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Illitization of Potassium, Cesium, and Ammonium Exchanged Smectite

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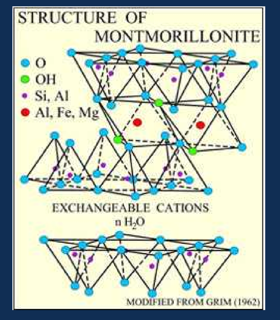
Motivation

Bentonite clay is a primary choice for engineered barrier systems within geologic repositories for disposal of radioactive wastes due to its low permeability at saturated states, warranting diffusion as the dominant transport mechanism, and large swelling pressures that promote sealing. In order to predict how well the barrier will function over time at repository relevant temperatures, it is important to understand thermal alteration effects on montmorillonite, better known as smectite, a main constituent of bentonite. One type of thermal alteration is the conversion to illite, thereby weakening barrier functions, when exposed to elevated temperatures and a sufficient amount of potassium ions. The path of illitization is complex and the kinetic reaction for all conditions is not fully understood, especially in terms outside of natural earth processes (i.e. nuclear waste temperatures and constituents). To facilitate the conversion of smectite to illite and examine the influence of interlayer cations, illitization experiments on cation exchanged smectite were performed within hydrothermal reaction vessels. The conversion has typically been thought to take a long time (months), but results here show alteration over one week timescales.

Background

Illitization is the formation of illite from smectite clay by diagenetic processes. The rate and extent of illitization is affected by the concentration of silica and potassium in solution, as well as time, temperature, initial composition of clay material, liquid to solid ratio, and pressure. The transformation from smectite to illite has been most commonly observed in natural sediments taken from various aged formations and at multiple depths. Laboratory studies (Roaldset et al. 1998, Huang et al. 1993, Mosser-Ruck et al. 2001, Velde and Vasseur 1992, and Inoue 1983 among others) have tried to reproduce the transformation under a wide variety of conditions. However, the conditions were based on efforts to replicate natural earth processes with commonly found elements, unlike results presented here.



$$2Na_{0.4}(Al_{1.47}Mg_{0.29}Fe_{0.18})Si_4O_{10}(OH)_2 + 0.85K^+ + 1.07H^+$$

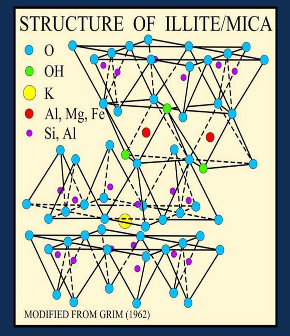
Na-Smectite

$$1.065K_{0.8}(Al_{1.98}Mg_{0.02})(Si_{3.22}Al_{0.78})O_{10}(OH)_2$$

Illite

$$+ 4.6SiO_2 + 0.36Fe(OH)_3 + 0.56Mg^{2+} + 0.8Na^+ + 0.9H_2O$$

From Huang et al. 1993



Approach

The reactor liquid to solid clay ratio is known to affect illitization rates, yet has only marginally been focused on it previous studies. Therefore, the approach in this study was to alter liquid to solid ratios reacted within 200mL acid digestion Parr Vessels, thereby examining if there is a critical point for conversion. In order to mitigate potential hazards by using the Parr Vessels, temperatures were limited to a max of 200ºC and liquid volumes to 150 mL. To determine the mass of clay, the amount of smectite needed to convert to 1 mole of illite was calculated based on their stoichiometric equations (above) and the solubility of SiO_2 at 200ºC. The optimal amount of smectite calculated was 0.169g, yielding a liquid to solid ratio of 1000. Various exchanged cation versions of SWy-2 Na-Smectite from the Clay Minerals Society Source Clays were utilized to see affects of initial clay composition. Reactor fluid consisted of 1M KCl for all reactions.

Experimental Procedure

Liquid to Solid Ratio	Clay Mass (g)	Liquid Volume (mL)
100	1.69	150
500	0.338	
1000	0.169	

Sample Preparation

- <75µm fraction: Crush and sieve SWy-2 Na-Smectite
- <2µm fraction: Suspension and settling of <75µm fraction
- Exchanges: Exchange <2µm fraction with 1M KCl, CsCl, and NH4Cl

Hydrothermal Alteration

- Parr Vessel Reaction: Place exchanged clay in Parr Vessel at various load ratios at 200°C

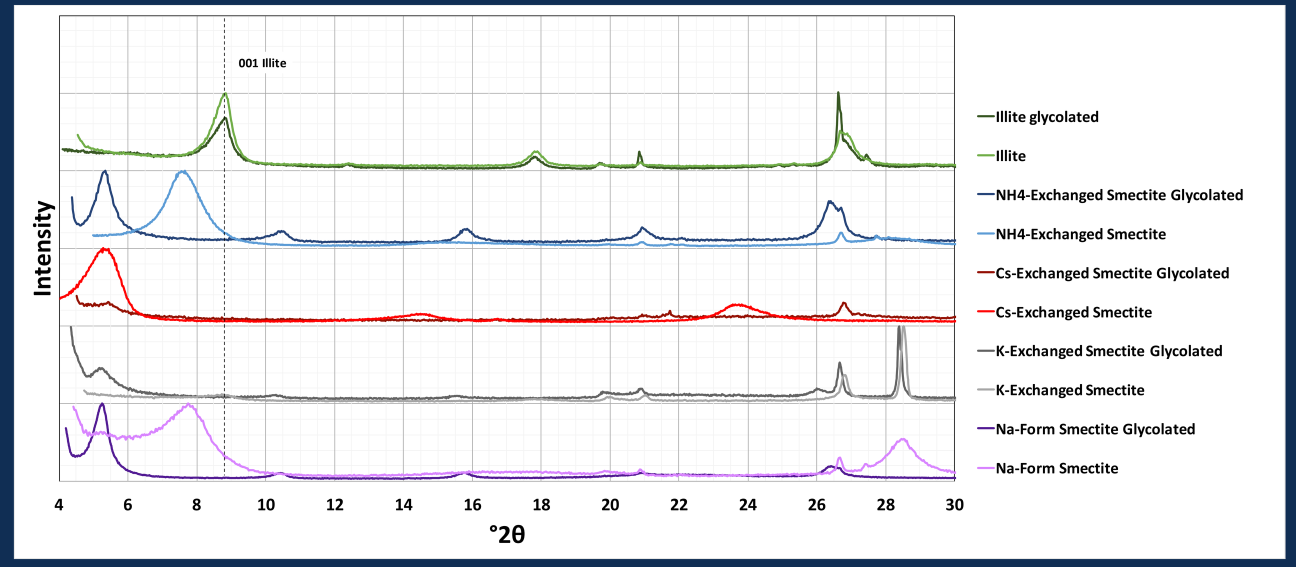
Conversion Investigation

- XRD Analysis: 001 peak from oriented and glycolated mounts

- Cation Exchange Capacity: $BaCl_2$ exchange method by Gillman (1986)
- Solid Recovery
- Released Elements
- Morphology from SEM

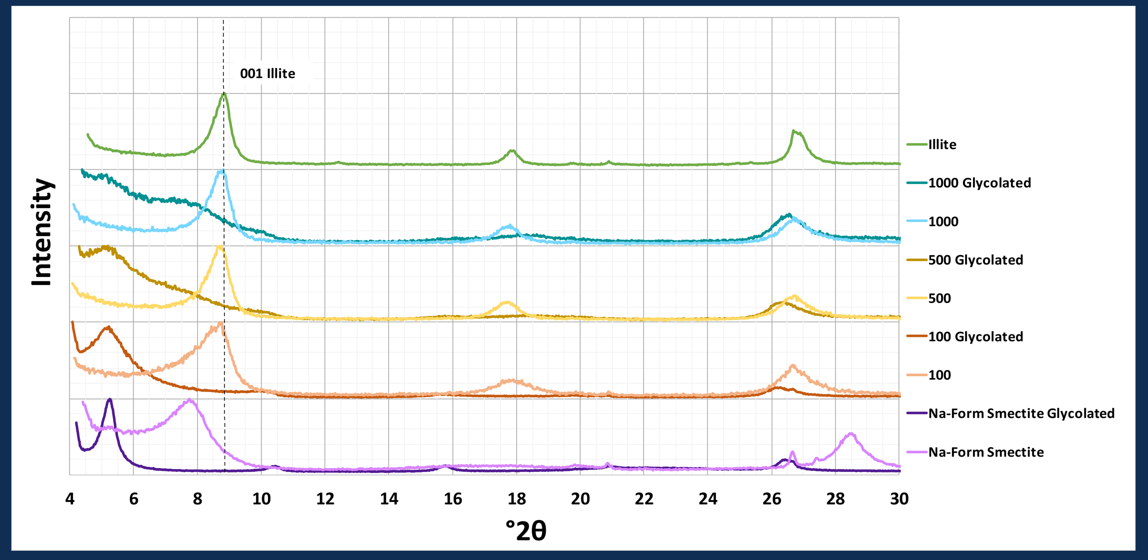
XRD Results

Clay oriented powder mounts were prepared on zero background silicon wafers. Glycolated samples were placed in a desiccator over a pool of ethylene glycol and put in an oven at 60°C for 24 hours. The powder diffraction data displayed here was collected in the 3°- 70° 2θ range using a Bruker Phaser Desktop Diffractometer and Cu*K* α radiation (1.54 Å). The time step was 0.2 seconds, with a total of 2556 steps.

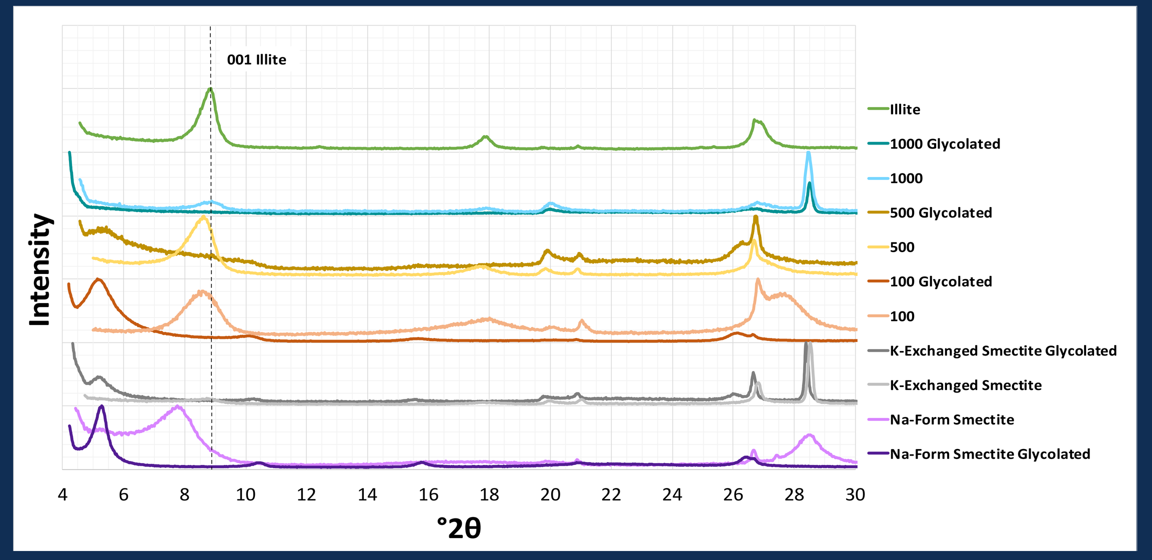


Starting Material

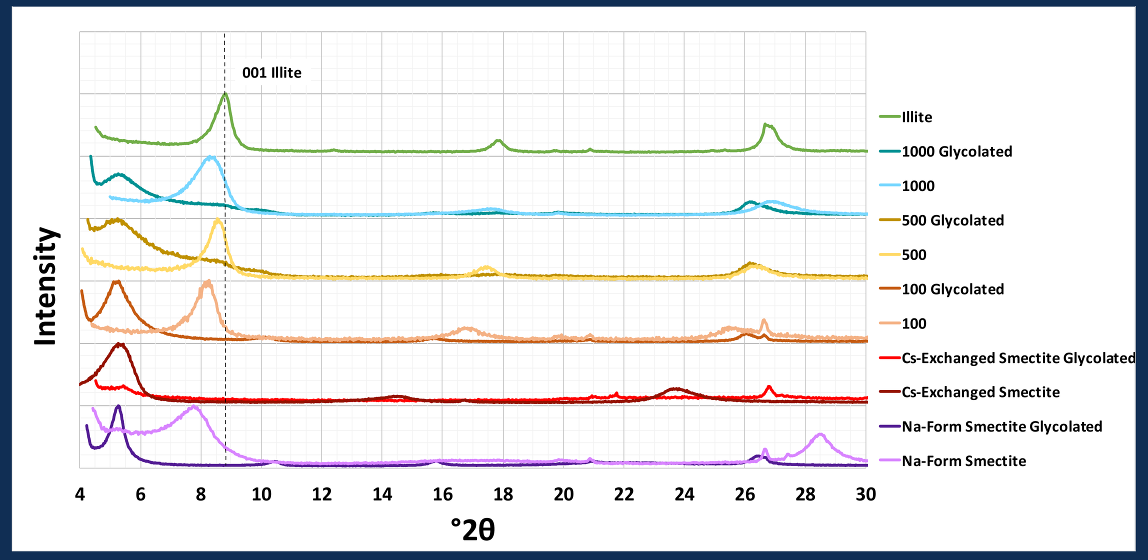
- 001 peaks of dry mount reacted clays shift closer to the illite 001 peak (noted in graphs) with increasing liquid to solid ratio, regardless of the starting interlayer cation.
- Glycolation in the higher liquid to solid ratios (1000), disrupts the crystalline structure shown by a diminished peak response. This indicates a weak structure or absent periodicity



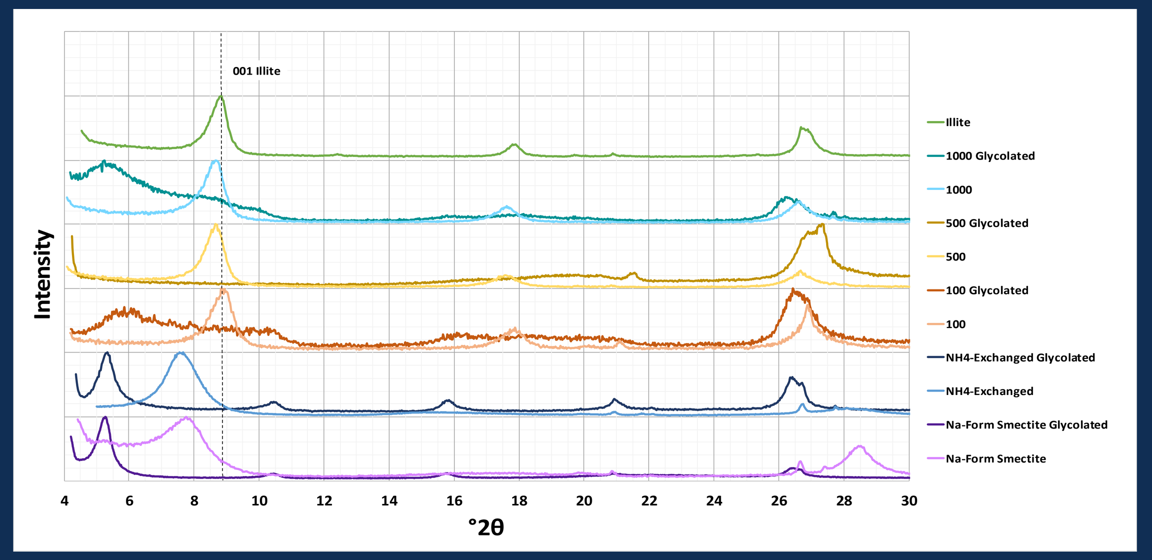
Na-Form Smectite



K-Exchanged Smectite

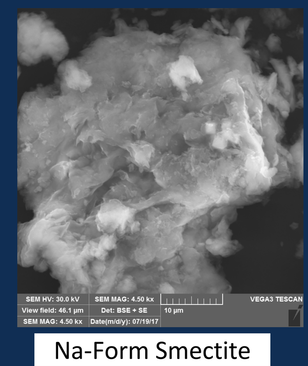


Cs-Exchanged Smectite

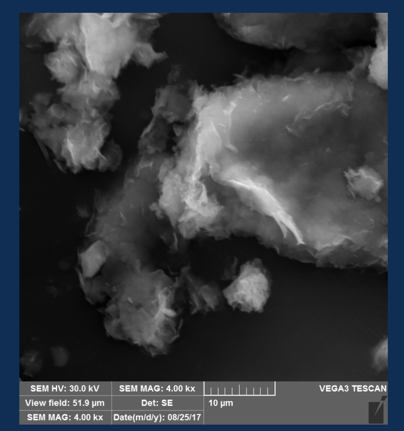


NH_4-Exchanged Smectite

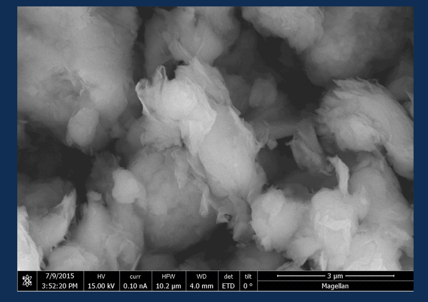
SEM



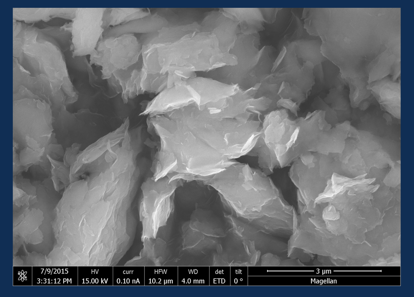
Na-Form Smectite



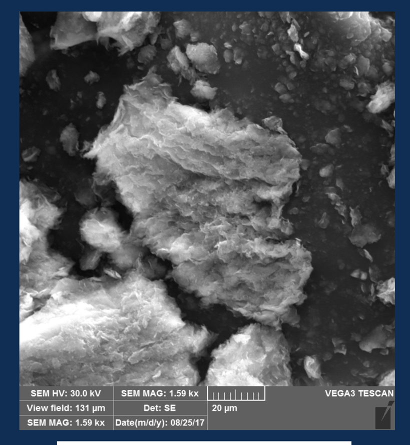
Na-Form Smectite: 1000 liquid/solid ratio



K-Exchanged Smectite

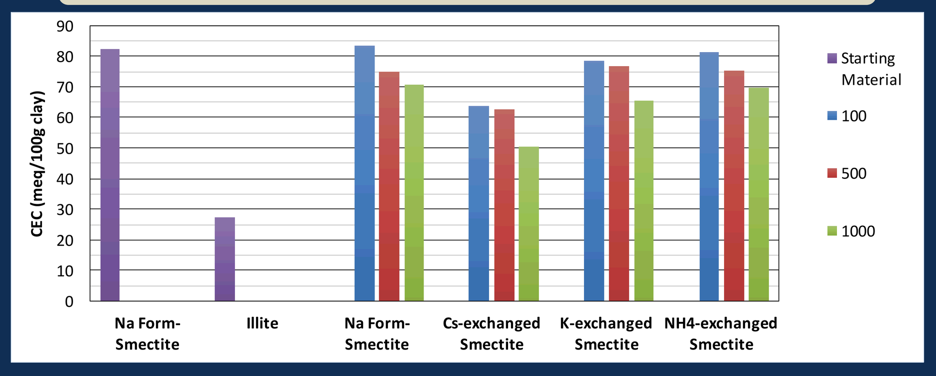


Cs-Exchanged Smectite



Cs-Exchanged Smectite: 1000 liquid/solid ratio

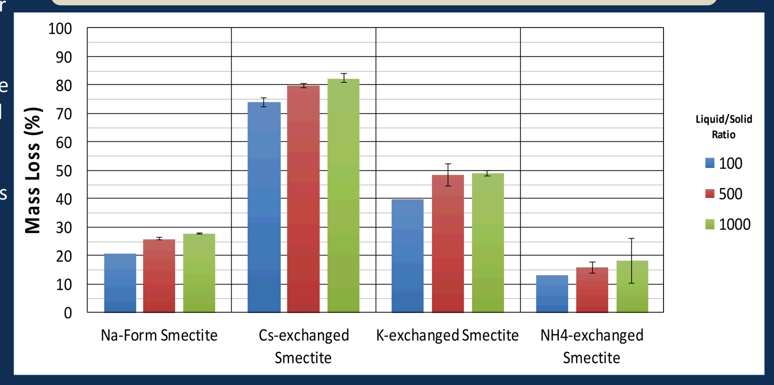
Cation Exchange Capacity of Reacted Clays



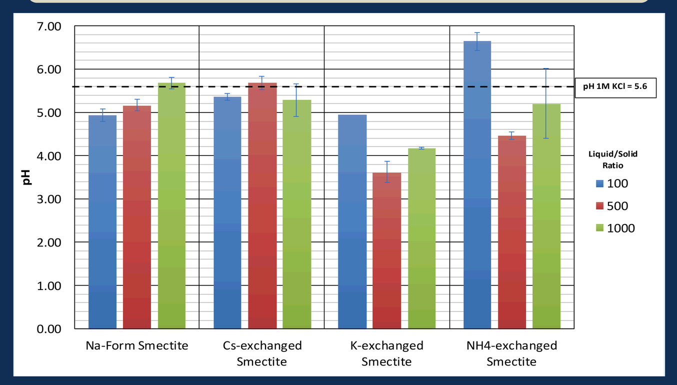
- Cation exchange capacity (CEC) of the reacted clays decreased as the liquid to solid ratio increased. This is encouraging since a lower CEC means the structure of the clay clearly changes, proceeding towards illite.

Mass Loss of Clay After Reaction

- Mass loss was seen after the clays were reacted, demonstrating the dissolving and/or release of interlayer cations and silica. This agrees with the derived stoichiometric equations by Huang et al. 1993. Cesium samples experienced a higher mass loss due to the much larger atomic weight of the cation.



pH Change of Reacted Solution



Take Aways:

- Illitization was shown to convert much faster than previously thought, within one week timeframe
- A higher liquid to solid solution ratio produced a clear change within the clay structure demonstrated by the shift in the smectite 001 peak towards illite.
- Glycolation still produced a peak shift in lower liquid to solid ratios, yet eliminates 001 peak at higher liquid to solid ratios. This indicates the reacted material has a weak crystallized structure and glycolation disrupts crystallites, making it amorphous.
- Cation exchange capacity of reacted clays decreased with increasing solid to solution ratio

Ongoing Work:

Further analysis of clay structure, properties, and composition will be attempted on reacted clays. Techniques include BET for surface area measurements, XRF or microprobe for composition, XRD source match comparisons, and additional SEM photomicrographs for morphology changes. Different reaction conditions will also be investigated such as including mixed layer clays (illite/smectite), vermiculite, adding mica or quartz to the system, and changing the reactor solution.

References:

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Acknowledgements:

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