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Adsorption and Desorption of Cesium in Clay Minerals:

Effects of Natural Organic Matter and pH

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Outline

- Introduction & Methodology
- Cs Adsorption
- Cs Desorption
- Future work

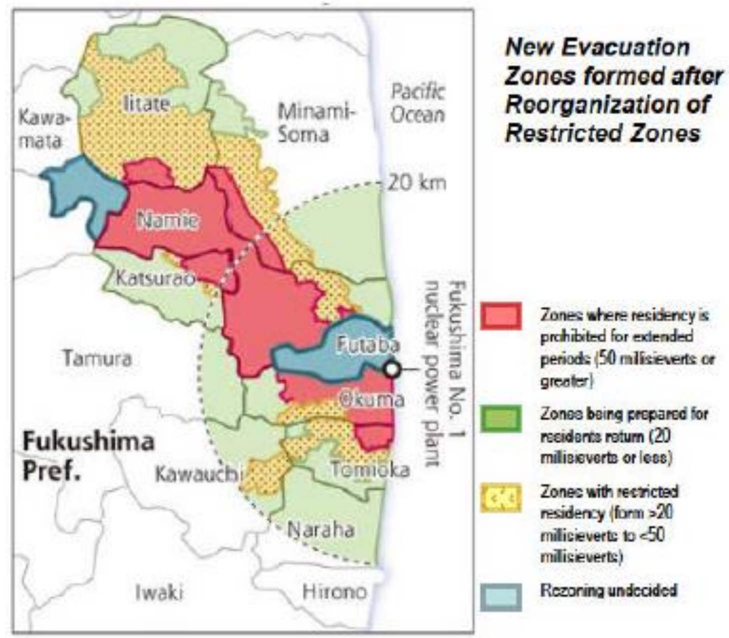
Cs Release into Environment

- Radioactive material released into the environment due to accidents and/or testing , resulting in soil contamination over large areas

  - Remediation efforts to cleanup seawater, groundwater, and cesium-contaminated soils

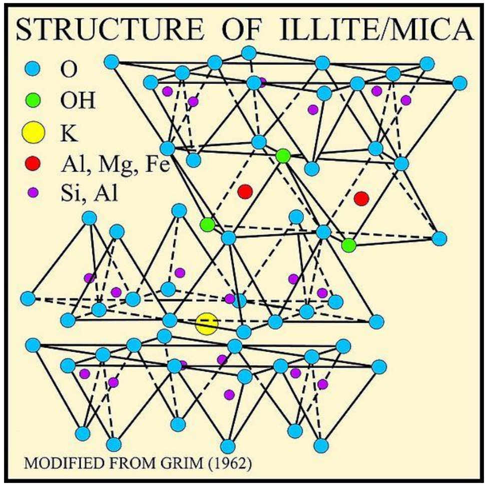
  - The fate and transport of Cs in the environment depends on clay mineral type and content, pH, temperature, ionic strength, and natural organic matter (NOM)

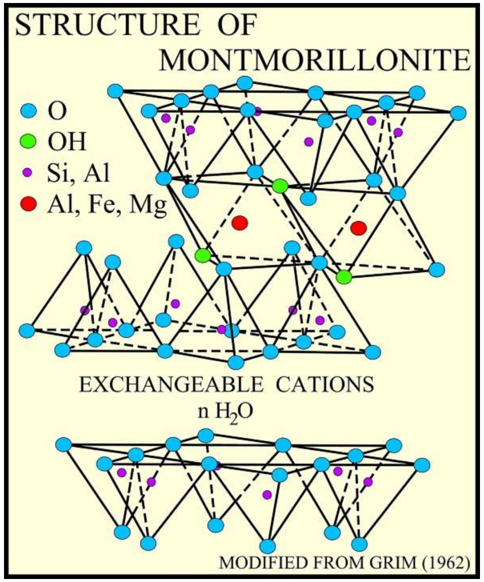
Contaminated zones due to the Fukushima accident

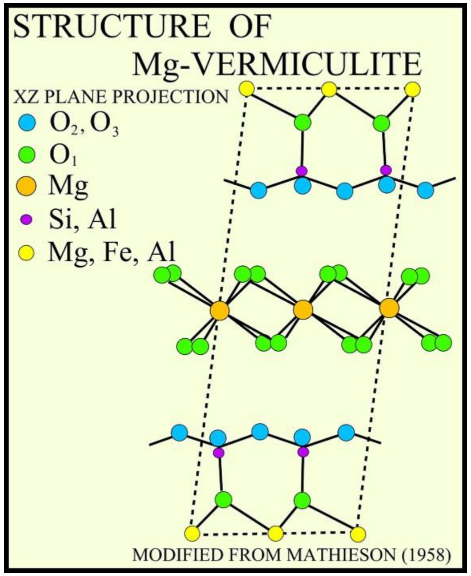


http://www.srs.gov/general/outreach/srs-cab/library/meetings/2013/slm/0611_fukushima.pdf

Clay Minerals

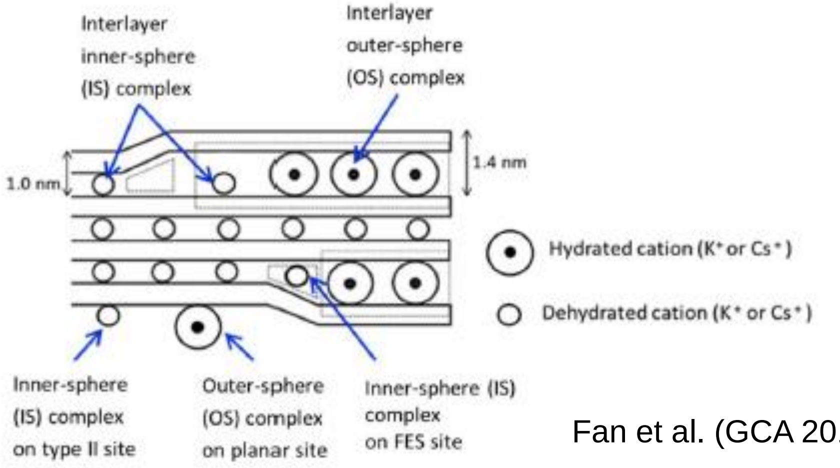






http://pubs.usgs.gov/of/2001/of01-041/htmldocs/clay.htm

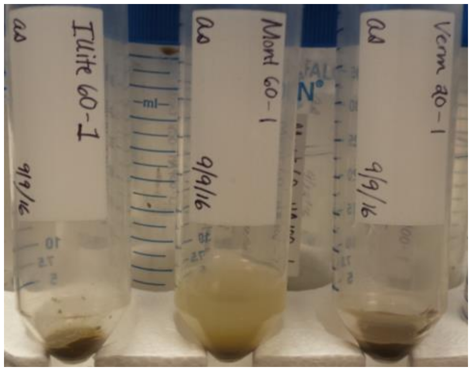
Adsorption species
Adsorption sites
Layer expansion of
Micaceous minerals



Fan et al. (GCA 2014)

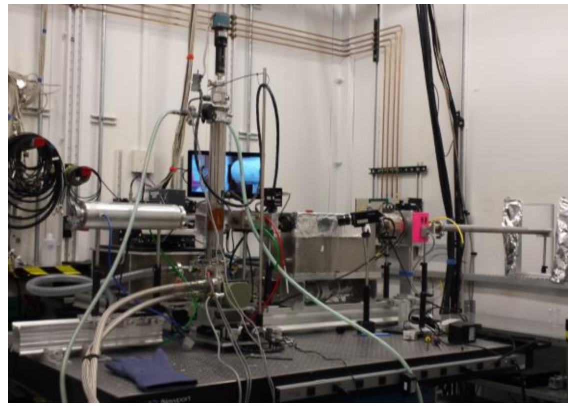
Methods

Batch Experiments



Humic acid (HA)
as a surrogate of NOMs

X-ray spectroscopy (XAFS)



Cesium L_{III}-edge XAFS was collected in fluorescent mode using a solid state detector at sector 20 at Advanced Photon Source

TEM

https://www.fei.com/products/tem/tecnai/

Cs adsorption conditions:

- ▶ Clay to solution ratio=0.5,2.5,5 g/L
- ▶ pH=6
- ▶ Ionic strength = 0.1M (NaCl base)
- ▶ Initial Cs conc = 1 to 250 ppm
- ▶ Humic Acid (HA) = 50 to 400 mg/L

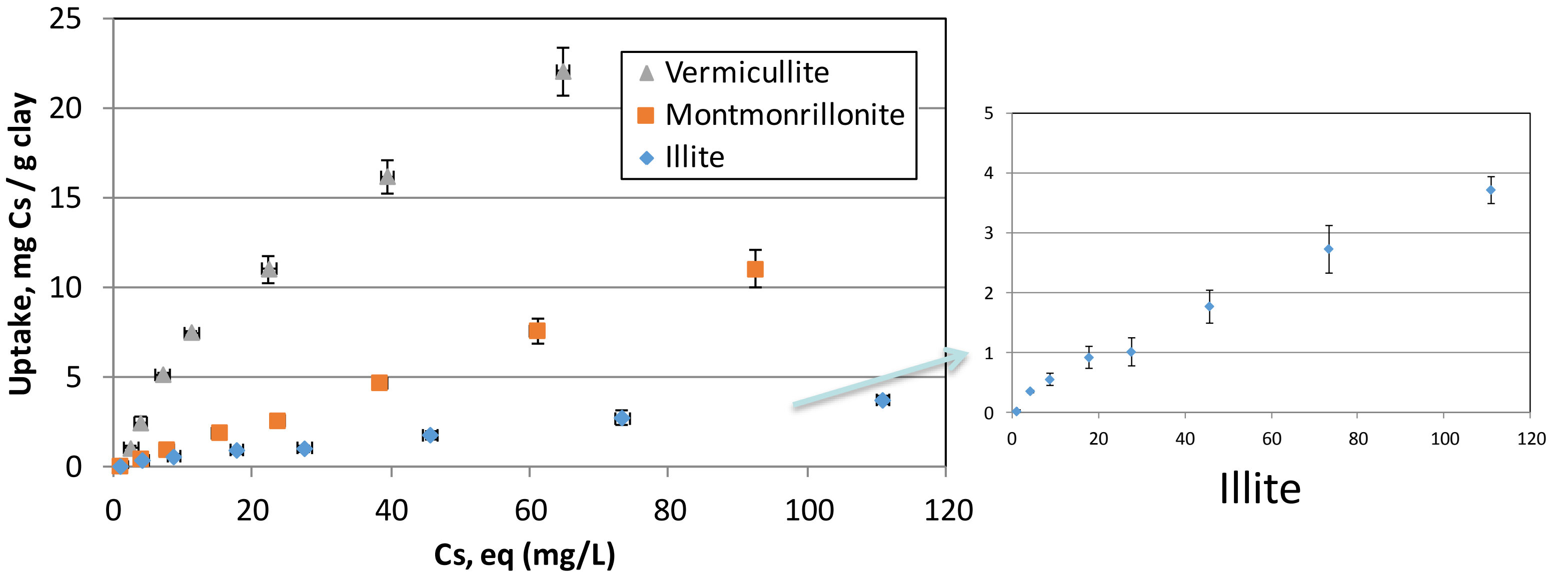
Cs desorption conditions:

- ▶ Step1: NaCl (0.01 M and 0.2M) and pH=8 and 10
- ▶ Step2: NH_4Cl (1 M)
- ▶ Step3: CH_3COOH (0.11 M)

XAFS: X-ray absorption fine structure spectroscopy

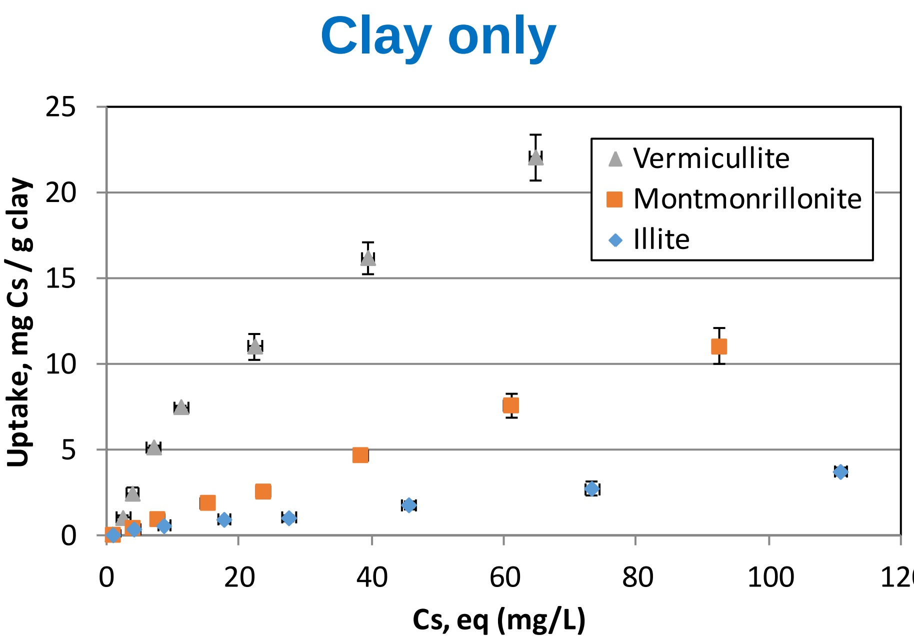
Cs Adsorption Isotherms

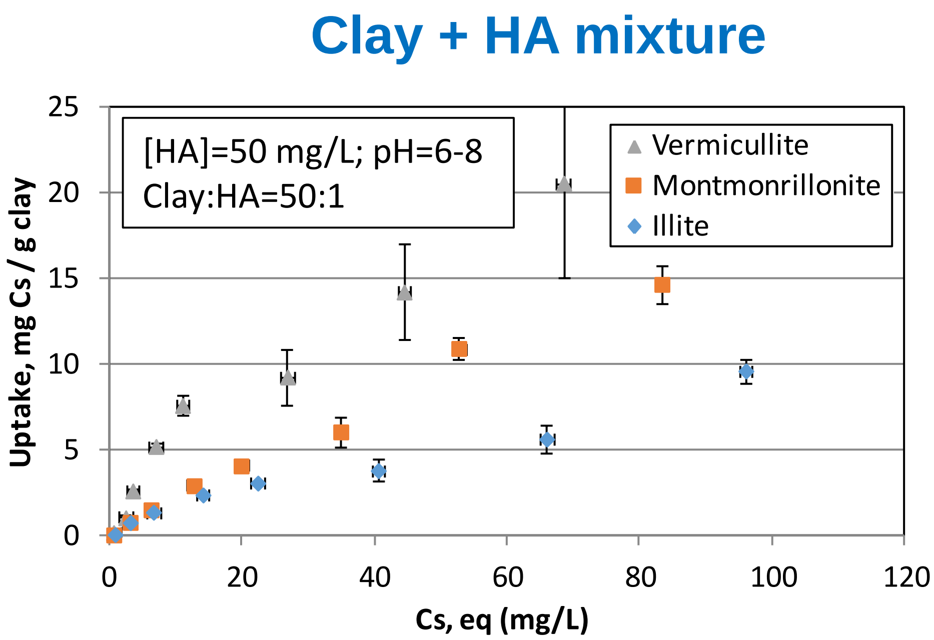
I=0.1 M NaCl
Clay to solution ratio=2.5g/L
pH=6-7



- Cs adsorption on different surface sites: easily accessible planar surface, selective frayed edge site (FES), and the interlayer sites
- Expandable clay minerals (e.g., montmorillonite and vermiculite) provide interlayer sites
- Non-expandable clay minerals (e.g., illite and mica) provide FES
- Different bonding sites have different adsorption mechanisms, resulting in different adsorption capasity

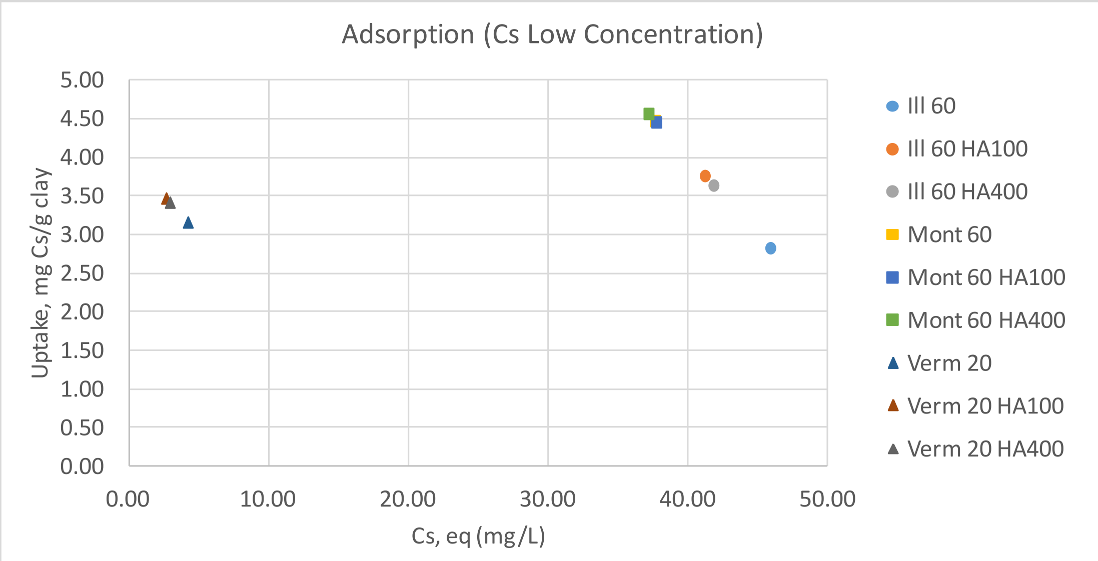
Cs Adsorption with HA



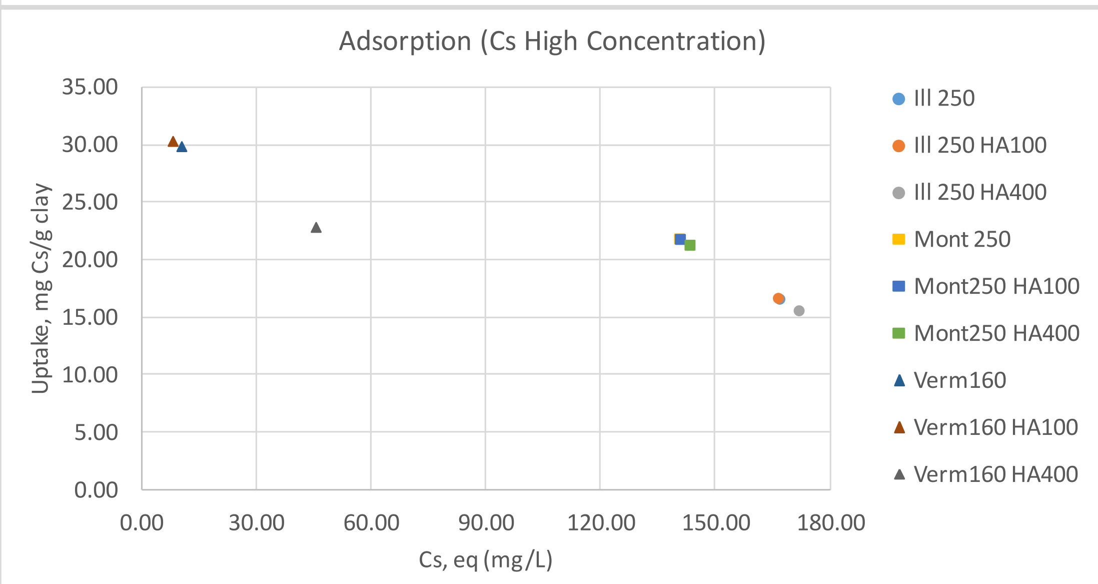


- For montmonrillonite and illite, the addition of HA increases Cs adsorption
- For vermiculite, the interlayer sites and inter-sphere complexes at the external basal sites are predominant. With HA addition (50 mg/L), the interlayer sites may decrease, but still provide large surface areas

Impact of HA on Cs Adsorption



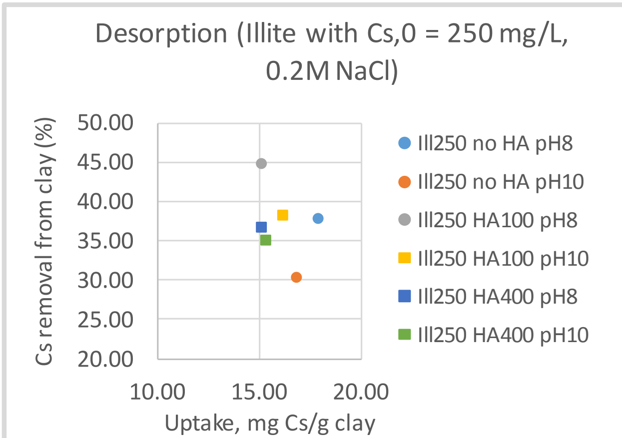
- At low Cs conc., the presence of HA increases Cs adsorption in the order of Illite, Vermiculite, and Montmorillonite
- HA may form Cs-HA complexes instead of blocking Cs adsorption sites on clays at low Cs conc.

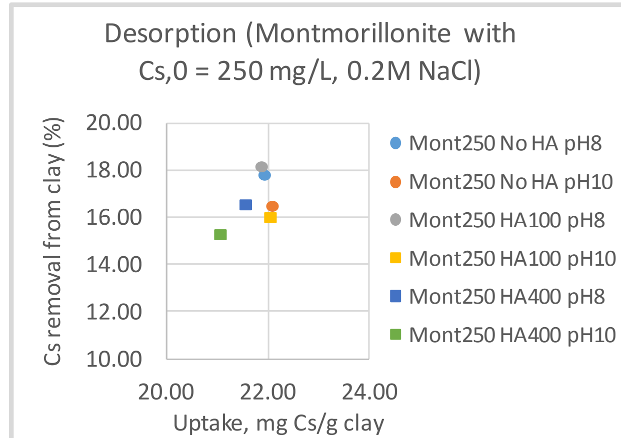


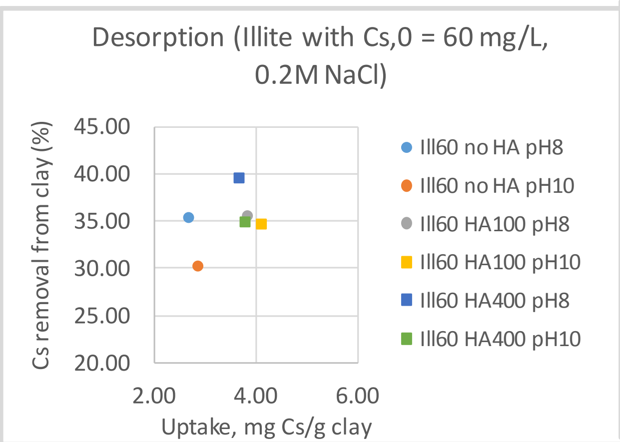
- At high Cs conc., the presence of HA decreases Cs adsorption in the order of Vermiculite, Illite, and Montmorillonite
- The effect of HA blocking Cs adsorption sites would be greater than additional Cs-HA complexes

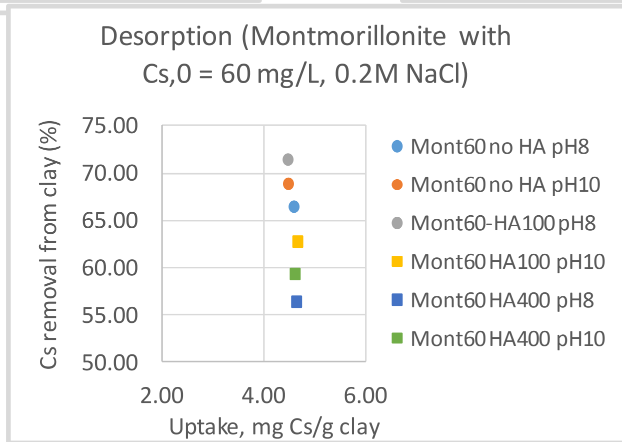
Ill60HA100 represents illite sample with 60 mg/L of initial Cs aqueous concentration and 100 mg/L of humic acid. All data are average values in triplicate.

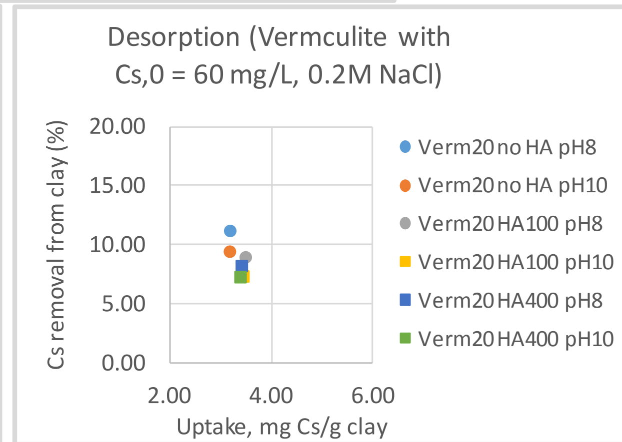
Cs Desorption





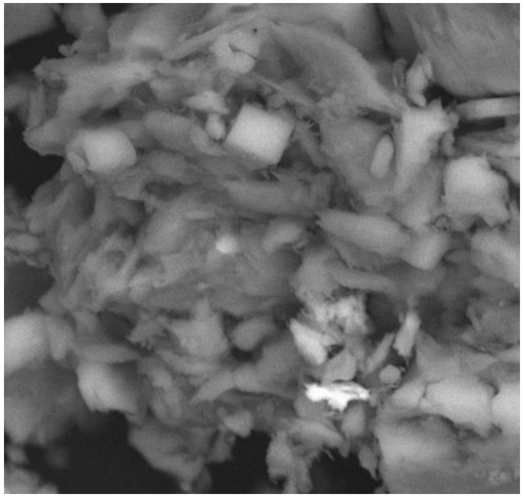
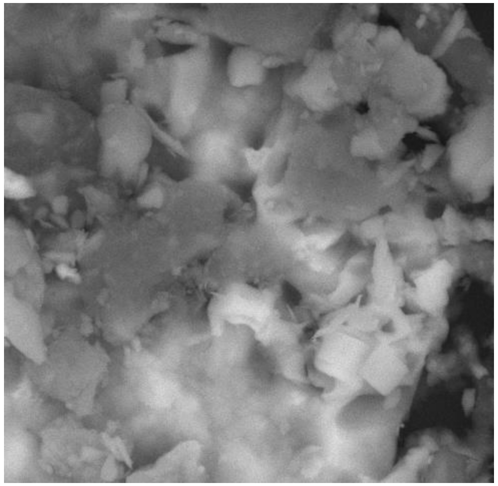
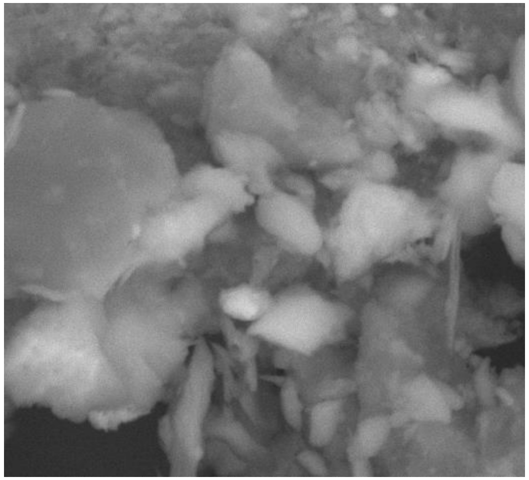
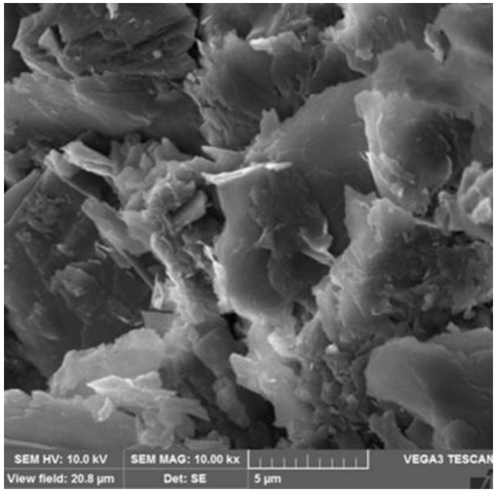
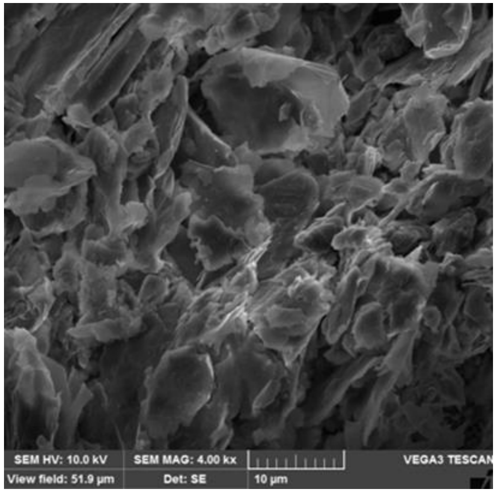
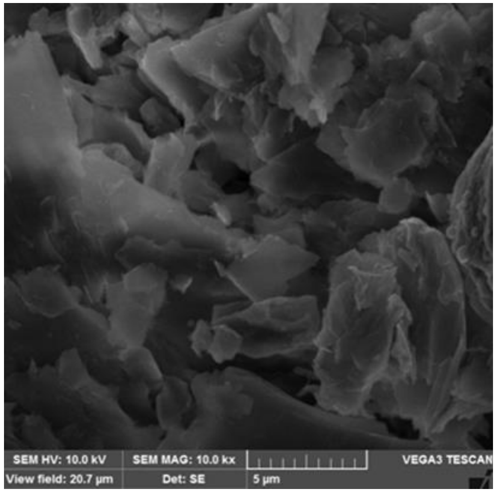






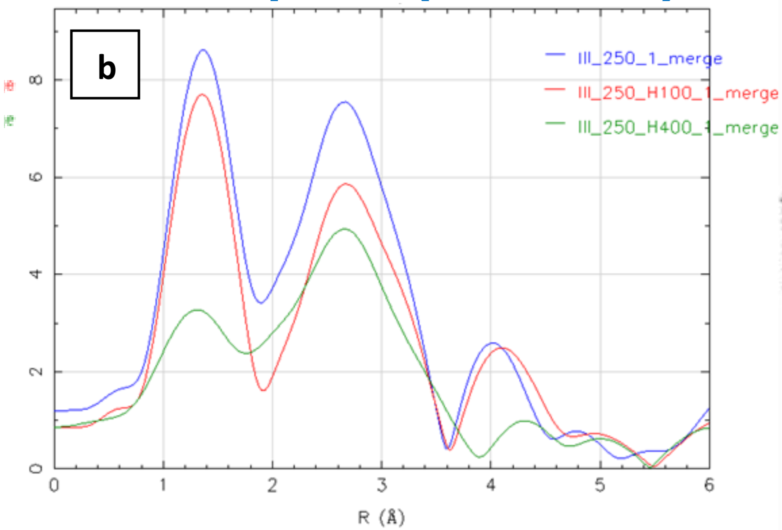
- The impact of pH, HA, and ([Na+]) on desorption is evaluated
- For high [Na+]=0.2M, Cs desorption tends to slightly increase at pH=8 than at pH=10, but the effect was not significant
- Desorption efficiency tends to depend on the amount of HA and clay type

Clay Morphology

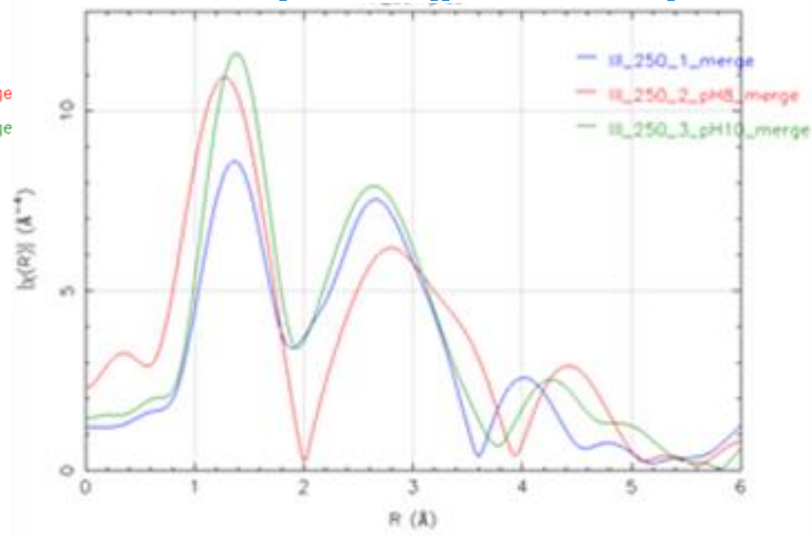
	Cs=120mg/L (No HA)	Cs=120 mg/L Clay and HA were mixed simultaneously with Cs	Cs=120 mg/L Clay and HA were mixed for 2 weeks, followed by Cs addition
Illite			
Vermicul-ite			

Cesium L_{III}-edge XAFS results (Illite)

Adsorption (HA effect)



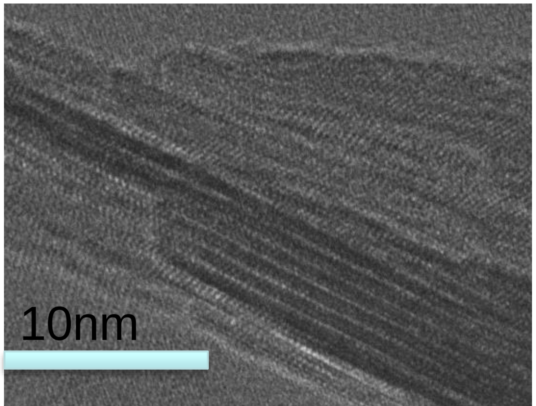
Desorption (pH effect)

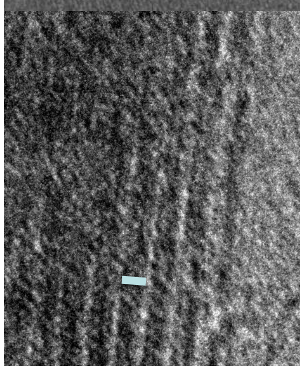


- Qualitative analysis shows the local coordination environment of cesium adsorbed onto illite depends on the concentration of HA
- For a high HA=400 mg/L with [Na+]=0.2M, the amplitude of the first coordination shell is lower, indicating that first shell of Cs has a lower coordination number
- For desorption samples, the difference in the Fourier transform spectra is less pronounced (right figure), indicating that after the desorption treatment, cesium remaining on the surface has the same speciation in all examined systems.

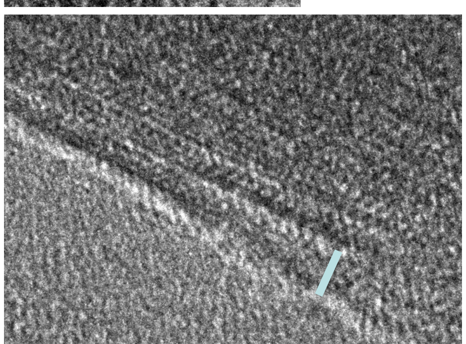
TEM Imaging (Illite)

Bright field TEM (No Cs)

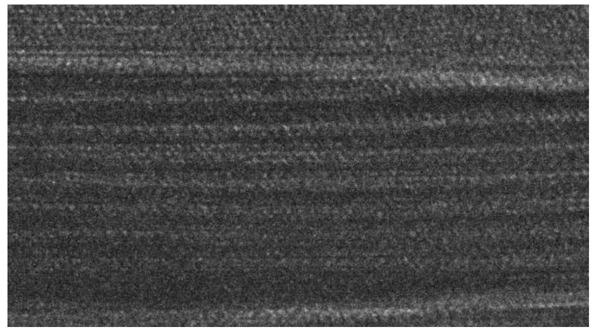


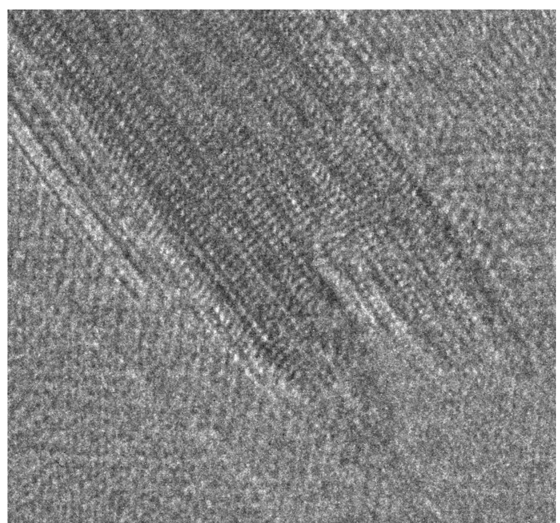


K interlayer
1nm

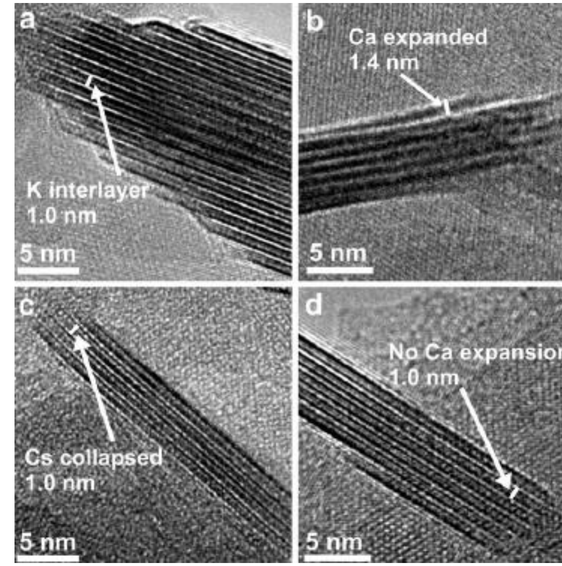


Cs,0=250mg/L
HA=400 mg/L

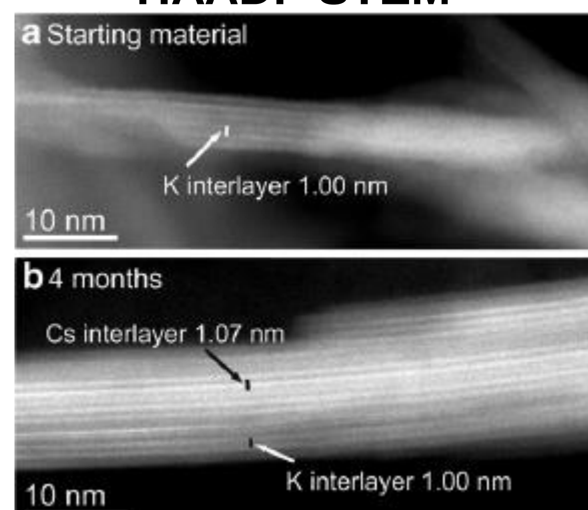




Bright field TEM



HAADF STEM



Fuller et al. (Applied Clay Sci., 2015)

Summary and Future works

- Cesium adsorption is affected by selective adsorption sites of clay minerals
- The presence of humic acid has different impacts on Cs adsorption for different clay minerals
- High Na+ concentration increases Cs desorption significantly (a three step sequential extraction with sodium, ammonium acetate and acetic acid will be optimized)
- For both adsorption and desorption (s)TEM and EXAFS analysis are being analyzed to account for Cs behavior in different clay minerals under different pH and HA amount

Acknowledgments

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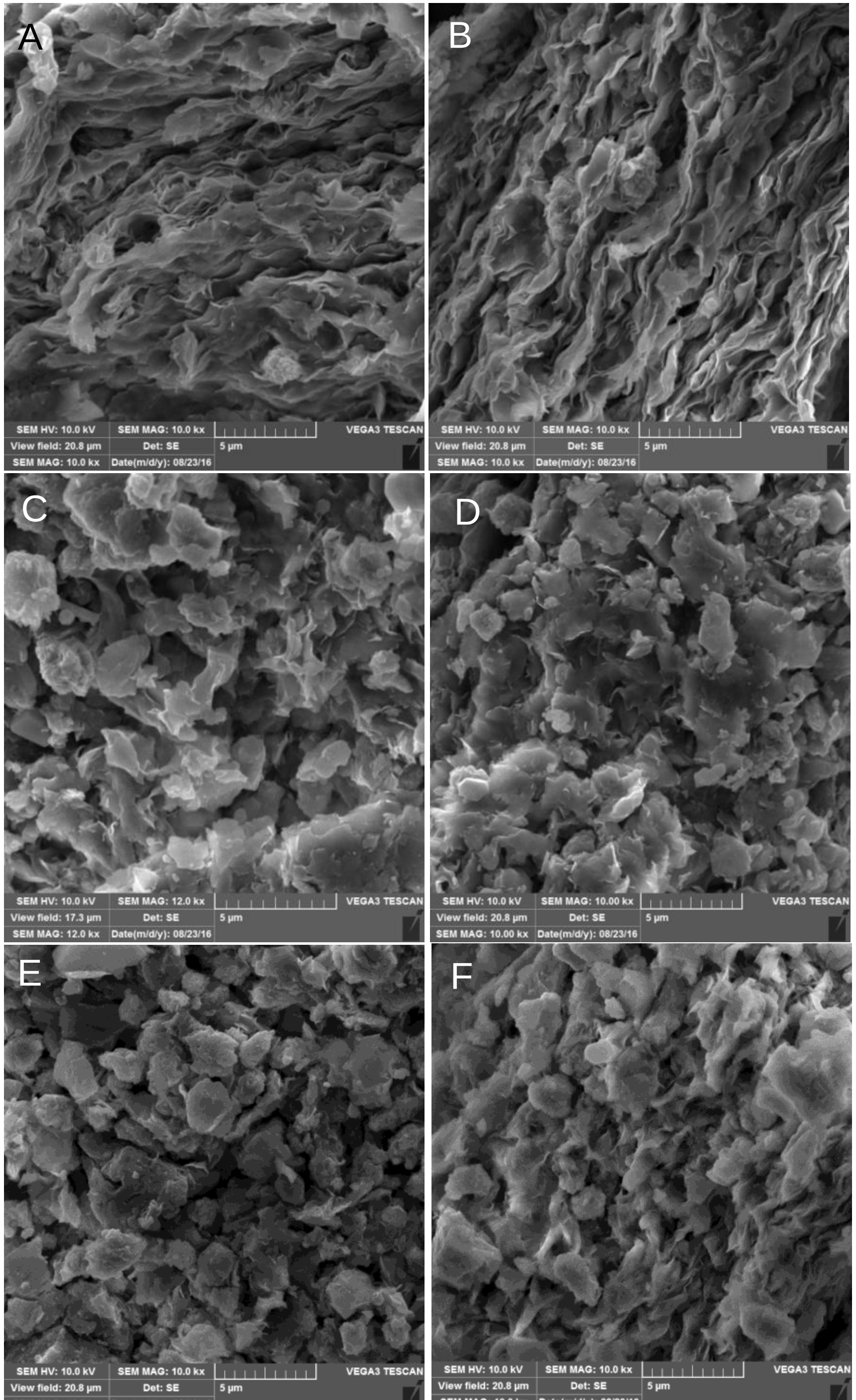
- This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science.
- Scientists Dr. Chengjun Sun (APS) and Dr. Katherine Jungjohann (CINT) for their supports on XAFS and TEM imaging, respectively
- Students – Amanda Sanchez, Lydia Boisvert, Joseph Mohagheghi for batch experiments

Backup



Scanning electron microscopy (SEM) images of montmorillonite contaminated with (a) cesium (1mg/L) without HA, (b) cesium (120 mg/L) without HA, (c) cesium (1 mg/L) with HA, (d) cesium (120 mg/L) with HA (c&d: HA and Cs were added simultaneously), (e) cesium (1 mg/L) with HA and (f) cesium (120 mg/L) with HA (e-f: HA was added 2 wks before Cs was added). The size of image is ~ 20 microns.