Uptake will be reported as a function of lattice substitution (CEC) and clay structure (fibrous vs. layered clays)

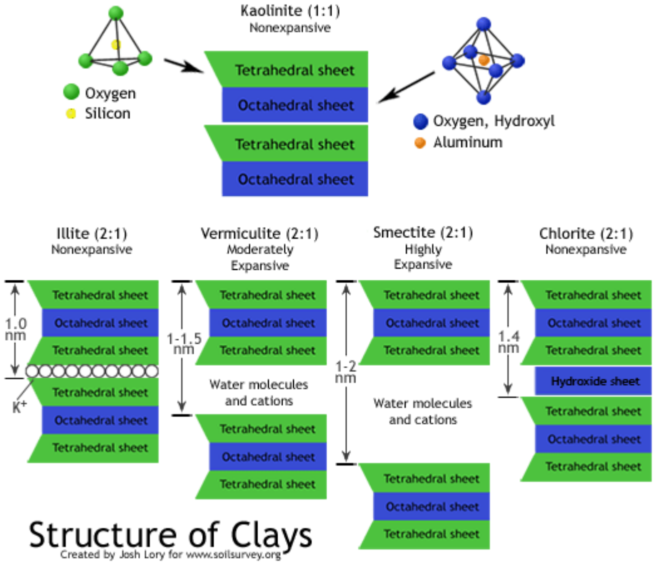


Clay

- Clays are silica (tetrahedral) and alumia (octahedral) sheets
- 7 total clays were used:
- Fibrous: sepiolite and palygorskite



- Layered: Kaolinite, ripidiolite, illite, montmorillonite, and illite/smectite mixed layer



Structure of Clays

Created by Josh Lory for www.soilsurvey.org

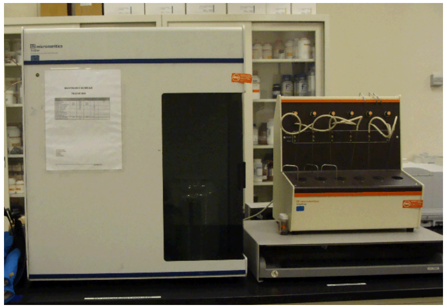
http://soils.missouri.edu/tutorial/page8.asp

Experimental Plan

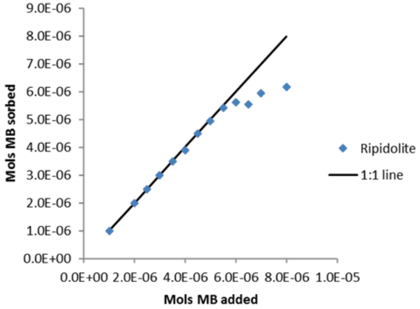
- Surface area determinations
- Cation exchange capacity (CEC)
- Iodine sorption experiments

Surface area determinations

- BET (NAD)- Using N2 gas represents the external surface area of the clay
  (N2 unable to enter the interlayers)



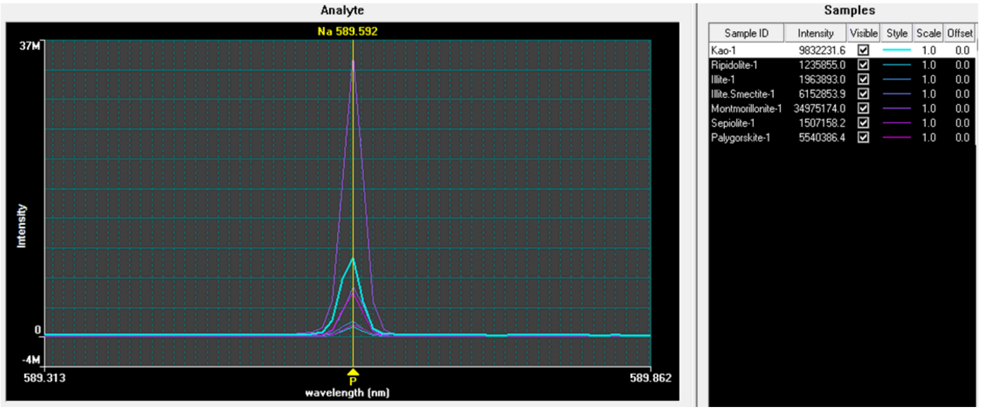
- Methylene Blue adsorption- represents the total surface area (aqueous solutions where the clays can de-laminate)
  - Requires sodium exchanged clays
  - Solid:liquid ratio (20g/L) varying MB concentration
  - Measure MB uptake using UV-vis (660nm)
  - Sorption isotherms are plotted, and the surface is assumed to be saturates at the point where the isotherm shifts from being linear



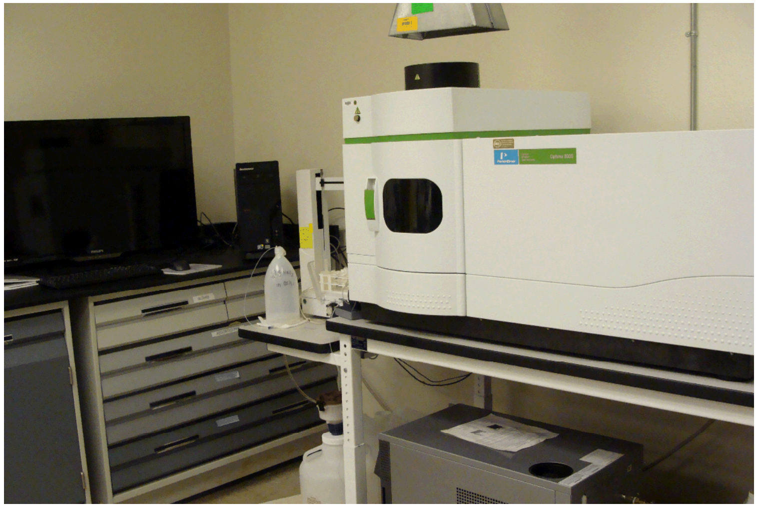
- Internal surface area- Methylene blue SA minus BET SA

Cation exchange capacity

- Barium exchange- Barium is added in excess 0.1M BaCl2 to a clay slurry (solid:solution= 6.25g/L) displacing all native cations
- Major cations- Na, Ca, K, Mg, Fe- exchange capacity determined
- Cations measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES)

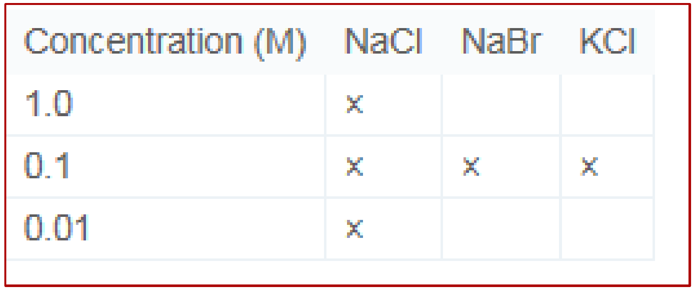


Sample ID	Intensity	Visible	Style	Scale	Offset
Kao-1	9832231.6	☑	—	1.0	0.0
Ripidolite-1	1235855.0	☑	—	1.0	0.0
Illite-1	1963893.0	☑	—	1.0	0.0
Illite.Smectite-1	6152853.9	☑	—	1.0	0.0
Montmorillonite-1	34975174.0	☑	—	1.0	0.0
Sepiolite-1	1507158.2	☑	—	1.0	0.0
Palygorskite-1	5540386.4	☑	—	1.0	0.0

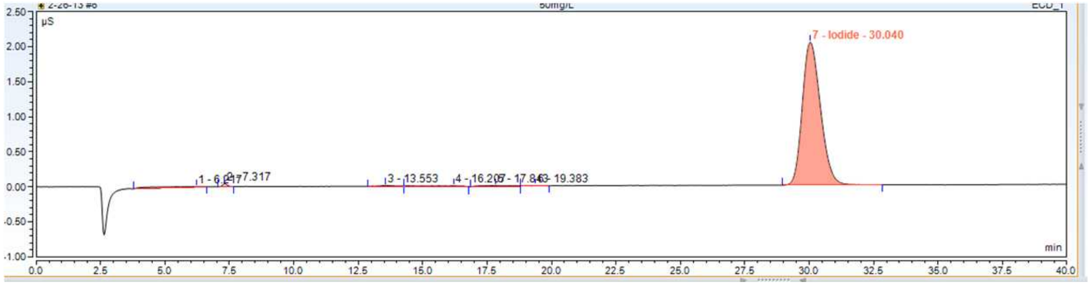


Iodine sorption experiments

- Batch reactors:
  - In 50mL centrifuge tubes
  - Clay in electrolyte solutions with a solid: solution ratio of 100g/L
  - Equilibrate overnight
  - Spiked with IC (ion chromatography iodide standard) 50mg/L
  - 7 day reaction time in the dark at room temperature
  - Centrifuged and supernatant was analyzed using Dionex 1100 ion chromatography (IC)
  - pH reading before iodide spike, after 7 days before and after centrifugation

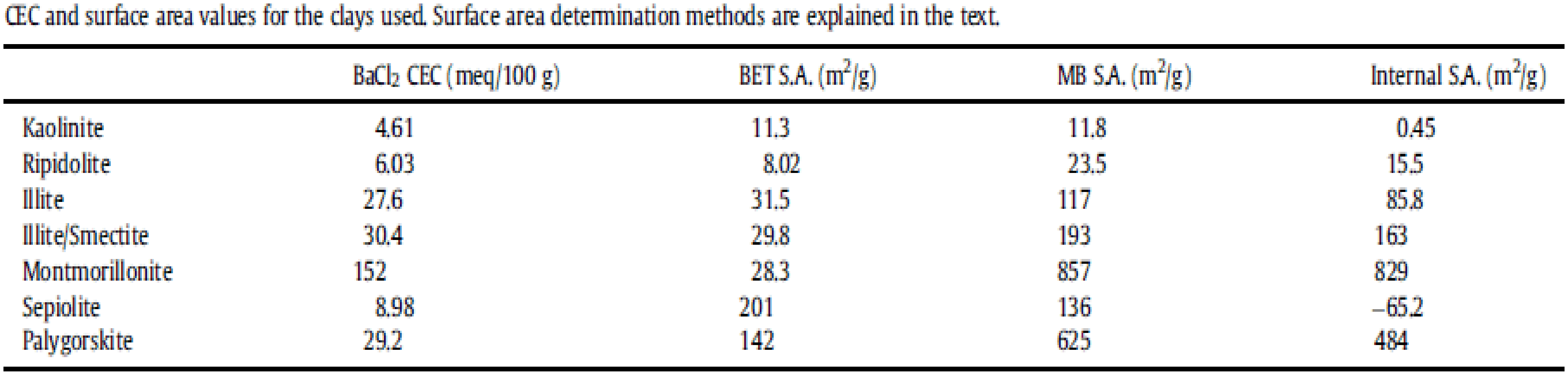


Concentration (M)	NaCl	NaBr	KCl
1.0	x		
0.1	x	x	x
0.01	x		



Results: surface area and CEC

- CEC and surface area determinations are in good agreement with published values approx. within a factor of 2
- Sepiolite is the one exception- negative internal surface area



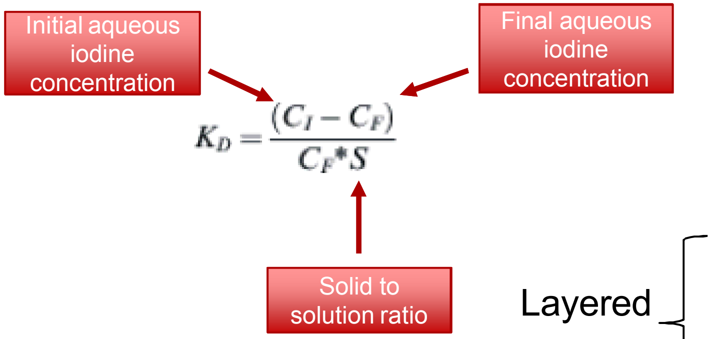
CEC and surface area values for the clays used. Surface area determination methods are explained in the text.

	$BaCl_2$ CEC (meq/100 g)	BET S.A. (m^2/g)	MB S.A. (m^2/g)	Internal S.A. (m^2/g)
Kaolinite	4.61	11.3	11.8	0.45
Ripidolite	6.03	8.02	23.5	15.5
Illite	27.6	31.5	117	85.8
Illite/Smectite	30.4	29.8	193	163
Montmorillonite	152	28.3	857	829
Sepiolite	8.98	201	136	–65.2
Palygorskite	29.2	142	625	484

Results Iodine uptake

Iodine uptake is dependent on ionic composition of swamping electrolyte

Solid: liquid partitioning coefficients (KD values, mL/g) were calculated using equation below

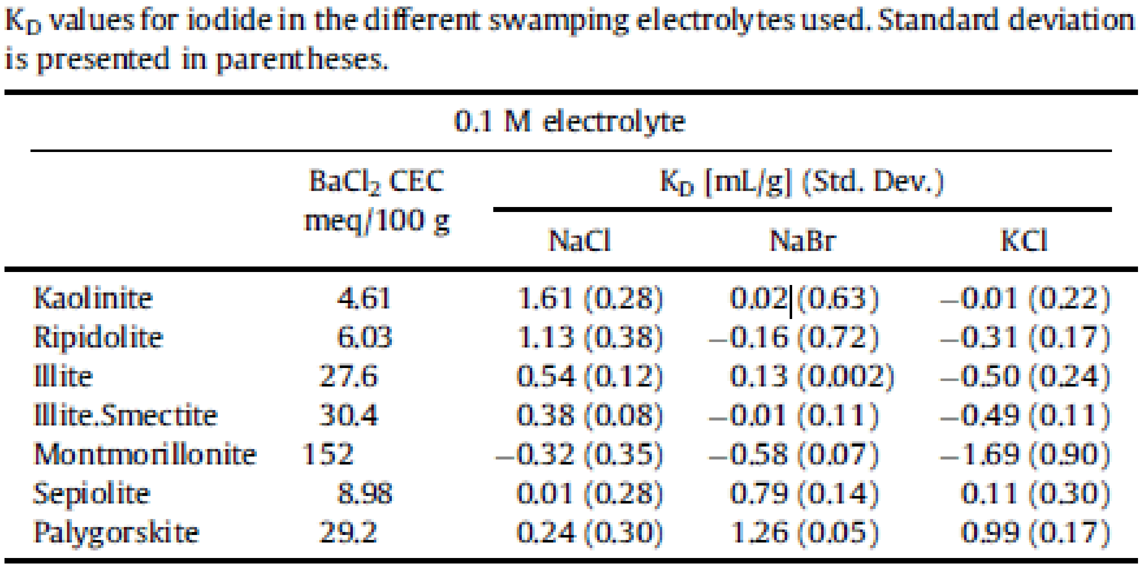


Initial aqueous iodine concentration

Final aqueous iodine concentration

$$K_D = \frac{(C_I - C_F)}{C_F{}^*S}$$

Solid to solution ratio

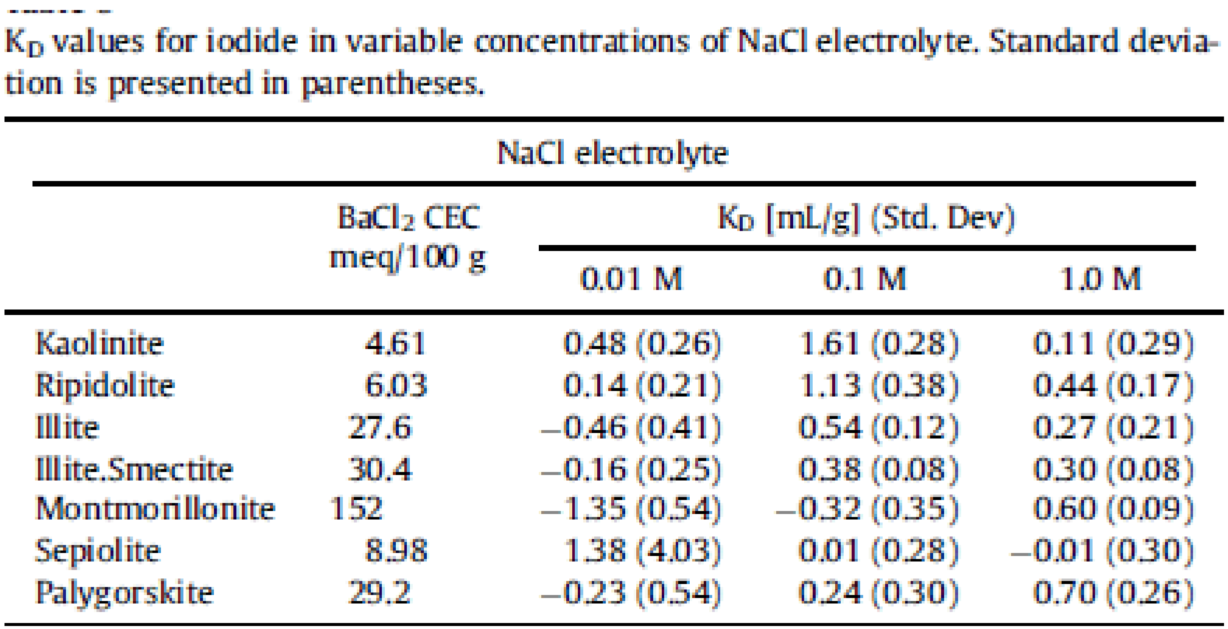


K_D values for iodide in the different swamping electrolytes used. Standard deviation is presented in parentheses.

	0.1 M electrolyte				
		$BaCl_2$ CEC meq/100 g	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	27.6	0.54 (0.12)	0.13 (0.002)	−0.50 (0.24)
	Illite.Smectite	30.4	0.38 (0.08)	−0.01 (0.11)	−0.49 (0.11)
	Montmorillonite	152	−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	29.2	0.24 (0.30)	1.26 (0.05)	0.99 (0.17)

Results- Iodide uptake

Iodine uptake depends on swamping electrolyte concentration



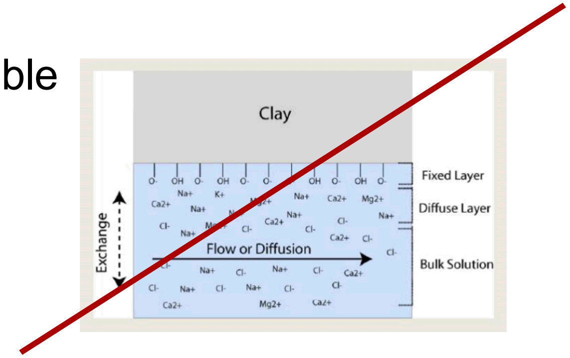
K_D values for iodide in variable concentrations of NaCl electrolyte. Standard deviation is presented in parentheses.

		NaCl electrolyte			
		BaCl$_2$ CEC meq/100 g	K_D [mL/g] (Std. Dev)		
			0.01 M	0.1 M	1.0 M
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	27.6	−0.46 (0.41)	0.54 (0.12)	0.27 (0.21)
	Illite.Smectite	30.4	−0.16 (0.25)	0.38 (0.08)	0.30 (0.08)
	Montmorillonite	152	−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	29.2	−0.23 (0.54)	0.24 (0.30)	0.70 (0.26)

Discussion

K_D relationship as a function of electrolyte composition:
Anion exchange mechanisim can be ruled out- iodide behavior would be similar for NaCl and KCl

Surface charge properties and the nature of the electrical double layer mechanism can be ruled out- iodide behavior would be expected to be similar between NaCl and NaBr
Underlying mechanism is dependent on the cation and anion present



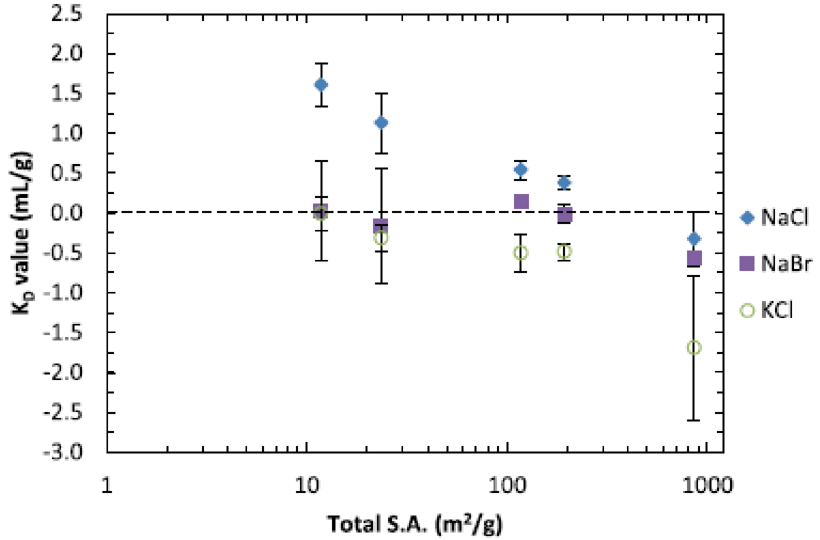


Fig. 1. K_D values for the layered clays as a function of the total surface area for the three electrolytes considered.

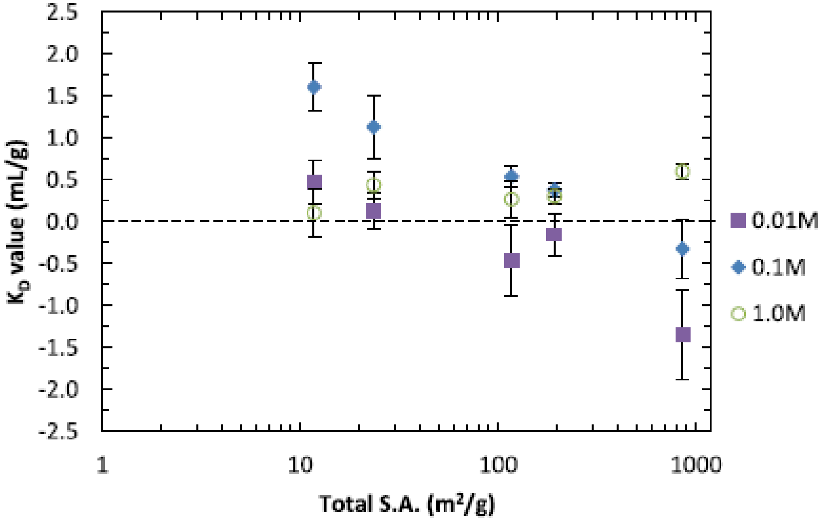
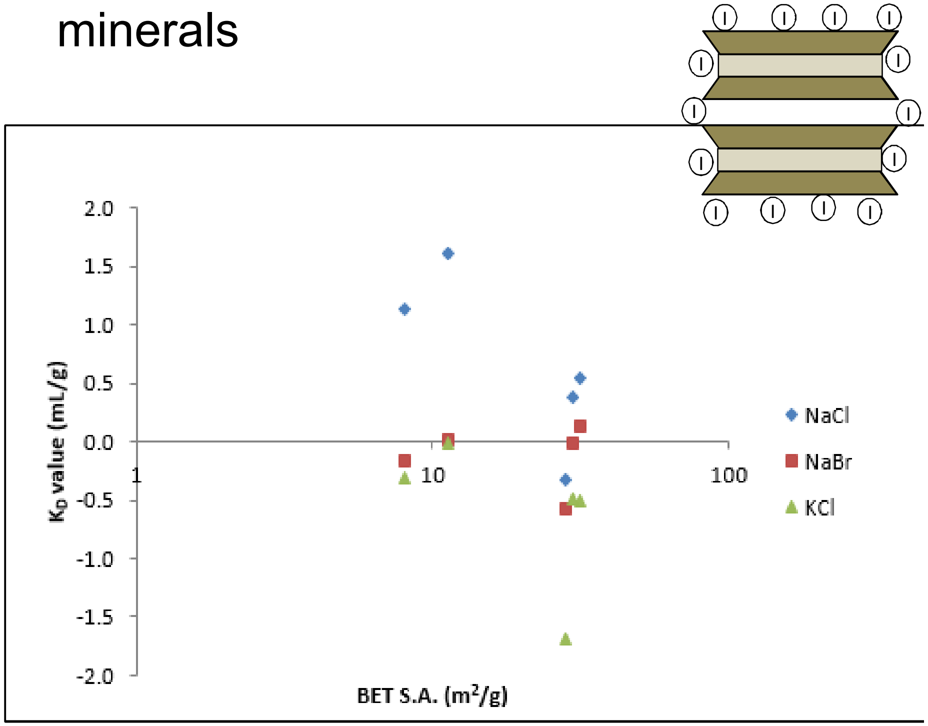


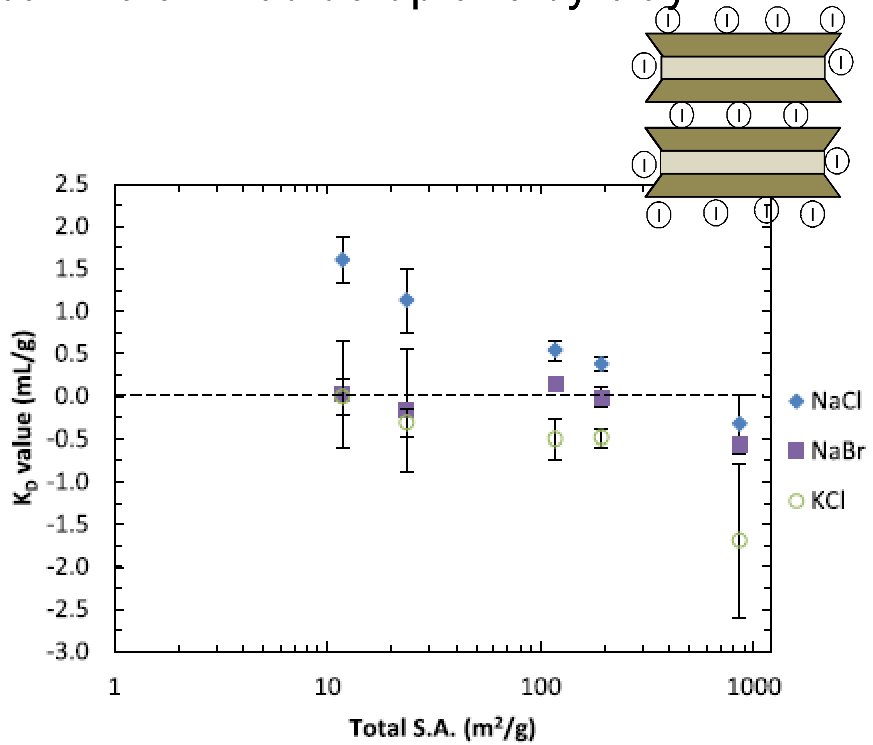
Fig. 2. K_D values for the layered clays as a function of total surface area for each of the NaCl concentrations used.

Discussion

The trend between K_D and CEC with total surface area and lack of trend with BET surface area suggest iodide interacts with the negatively charged sites in the interlayers

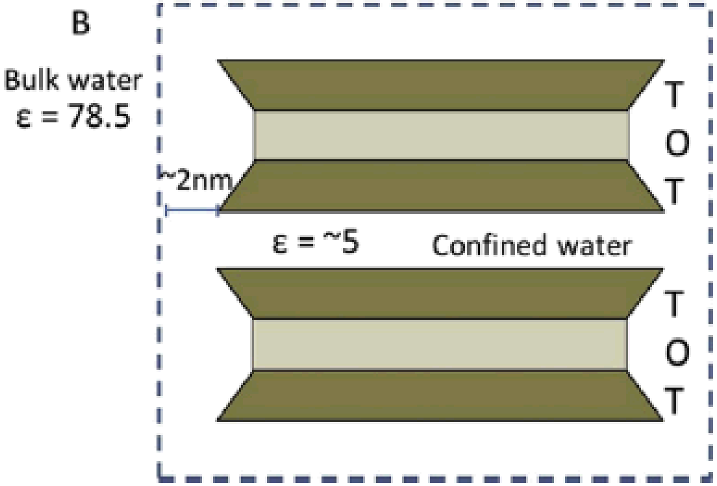
External surface sites do not play a significant role in iodide uptake by clay minerals





What about charge repulsion?

- Ion pair formation is increasing as the dielectric constant decreases (confined water vs. bulk).
- Clay interface (2nm) →confined structure →decrease in dielectric constant →ion formation favored
- Free iodide is less likely within the confined spaces of the clay interlayer



Iodide concentrations

- Halogen concentrations follow the Hofmeister series F<Cl<Br<I within the 2nm of the clay water interface.
- Bromide and iodine concentrations are higher at the interface than in the bulk
- It is more thermodynamically favored for the highly polarizable iodide to be present in areas where water is more structured

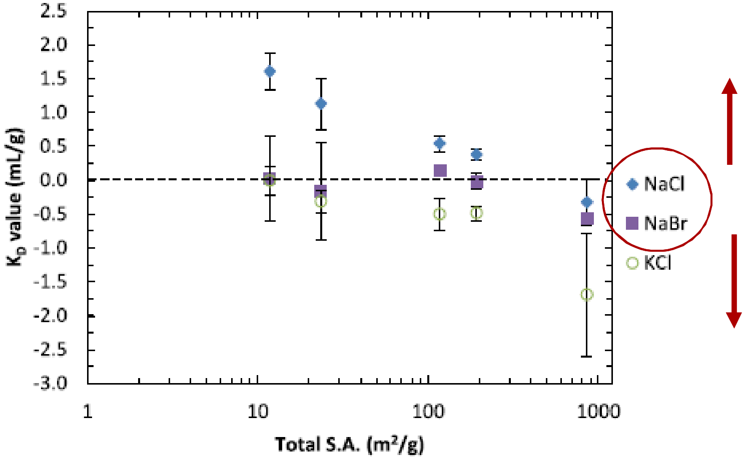
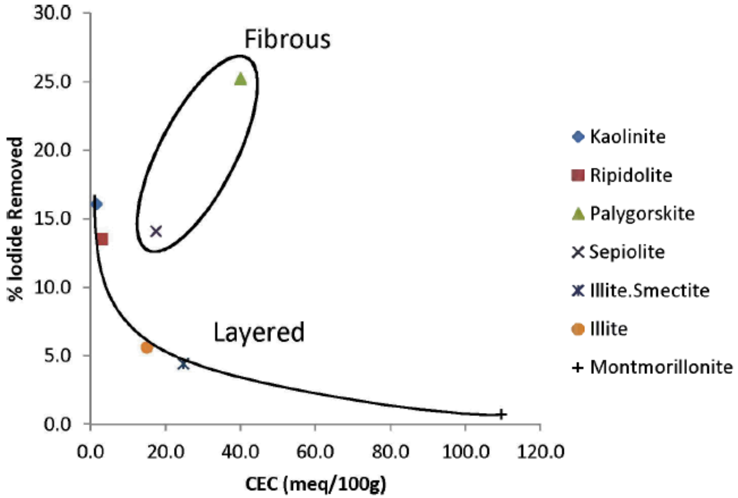
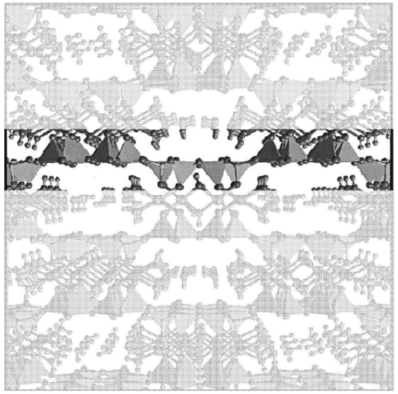


Fig. 1. K_D values for the layered clays as a function of the total surface area for the three electrolytes considered.

Clay structure differences

- Comparing uptake between palygorskite and sepiolite-based on charge exclusion less iodide uptake for the more highly negative palygorskite.
    - Palygorskite showed a higher uptake compared to sepiolite.
- Conformational differences between fibrous and layered clays and the different sizes of the pore channels may lead to variable water properties leading to increased uptake despite higher structural charge

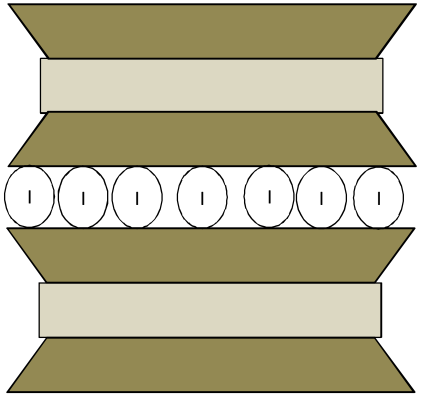




Fois et al., 2003. **Microporous and Mesoporous Materials**. 57, 263-272.

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

Project summary



- Data suggests unexpected interlayer concentration of iodide
- Iodide uptake is heavily related to CEC
    - For layered clays higher CEC (larger negative charge) led to smaller iodide sorption
- Iodide uptake is heavily related to ionic composition of electrolyte
- Iodide uptake is dependent on clay textures and structures

Current and future work on clay

- Investigate the thermal effects of the chemical behaviors of the clays (~300C- repository conditions)
- Diffusion experiment with varied clay minerals, compactions and ionic strengths/compositions
- Hydrothermal alteration of clay

Net positive surface charge; anion exchange

Net negative surface charge; cation exchange

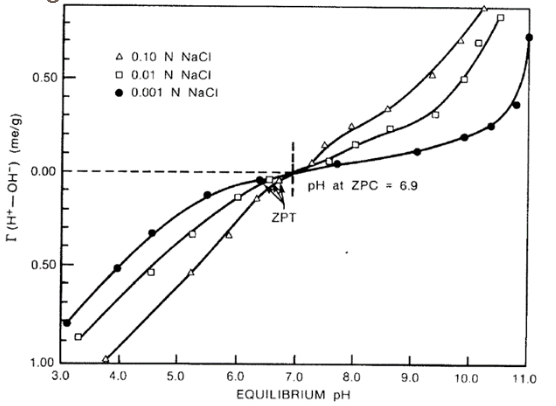
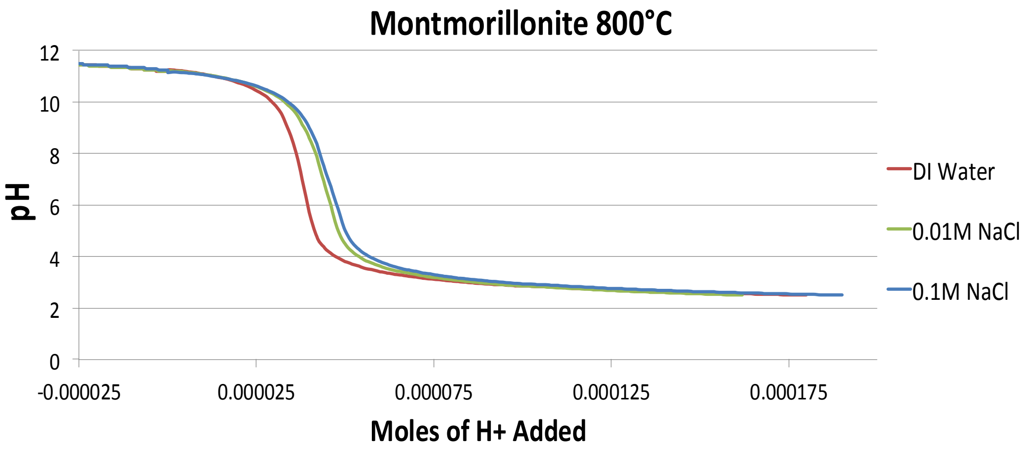


Figure 3.2. pH titration curve for amorphous hydrated iron oxide showing zero points of titration (ZPT) and zero point of charge (ZPC). (From Gast, 1977, Fig. 2.3).

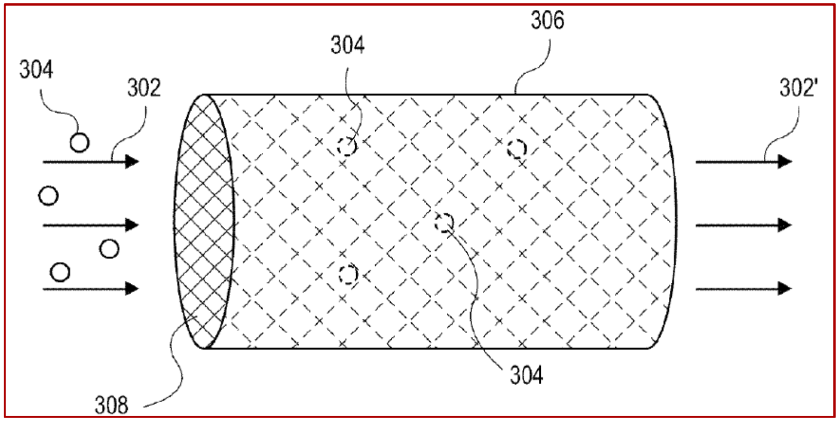


Patent- Background

- Concerns- Safe disposal and isolation of used fuels from reactors or waste streams from reprocessing plants
- ^{129}I and ^{99}Tc are highly mobile fission products produced from a fission processes
- They both have very long half lives
  - ^{129}I 15.7 million years
  - ^{99}Tc 211,000 years
- Can exist as gaseous or anionic species that are highly soluble and poorly sorbed.

Claim

- Includes flowing a gas stream through an exhaust apparatus. The exhaust apparatus includes a metal-fluorite based inorganic material. The gas stream includes a radioactive species. The radioactive species is removed from the gas stream by absorbing the radioactive species to the metal fluorite-based inorganic material.

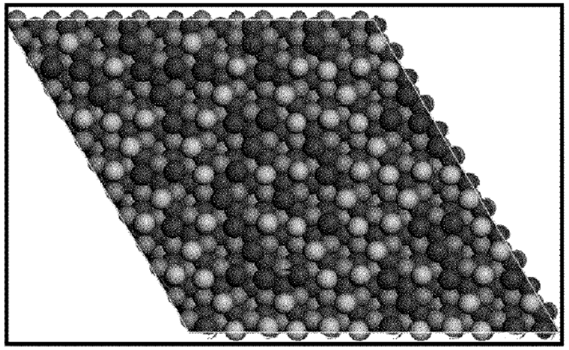


Radioactive species is captured by the metal fluorite-based inorganic material

306-exhaust apparatus
308-Metal fluorite-based inorganic material
304-Radioactive species (iodine)
302-gas stream

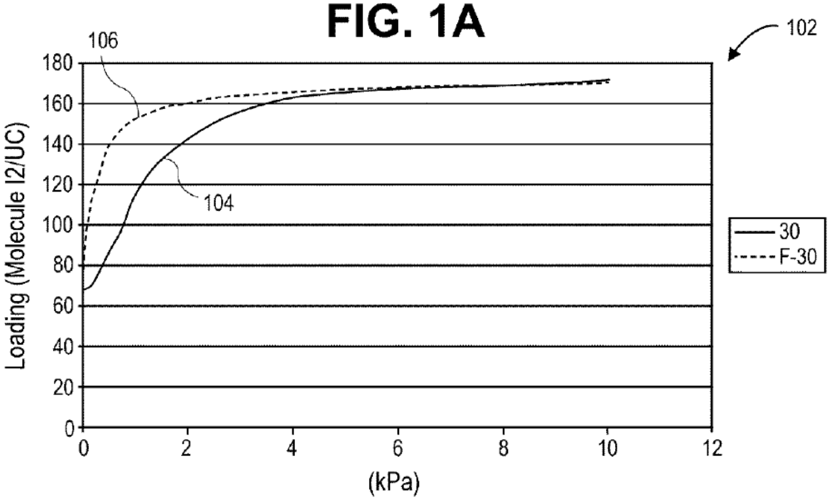
System simulations

- Grand Canonical Monte Carlo (GCMC) simulation of iodine gas adsorption on a modified ɣ-alumina (Al2O3) surface, in accordance with invention



60% Fluorinated alumina surface
Lightest balls- fluorine atoms
Dark balls- oxygen atoms
Intermediate balls- aluminum atoms

FIG. 1A



Modified material show improvement versus conventional oxide-based material with respect to radionuclide sorption

Synthesis

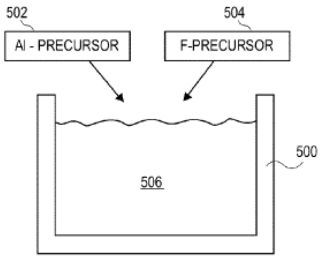


FIG. 5A

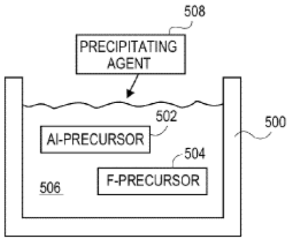
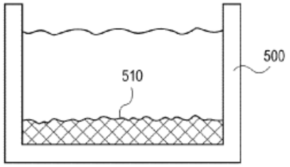


FIG. 5B



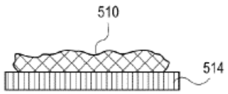


FIG. 5D

AlCl3 and trifluoroacetate in a water/ethanol solution

Precipitating agent is polyethylene oxide

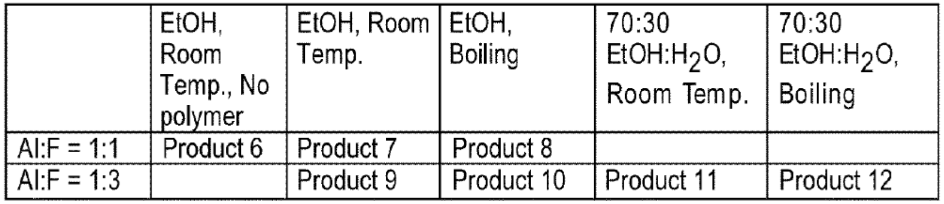
Filter and rinse with water and dry

Add block co-polymer (fabricate porosity) poly)ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)- know as P-123.

Calcine at 550°C to remove polymer

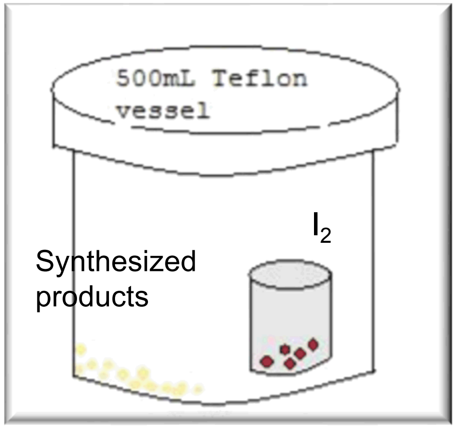
Results

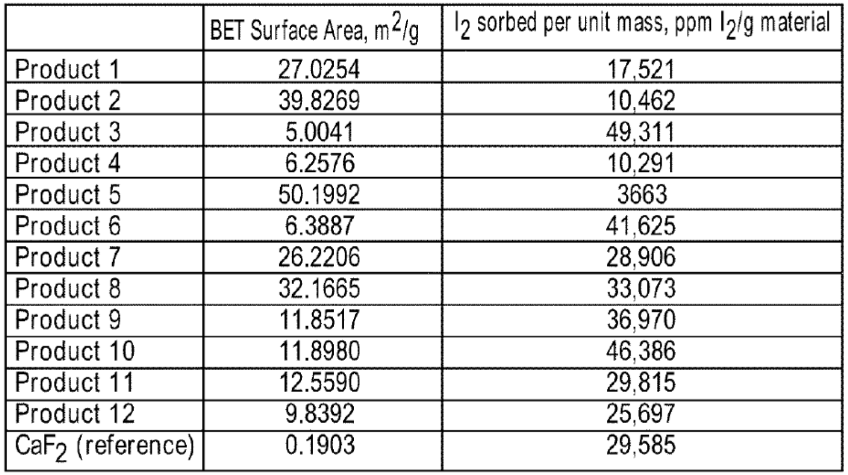
- Despite lower surface area in respect to Al-O material, the fluorinated compounds will outperform existing oxide-based adsorbents in total iodine removal



	EtOH, Room Temp., No polymer	EtOH, Room Temp.	EtOH, Boiling	70:30 EtOH:H_2O, Room Temp.	70:30 EtOH:H_2O, Boiling
Al:F = 1:1	Product 6	Product 7	Product 8		
Al:F = 1:3		Product 9	Product 10	Product 11	Product 12

90°C for 6 hours

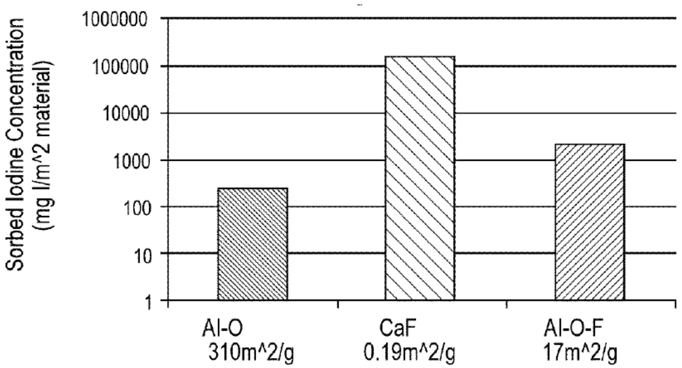




	BET Surface Area, m^2/g	I_2 sorbed per unit mass, ppm I_2/g material
Product 1	27.0254	17,521
Product 2	39.8269	10,462
Product 3	5.0041	49,311
Product 4	6.2576	10,291
Product 5	50.1992	3663
Product 6	6.3887	41,625
Product 7	26.2206	28,906
Product 8	32.1665	33,073
Product 9	11.8517	36,970
Product 10	11.8980	46,386
Product 11	12.5590	29,815
Product 12	9.8392	25,697
CaF_2 (reference)	0.1903	29,585

Project Summary

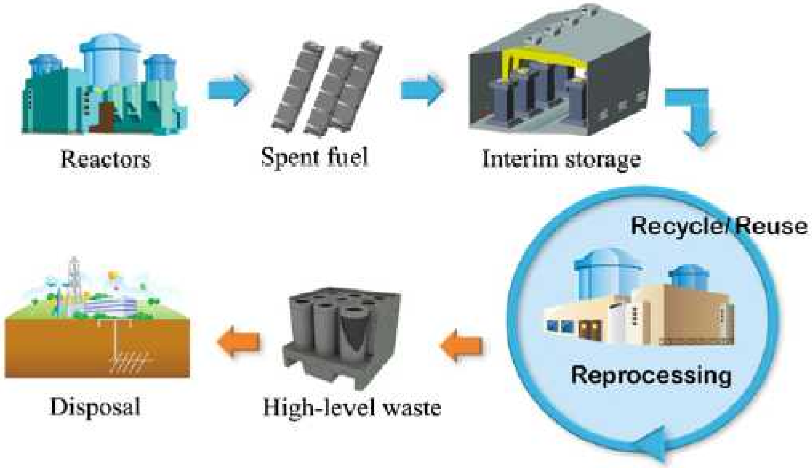
- This nanoporus aluminum fluorite represents a class of highly efficient materials for uptake of gaseous iodine.
- The high performance inorganic solid adsorbents may be applied to capturing gaseous radionuclides in:
  - Process operations of advanced fuel cycle from novel fuel concepts
  - Off-gas treatment of used fuel reprocessing
  - Nuclear waste disposal
- Potentially used to capture, separate, and immobilize non-radioactive chemicals.



UFD now SFWST (Spent Fuel and Waste Science and Technology)

- The U.S. Department of Energy Office of Nuclear Energy (DOE-NE), Office of Fuel Cycle Technology (OFCT) has established the Used Fuel Disposition Campaign (UFDC) to conduct the research and development (R&D) activities related to storage, transportati and disposal of used nuclear fu (UNF) and high level nuclear waste (HLW).

The objective of the Crystalline Disposal R&D Work Package is to advance our understanding of long-term disposal of used fuel in crystalline rocks and to develop necessary experimental and computational capabilities to evaluate various disposal concepts in such media.



Kim, J. et al 2011.

Thank you for your time

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