

Sorption and Desorption of Cs(I), Sr(II), Eu(III), Nd(III), and Ce(IV) on Culebra Dolomite

LA-UR

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Introduction

The Waste Isolation Pilot Plant (WIPP) is the only deep geologic transuranic (TRU) waste repository operating in the United States. This repository is located in a salt deposit near Carlsbad, New Mexico over 600 meters below the surface. This salt deposit is beneath several different geologic formations, including various layers of dolomite. Below the repository, brine pockets at high pressures exist that could create a mechanism for the accidental release of radioactive material to the accessible environment through an accidental intrusion from boreholes drilled in association with efforts to extract resources in the Permian Basin. This brine could then carry radioactive material to the geologic layers above the repository and result in a far-field transport due to the transmissivity of the fractured culebra dolomite. The objective of this work is to investigate the sorption and desorption behavior of several different metal ions representing oxidation states from +I to +IV as a function of time. The metal ions are used as analogs for actinides found in the WIPP waste.

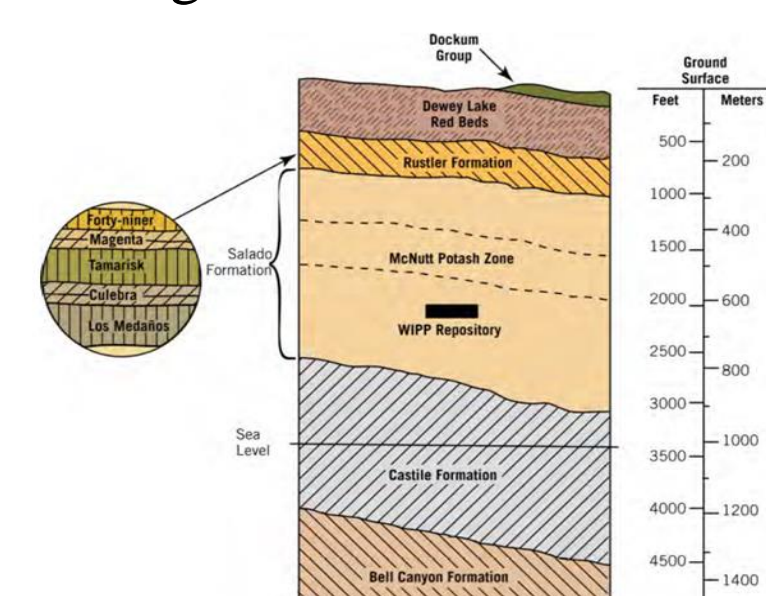


Fig. 1. Depiction of different layers below and above the WIPP.

Metal	Ox. State	Analog
Cs	1+	Cs
Sr	2+	Sr
Eu, Nd	3+	Am, Pu
Ce	4+	U, Pu, Np

Table 1. Oxidation State and Analog for Metal Ions in Studies.

Methods & Materials

Culebra and Brine Preparation

Culebra dolomite material was collected from the Culebra Bluff outcropping near the WIPP site and taken to the lab for further preparation. The rock was crushed using a percussion mortar and pestle and sieved to a 150-355 μm particle size range. These particles were washed and dried to be used in the experiments.

The sodium chloride brine was prepared in 2L batches and made to a concentration of 15 (w/v) % NaCl with 3mM of NaHCO_3 to act as a buffer to maintain the brine at pH 8-9.

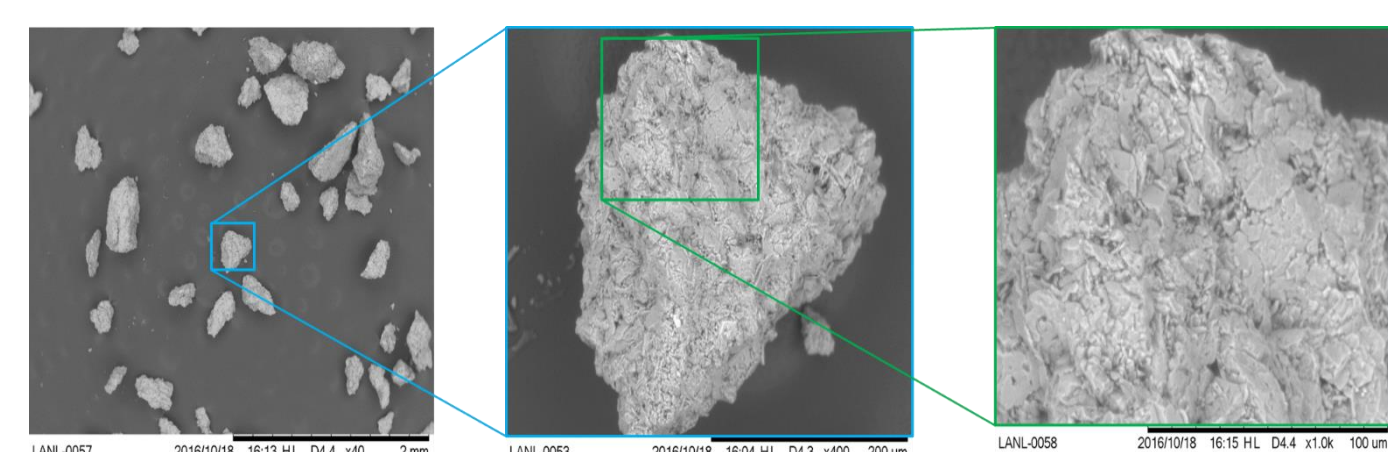


Fig. 2. SEM images of culebra used in experiments

Sorption Batch Setup and ICP-MS Sampling

Several different concentrations of each metal ion was selected to ensure sorption and saturation was measurable. Each concentration was done in duplicate as well as duplicate controls to account for sorption and desorption from the 60 mL polypropylene bottles. Each sample was 50 mL of brine with 0.05 g of Culebra dolomite.

ICP-MS Samples were taken approximately every 48 hours for sorption for 14 days and intermittently for the desorption for 7 days. Both total samples and samples filtered through 100 kDa cellulose filters were prepared for analysis.

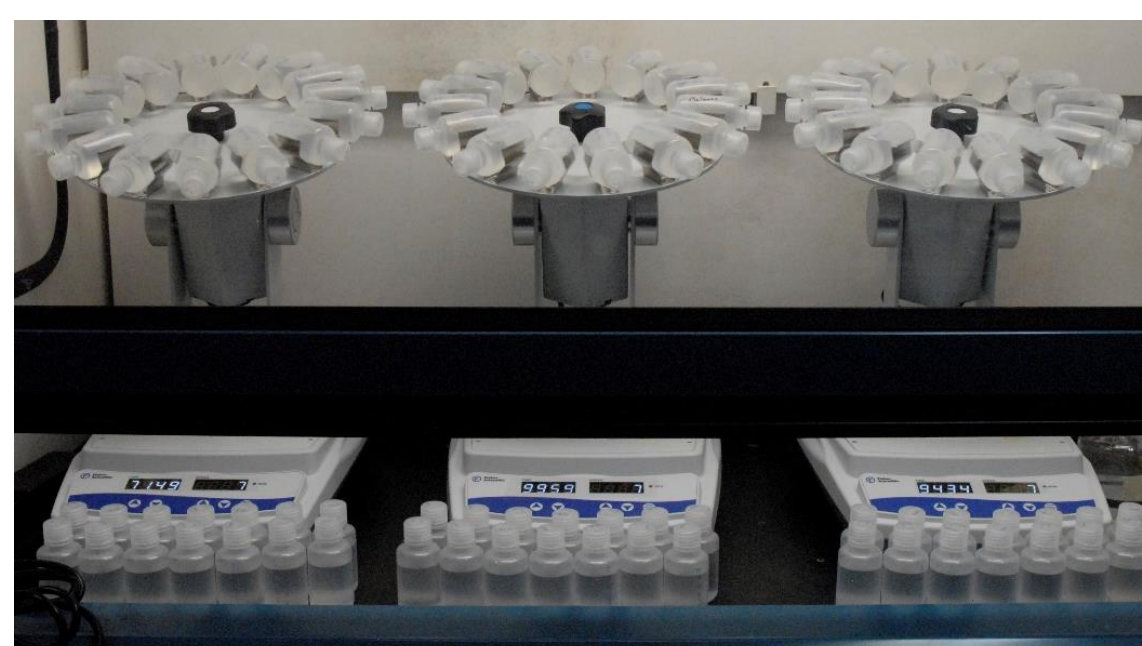


Fig. 3. Rotating samples with culebra and non-rotating controls

Results

Eu Sorption and Desorption

Fig. 4a shows the sorption curve with no Eu added to the solution. This was to ensure that the culebra did not have any Eu desorbing into the solution as the experiment progressed. Fig. 4b shows the 10,000 ppb Eu sorption curve. This shows that the highest concentration was enough to saturate the culebra with Eu ions to see the maximum amount of Eu the dolomite could sorb onto the surface. The data for 10, 300, 1000, 5000, and 10,000 ppb cases are not shown, but were sampled and being analyzed.

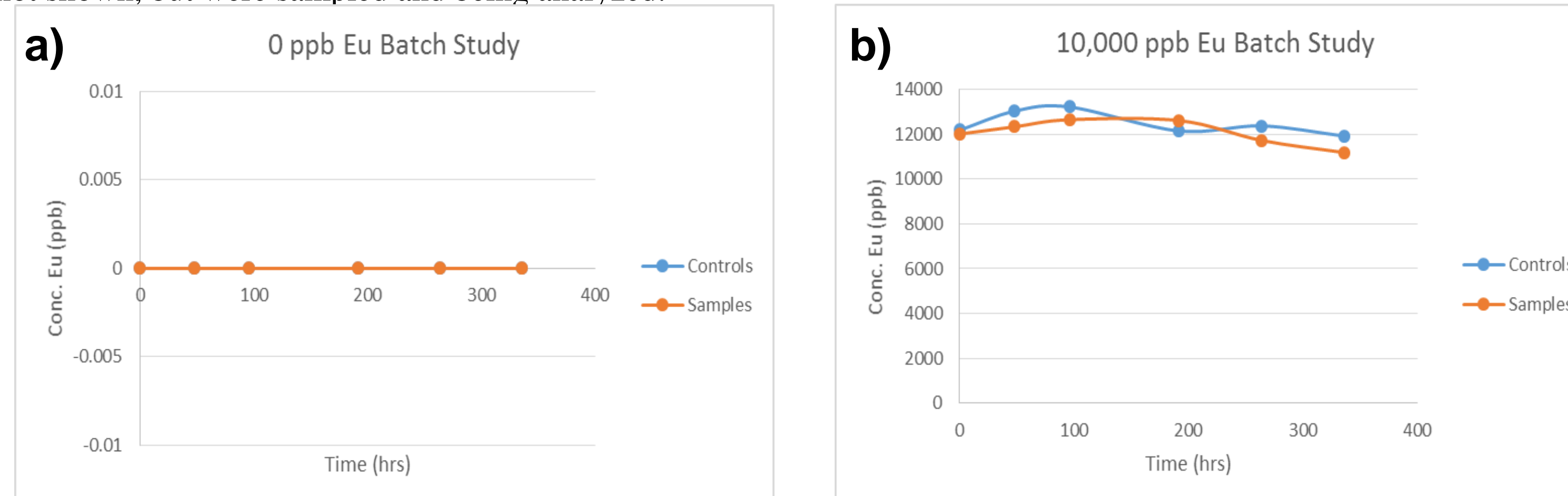


Fig. 4. Averaged sorption curves for (a) 0 ppb and (b) 10,000 ppb Eu onto culebra dolomite in 15(w/v)% NaCl brine solution. Error bars are shown in all figures, but are smaller than data points.

Fig. 5a shows sorption curve with 100 ppb Eu in the brine solution. As seen in the figure, the controls show no loss of Eu in the brine, indicating no sorption of Eu onto the polypropylene bottles themselves. The sample curve shows a steady decline of Eu in the solution until a steady state is achieved. This proves that the dolomite is being sorbed onto the culebra. Fig. 5b shows the desorption curve of 100 ppb Eu in the brine solution. The flat curve of the controls suggest that the polypropylene bottles did not sorb any Eu and did not desorb any material into the brine. The increasing concentration of Eu in the samples with culebra suggest that the sorption seen in the first phase of the experiment was physisorbed and can be easily desorbed off of the culebra.

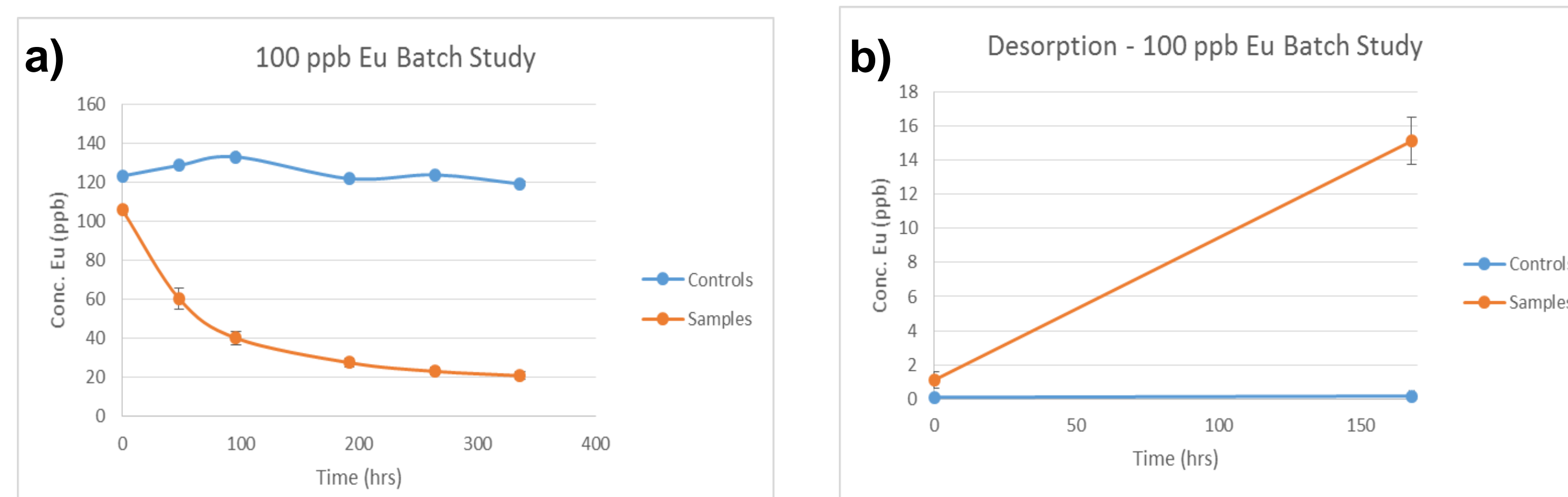


Fig. 5. (a) Averaged sorption curves and (b) averaged desorption curves of 100 ppb Eu onto culebra dolomite in 15(w/v)% NaCl brine solution.

Cs and Sr Sorption and Desorption

The sorption curves for Cs and Sr (fig 6a) show that the concentration of the ion stayed constant throughout the duration of the experiment. This would suggest that high concentration of Na from the brine sorbing to the surface of the culebra dolomite is more favorable than the Cs and Sr sorbing to the surface of the culebra. With none of the metal ions sorbing to the dolomite, there was no desorption curve observed.

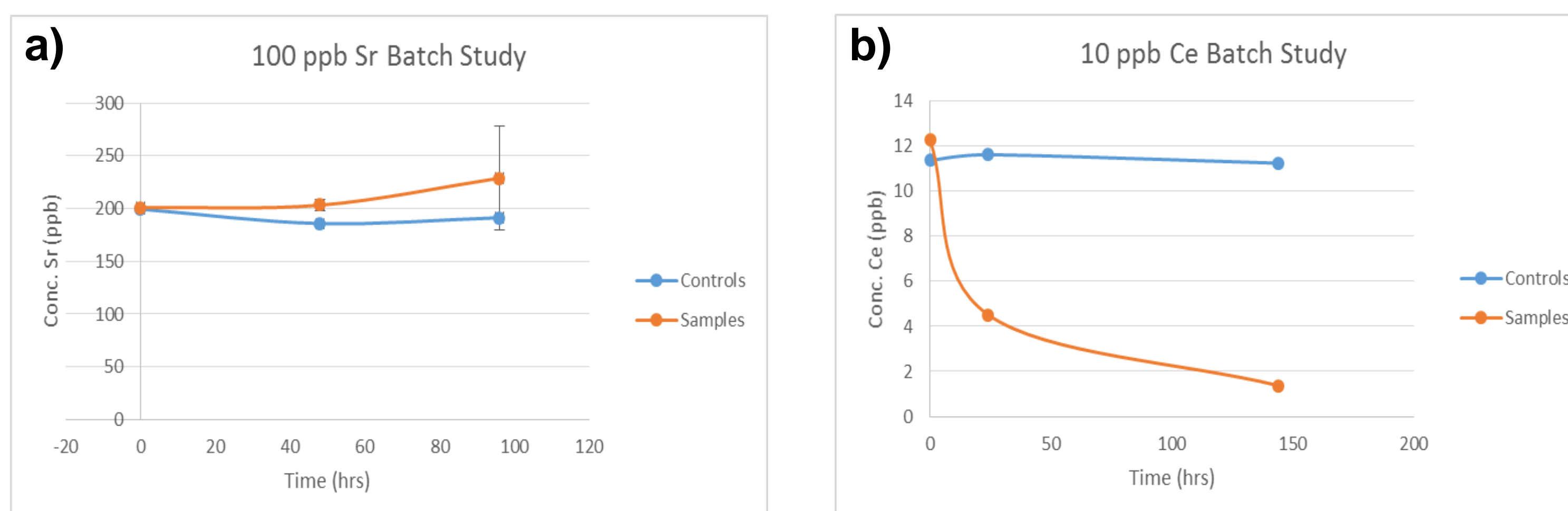


Fig. 6. Average sorption curves for (a) Sr and (b) Ce onto culebra dolomite in 15(w/v)% NaCl brine solution.

Nd and Ce Sorption and Desorption

The sorption curves for neodymium and cerium (fig 6b) show that the ions did not bind to the polypropylene bottles. The sample curves demonstrate that the cerium ions do sorb to the culebra faster than the neodymium or europium ions. However, the higher concentrations show some instability in terms of solubility for neodymium and cerium in the brine.

Conclusions

This project demonstrated that as the oxidation state increases in the metal ions, the more the ion will sorb onto the culebra dolomite and outcompete the Na ions in the brine. Figure 7 illustrates this effect.

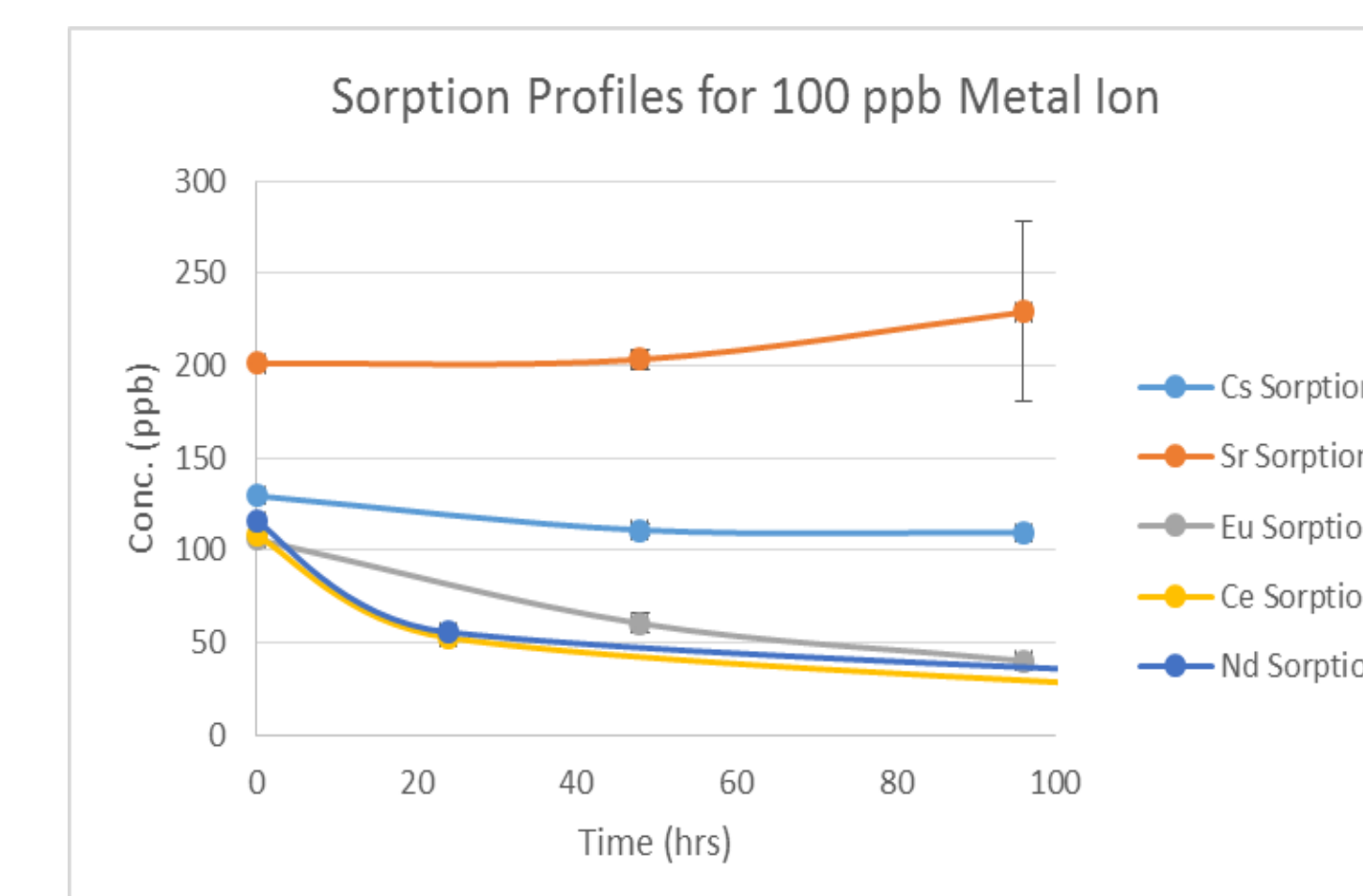


Fig. 6. 100 ppb sorption curves for all metal ions investigated

This project also showed that the heavier metal ions do experience solubility instabilities in the NaCl brine solution. This could be due to the high ionic strength of the brine, the higher pH, or a colloidal formation from the carbonate in the culebra. The solubility issue will need to be studied more closely to determine the cause.

Future Work

More samples are being analyzed by ICP-MS in order to fully understand the sorption and desorption behavior as well as investigate the issue of solubility and stability in the experiments. These samples include the filtered samples to investigate if there was generation of dolomite colloids. This would require further interpretation of the data.

In addition, more metals are planned to be tested, such as Np(V) and U(VI), as well as other actinide metals to determine the best analogs for radioactive material.

Lastly, the kinetics of these experiments will be investigated to determine the K_d values and sorption capacity of the system.

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