



Solid-State NMR Studies of Hydroxyl-Promoted Kaolinite Dissolution under Simulated Tank Waste Conditions

Environmental Problem

- The Vadose Zone at the Hanford Reservation (HR) in Richland, WA is contaminated with hazardous and radioactive contaminants.
 - The HR is one of the most contaminated sites in the world.
 - Nuclear weapons production led to the release of 1.7 trillion liters of liquid waste to the ground at Hanford.
 - 67% of waste storage tanks are known to have leaked or are currently leaking.
 - ¹³⁷Cs and ⁹⁰Sr are the main contributors to site radioactivity.
 - Although not used for human consumption, HR water feeds into the Columbia River posing a threat to salmon habitats.
- ¹³⁷Cs/⁹⁰Sr fate and mobility may be affected by mineral weathering processes at the site (Buck et al. 2004 and Chorover et al. 2003).
 - Field and laboratory studies suggest that mineral weathering reactions produce mineral phases which can entrap Cs and Sr.
 - Nitrate-cancrinite, a Cs and Sr sorbent, was found in Hanford tank sludge.
 - Limited data exists pertaining to mineral weathering processes occurring under HR geochemical conditions, thus more studies are needed to better assess potential threats and to help develop better remediation and preventative strategies.

References

- Buck, E.C. and B.K. McNamara, *Environ. Sci. Technol.* **2004**, *38*, 4431.
 Chorover, J. et al., *Environ. Sci. Technol.* **2003**, *37*, 2200.

Hypothesis

- Hydroxyl-promoted dissolution of minerals in simulated tank waste leachates (STWL) lead to the formation of new phases that can influence the mobility of Cs and Sr in Hanford soils.

Research Plan

- Evaluate the weathering behavior of Kaolinite (K) in STWL.
 - Prepared batch reactors of simulated tank waste leachate with ¹³³Cs and ⁹⁰Sr and monitored kaolinite dissolution.
 - ²⁷Al nuclear magnetic resonance (NMR) spectroscopy, in conjunction with other spectroscopic and microscopic methods, was used to evaluate the weathering behavior of kaolinite and the formation of new mineral phases in reactors.
 - ²⁷Al NMR was used to assess the effects of ¹³³Cs and ⁸⁷Sr concentrations on neophase formation.
 - ²⁷Al NMR was used to quantify the relative amount of neophases forming in the reactor.
- Propose mechanisms of ¹³³Cs and ⁸⁷Sr removal from STWL leachate
 - ¹³³Cs and ⁸⁷Sr have different hydration properties and different solubilities thus, removal mechanisms are likely different.

Results

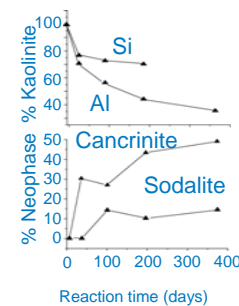


Fig. 1: ²⁹Si and ²⁷Al NMR of kaolinite dissolution in STWL (top); ²⁷Al NMR of cancrinite (C) and sodalite (S) formation in STWL (bottom).

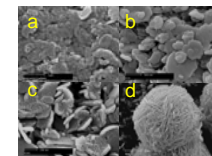


Fig. 2: SEM images: (a) 0 days kaolinite, (b) 1 day w/ S and K, (c) 30 days w/ S, C, and K, (d) Unidentified aluminum phase at 190 days.

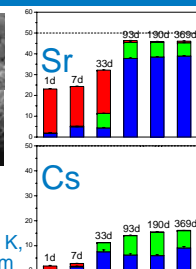


Fig. 3: Sr and Cs uptake from solution.

Conclusions

- Hydroxyl-promoted dissolution reactions of kaolinite are incongruent and lead to the formation of cancrinite and sodalite.
- The overall rate of dissolution is determined by Si release to solution.
- Sr removal is rapid and likely occurs via precipitation.
- Cs removal is gradual, occurs via an ion-exchange mechanism, and correlates to the formation of cancrinite and sodalite.
- Cs likely absorbs to cancrinite and sodalite phases.

Research Implications

- Knowledge gained from this simulated system can be combined with other studies to better decide how to allocate resources for the environmental management of this site.
- ¹³⁷Cs and ⁹⁰Sr are contaminants at the DOE Savannah River site, and as such, the results of this study should provide knowledge about the likelihood of radionuclide transport at this site.