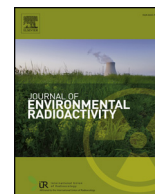




Contents lists available at ScienceDirect

## Journal of Environmental Radioactivity

journal homepage: [www.elsevier.com/locate/jenvrad](http://www.elsevier.com/locate/jenvrad)

## Retention of neodymium by dolomite at variable ionic strength as probed by batch and column experiments

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## ARTICLE INFO

## Keywords:

Dolomite  
Neodymium  
Lanthanide  
Actinide analogs  
Carbonates  
Sorption  
Incorporation Abbreviations:  
BET  
Brunauer Emmett Teller  
DOE  
Department of Energy  
EMPA  
Electron microprobe analysis  
ERDA-6  
Energy research and development administration well 6 brine  
GWB  
Generic weep brine  
ICP-MS  
Inductively coupled plasma mass spectrometer  
ICP-OES  
Inductively coupled plasma optical emission spectrometer  
PA  
Performance assessment  
PTFE  
Polytetrafluoroethylene  
SEM-EDS  
Scanning electron microscope with energy dispersive x-ray spectroscopy  
TRLFS  
Time resolved laser fluorescence spectroscopy  
WIPP  
Waste Isolation Pilot Plant  
XRD  
X-ray diffraction

## ABSTRACT

The results presented in this paper highlight the complexity of adsorption and incorporation processes of Nd with dolomite and significantly improve upon previous work investigating trivalent actinide and lanthanide interactions with dolomite. Both batch and mini column experiments were conducted at variable ionic strength. These data highlight the strong chemisorption of Nd to the dolomite surface (equilibrium  $K_d$ 's > 3000 mL/g) and suggest that equilibrium adsorption processes may not be affected by ionic strength based on similar results at 0.1 and 5.0 M ionic strength in column breakthrough and equilibrium batch (> 5 days) results. Mini column experiments conducted over approximately one year also represent a significant development in measurement of sorption of Nd in the presence of flow as previous large-scale column experiments did not achieve breakthrough likely due to the high loading capacity of dolomite for Nd (up to 240 µg/g). Batch experiments in the absence of flow show that the rate of Nd removal increases with increasing ionic strength (up to 5.0 M) with greater removal at greater ionic strength for a 24 h sampling point. We suggest that the increasing ionic strength induces increased mineral dissolution and re-precipitation caused by changes in activity with ionic strength that lead to increased removal of Nd through co-precipitation processes.

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## 1. Introduction

Dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ] is a major mineral constituent in shallow aquifers and deep geologic formations including those used for injection of wastewater brines and long-term disposal of radioactive wastes; therefore, there is a need to understand long-term behavior and sorption processes for contaminant interactions with dolomite. For example, the Waste Isolation Pilot Plant (WIPP) is a deep geologic repository used for the disposal of transuranic defense nuclear waste located over 650 m deep in a halite salt formation located near Carlsbad, NM, USA. Culebra dolomite member is the most transmissive geologic layer above the halite and has been suggested as the most susceptible release pathway in the unlikely event of contaminant-laden brine release from the repository (Meigs et al., 1997; Perkins et al., 1999).

Trivalent actinide partitioning to dolomite has been the focus of multiple reports for the WIPP due to their significance in the waste stream (Brady et al., 1999; Brush and Storz, 1996; Perkins et al., 1999). Researchers have previously utilized trivalent lanthanides as chemical analogs for trivalent actinides such as Am(III) and Pu(III) that are expected to exist in the WIPP environment (Brady et al., 1999; Lucchini et al., 2007). Lanthanides can be used as non-radioactive, invariant oxidation state analogs to understand the chemical behavior of actinides in the trivalent oxidation state. The stable oxidation state and similar chemical behavior allows for understanding of the chemical behavior of the +3 oxidation state in the absence of redox transformations (e.g. as would be expected with Pu) (Silva and Nitsche, 1995).

Previous work has observed strong sorption of trivalent actinides to dolomite; however, a wide range of partitioning coefficients ( $K_d$ 's) have been reported for both trivalent actinides and lanthanides as summarized in Table 1. Potential experimental artifacts complicate the universal application of these values for risk assessment (Brady et al., 1999; Brush and Storz, 1996; Perkins et al., 1999; Stout and Carroll, 1993). For example, Perkins et al. conducted intact-core experiments but did not record breakthrough of Am(III) after many months of injection (Perkins et al., 1999). In addition to sorption of Am(III), it is likely that precipitation occurred near the inlet due to exceedance of solubility. Batch-type laboratory experiments have also produced limited datasets describing trivalent actinide and lanthanide sorption to dolomite. Brady et al. used a limited residence time reactor technique and provided valuable insight into the challenges of the dolomite-lanthanide system. However, these experiments approached or exceeded Nd(III) solubility for pH 6–8 and reported a large uncertainty in data points which was likely due to measurements nearing analytical detection limits (Brady et al., 1999).

It is expected that trivalent actinides and lanthanides will interact with carbonate minerals through a fast initial adsorption process (by

electrostatic association or chemisorption) followed by a slower incorporation process observed and reported by others (Martin-Garin et al., 2003; Morse and Mackenzie, 1990). The second process may include diffusion into the surface, formation of  $\text{Me-CO}_3$  solid phases, and/or formation of a solid solution (Brady et al., 1999). Previous research by Martin-Garin et al. investigated the rapid adsorption of  $\text{Cd}^{2+}$  to calcite followed by slower uptake and incorporation and concluded that adsorption dominated for residence times of less than 30 min as compared to incorporation in flow cell reactors (Martin-Garin et al., 2003). Brady et al. reported equilibrium within 30 s for Nd and Am adsorption to dolomite with stirred reactors at variable pH in 0.05 and 0.5 M NaCl (Brady et al., 1999). Zavarin et al. observed equilibrium within 24 h for sorption without differentiating between adsorption and incorporation of actinides and lanthanides to calcite for pH from 7.5 to 9.75 (Zavarin et al., 2005). These previously reported results are highly variable with respect to the sorption equilibration time and the consideration of a secondary incorporation process for carbonate minerals.

Because research investigating the sorption of trivalent actinides and lanthanides to dolomite is limited, their interactions with calcite minerals can provide insight into dolomite sorption mechanisms as dolomite is comprised of alternating layers of calcite and magnesite (Brady et al., 1999; Stout and Carroll, 1993). Very strong sorption of trivalent actinides and lanthanides to calcite has been shown in laboratory experiments (Mecherri et al., 1990; Shanbhag and Morse, 1982; Zavarin et al., 2005; Zhong and Mucci, 1995) with negligible desorption likely due to strong chemisorption and incorporation (Brady et al., 1999; Mecherri et al., 1990; Shanbhag and Morse, 1982). Time-resolved laser fluorescence spectroscopy (TRLFS) experiments identified two surface species for Cm on calcite at pH 8.1: (1) a surface sorbed species and (2) an incorporated species (Fernandes et al., 2008; Stumpf and Fanghänel, 2002). These results suggest that Cm is initially sorbed at the hydrated calcite surface and, over time, slow dehydration and incorporation can occur (Stumpf and Fanghänel, 2002). Cm coordination is expected to be similar to a tetracarbonato species and may also substitute for  $\text{Ca}^{+2}$  in the calcite crystalline lattice. Similar behavior has also been observed for Eu and is expected for other trivalent actinides and lanthanides (Piriou et al., 1997).

The objective of this research was to understand the sorption of neodymium to dolomite under variable ionic strength including simplified conditions relevant to subsurface environments near the WIPP repository. The WIPP repository is located within the Salado geologic formation which is largely composed of halite (NaCl) and potash salts and results in high ionic strength porewater ( $I \geq 5$  M with Na, Mg, K, Cl) (Brady et al., 1999). However, in the event of a release from the repository, the ionic strength would change significantly as it is diluted with lower ionic strength groundwater. In order to understand the variability in actinide sorption capacity of dolomite related to solution ionic strength, we investigated a range from 0.01 to 5.0 M NaCl. Both batch sorption and mini-column experiments were conducted to evaluate sorption processes in the presence and absence of flow and under different solid to liquid ratios. Nd is used as a non-radioactive, invariant oxidation state analog to understand the chemical behavior of actinides in the trivalent oxidation state including Am(III) and Pu(III).

## 2. Materials and methods

### 2.1. Mineral collection and characterization

Dolomite mineral samples were collected from the Culebra bluff outcrop located on the bank of the Pecos River near the WIPP. Rock samples were crushed, cleaned and characterized prior to experiments. First, dolomite rock samples were crushed in an impact mortar and pestle (Chemplex, catalogue no. 850), washed with Milli-Q  $\text{H}_2\text{O}$  ( $> 18 \text{ M}\Omega\cdot\text{cm}$ ), and sieved through No. 45, 100 and 200 sizes (Fisher, Stainless steel). After repeated washing and sieving, all solids were dried for 24 h at 40 °C and re-sieved. To ensure consistent surface area

**Table 1**

Summary of previous research investigating actinide and lanthanide partitioning to dolomite.

Experimental Setup	Element	Conditions	$K_d$ (mL/g)	Reference
Batch	Am	NaCl brine	2570	(Dosch, 1979)
Batch	Am	Brine	2005	(Brush and Storz, 1996)
Intact core	Am	Brine	1000000 <sup>a</sup>	(Perkins et al., 1999)
Mixed reactor	Nd	0.05 M NaCl	300–3000 <sup>b</sup>	(Brady et al., 1999)
Mixed reactor	Am	0.05 and 0.5 M NaCl	$> 400^c$	(Brady et al., 1999)
WIPP PA assumption	$\text{Am}^{+3}$	WIPP conditions	20 to 500	(Brush and Storz, 1996)

<sup>a</sup> Possible precipitation of Am.

<sup>b</sup> Exceeded solubility above pH 8.

<sup>c</sup>  $K_d$ 's unmeasurable above pH 6.

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