CORASSE, Fukushima/Japan, September 30th - October 3rd, 2013

Fundamental approaches toward development of radiocesium removal methods from soil and the other related materials, waste reduction and management optimization

Chair, T. Yaita, Facilitator, I. McKinley

Talks in this session

Session 2: Fundamental approaches toward development of radiocaesium removal methods from soil and other related materials, waste reduction and management optimization

Monday September 30th 14:20-17:20

14:20~15:00 Introduction of study on the Cs adsorption-desorption on clay minerals for waste reduction and adsorption mechanism from the standpoint of materials science (T. Yaita)

15:20~16:00 Validation of uptake processes of radionuclides such as Cs on clay minerals by EXAFS (R. Dähn, PSI)

16:00~16:40 Molecular mechanisms and selectivity of Cs binding to phyllosilicate minerals with implications for fate and transport in the environment (K.M. Rosso, PNNL)

16:40~17:20 Caesium and other radionuclide retention by geochemical and engineered barriers (S.N. Kalmykov, MSU)

Talks in this session

Tuesday October 1st - 9:00-17:20

9:00~9:20 Cs Adsorption and related reactive dynamics in frayed edges of micaceous minerals (M. Machida, JAEA)

9:20~9:40 Molecular dynamics simulation for Cs adsorption behaviour under various kinds of conditions (T. Ikeda, JAEA)

9:40~10:00 Finding and analyses of soil particles adsorbing radioactive cesium in Fukushima (T. Kogure, Tokyo University)

10:00~10:20 Interpretation of Cs behaviour in waste reduction process by X-ray imaging and position sensitive XAFS methods (Y. Okamoto, JAEA)

10:40~11:20 Sorption-desorption behavior of Cs in subsurface materials: observations and modelling approaches (M. Ochs, BMG)

Talks in this session

11:20~12:00 Overview of chemical treatments for radioactive waste (S. Yokoyama, CRIEPI, T. Kobayashi, JAEA)

13:00~13:40 Importance of understanding clay-Cs association for reduction, storage and disposal of waste from decontamination activities in Fukushima (T. Sato, Hokkaido University / K. Ito, Miyazaki University)

13:40~14:20 Discussion / brainstorming (T. Yaita, JAEA)

Session 2 -Question

1. How we make efficient use of basic results for practical waste reduction? *Relationship between field work and laboratory scale experiment?*

2. Are there any effective chemical treatments and the other active methods for waste reduction? *These methods position for overall waste reduction?*

3. How we make fundamental results apply for elucidation of long-term radioactive cesium behavior?

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Introduction of study on the Cs sorption-desorption on clay minerals for waste reduction and sorption mechanism from the standpoint of materials science

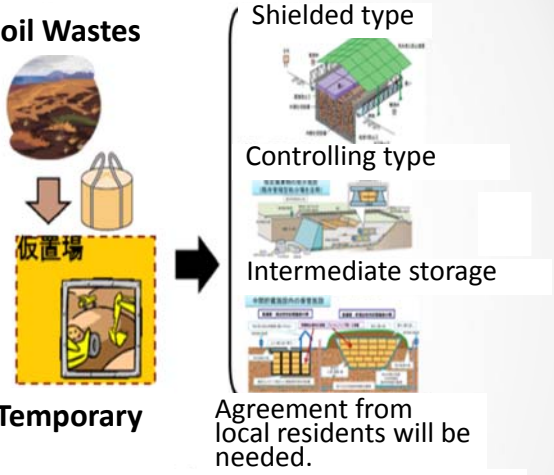
Tsusyoshi YAITA
Japan Atomic Energy Agency

Why do we need waste reduction?

Fukushima Dai-ichi Accident

Current treatment

Removal and deep plowing



Strategy for Waste treatment

We have to reduce waste volume

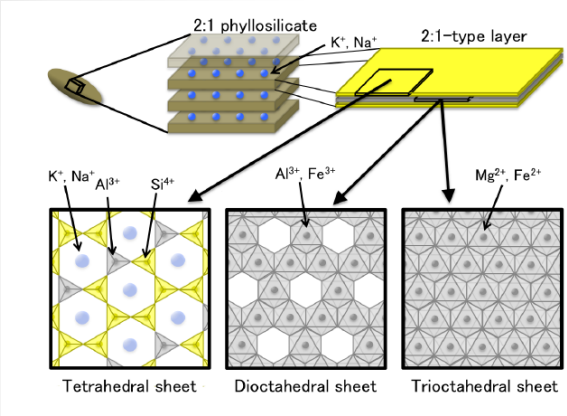
What is soil waste reduction?

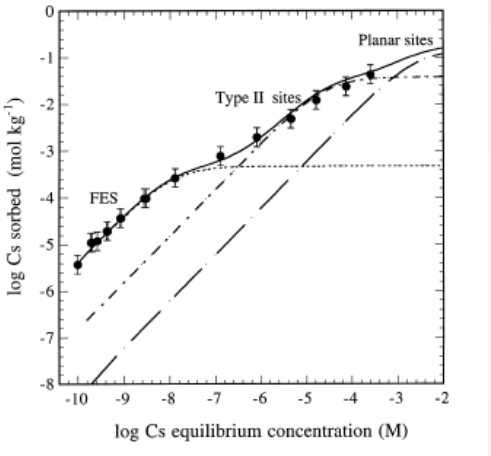
1) Wet Classification, incineration and Chemical Treatment (positive)
2) Deep Plowing etc. (passive)

On assumption that decontamination methods should be applied for actual spot based on effectiveness, cost, secondary waste production, environmental impact and so on,

1) We have to develop reasonable chemical treatment methods,
2) We have to evaluate stability in soil especially against weathering.

Clay mineral structure and Cs sorption





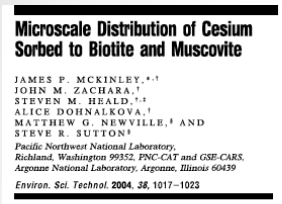
Cs sorption isotherm for Na-illite in 0.1 M $NaClO_4$ (Potnssot et al.,1999)

Vermiculite, Illite the others

- Important clay minerals in Fukushima
- Dominant adsorptive clay minerals
- Irreversible Cs was included.

There are three Cs sorption sites for in illite.

Cesium distribution in muscovite

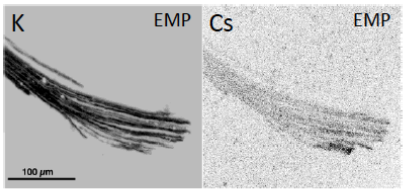


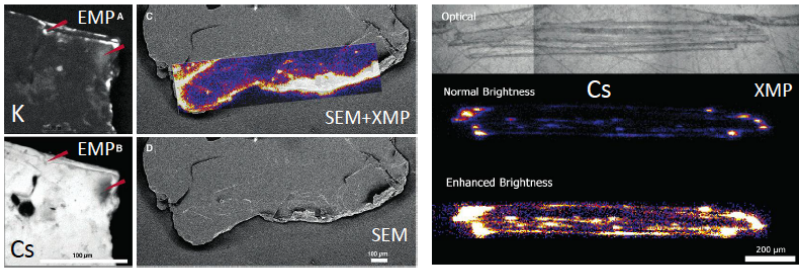
Microscale Distribution of Cesium Sorbed to Biotite and Muscovite

JAMES P. MCKINLEY,*,† JOHN M. ZACHARA,† STEVEN M. HEALD,†,‡ ALICE DOHNALKOVA,† MATTHEW G. NEWVILLE,§ AND STEVE R. SUTTON§

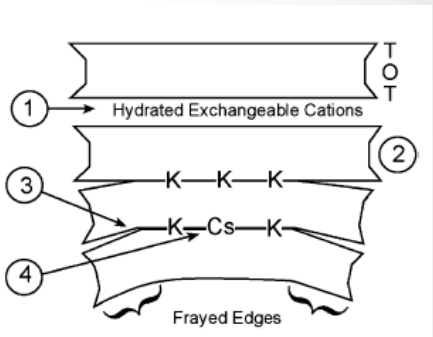
Pacific Northwest National Laboratory, Richland, Washington 99352, PNC-CAT and GSE-CARS, Argonne National Laboratory, Argonne, Illinois 60439

Environ. Sci. Technol. **2004**, *38*, 1017–1023





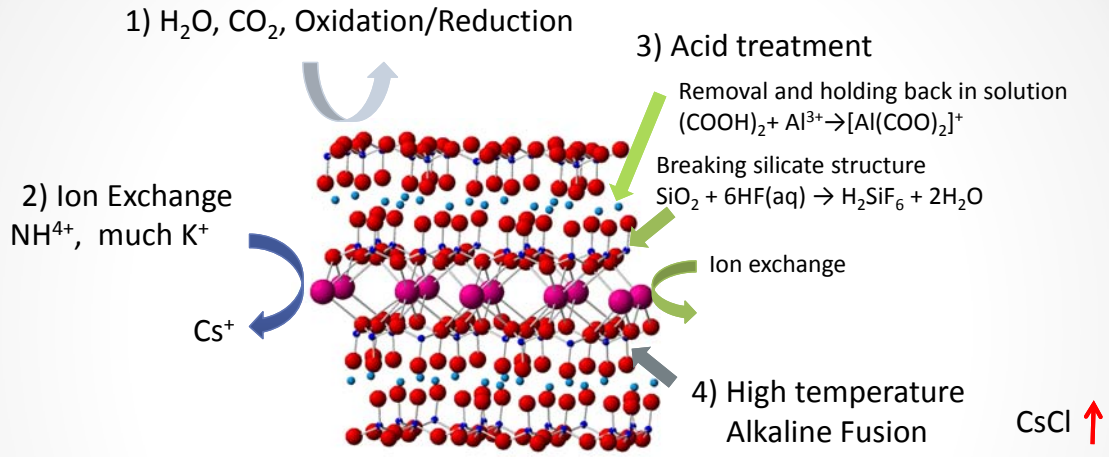
EMP: electron microprobe, SEM: scanning electron microscopy, XMP: X-ray microprobe



Schematic diagram of the mica structure: TOT, Tetrahedral-octahedral-tetrahedral sheet structure; K and Cs, interlayer cations; edges are "frayed" by the removal of interlayer K^+. Potential sites for Cs^+ sorption: (1) cation exchange sites on the basal plane, (2) edge sites, (3) frayed edge sites, (4) replacement of K^+ by Cs^+ in interlayer sites.

Mckinley et al., 2004

How to decontaminate radioactive Cs from soil ? How to evaluate Cs stability in soil?



Reversible

Van der waals bonding (Physisorption)

0.25eV (25kJ/mol)

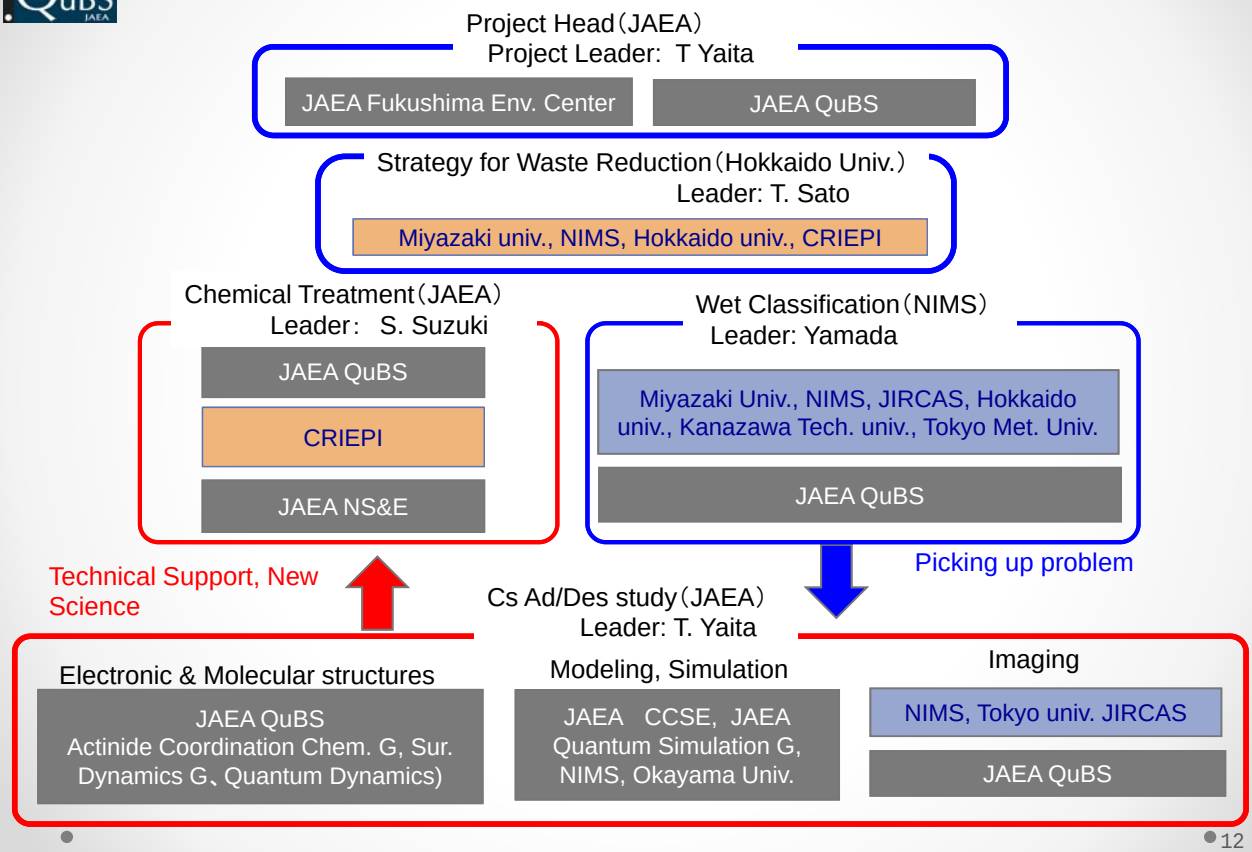
Reversible and irreversible

Ionic and Covalent bonding (Chemisorption)

0.42～4.2eV （40～400kJ/mol）

Detailed speciation of cesium in soil (clay mineral) would be important to develop decontamination method. In addition, weathering resisting properties would be also evaluated.

Project Structure

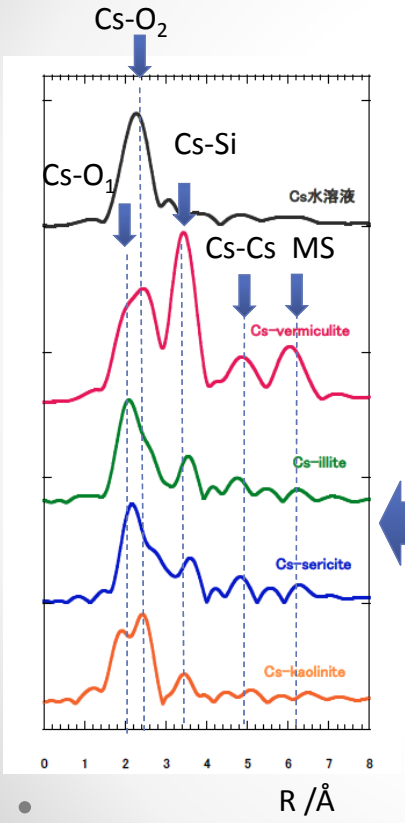


Elucidation studies on Cs sorption and desorption toward Clay Minerals

Cs adsorption/desorption structures by EXAFS, STXM and DFT calculation.

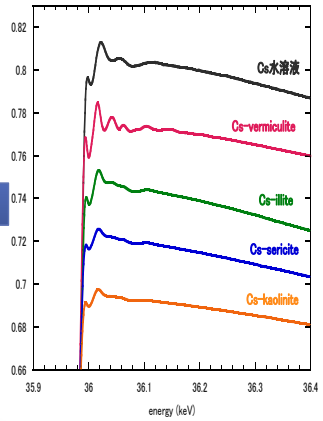
Cs-K EXAFS

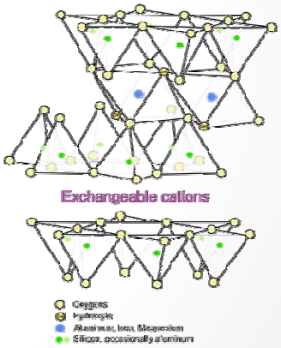
SPring-8 BL11XU



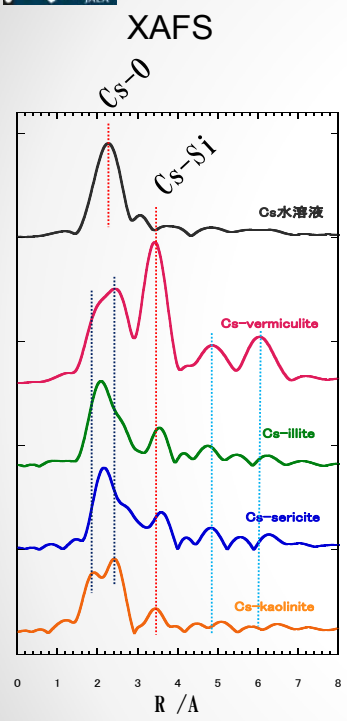
・Sample preparation of Cs-clay mineral system

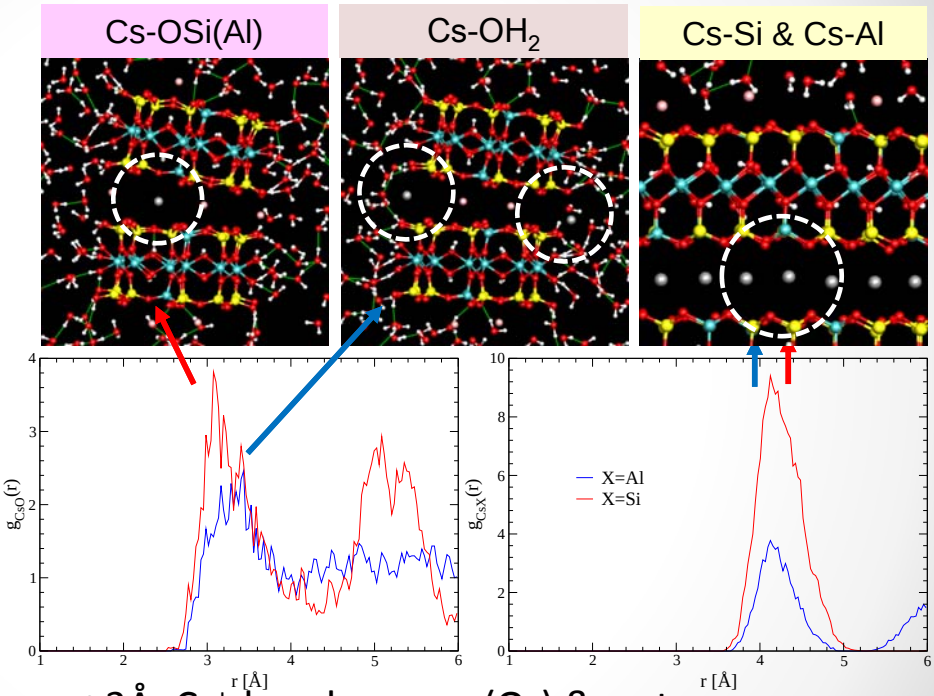
Cesium and water was added to 300mg clay minerals to adjust 100 ppm mixed solution. This mixed solution was shaking gently under RT for two days, and then, was filtered with membrane filter. The Cs adsorbed clay mineral was evaporated to dryness extremely gently under atmospheric pressure for one night.





Comparison with XAFS experiments

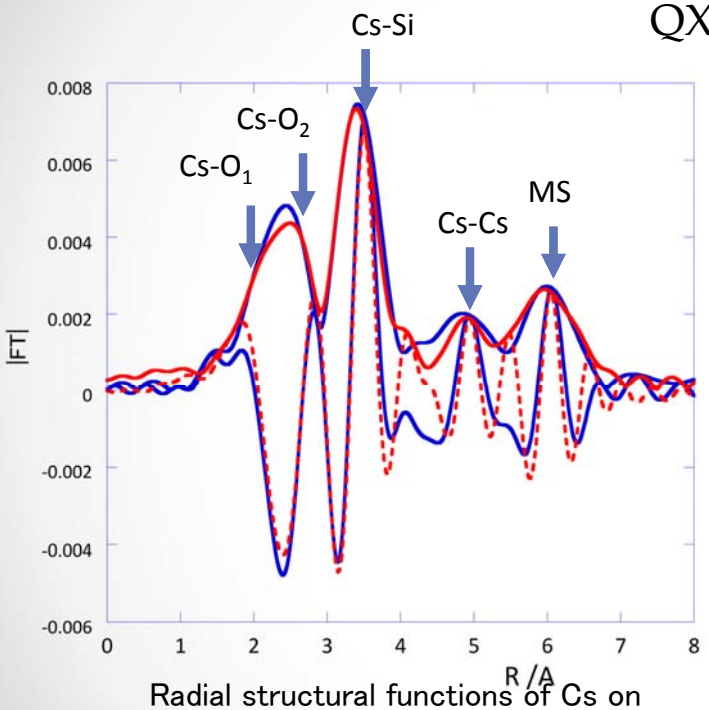




- ~3Å: Cs^+-basal oxygen (O_b) & water oxygen
- ~4Å: Cs^+-Si (Al) of tetrahedral sheet
- ~5Å: Cs^+-apical oxygen(O_a)

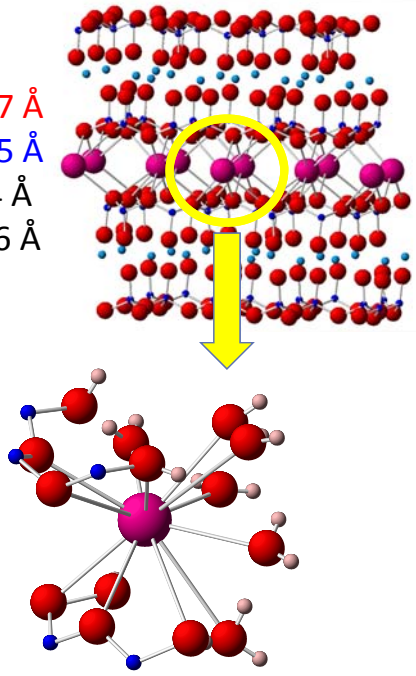
Cs-Vermiculite by EXAFS

QXAFS SPring-8 BL11XU



Radial structural functions of Cs on vermiculite

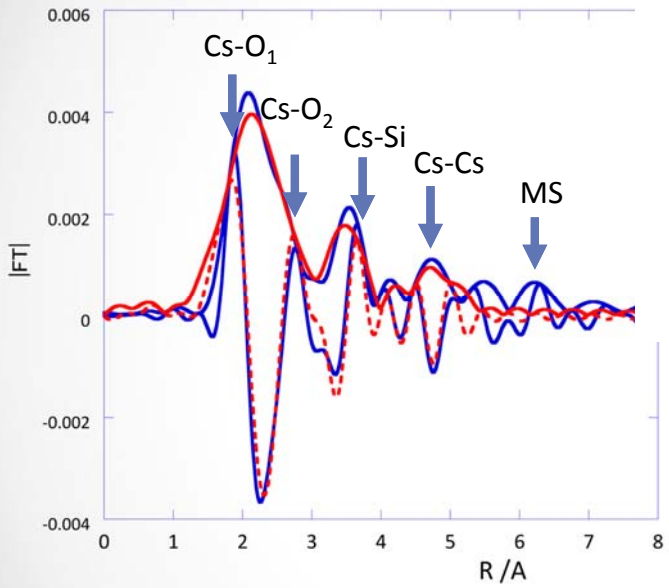
Cs-O_1: 2.97 Å
Cs-O_2: 3.25 Å
Cs-Si: 4.04 Å
Cs-Cs: 5.56 Å



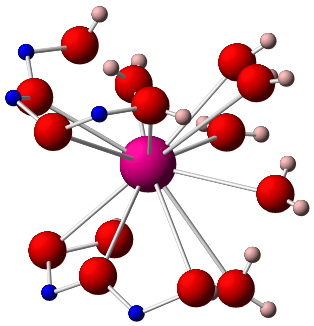
Used model on curve fitting

Cs-illite by EXAFS

SPring-8 BL11XU



Radial structural functions of Cs on illite



Used model on curve fitting

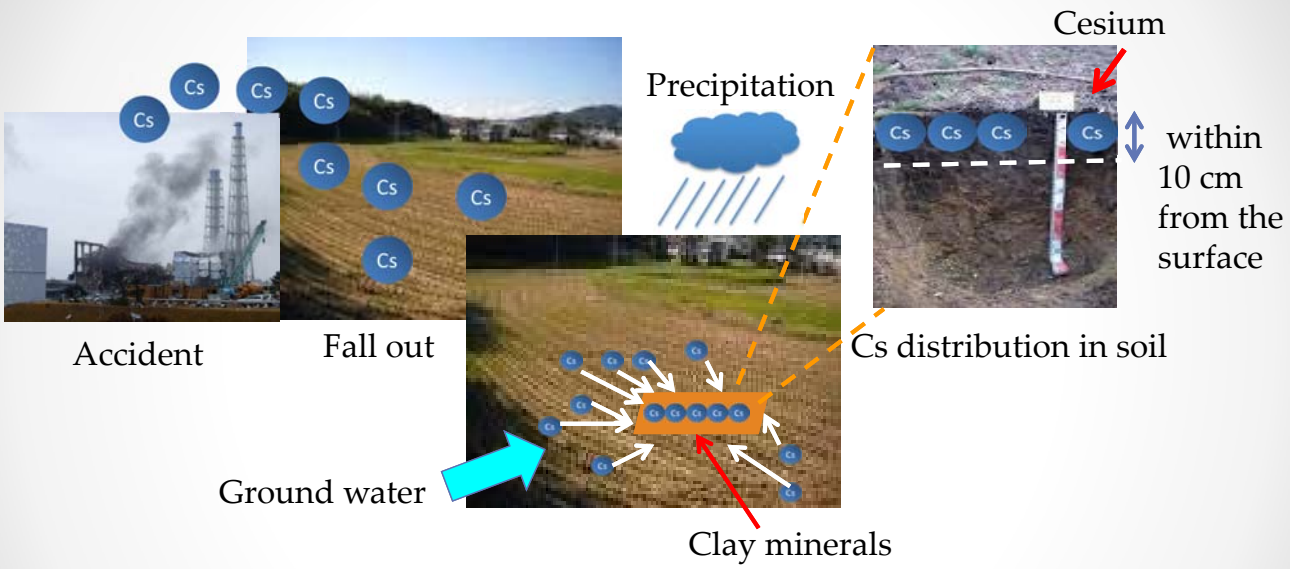
Cs-O_1: 2.98 Å ← Slight covalency?
Cs-O_2: 3.20 Å ← Same as Cs–O_{H2O}
Cs-Si: 4.01 Å
Cs-Cs: 5.50 Å

* Same distances as Vermiculite

Cs adsorption Dynamics by DXAFS

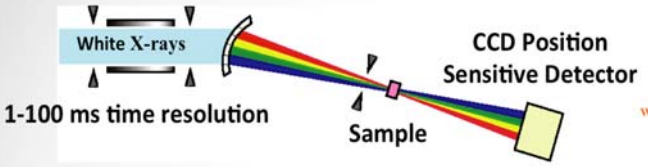
How does Cs sorb on clay minerals ?

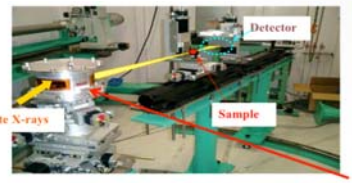
Estimated Phenomena



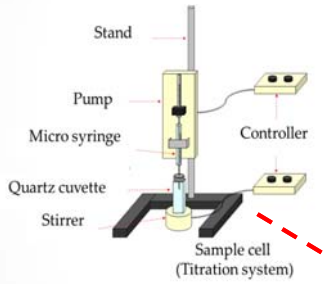
Radioactive cesium derived from Fukushima Dai-ichi power plants deposited on the ground, and moved slightly through ground water or precipitation. Finally, Cs generally adsorped on clay minerals and stabilized.

Cs adsorption dynamic studies by DXAFS





SPring-8 BL14B1 (JAEA beamline)



Water (Precipitation and Ground water)

drop

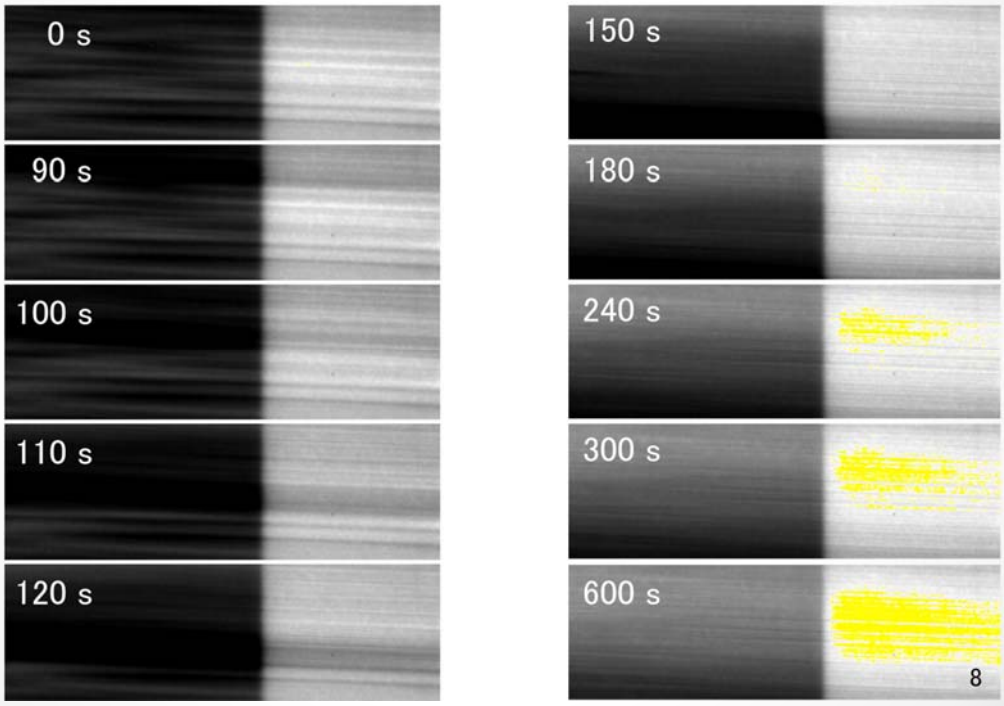
Vermiculaite with $CsCl_2xH_2O$

SPring-8

X-ray

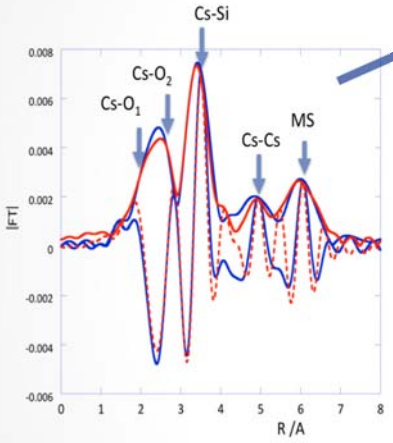
Snapshot of sorption on vermiculite

Post edge Pre edge



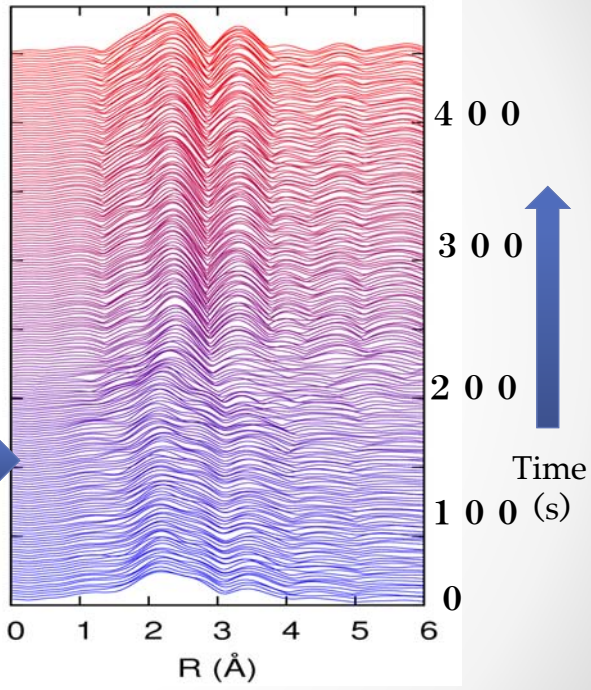
Results of Time dependent RSF

EXAFS



Conventional XAFS data

Water



Time dependence RSF

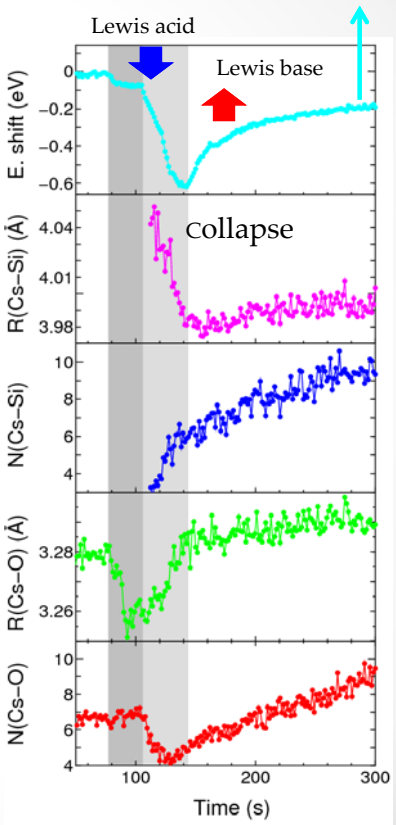
Time dependent EXAFS parameters

Physical mixture (CsCl)

Water-in and hydration
E. shift, R(Cs-O) decreases
⇒ CsCl → $Cs^+(H_2O)_n$

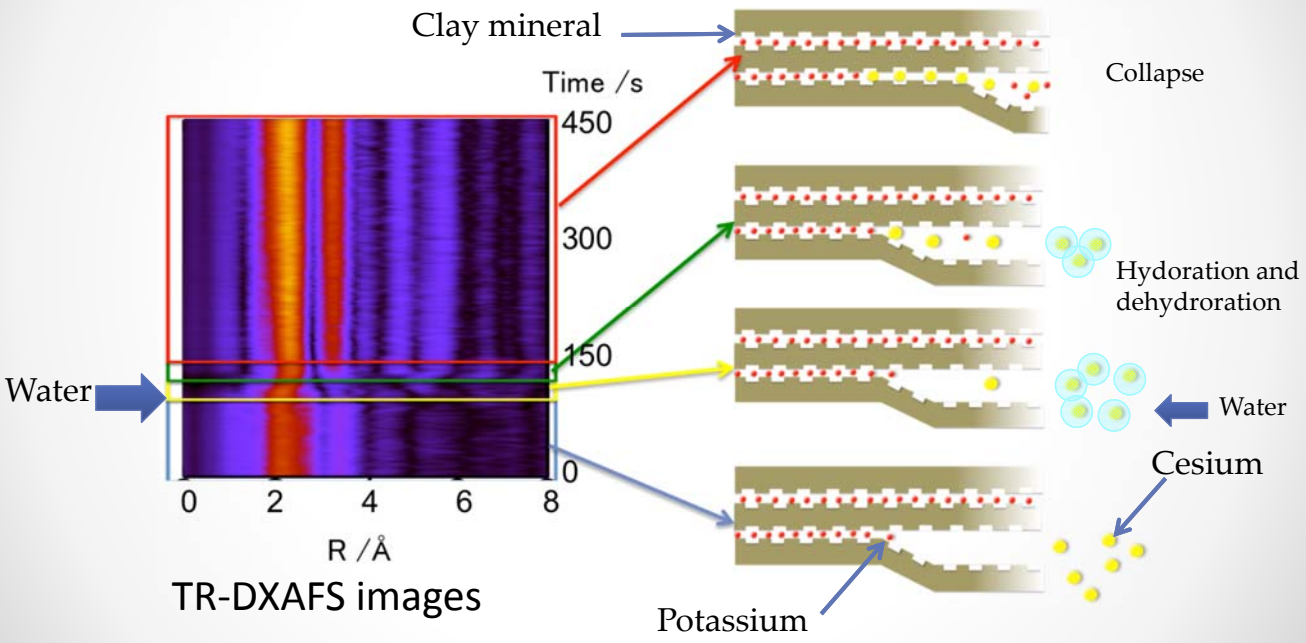
R(Cs-Si) decreases
N(Cs-Si) increases
⇒ layer collapse
E shift still decreases
⇒ dehydration & forming ionic bond with clay

E shift gradually increase
N(Cs-O) increase & R(Cs-O) apparently keep constant
⇒ forming covalent and ionic bonds



Interpretation of TR-DXAFS

Cs adsorption model based on TR-DXAFS



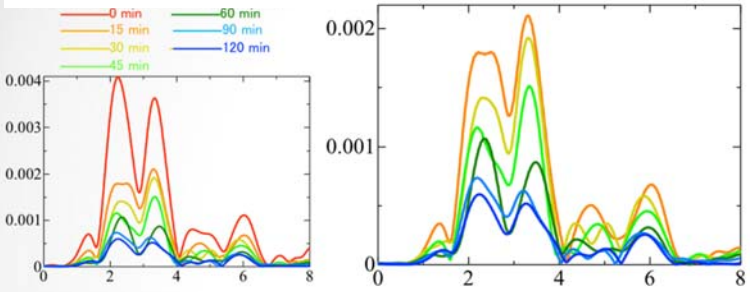
Cesium concentrated at Frayed edge site

Cs desorption behavior by acid treatment

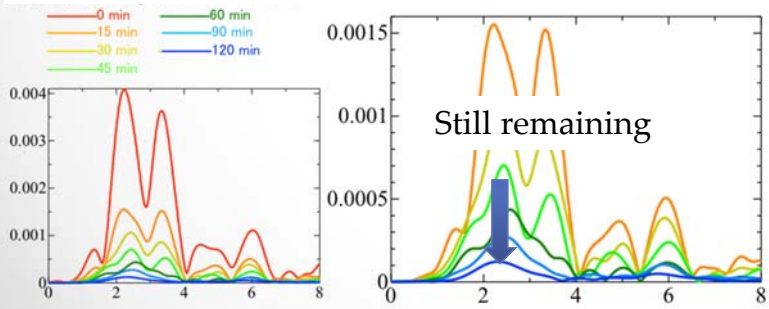
We can observed several sorption sites in clay mineral?

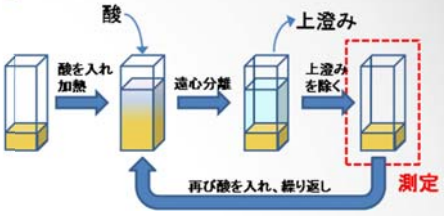
Time dependent EXAFS analysis on acid treatment

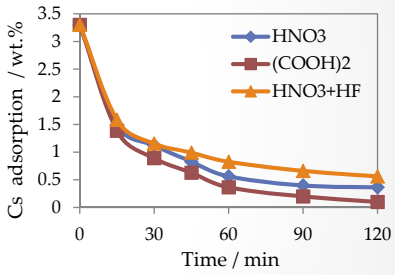
1M HNO_3, 100˚C



1M Oxalic acid, 100˚C



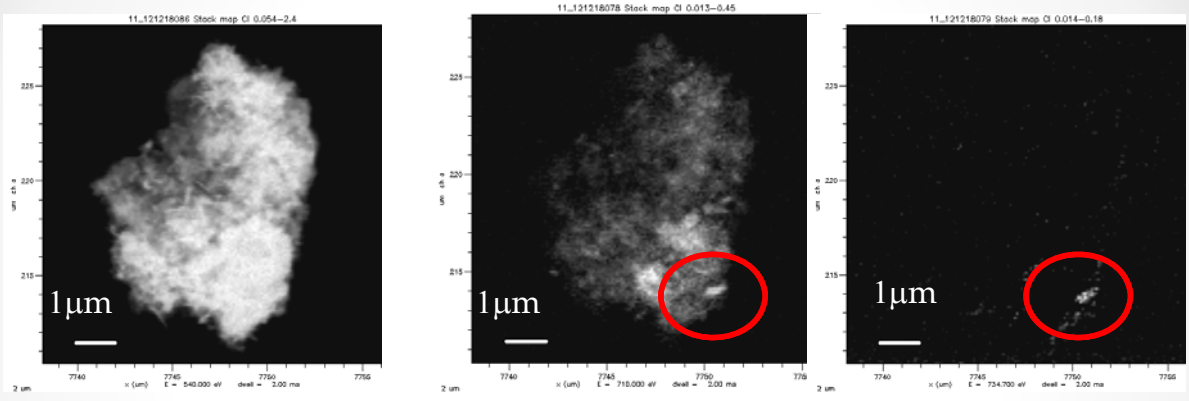




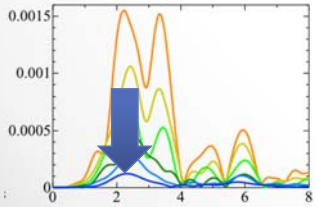
Cs-O_1 interaction (2.97 Å) was acid resisting property.

This result would probably relate with ultra cesium behavior .

STXM analysis of Cs-Vermiculite Cs Map after Treatment by Oxalic Acid



O Map Fe Map Cs Map

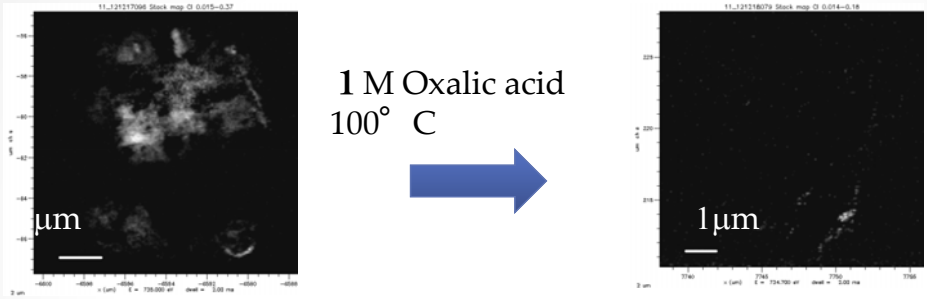


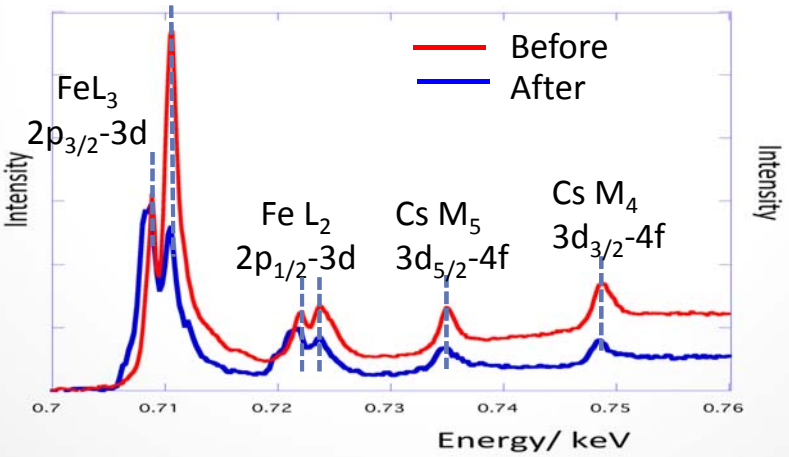
120min, oxalic acid tr.

RSF aftrer treatment of Oxalic acid

After oxalic acid treatment, soluble Fe disappeared, while insoluble Fe distribution was correlated with Cs.

Comparison of XANES for Cs and Fe between before and after treatment

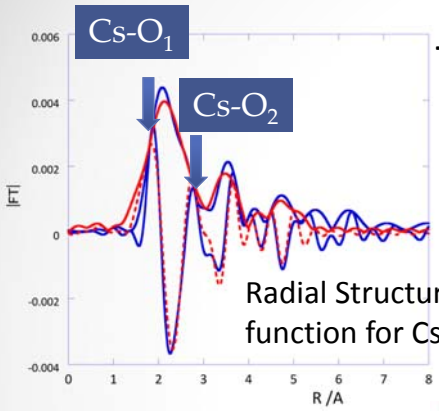




Chemical bond of Cs in clay minerals

How strong is the chemical bond of Cs with clay minerals?

Covalent bond of Cs in clay mineral



Radial Structural function for Cs-illite

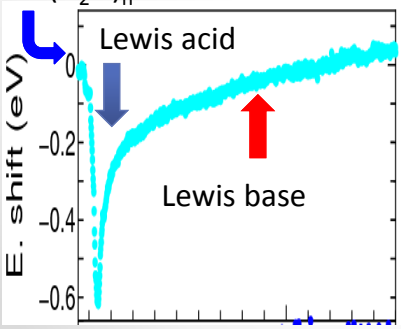
There are two sites in clay minerals from Cs-O.

$Cs\text{-}O_1$: 2.98 Å ≈ $Rcov_{Cs+O}$=2.95Å*

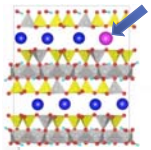
$Cs\text{-}O_2$: 3.20 Å ≈ $Rionic_{Cs+O}$=3.28Å**

*Pekka et al.,2009, **Shannon et al., 1976.

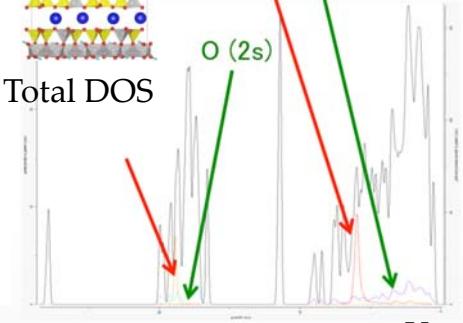
$CsCl(H_2O)_n$



Cs

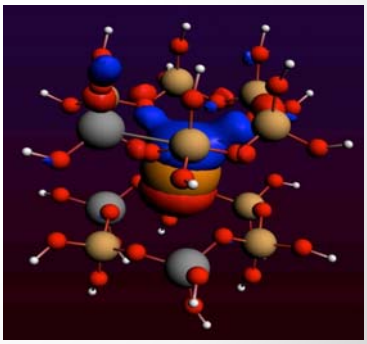


Total DOS

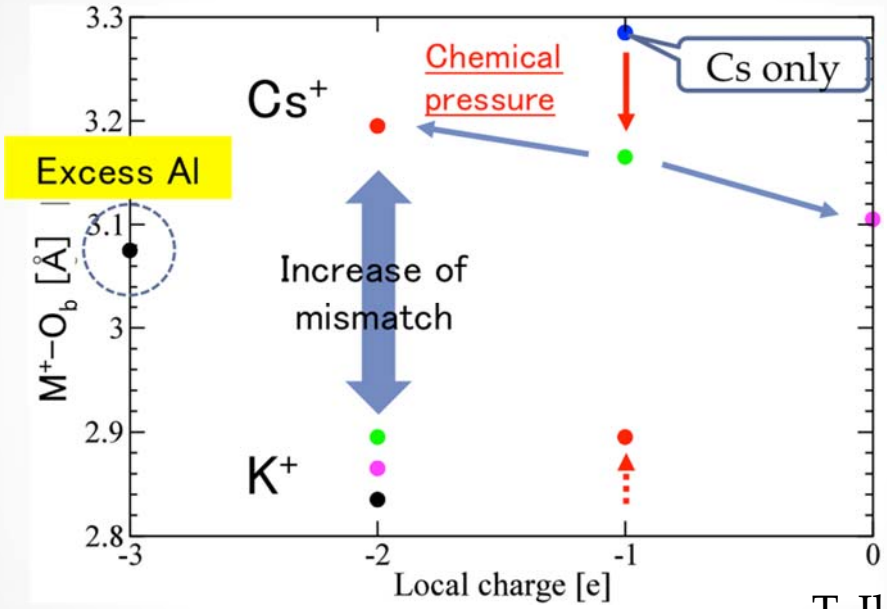


Okumura et al., 2013

$Cs\text{-}O_1$<3 Å



Relationship between local charge and M^+-O_b distance



T. Ikeda, 2013

A Cs-O distance contains several type of interaction between Cs and clay mineral.

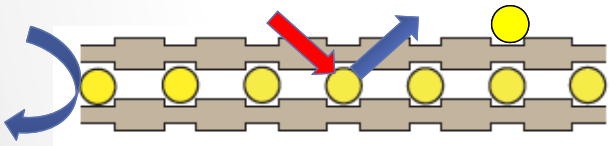
Reversible or Irreversible?

$$A{\cdot}B \underset{}{\overset{K_n}{\rightleftharpoons}} A+B$$

$$-RT\ln K_n = \Delta G = \Delta H - T\Delta S$$

several processes?
Breaking clay structure?

$\Delta H \approx$ 50 kJ/mol

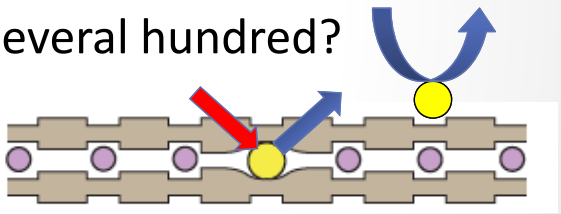


$Cs\text{-}O_2 = 3.25$ Å

Weak covalent bond

$\Delta H \approx$ 20 kJ/mo

ΔH several hundred?



$Cs\text{-}O_1 = 2.97$ Å

strong covalent bond

Summary and Conclusion

1) From EXAFS and DFT analyses for Cs-Vermiculite and Illite, local structure around Cs were determined.

1) From Cs adsorption dynamics study by DXAFS, sorption mechanism of Cs on clay minerals was observed.

2) Chemical treatment and following STXM analysis suggested that there are several specific sorption site toward Cs in clay minerals.

Summary and Conclusion (continued)

4) DFT , MD calculations, and EXAFS results suggested that chemical bonds of Cs with clay minerals showed covalent bond features, and we begin to consider reasonable decontamination methods.

End of Talk

Thank you for your attention