Role of Ionic Strength on Sorption of Neodymium on Dolomite

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Background

The Waste Isolation Pilot Plant (WIPP) is a deep geologic repository for permanent disposal of transuranic, radioactive waste that is a byproduct of the nation’s nuclear defense program. In the most likely WIPP Release scenario, human intrusion (cuttings, cavities, spallings) can lead to direct and/or long-term brine release (US DOE 1995, US DOE 1996, Perkins et al. 1999). Once the brine is released, it may proceed through the Ruelster formation (the most transmissive layer being the Caliche dolomite) and pose a potential threat to the environment (Perkins et al., 1999).

The chemical behavior of actinide series elements (the most long-lived byproduct of the waste created from development of nuclear weapons) is a major concern for the WIPP due to their long half-lives and unknown mobility in the WIPP environment. In this work, we are investigating the fate and transport of trivalent actinides with neodymium as a non-radioactive, chemical analog.

These data are important for the WIPP performance assessment (PA). The previous PA assumed a Kd of 20-40 M/L g for Ps and Am. In literature, previous Kd’s have been measured from 10^4 to 10^6 M/L g for dolomite (e.g. Brady et al., 1999, Perkins et al., 1999, Brush & Storz, 1996). However, there is a need to refine these data under relevant conditions for the WIPP repository.

Objective

To update experimental sorption data for trivalent actinides and lanthanides under simplified systems to complement LANL ACRSP research for the WIPP 5-year re-certification. Kinetic and equilibrium sorption Kd’s as well as sorption capacity of dolomite will be measured to better evaluate the mobility of trivalent actinides and lanthanides.

Materials and Methods

Batch Experiments
- 20 ppb Nd, pH 8.5
- 0.01 to 5.0 M IS (3 mM NaHCO₃ + NaCl)
- 0.5 to 5.0 g/L crushed dolomite (335 – 500 µm)
- Placed on an end-over-end mixer at 40 rpm
- Sampling from 15 minutes to 48 hours

Continuous injection mini columns
- 1 cm Teflon column (+1 gram dolomite, porosity 0.32, 0.45 mL pore volume)
- 0.01 and 5.0 M IS (3 mM NaHCO₃ + NaCl)
- 20 ppb Nd, Target pH 8.5
- Continuous injection of Nd at 1.5 mL/hr flow rate (~20 min retention time)

Results

Batch kinetics experimental results at variable ionic strength from 0.01 to 5.0 M

What is a Kd?

A contaminant partitioning coefficient between the solid and aqueous phase. Generally, only equilibrium Kd’s are reported but kinetic data will also be shown as Kd’s for simplicity.

Where:

Kd = [Nd]solid / [Nd]aqueous

R = 1 + Pd / nKd

Figure 1: Sorption of Nd (initially 20 ppb) with respect to time at variable ionic strength (as 3 mM NaHCO₃ + NaCl) at pH 8.5 in the presence of 5 g/L dolomite as expressed by Kd partitioning coefficients (mL/g)

Discussion

Increasing ionic strength leads to an increase in activity which may impact both aqueous speciation and mineral solubility

(1) Changes in aqueous speciation of Nd due to increases in activity (hydrolysis and carbonate complexation) => SORPTION?

Previous work has shown increases in sorption with ionic strength consistent with batch results presented here. (1) Neptunium sorption to minerals at 4 vs. 2 M ionic strength (Almas et al., 2013), (2) Th(IV) sorption to hematite at 0.1 vs. 1.0 M ionic strength (Powell et al., 2016), (3) U(VI) sorption to hematite and montmorillonite at 0.1 vs. 1.0 M ionic strength (Powell et al., 2016)

(2) Increases in solubility and exchange of mineral with the aqueous phase due to increases in activity => INCORPORATION?

Previous work suggests that both processes likely play a role in the removal of trivalent actinides and lanthanides from the aqueous phase.

TRILFS measurements at pH 8.1 in 0.01 M IS (as NaClO₄) identified two surface species for Cu⁴⁺ interacting with calcite including (1) a surface adsorbed species and (2) an incorporated species (Fernandez, et al. 2008).

Our work suggests incorporation as a major factor leading to changes with ionic strength in batch experiments. However, due to constant flow and a short (20 minute) retention time, we expect co-precipitation processes that lead to incorporation to be negligible in the mini column experiments. Hence, a lack of effect of ionic strength in column experiments suggesting adsorption is not ionic strength dependent.

Relevance to the Waste Isolation Pilot Plant

Based on this work in simplified NaCl brines, the assumed Kd range of 20-400 M/L g for the WIPP performance assessment likely over predicts the mobility of the trivalent actinides as the maximum Kd from batch experiments is more representative of column results. However, additional work is ongoing to investigate more complex brines and the effect of ligands.

Future Work

Future experiments will focus on understanding the chemistry in the solid phase of these experiments via scanning electron microscopy and electron microprobe analysis. Polished grain mounts are currently under preparation for dolomite loaded with Nd under batch and column experimental conditions for comparison.

This work will also be extended to include (1) MgCl₂ systems to account for Mg⁰ addition to the WIPP and its effect on chemistry, (2) Eu and Am to understand the applicability as an oxidation state analog, and (3) ligands including EDTA (due to its prevalence in the waste stream) and Chromohalobacter (as it has been isolated from near the WIPP) to quantify their effects on mobility.

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Full references available (email: hemerson@fiu.edu)