SAND2018-3415C

Sandia National Laboratories

Cesium adsorption and desorption in Clay Minerals: *Effects of Natural Organic Matter and pH*

by Hongkyu Yoon, Anastasia Ilgen, Melissa M. Mills, Moo Y. Lee, Sandia National Laboratories, Albuquerque, NM, USA

Fukushima Daiichi Reactor Accident

- Radioactive material release, resulting in contamination of a large area of soils
- Remediation efforts to cleanup seawater, groundwater, and cesium-contaminated soils
- Disposal of radioactive wastes and decommission of reactors

http://enformable.com/2012/07/photo-of-the-week-fukushima-daiichi-reactor-4-building-debris-removal/

Batch Experiments

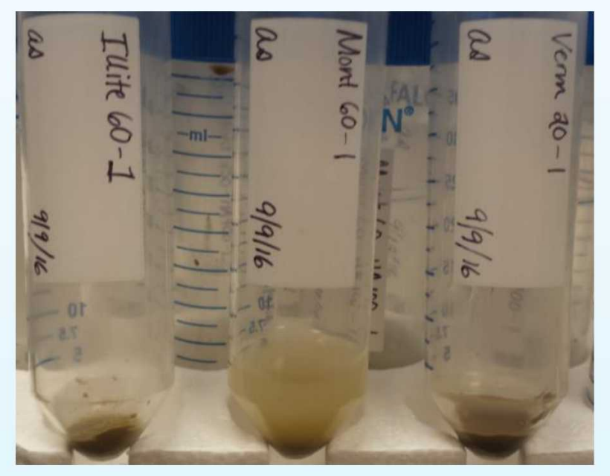
	Clay to Solution (g clay/ L solution)	pH*	Ionic strength (NaCl base)	Initial Cs conc (mg/L)	Minerals	Humic Acid conc (mg HA/L)	Notes
Set 1	5	6	0.1 M	60,250	Illite Montmorillonite	0, 100, 400 mg/L	Clay and HA are equilibrated for 1 wk before Cs is added
Set 2	5	6	0.1 M	20, 160	Vermiculite	10 & 50 mg/L	

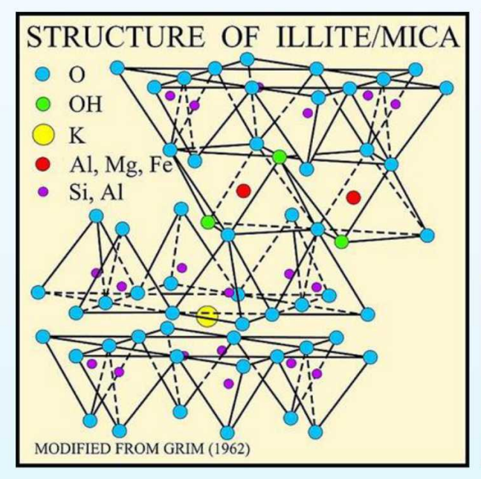
All adsorption experiments are repeated seven times for different desorption tests.

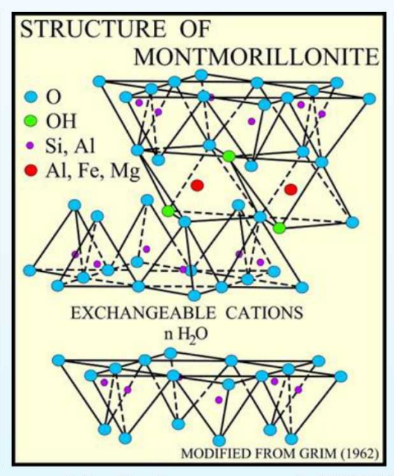
* All adsorption experiments are performed for 7 days and pH was adjusted to 6 at 1, 3, 5, and 7 days. Final pH values range between 5.91 and 6.34.

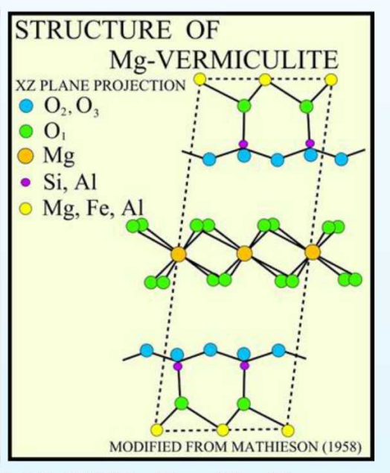
Adsorption: Clay suspensions with Cs were equilibrated for 3 days and then centrifuged for 15 min at 3000RPM. Supernatant of 6mL from each vial was filtered using 0.2 µm nylon filter, acidified with ultrapure nitric acid, and kept at 4 ºC until analysis by ICP-MS. The rest of supernatant was discarded. The mass of the vials with the pellet formed at the bottom after centrifuge was measured to estimate the mass of clay and water, so initial Cs mass for desorption can be calculated. .

Desorption: a sequential extraction scheme is performed to evaluate the Cs desorption using NaCl solution, NH4Cl solution, and Acetic acid solution. Each fraction of desorbed Cs corresponds to the weak exchangeable fraction, strong exchangeable fraction, and carbonate fraction, respectively. Detailed description of the sequential desorption can be found in Fan et al. (2014). For Cs desorption, low and high initial adsorbed Cs concentration are chosen depending on Cs adsorption results.



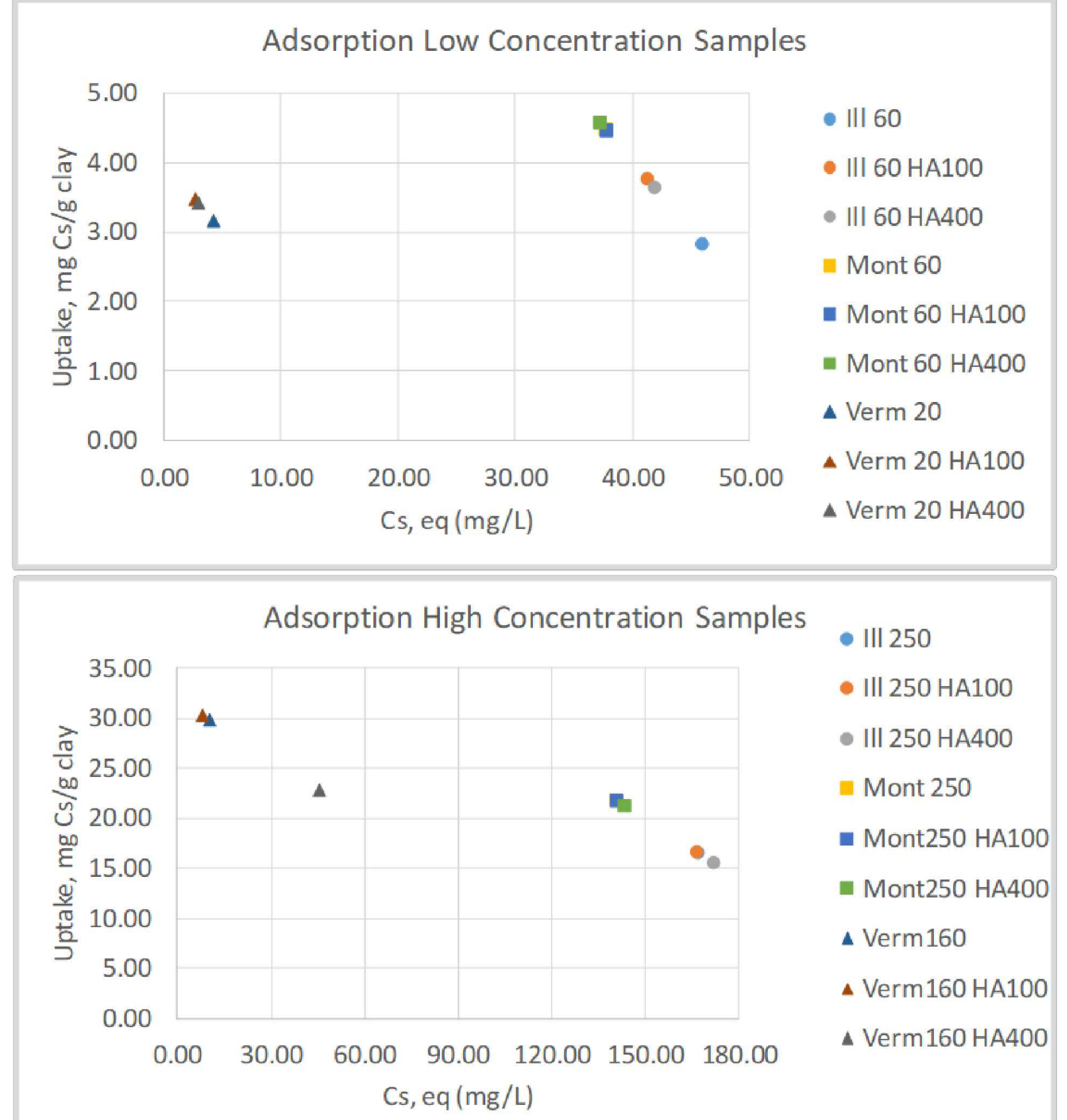




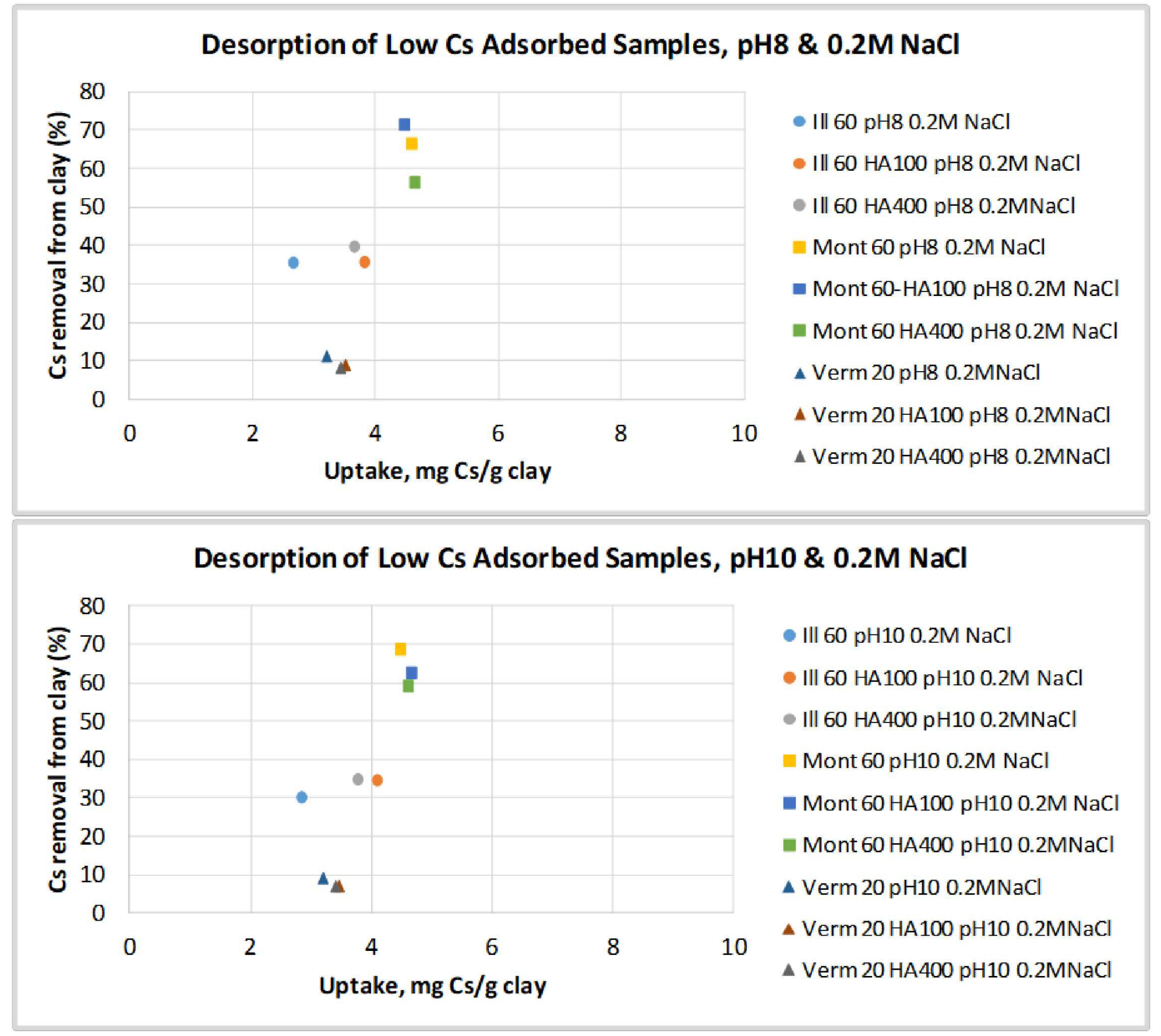


http://pubs.usgs.gov/of/2001/of01-041/htmldocs/clay.htm

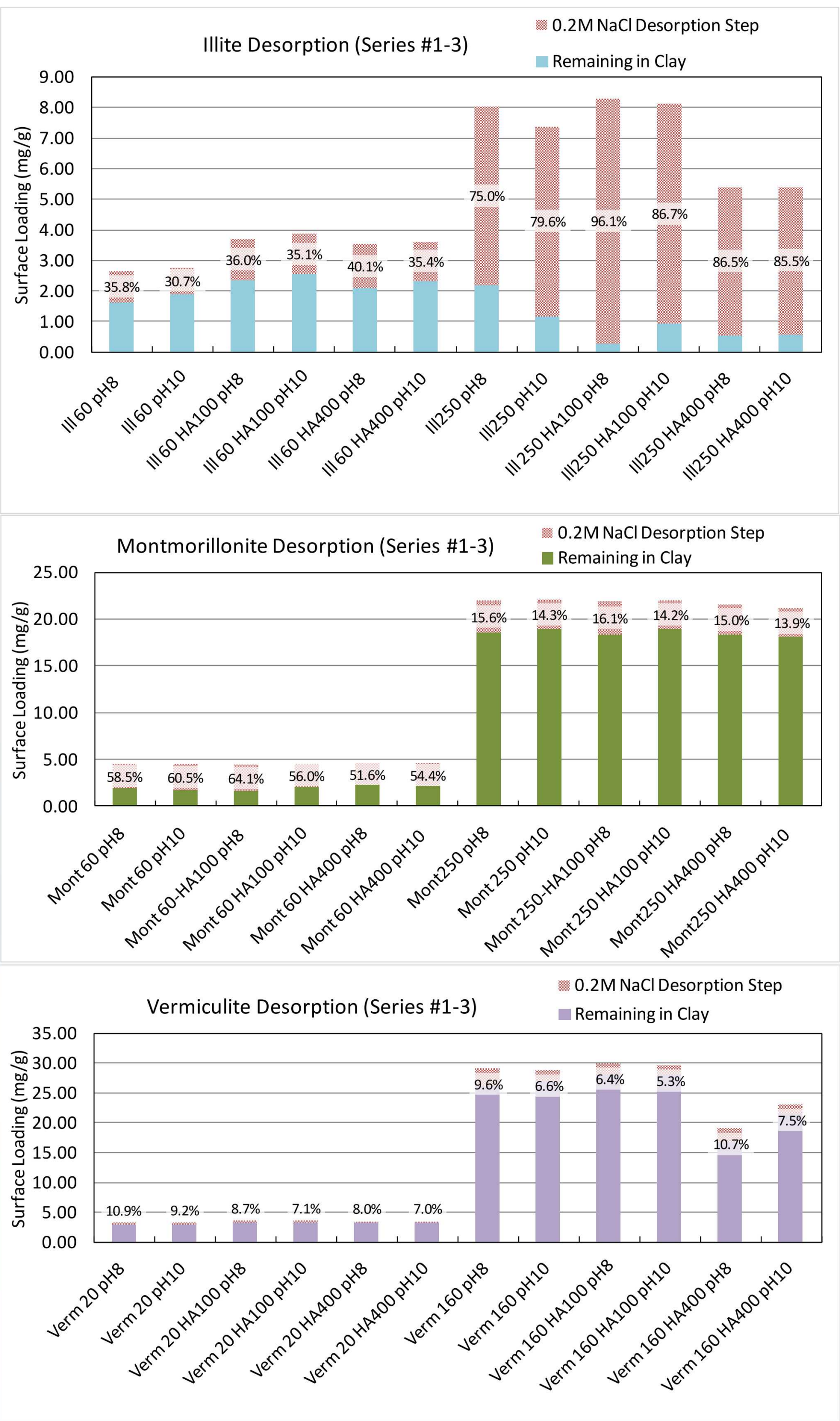
Adsorption results in 5 g/L of clay to solution ratio with low (top) and high (bottom) initial Cs aqueous concentration. Ill60HA400, for example, represents illite sample with initial Cs aqueous concentration of 60 mg/L and 400 mg/L of humic acid.



Cs removal (%) from clay minerals under pH=8 (top) and 10 (bottom) with 0.2M NaCl concentration.

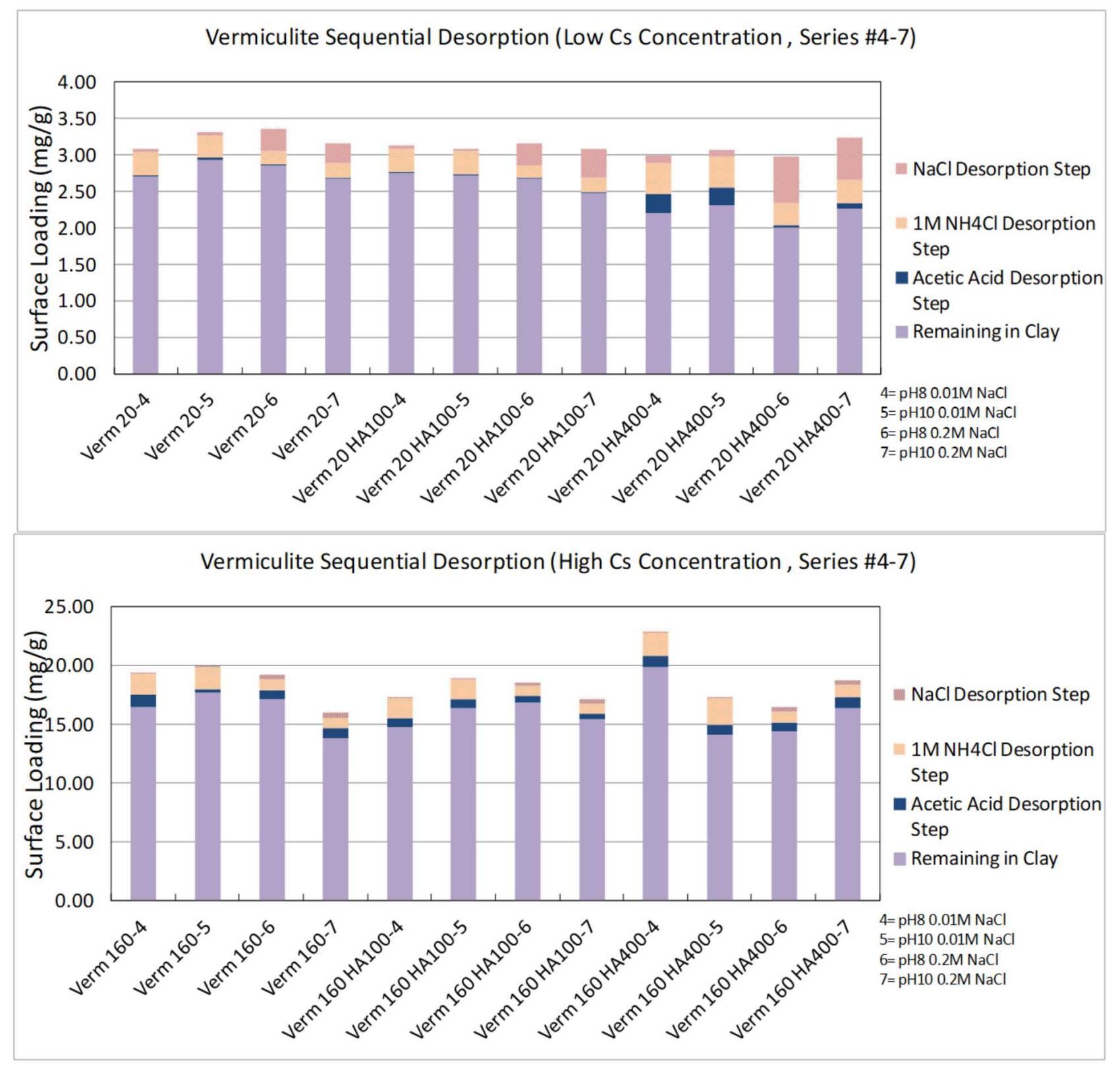


Sequential Desorption

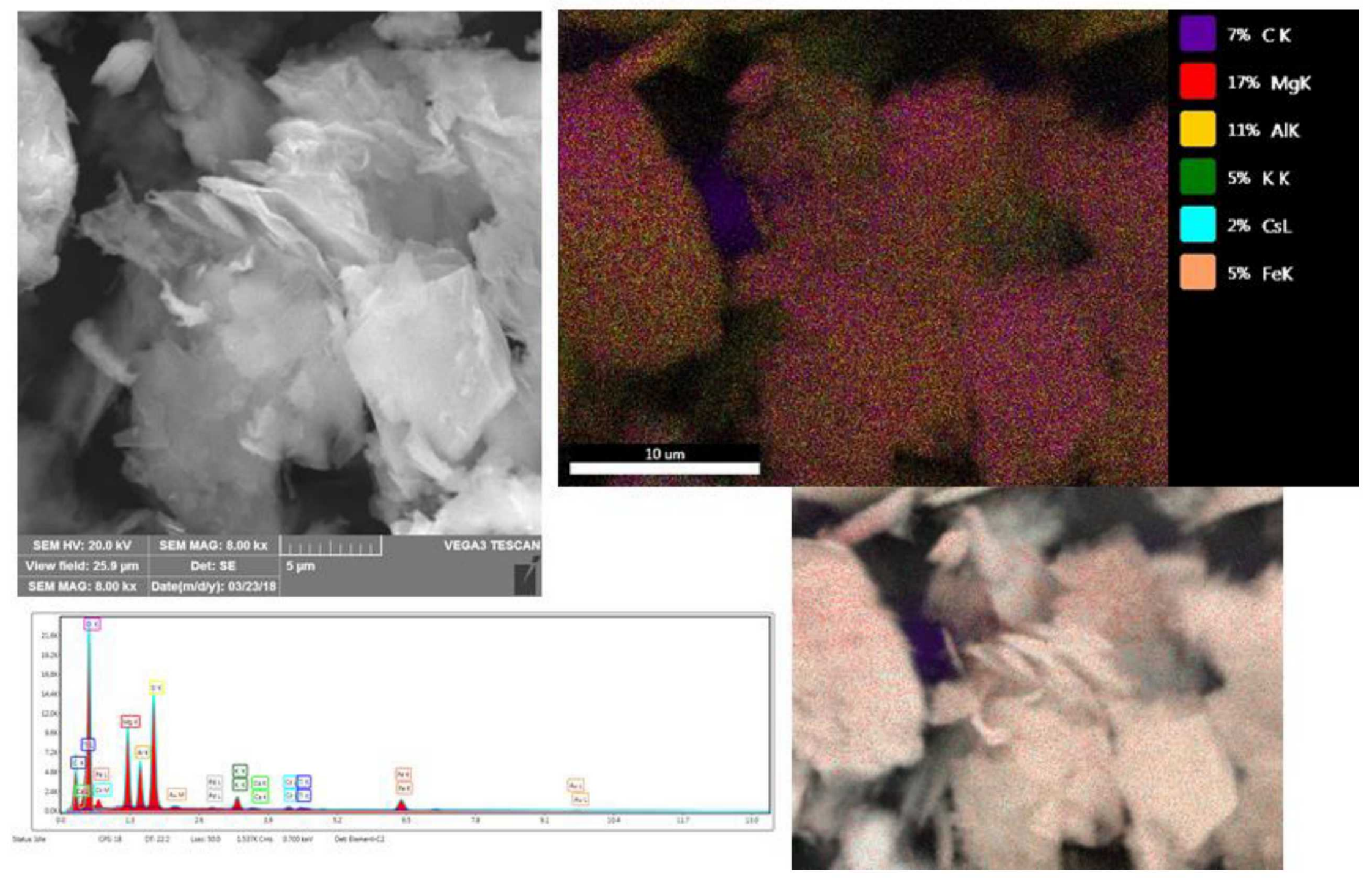


Results

- Cesium adsorption is affected by selective adsorption sites of clay minerals
- The presence of humic acid has a different impact on Cs adsorption for different clay minerals
- High Na+ concentration at high pH increases Cs desorption significantly
- For both adsorption and desorption TEM and EXAFS analysis will be performed to account for Cs behavior in different clay minerals under different pH and solution chemistry



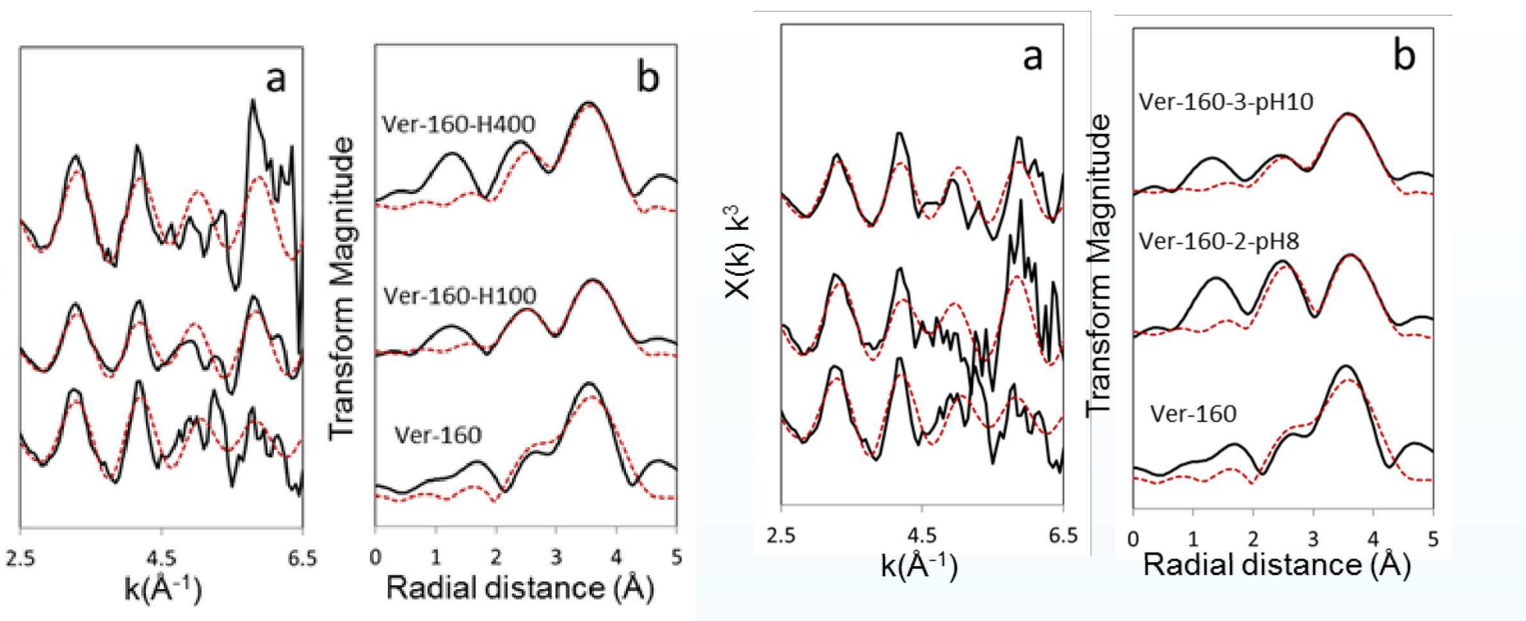
Vermiculite 160-4 (pH8 0.01M NaCL)



X-ray absorption fine structure spectroscopy (XAFS)

Table 4-2. Outer-sphere (OS) and inner-sphere (IS) cesium complexes on the examined quantified using the ratio of coordination numbers from shell-by-shell fitting.

Substrate	Sample Name	Surface loading, µmoles m⁻²	OS	IS
Montmorillonite	HCs-M standard	9.04	0.5	0.5
Illite	Ill 250-1	3.99	0.2	0.8
Illite	Ill 250-2-pH8	2.56	0.2	0.8
Illite	Ill 250-3-pH10	2.50	0.4	0.6
Vermiculite	Ver 160-1	35.14	0.2	0.8
Vermiculite	Ver 160-2-pH8	31.65	0.3	0.7
Vermiculite	Ver 160-3-pH10	32.42	0.2	0.8
Illite	Ill 250-H100-1	4.01	0.4	0.6
Illite	Ill 250-H100-2-pH8	2.12	0.2	0.8
Illite	Ill 250-H100-3-pH10	2.30	0.2	0.8
Vermiculite	Ver 160-H100-1	35.91	0.2	0.8
Vermiculite	Ver 160-H100-2-pH8	33.78	0.3	0.7
Vermiculite	Ver 160-H100-3-pH10	33.78	0.2	0.8
Illite	Ill 250-H400-1	3.75	0.2	0.8
Vermiculite	Ver 160-H400-1	26.43	0.2	0.8
Vermiculite	Ver 160-H400-2-pH8	22.30	0.3	0.7
Vermiculite	Ver 160-H400-3-pH10	27.14	0.2	0.8



(Left) Cs X-ray absorption fine structure spectroscopy data (black lines) for vermiculite with corresponding fits (red dashed lines) with high, low, and absent humic acid. (a) plotted as normalized k³-weighted χ(k); and (b) Fourier transform of the XAFS spectra.

(Right)Cs X-ray absorption fine structure spectroscopy data (black lines) for vermiculite with corresponding fits (red dashed lines) before and after two desorption treatments. (a) plotted as normalized k³-weighted χ(k); and (b) Fourier transform of the XAFS spectra.

U.S. DEPARTMENT OF ENERGY
NNSA National Nuclear Security Administration
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology &Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.
SAND No. ___________

Supported in part by the Strategic Partnership Project, the KEPCO Nuclear Fuel to develop non-acid based decontamination technology for cesium contaminated soils
This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

Sandia National Laboratories