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M3SF-24LL010302052-Comprehensive Analysis of Radionuclide Interaction with Hydrothermally Altered Repository Materials

E. Balboni, F. Caporuscio, A. E. Zandanel, M. Mills, Y. Wang, M. Zavarin

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M3SF-24LL010302052- Comprehensive Analysis of Radionuclide Interaction with Hydrothermally Altered Repository Materials

Crystalline Disposal R&D

Prepared for
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Work Package Title and Number	Crystalline Disposal R&D – LLNL SF-24LL01030205
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ACKNOWLEDGMENTS

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CONTENTS

M3SF-24LL010302052-COMPREHENSIVE ANALYSIS OF RADIONUCLIDE INTERACTION WITH HYDROTHERMALLY ALTERED REPOSITORY MATERIALS

1 INTRODUCTION

This progress report (Level 3 Milestone Number M3SF-24LL010302052) summarizes research conducted at Lawrence Livermore National Laboratory (LLNL) within the Crystalline Work Package Number SF-24LL01030205. The research is focused on actinide and radionuclide sequestration in hydrothermally altered repository materials.

In FY24, we completed a rigorous analysis of Se sorption to iron oxide phases using our L-SCIE sorption database. This effort explicitly accounts for surface titration behavior of oxide surfaces that was the subject of a recently published manuscript (Han et al., 2023). With this in mind, our Se sorption analysis now yields a more robust workflow for developing self-consistent surface complexation modeling approaches that can be adapted to specific SCM conceptual and numerical approaches (i.e. non-electrostatic, diffuse layer, triple layer models). In late FY24, we plan to publish the results of our comprehensive surface complexation modeling of Se(IV) and Se(VI) sorption to iron oxide mineral phases and provide a path forward to developing robust radionuclide sorption models for use in performance assessment.

In FY24, we also submitted a manuscript summarizing our approach to integrating radionuclide sorption and coprecipitation phenomena and evaluation of radionuclide partitioning values across a range of radionuclides relevant to performance assessment. We demonstrated our approach in detail using Se sorption and coprecipitation with iron oxide minerals as a test case. This manuscript was recently accepted for publication in Applied Geochemistry (Balboni et al., Accepted).

We also continued experiments to identify radionuclide interaction with hydrothermally altered crystalline repository and backfill materials. Recent research performed at Los Alamos National Laboratory (LANL) and Sandia National Laboratory (SNL) has provided key insights regarding the hydrothermal alteration behavior of bentonite backfill in the presence of repository materials (steel, concrete, etc.). We are now examining how mineral alteration affects retardation behavior of a suite of radionuclides of interest to repository performance assessment. These experiments also allow us to test the predictive ability of our component additivity approach to surface complexation and ion exchange. Our guiding hypothesis is that a robust surface complexation/ion exchange model and associated database, developed using our L-SCIE approach, can effectively predict changes in radionuclide sorption behavior resulting from the hydrothermal alteration of mineralogy in a repository near field. A short update of results to date is presented below.

2 EFFECTS OF BENTONITE HEATING ON RADIONUCLIDES ADSORPTION

One of the more accepted ideas for high-level nuclear waste disposal is to emplace steel waste canisters in a geological repository with a bentonite/clay barrier between the canister and host rock (Meunier et al., 1998; Pusch, 1979). Bentonite is used to provide 1) a physical barrier to prevent fluid seeping in from natural surroundings and interacting with the waste package and 2) a chemical barrier by attenuating actinide migration if a release occurs.

High temperatures (100–200 °C) near waste canisters resulting from radioactive decay may alter the bentonite clay's ability to adsorb contaminants. Temperature effects on the bentonite/clay barrier may include changes to the clay's hydrological and mechanical properties, changes to pore water chemical compositions, and changes to the clay and accessory mineral composition (Cuadros and Linares, 1996; Wersin et al., 2007; Zheng et al., 2017). For these reasons the effects of

elevated temperature on the engineered barrier must be considered when designing a nuclear waste repository.

In this study, we examine the capacity of hydrothermally altered clay samples (Table 1) to adsorb radionuclides (Table 2) in batch sorption experiments. The hydrothermally altered samples were subjected to short-term (days to months) high temperature (200-300 °C) heating in the laboratory (Table 1).

2.1 MATERIALS AND METHODS

The hydrothermally altered samples used in this study were provided by collaborators from LANL and SNL (Table 1). All the samples received at LLNL were prepared for surface area analysis using BET, but no further characterization was performed at LLNL as complete chemical and mineralogical characterization of the selected samples was presented in previous publications (Caporuscio, 2014, 2015; Caporuscio, 2018; Caporuscio, 2019; Caporuscio, 2020; Cheshire et al., 2014; Mills et al., 2023).

In this work, batch sorption experiments with hydrothermally altered barrier materials (Table 1) and different radionuclides (Table 2) are performed at a pH range of 7-8 using either a low (NaCl 0.01M, $NaHCO_3$ 0.01M) or high (NaCl 1M, $NaHCO_3$ 0.01M) ionic strength buffer solution as background electrolyte. In both low and high ionic strength solutions, a 0.01M HEPES buffer is used to maintain the pH in the desired range. Each sorption experiment is performed in triplicate using a solid to solution ratio of 5 g/L. To monitor the effects of heating on the adsorption properties of bentonite, batch sorption experiments are also performed using control, unheated samples (Table1). The linear distribution coefficient (Kd), was calculated as the ratio between the solid phase and aqueous phase concentrations using the formula below:

$$K_d(\mathrm{mL/g}) = \frac{C_s(\frac{\mathrm{mol}}{\mathrm{g}})}{C_{aq}(\frac{\mathrm{mol}}{\mathrm{mL}})}$$

where C represents the concentration of an ion either adsorbed onto a solid (s) or in the aqueous solution (aq). A list of all the radionuclides and materials used for sorption experiments is reported in Table 1 and Table 2.

Table 1. List of samples used for sorption experiments. Samples (unheated and hydrothermally altered) were provided by collaborators at Los Alamos National Laboratory (LANL) and Sandia National Laboratory (SNL). Cation exchange of selected unheated samples was performed at SNL (K, Na) and Lawrence Livermore National Laboratory (LLNL).

Mineralogical composition	Sample origin	Sample Name			
Unheated samples					
Wyoming Bentonite	LANL	**WY**			
Opalinus Clay	LANL	**OPC**			
Grimsel Granodiorite	LANL	**GG**			
Illite	SNL	**IMt-1**			
Illite/Smectite (70:30) mixed layers	SNL	**ISCz-1**			
Cation exchanged unheated samples			**Cation Exchange Solution**		
Na-exchanged Wyoming Bentonite	LANL/LLNL	**Na-WY**	1M $NaC_2H_3O_2$		
Na-exchanged Opalinus Clay	LANL/LLNL	**Na-OPC**	1M $NaC_2H_3O_2$		
K-exchanged Smectite	SNL	**K-Swy-2-SNL**	1M KCl		
Na-exchanged Wyoming bentonite	SNL	**Na-SWy-2-SNL**	1M NaCl		
Hydrothermally altered samples			**Hydrothermal Alteration Conditions**		
			Synthetic Ground Water Type	**Temperature (C)**	**Duration of Hydrothermal Experiment**
Wyoming Bentonite and 304 SS	LANL	**EBS 5**	Stripa V2.1	300	6 weeks
Wyoming Bentonite and Quartz Sand	LANL	**EBS 9**	Stripa V2.2	25/100/200/300/25	5 weeks
Wyoming Bentonite and 316 SS	LANL	**EBS 10**	Stripa V2.3	300	6 weeks
Wyoming Bentonite	LANL	**EBS 12**	Stripa V2.3	300	7 weeks
Wyoming Bentonite, Opalinus Clay, and 316 SS	LANL	**EBS 15**	Synthetic Opalinus GW	300	6 weeks
Wyoming Bentonite, Opalinus Clay, and 304 SS	LANL	**EBS 19**	Synthetic Opalinus GW	300	6 weeks
Wyoming Bentonite, Opalinus Clay, and 316 SS	LANL	**EBS 20**	Synthetic Opalinus GW	300	6 months
Wyoming Bentonite, Opalinus Clay, and Portland Cement	LANL	**EBS 28**	Synthetic Opalinus GW	300	8 weeks
Wyoming Bentonite, Grimsel Granodiorite, and 316 SS	LANL	**IEBS 5**	Synthetic Grimsel GW	250	8 weeks
Wyoming Bentonite, Grimsel Granodiorite, and Portland Cement	LANL	**IEBS 6**	Synthetic Grimsel GW	250	8 weeks
K exchanged Wyoming bentonite	SNL	**K-1000-KCl-28**	1M KCl	200	28 days

Table 2. List of radionuclides chosen for adsorption studies with hydrothermally altered samples. The column labeled FY indicates the status of the work and/or when it will be completed.

Radionuclide	Oxidation state	FY
^{137}Cs	(I)	2024 (complete)
^{90}Sr	(II)	2024 (complete)
^{243}Am	(III)	2023 (complete)
^{238}Pu	(IV)	2025
^{237}Np	(V)	2025
^{233}U	(VI)	2024 (started, near completion)
^{99}Tc	(VII)	2025

2.2 RESULTS

In FY24, we completed and analyzed data for ^{137}Cs, ^{90}Sr, ^{243}Am sorption experiments using samples provided by LANL and SNL and results of our findings are reported below. Batch sorption experiments with ^{233}U are underway. The overall goal of this work is to 1) monitor the changes in Kd values between original, non-altered materials and hydrothermally altered samples; 2) determine the factors that control changes in sorption capacity of radionuclides after hydrothermal alteration of bentonite, host rock, and structural materials

Sorption experiments with hydrothermally altered materials provided by LANL

In the figures below (1-3) the Kd values measured in sorption experiments using the hydrothermally altered materials (EBS 5 though IEBS 6) are reported on the x axis; whereas the Kd measured for the original, non-hydrothermally altered materials (Wy, Na-Wy, OPC, Na-OPC, GG) are plotted on the y axis. For samples that included mixtures of starting materials (Wy, OC, GG) in the hydrothermal experiments (EBS 15, EBS 19, EBS 20, EBS28, IEBS 5, IEBS 6), we calculated the expected Kd values of the unaltered substrate as weighted averages of Kd measured for the starting materials. In Figure 1, 2, and 3 the dashed line represents a 1-to-1 line. In the figures, if a hydrothermally altered sample has a Kd that is unchanged from the starting material, then its Kd will plot on (or around) the 1-to-1 line. If hydrothermally altered samples have larger Kd values compared to their starting material, then they will plot below the 1-to-1 line, whereas if Kd values are reduced during hydrothermal processing, samples will plot above the 1-to-1 line.

Figure 1 shows the results for the 137Cs sorption experiments. Data shows that the measured Kd values are overall lower (4-10 times) for sorption experiments conducted in high ionic strength solution (triangles) compared to those conducted in low ionic strengths (circles). In experiments conducted at either low or high ionic strength (circles or triangles) most hydrothermally altered samples exhibit some decrease in Kd after hydrothermal alteration (plot above the 1:1 line) including samples containing quartz (EBS 9), portland cement (EBS 28, IEBS 6), and the sample hydrothermally altered under dry conditions (EBS 12). At low ionic strength three samples show an increase in Kd compared to the starting material (EBS 15, 19, 20); however, this is not observed for experiments at high ionic strength where about half the samples plot on the 1-to-1 line.

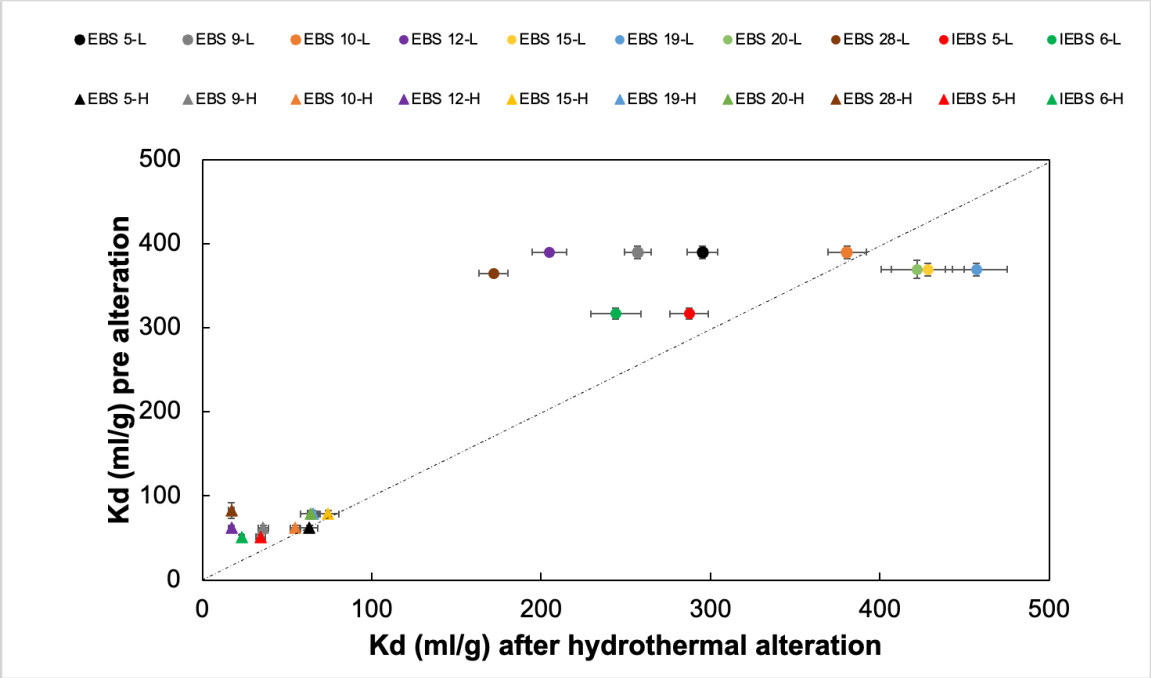

Figure 1. Kd measured for ^{137}Cs batch sorption experiments in hydrothermally altered samples (EBS 5, EBS 9, EBS 10, EBS 12, EBS 15, EBS 19, EBS 20, EBS 28, IEBS 5 and IEBS 6) compared to Kd measured for unaltered starting materials. Sorption experiments were conducted in either low (circles) and high (triangles) ionic strength background electrolyte solutions. In the legend the -L or -H represents Kd values measured using low (L) or high (H) ionic strength electrolyte. Each experiment was performed in triplicates.

Figure 2 shows the Kd values measured for ^{90}Sr sorption experiments. The results reveal that the Kd values are significantly lower (by 2 to 16 times) for sorption experiments conducted in high ionic strength solution (triangles) compared to those in low ionic strength solution (circles). For ^{90}Sr, the Kd values for hydrothermally altered samples at high ionic strength (triangles) remained the same or increased in all samples but decreased (less than 1) in a few samples, at low ionic strength. At low ionic strength, sample IEBS 6 shows the highest increase in Kd after hydrothermal alteration.

For ^{243}Am, a relative small decrease in Kd is observed in only a few samples including EBS 12 (dry sample), EBS 15 at low ionic strength, EBS 19 and EBS 20 while in most samples, the Kd values measured in hydrothermally altered samples are 2 to 10 times higher compared to the unaltered materials. Overall, ionic strength in ^{243}Am experiments did not significantly affect Kd values.

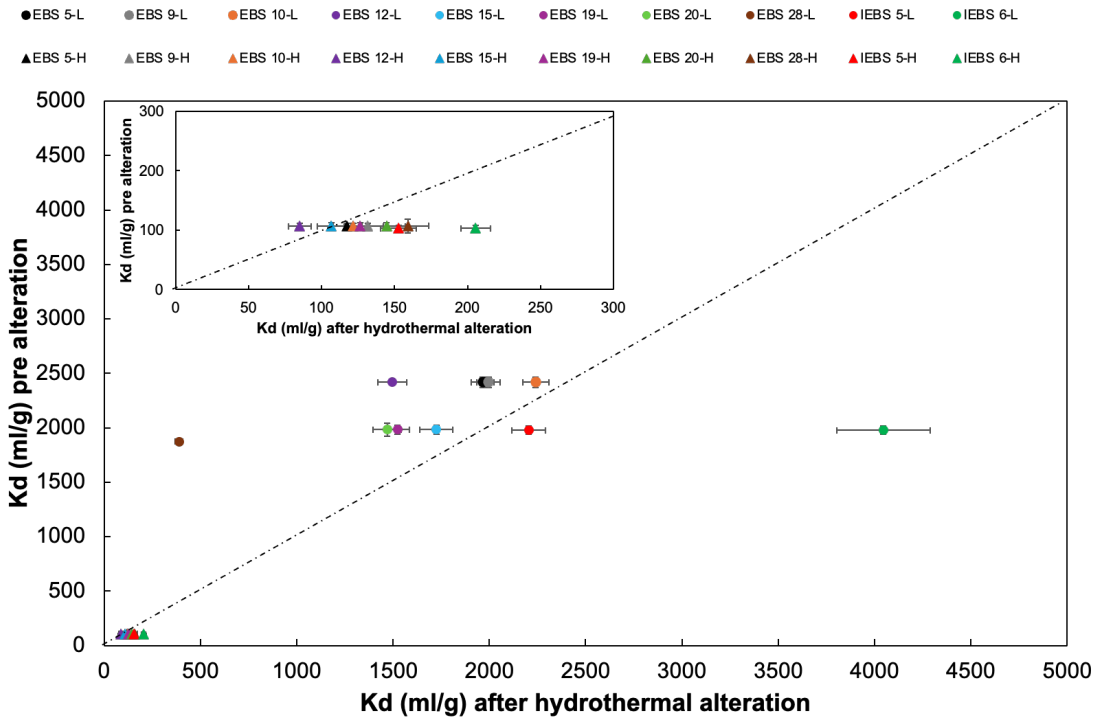

Figure 2 Kd measured for ^{90}Sr batch sorption experiments in hydrothermally altered samples (EBS 5, EBS 9, EBS 10, EBS 12, EBS 15, EBS 19, EBS 20, EBS 28, IEBS 5 and IEBS 6) compared to Kd measured for unaltered starting materials. Sorption experiments were conducted in either low (circles) and high (triangles) ionic strength background electrolyte solutions. The inset in the Figure (top left) zooms in to display the Kd measured in high ionic strength solutions. In the legend the -L or -H represents Kd values measured using low (L) or high (H) ionic strength electrolyte. Each experiment was performed in triplicates.

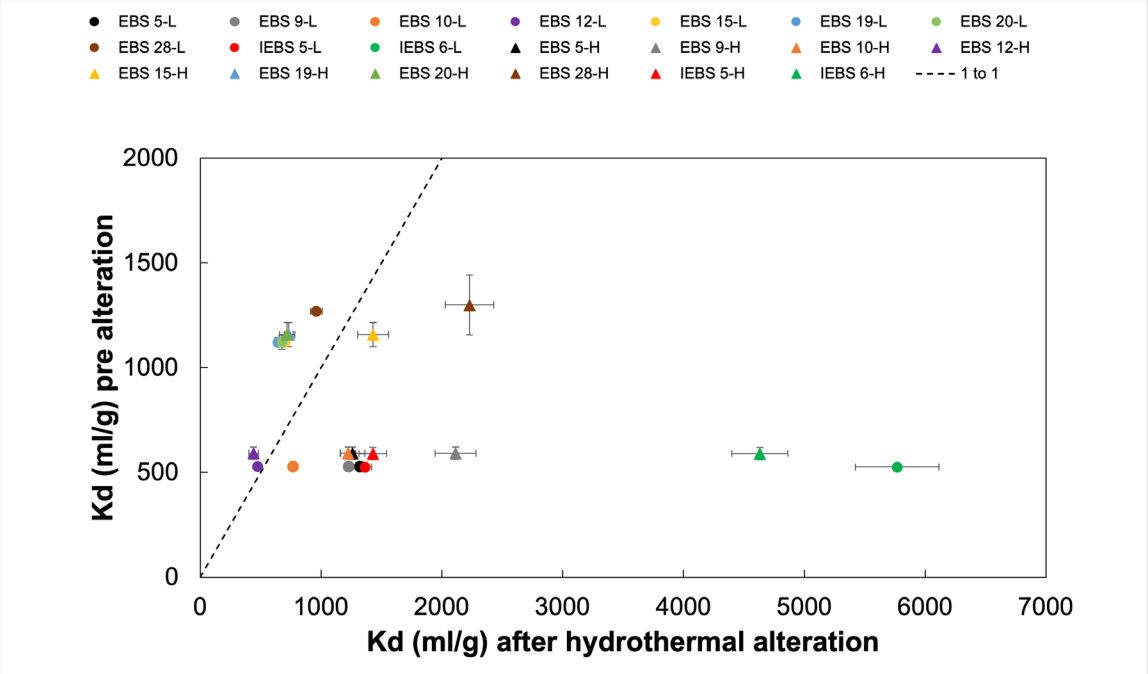

Figure 3 Kd measured for ^{243}Am batch sorption experiments in hydrothermally altered samples (EBS 5, EBS 9, EBS 10, EBS 12, EBS 15, EBS 19, EBS 20, EBS 28, IEBS 5 and IEBS 6) compared to Kd measured for unaltered starting materials. Sorption experiments were conducted in either low (circles) and high (triangles) ionic strength background electrolyte solutions. In the legend the -L or -H represents Kd values measured using low (L) or high (H) ionic strength electrolyte. Each experiment was performed in triplicates.

Hydrothermal alterations of bentonite and host rock materials can affect the sorption capacity of radionuclides in some instances. For 90Sr and 137Cs lower Kd values are measured in sorption experiments performed using a high ionic strength background electrolyte, but this effect is not observed for 243Am, indicating different processes (cation exchange versus surface complexation). In the "dry sample" EBS 12, a reduction in Kd in both high and low ionic strength was observed for both 137Cs and 90Sr and to a lesser extent for 243Am. The addition of Portland cement also affected sorption capacity, although the effects are unpredictable. Numerous variables must be considered when interpreting these results. The triplicate results from our experimental setup provided reproducible data. However, data interpretation is ongoing and a more detailed analysis of the results will be presented in a future publication.

Sorption experiments with hydrothermally altered materials provided by SNL

The samples received from the Sandia collaborators are listed in Table 1 and include Na-smectite (SWy-2), illite (IMT-1), illite/smectite (70:30) mixed layers (IsCz-1) standards from the Clay Mineral Society, a K-exchanged smectite (K-SWy-2), and the hydrothermally altered sample K-1000-KCl-28. Information on the preparation of sample K-1000-KCl-28 (abbreviated to K-1000 in figure 4) can be found in (Mills et al., 2023). Briefly, a Na-SWy aliquot was hydrothermally altered in a 1M KCl suspension with a 1000:1 liquid/solid ratio for 28 days. Results showed that after the hydrothermal alteration, the original smectite (SWy-2) had lost expandability, which was related to the presence of smectite/illite layers. The sorption of 137Cs, 90Sr and 243Am was studied under the same experimental conditions used for the LANL samples, as discussed above.

For the four standards that did not undergo hydrothermal alterations, we observe that the Kd values have a broader range in experiments performed at low ionic strengths, compared to the values measured at high ionic strength (Figure 4 a, c, d left panel). The Kd values measured in experiments at low ionic strength background electrolyte are generally higher for 137Cs and significantly higher for 90Sr, but unchanged for 243Am, consistent with our previous observations.

The Kd measured for 137Cs in the K-1000 sample is significantly elevated compared to the starting material (Na-SWy) and the other control samples (K-SWy-2, IsCz-1, and IMt-1). The stark difference in Kd between K-1000 and the illite standard IMt-1 is somewhat surprising, as Cs is expected to be favorably sorbed by illite. This strong increase in Kd in K-1000 could be related to the high surface area of the sample. BET measurements reveal that the surface area of K-1000 is 113 m^2/g, whereas the surface areas of Na-SWy-2, K-SWy-2, IsCz-1, and IMt-1 range between 25-50 m^2/g. When considering Ka rather than Kd (Ka=Kd/surface area), this difference becomes less pronounced (Figure 4 b). In Figure 4b, the sorption capacity expressed as Ka of IMt-1, a natural illite, is generally higher than that of the K-1000, a smectite/illite clay. At high ionic strength, the Ka values of both IMt-1 and K-1000 are approximately 1.5 times higher than the other samples, which is consistent with the expected Cs sorption behavior for illite.

The Kd measured for K-1000 do not show significant changes compared to the standard material in either 90Sr or 243Am experiments. The Kd values measured for 243Am in all samples are similar (Figure 4d), and differences in the ionic strength of the background electrolyte do not affect the measured Kd values.

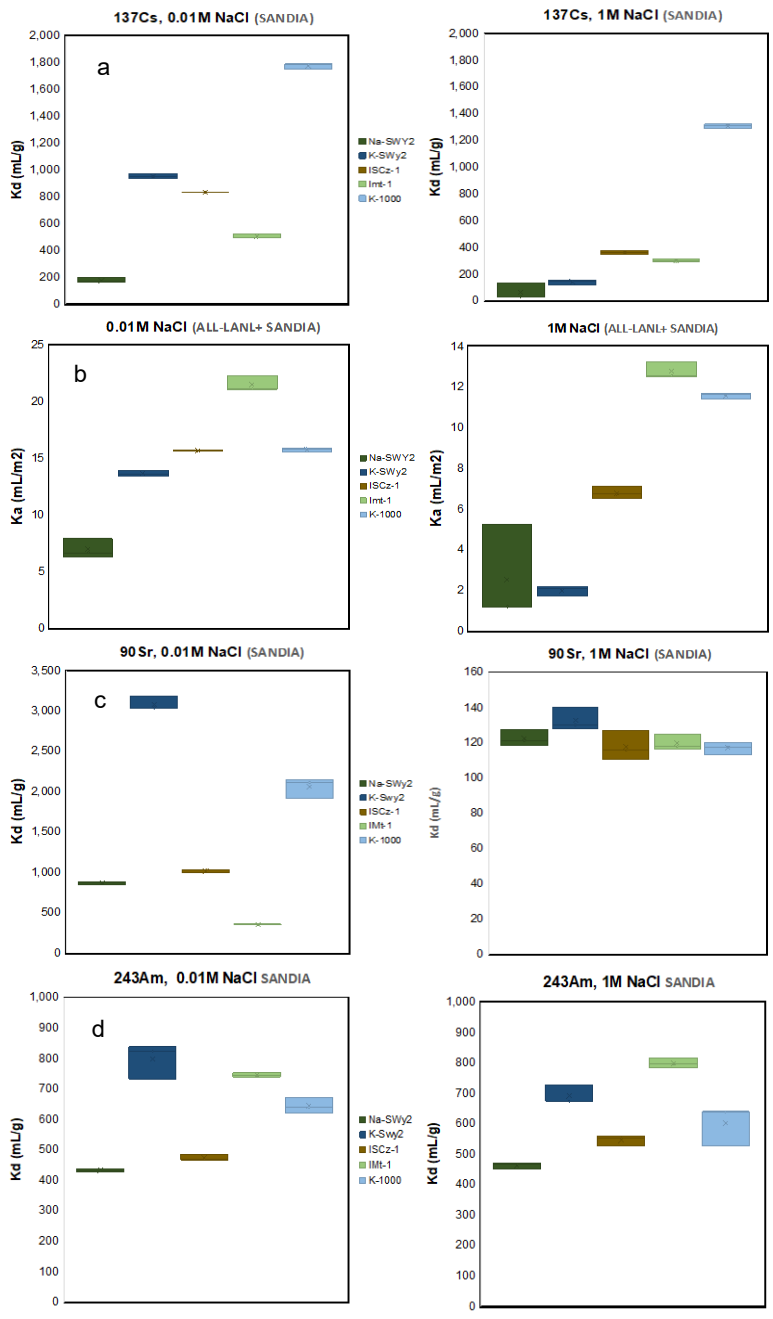

Figure 4 Results obtained from sorption experiments conducted using materials provided by SNL (Na-SWY2, K-SWY-2IScz-1, IMt-1 and K-1000-KCl-28 (name abbreviated to K-1000). a) Kd values calculated for ^{137}Cs sorption experiments in low and high ionic strength; b) Ka values calculated for ^{137}Cs sorption experiments in low and high ionic strength; c) Kd values calculated for ^{90}Sr sorption experiments in low and high ionic strength; d) Kd values calculated for ^{243}Am sorption experiments in low and high ionic strength.

2.3 OUTLOOK AND FUTURE WORK

Observed changes in radionuclide adsorption after bentonite/clay heating have implications for radionuclide diffusive transport through engineered barriers and must be considered when designing waste disposal repositories. Results from this comprehensive analysis will inform performance assessment models on how much reduction in Kd can be expected for the original barrier material as a result of heating under different ionic strengths.

Sorption experiments for ^{233}U will be completed by the end of FY24. In FY25, we will complete the sorption experiments for all radionuclides reported in Table 2. Additional radionuclides (e.g. ^{129}I) may be added to our analysis based on results from performance assessment model sensitivity analysis. Recent discussions suggest the importance of ^{129}I in repository performance and some effort may focus specifically on this isotope to address its retardation. We will also use statistical tools (i.e. PCA) to help us determine the major drivers in affecting changes in measured Kd values induced by hydrothermal alteration.

3 PAPER SUBMISSION: "SELENIUM INTERACTION WITH IRON MINERALS: QUANTITATIVE COMPARISON OF SORPTION AND COPRECIPITATION IMPACTS ON MOBILITY"

A paper titled "Selenium interaction with iron minerals: Quantitative comparison of sorption and coprecipitation impacts on mobility" authored by Enrica Balboni, Solchan Han, and Mavrik Zavarin was submitted to Applied Geochemistry in May 2024. This paper represents FY22-23 efforts and was recently accepted with minor revisions.

Summary of work

Given the significance of selenium (Se) as a micronutrient, the radioactive nature of some of its isotopes, and its affinity to iron (Fe) minerals, extensive research has been conducted on the sorption mechanisms between Se and these minerals. Here, we employ adsorption data sourced from the L-SCIE database and coprecipitation data from available literature to achieve the following objectives: i) establish coherence between adsorption and coprecipitation processes, ii) quantitatively evaluate the importance of these processes in nuclear waste repository science, and iii) propose a forward-looking approach for integrating coprecipitation into reactive transport models. Our findings indicate that a correlation between Se adsorption and coprecipitation can be established using the λ formalism. Our analysis confirms a stronger affinity of Se(IV) compared to Se(VI) for both adsorption and coprecipitation processes with hydrous ferric oxide, goethite, hematite, and magnetite. Moreover, the comparable log(λSe(IV)/ λSe(VI)) ratios derived from adsorption and coprecipitation experiments suggest that these processes can be quantitatively compared and evaluated using our numerical approach. Across all iron oxide phases examined, coprecipitation leads to significantly greater immobilization of Se compared to adsorption. Specifically, for hydrous ferric oxide, hematite, and goethite, coprecipitation is predicted to result in 100 to 1000 times more Se immobilization compared to adsorption, irrespective of the Se oxidation state (Se(IV) or Se(VI)); notably stronger immobilization potential via coprecipitation was observed for magnetite. The modeling approach and quantitative analysis presented herein clearly highlight the importance of including coprecipitation processes when simulating Se (and other elements) transport, particularly under conditions where mineral compositions are transient or evolving with time. Neglecting coprecipitation in models is likely to lead to significant overestimates of migration.

4 FY25 PLANNED EFFORTS

Observed changes in radionuclide sorption after bentonite/clay heating have implications for radionuclide diffusive transport through engineered barriers and must be considered when designing waste disposal repositories. Sorption experiments and data analysis for ^{233}U will be completed by the end of FY24. In FY25, we will complete the study including all other radionuclides reported in Table 2.

In addition, we have initiated discussion with PA modelers to identify radionuclides of importance to repository performance. We are particularly focused on ^{129}I as a driver in repository performance assessment models. As such, we are discussing the extension of our efforts to quantify the retardation behavior of this isotope and application of retardation parameters into PFLOTRAN generic repository performance assessment modeling conducted by our Sandia collaborators.

5 REFERENCES

Balboni, E., Han, S., Zavarin, M., Accepted. Selenium interaction with iron minerals: Quantitative comparison of sorption and coprecipitation impacts on mobility. Applied Geochemistry.

Caporuscio, F.A., Cheshire, M. C., Palaich, S., Norskog, K., Jove Colon, C. , 2015. Argillite Disposal R&D-LANL 2015. Summary of baseline experiments for generic repository engineered barriers. (FY 2015). (FCRD-UFD-2015-000356, LA-UR-15-26110). Los Alamos National Lab. (LANL), Los Alamos, NM (United States).

Caporuscio, F.A., Cheshire, M. C., Rearick, M. S., Jove Colon, C. , 2014. LANL argilliteEBS experimental program 2014. (FCRD-USED-2014-000491). Los Alamos National Lab. (LANL), Los Alamos, NM (United States).

Caporuscio, F.A., Migdissov, A., Rock, M. J., Sauer, K. B., van Hartesveldt, N. F. , 2019. Engineered Barrier System R&D and International Collaborations–LANL (FY19) (No. LA-UR-19-24222). Los Alamos National Lab. (LANL), Los Alamos, NM (United States).

Caporuscio, F.A., Sauer, K.B., Rock, M.J., 2020. Engineered System R&D and International Collaborations – Los Alamos National Laboratory (FY18). SF&WD R&D Work package # SF-02LA01030801 Rev2/SF-20LA01030805, LA-UR-20-25330.

Caporuscio, F.A., Sauer, K.B., Rock, M.J., Houser, L.M., 2018. Engineered System R&D and International Collaborations – Los Alamos National Laboratory SF&WD R&D Work package # SF18LA01030801/SF-18LA01030805, LA-UR-18- 27601.

Cheshire, M.C., Caporuscio, F.A., Rearick, M.S., Jove-Colon, C., McCarney, M.K., 2014. Bentonite evolution at elevated pressures and temperatures: An experimental study for generic nuclear repository designs. American Mineralogist 99(8-9), 1662-1675.

Cuadros, J., Linares, J., 1996. Experimental kinetic study of the smectite-to-illite transformation. Geochimica Et Cosmochimica Acta 60(3), 439-453. doi.org/Doi 10.1016/0016-7037(95)00407-6.

Han, S.-C., Chang, E., Zechel, S., Bok, F., Zavarin, M., 2023. Application of community data to surface complexation modeling framework development: Iron oxide protolysis. J Colloid Interf Sci 648, 1015-1024. doi.org/https://doi.org/10.1016/j.jcis.2023.06.054.

Meunier, A., Velde, B., Griffault, L., 1998. The reactivity of bentonites: a review. An application to clay barrier stability for nuclear waste storage. Clay Minerals 33(2), 187-196. doi.org/10.1180/claymin.1998.033.2.01.

Mills, M.M., Sanchez, A.C., Boisvert, L., Payne, C.B., Ho, T.A., Wang, Y., 2023. Understanding smectite to illite transformation at elevated (>100 °C) temperature: Effects of liquid/solid ratio, interlayer cation, solution chemistry and reaction time. Chemical Geology 615, 121214. doi.org/https://doi.org/10.1016/j.chemgeo.2022.121214.

Pusch, R., 1979. Highly Compacted Sodium Bentonite for Isolating Rock-Deposited Radioactive-Waste Products. Nucl Technol 45(2), 153-157. doi.org/Doi 10.13182/Nt79-A32305.

Wersin, P., Johnson, L.H., McKinley, I.G., 2007. Performance of the bentonite barrier at temperatures beyond 100 degrees C: A critical review. Phys Chem Earth 32(8-14), 780-788. doi.org/10.1016/j.pce.2006.02.051.

Zheng, L., Rutqvist, J., Xu, H., Birkholzer, J.T., 2017. Coupled THMC models for bentonite in an argillite repository for nuclear waste: Illitization and its effect on swelling stress under high temperature. Eng Geol 230, 118-129. doi.org/10.1016/j.enggeo.2017.10.002.

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