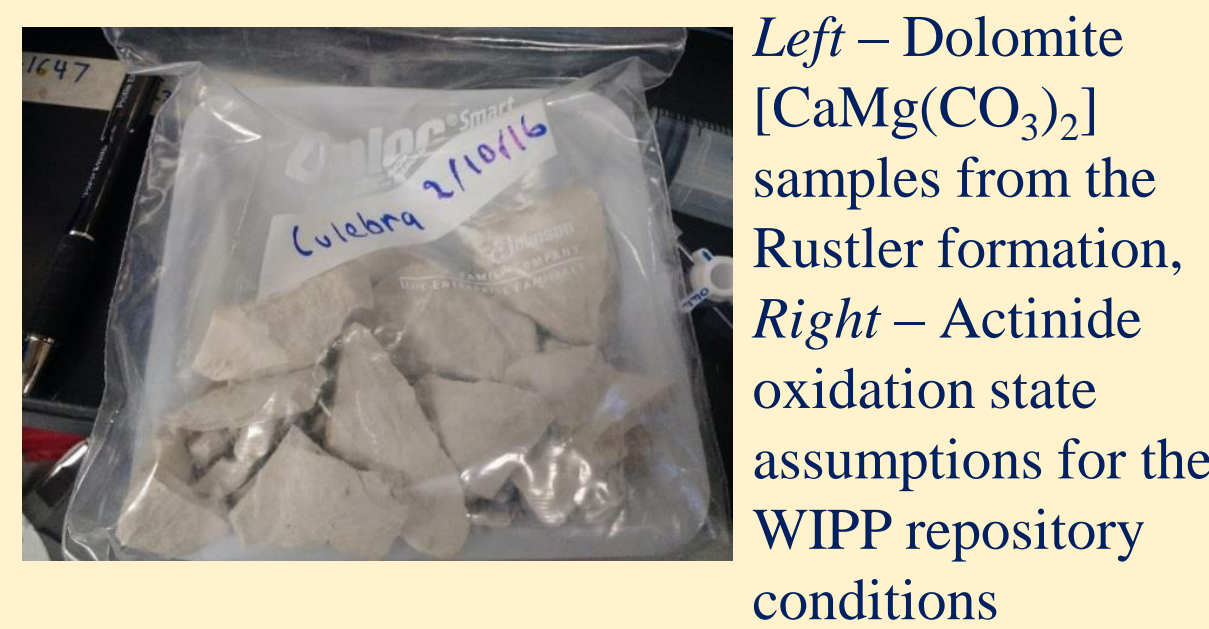


Background

The Waste Isolation Pilot Plant (WIPP) is a deep geologic repository for permanent disposal of transuranic, radioactive waste that is a byproduct from the nation's nuclear defense program. In the most likely WIPP Release scenario, human intrusion (cuttings, cavings, spillings) 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 Rustler formation (the most transmissive layer being the Culebra 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 K_d of 20-400 mL/g for Pu and Am. In literature, previous sorption K_d 's have been measured from $10^{3.4}$ to 10^6 mL/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.



Left – Dolomite [CaMg(CO₃)₂] samples from the Rustler formation, Right – Actinide oxidation state assumptions for the WIPP repository conditions

Actinide	Oxidation State				Speciation Data used in Model Predictions
	III	IV	V	VI	
Uranium		50%		50%	Thorium for U(VI), 1 mM fixed value for U(IV)
Plutonium	50%	50%			Am/Nd for Pu(III) and thorium for Pu(IV)
Americium	100%				Americium/neodymium

Species	Abundance
Nd(CO ₃) ₂ ⁻	67.45%
NdCO ₃ ⁺	32.23%
NdOH ⁺²	0.15%
NdHCO ₃ ⁺²	0.02%

Left - Vertical cross section of the Waste Isolation Pilot Plant deep geologic repository and surrounding geology with respect to depth, located near Carlsbad, NM, Above – Expected speciation for Nd in 0.1 M ionic strength (NaCl + 3 mM NaHCO₃) at pH 8.5

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 K_d '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 (355 – 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

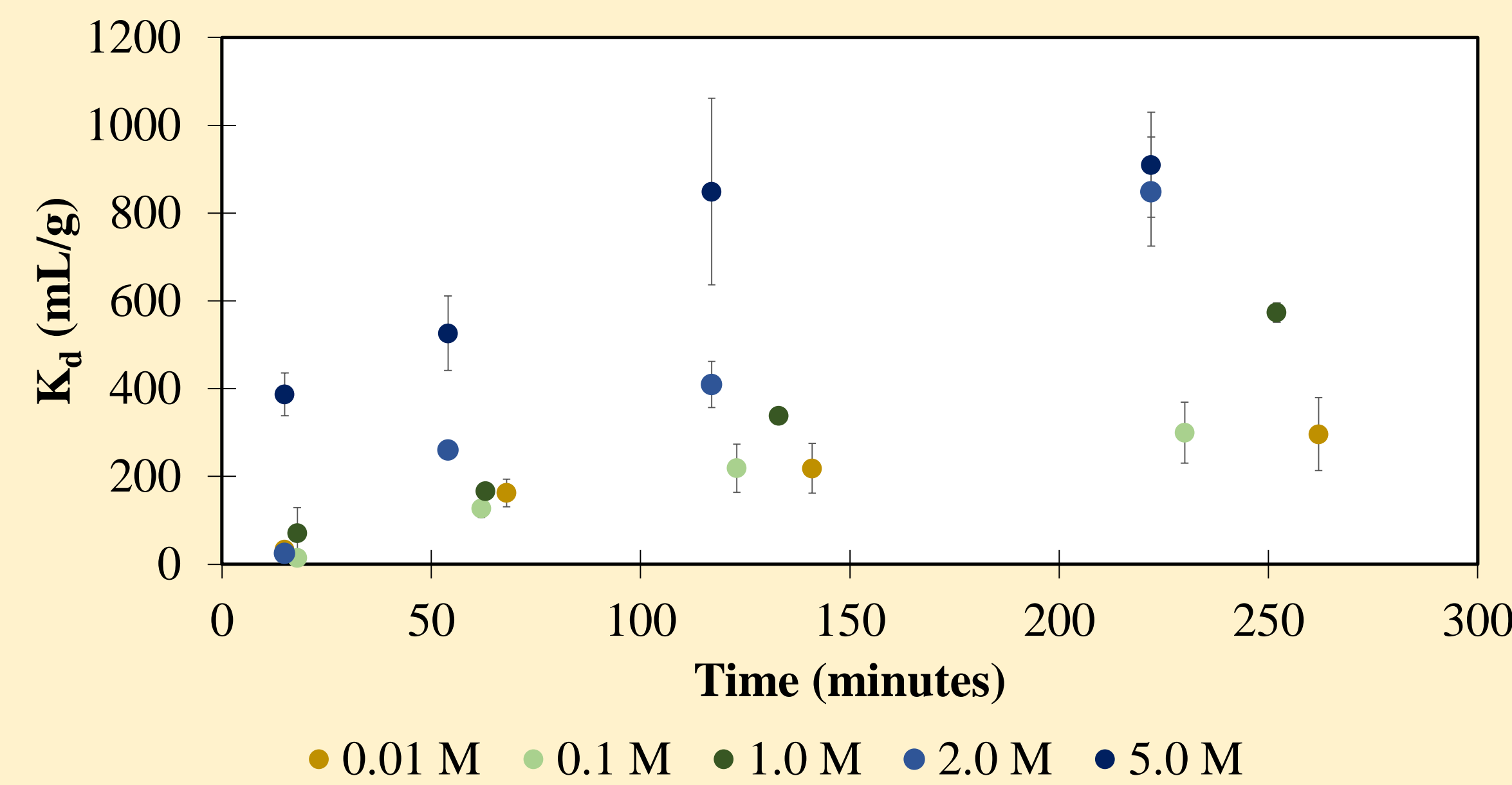


Figure 1: Sorption of Nd (initially 20 ppb) with respect to time at variable ionic strength (as 3 mM NaHCO₃ + NaCl) at pH 8.5 in the presence of 5 g/L dolomite as expressed by K_d partitioning coefficients (mL/g)

Table 1: Equilibrium K_d (24 hours) with respect to ionic strength based on batch experiments at 5.0 g/L dolomite and 20 ppb Nd, Note the increase in removal of Nd with increasing ionic strength

IS	pH	pC _{H+} [*]	K_d (mL/g)
5.0 M	7.42±0.11	8.28±0.13	6380±3060
2.0 M	7.92±0.23	8.22±0.24	1180±450
1.0 M	8.29±0.08	8.39±0.09	819±225
0.1 M	8.64±0.08	8.62±0.09	724±105
0.01 M	8.67±0.11	8.63±0.12	503±129

* pC_H calculated by empirical equation fit to previous data (Rai *et al.*, 2001)

What is a K_d ?

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

$$K_d = \frac{[Nd]_{solid}}{[Nd]_{aqueous}}$$

$$R = 1 + \frac{\rho_b}{n_e} K_d$$

Mini column saturation experimental results for 0.1 and 5.0 M ionic strength

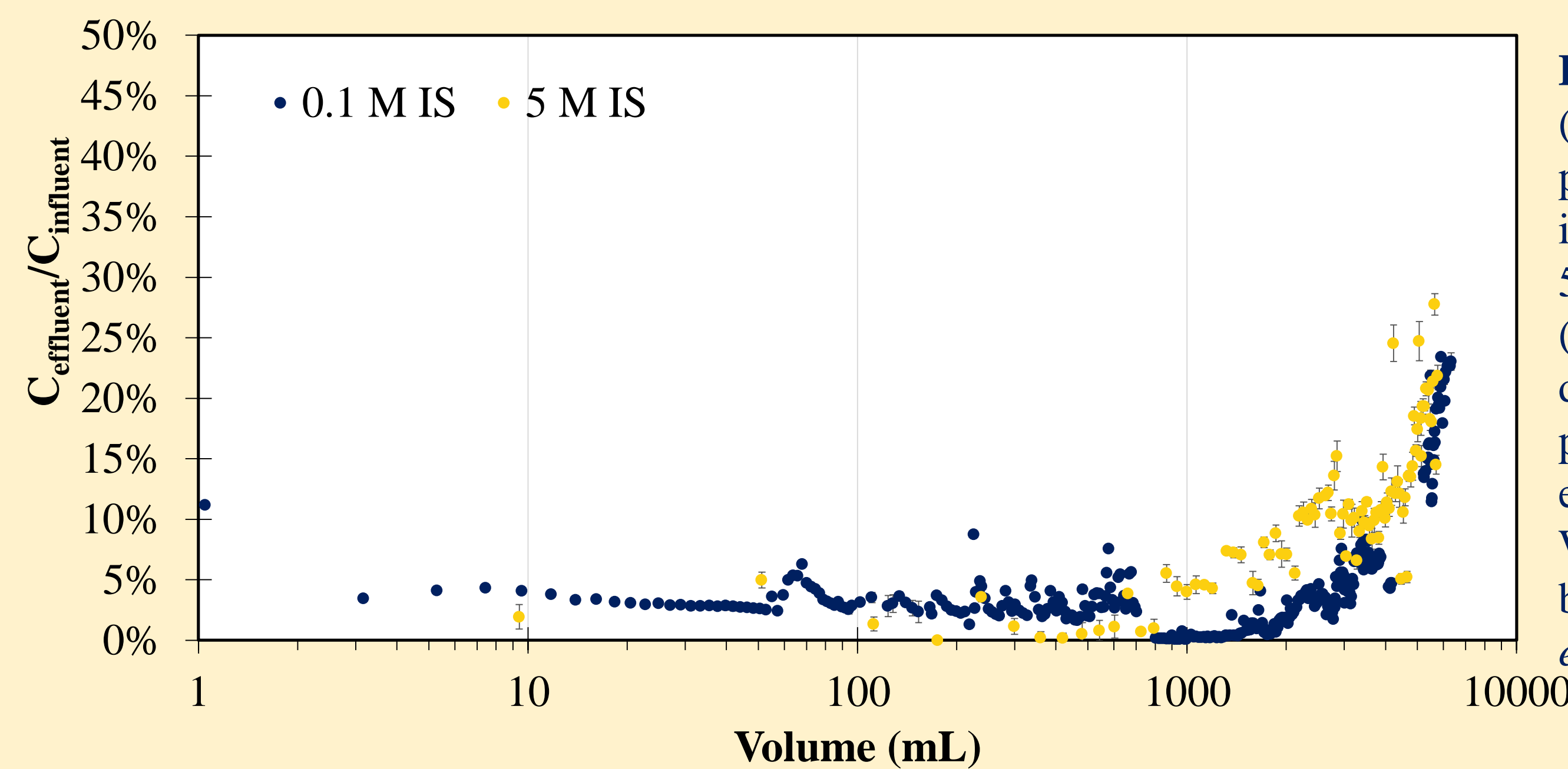
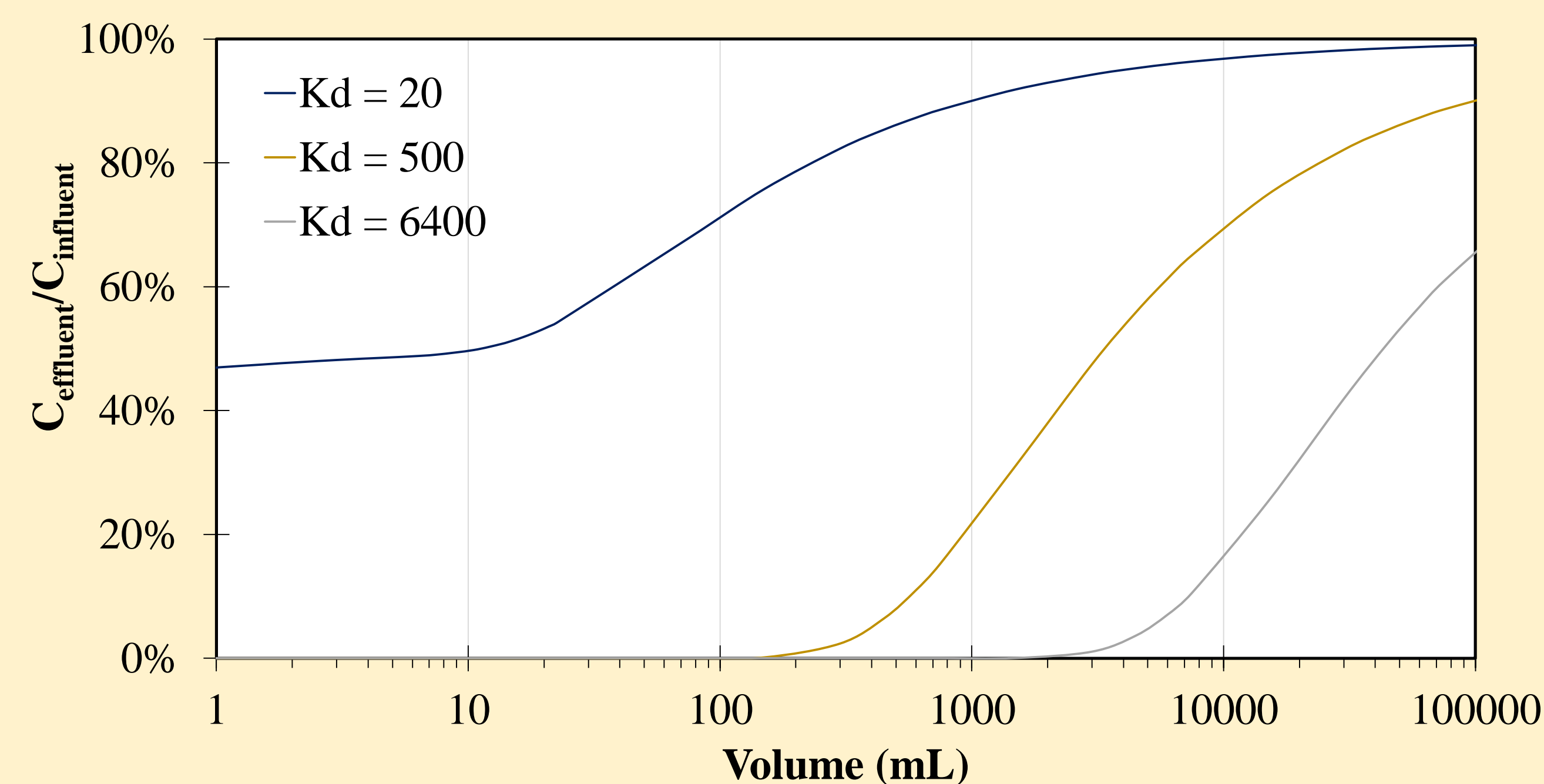


Figure 2: Breakthrough of Nd (influent concentration of 20 ppb) with respect to volume injected for 0.1 M (blue) and 5.0 M (yellow) ionic strength (3 mM NaHCO₃ + NaCl) for dolomite mini columns, Note: previous core column experiments for the original WIPP PA did not reach breakthrough for Am (Perkins *et al.*, 1999)

Figure 3: One-dimensional, constant dispersivity model of breakthrough of Nd (influent concentration of 20 ppb) with respect to volume injected for variable K_d 's from the lower range of the WIPP PA for Am (20 mL/g) to the upper range for batch experiments above (5 M IS, 6400 mL/g), dispersivity estimated by tracer breakthrough curves



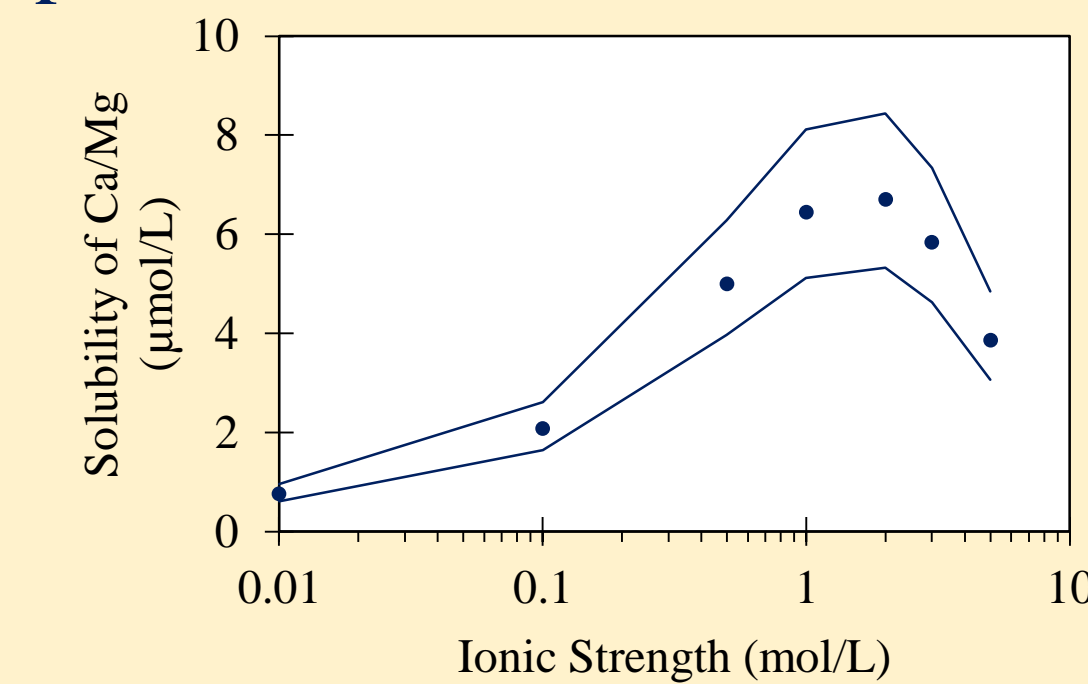
Discussion

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) Np(V) sorption to microbes at 4 vs. 2 M ionic strength (Ams *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?**



Aqueous concentration of Ca²⁺ and Mg²⁺ based on the solubility of dolomite at pH 8.5 in the presence of 3 mM NaHCO₃ at variable ionic strength as NaCl with activity corrections based on the SIT model. Note: lines represent the error on the K_{sp} value for dolomite as measured previously (Sherman and Barak, 2000).

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

TRLFS measurements at pH 8.1 in 0.01 M IS (as NaClO₄) identified two surface species for Cm³⁺ interacted with calcite including (1) a surface adsorbed species and (2) an incorporated species (Fernandes, *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 K_d range of 20-400 mL/g for the WIPP performance assessment likely over predicts the mobility of the trivalent actinides as the maximum K_d 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 MgO 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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