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Cation Retention by Montmorillonite in Constrained Environments

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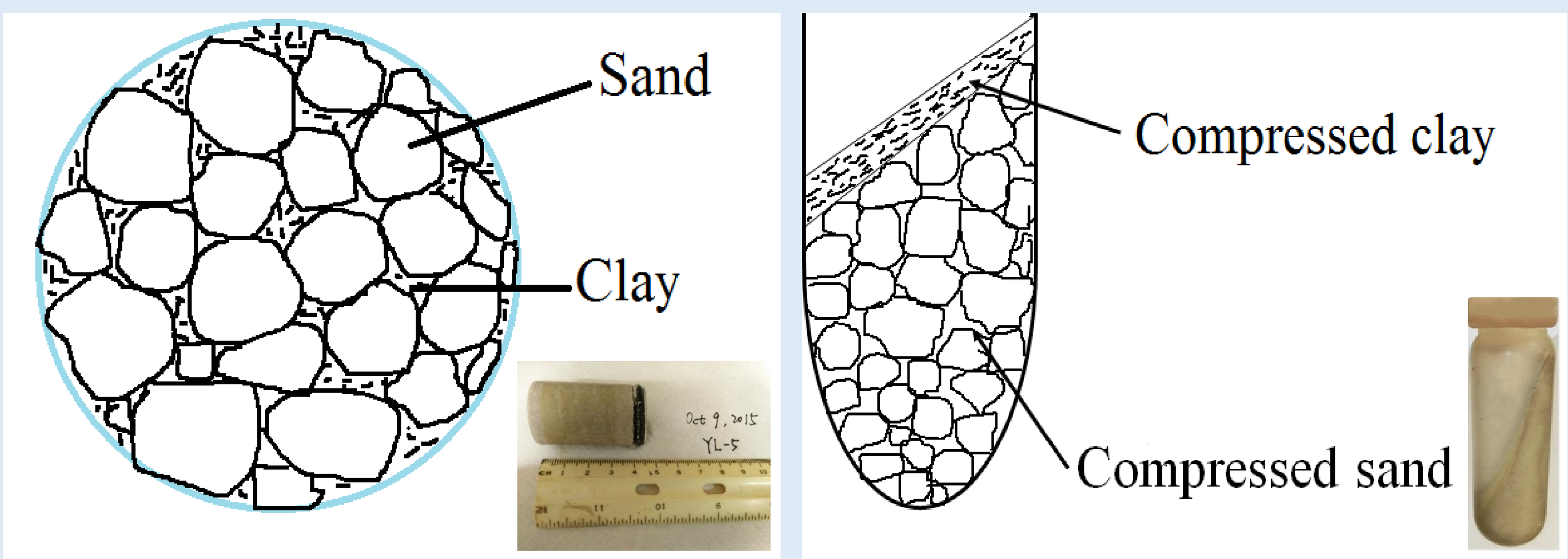
Introduction

Radioactive cesium contamination is a serious problem worldwide, and montmorillonite is widely used as an adsorbent to control its mobility. Understanding the retention mechanisms of cesium on montmorillonite will help us to better manage them.

Recent studies have found that cation retention increases significantly in constrained environments[1,2]. This is now known as the nanopore inner-sphere enhancement (NISE) effect. The NISE effect has been validated for some minerals, but not yet for montmorillonite clays. Because of the prevalence of this clay in nature, we seek to know if the NISE effect is also observed on this clay.

We used column and batch experiments to control the interlayer spacing of this clay. Since batch samples need to go through centrifugation before testing, it is possible that clays are compressed by this process. We also measured the interlayer spacing of clay by X-ray diffraction (XRD) method.



(A) Column (Non-constrained)

(B) Batch after centrifugation (Constrained)

Figure 1. Montmorillonite swelling in non-constrained and constrained environments.

Objectives

- ➢ Determine if NISE effect is applicable to montmorillonite.
- ➢ Explore the cation exchange process in constrained environments.

Materials & Methods

1) 2 g montmorillonite + 27 g sand + 30 mL 23.5 m*M* CsCl solution.

Non-constrained: column reaction at flow rate of 0.006 mL/min.

Constrained: batch reaction and then centrifuge at 39100 *g* for 30 min.

2) Analyze cation concentrations on ICP and d_{001} spacing with XRD.

Figure 2.
(A) Components of column
(B) Constructed column

Results & Discussion

The amount of K^+, Na^+, Ca^{2+} and Mg^{2+} adsorbed were higher in the non-constrained environments than the constrained environments, while Cs^+ adsorption was the opposite.

The amount of Cs^+ adsorbed was higher than Na^+ both in constrained and non-constrained environments.

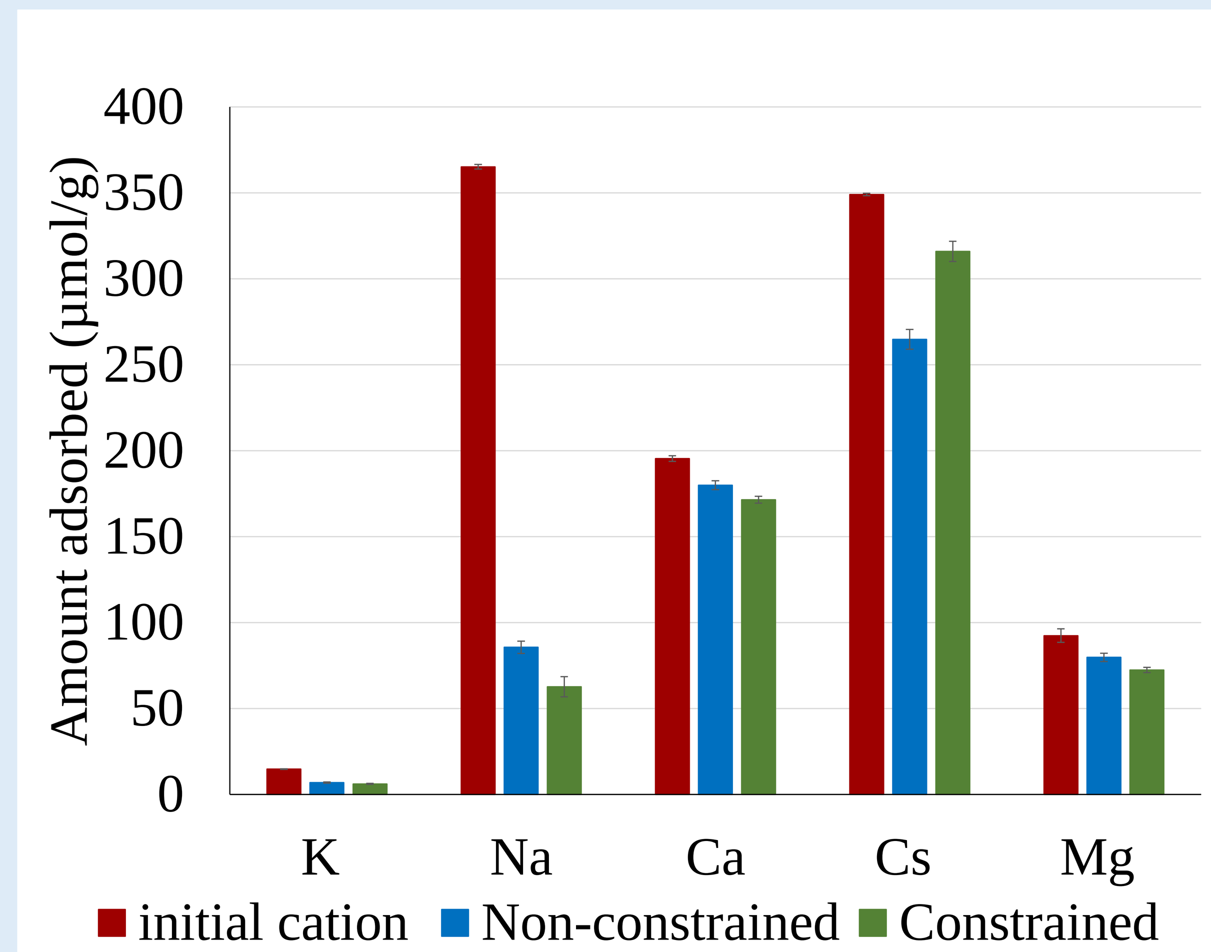


Figure 3. Cation adsorption on montmorillonite in constrained and non-constrained environments.

The interlayer spacing of montmorillonite in the column is higher than in batch after centrifugation.

Constrained interlayer = 3.089 Å

Non-constrained interlayer = 4.975 Å

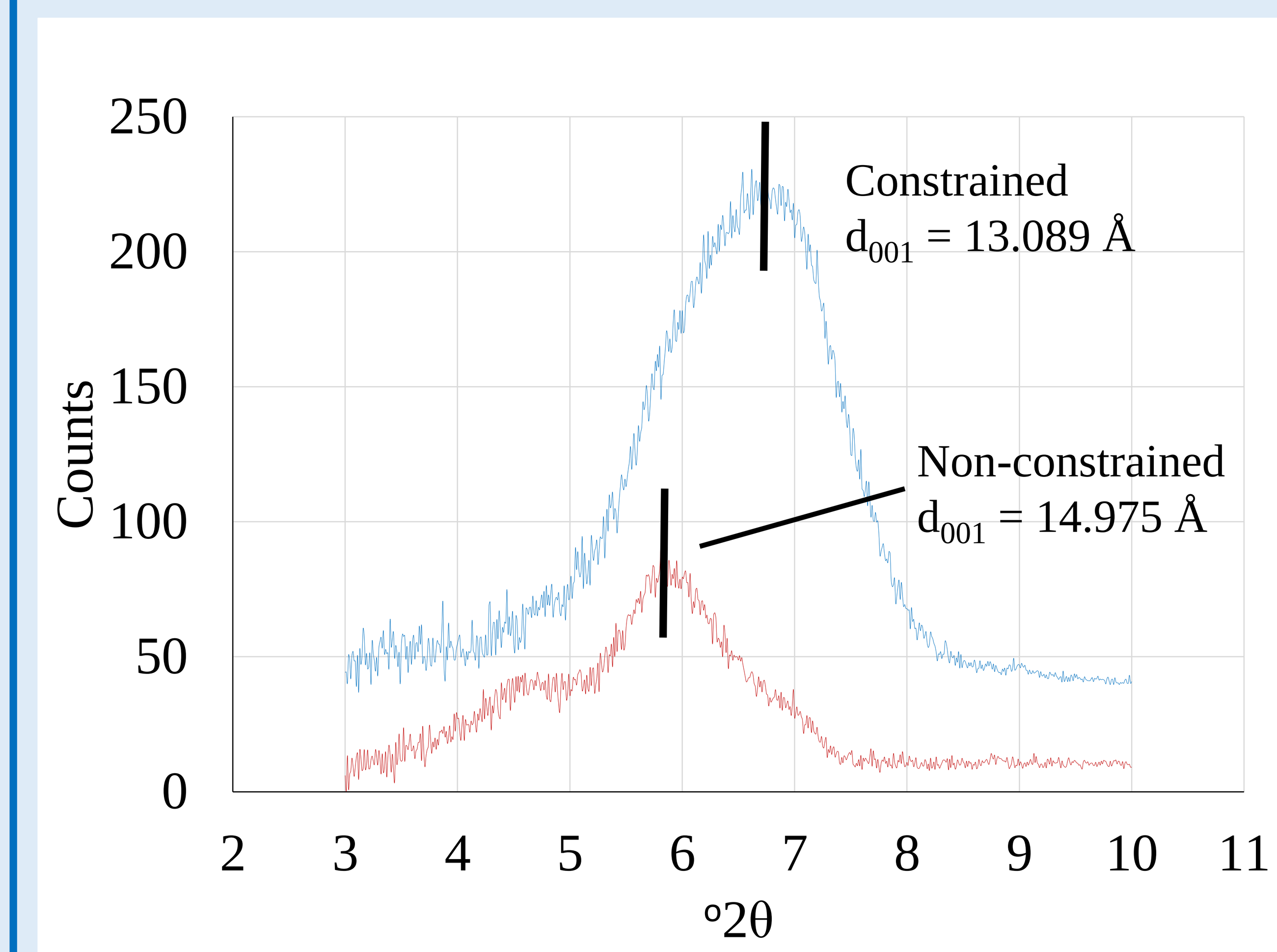


Figure 4. X-ray diffraction of montmorillonite in constrained and non-constrained environments.

The sum of K^+, Na^+, Ca^{2+}, Mg^{2+} adsorption difference (Δ = 55.33 ± 8.13 µmol$_c$/g) was close to Cs^+ (Δ = -51.14 ± 8.22 µmol$_c$/g).

Table 1. Cation adsorption in constrained and non-constrained environments. Unit of black colored numbers is µmol/g, unit of red colored numbers is µmol$_c$/g.

	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cs^+
Initial cation conc. (pH=4.74; n=6)	14.78 ± 0.23	365.20 ± 1.36	195.44 ± 1.64	92.47 ± 3.95	349.13 ± 0.69
Amount adsorbed					
Non-constrained (pH=7.62; n=11)	6.97 ± 0.38	85.68 ± 3.54	179.97 ± 2.58	79.84 ± 2.41	264.83 ± 5.76
Constrained (pH=7.95; n=24)	6.17 ± 0.29	62.75 ± 5.88	171.56 ± 1.98	72.45 ± 1.54	315.97 ± 5.87
Δ (Non-constrained – constrained)	0.80 ± 0.48	22.93 ± 6.86	8.41 ± 3.25	7.39 ± 2.86	**-51.14 ± 8.22**
$\sum$ (Δ of all except Cs)	**55.33 ± 8.13**				

Conclusions

- ➢ Adsorption of Cs^+ in constrained environments follows the NISE effect. That is, Cs^+ adsorption increases in constrained environments.
- ➢ However, other cations didn't follow the NISE effect. This may be due to cation competitive adsorption and cation exchange reactions in constrained environments. It may also be due to cation selectivity based on their relative hydration energies[1].

References

[1] Oba, M. 2015. Adsorption selectivity of cations in constrained environments. M.S. Thesis, University of Connecticut, Storrs, CT.

[2] Schulthess, C.P., R.W. Taylor, and D.R. Ferreira. 2011. The nanopore inner sphere enhancement effect on cation adsorption: Sodium and nickel. Soil Sci. Soc. Am. J. 75:378-388.

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