LLNL-TR-701737

M4FT-16LL080303052-State of Knowledge for Colloid Facilitated Radionuclide Transport and Update on Actinide Diffusion in Bentonite Backfill

M. Zavarin, C. Joseph

August 29, 2016

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Appendix E
FCT Document Cover Sheet

Name/Title of Deliverable/Milestone: M4FT-16LL080303052-State of Knowledge for Colloid Facilitated Radionuclide Transport and Update on Actinide Diffusion in Bentonite Backfill

Work Package Title and Number: FT-16LL08030305 (Rev. 2) DR Crystalline Disposal R&D - LLNL

Work Package WBS Number: 1.02.08.03.03.05

Responsible Work Package Manager: Mavrik Zavarin
(Name/Signature)

Date Submitted

Quality Rigor Level for Deliverable/Milestone	☒ QRL-3	☐ QRL-2	☐ QRL-1 ☐ Nuclear Data	☐ N/A*

This deliverable was prepared in accordance with Lawrence Livermore National Laboratory's QA program which meets the requirements of

☒ DOE Order 414.1 ☐ NQA-1-2000

This Deliverable was subjected to:

☒ Technical Review

Technical Review (TR)

Review Documentation Provided

☐ Signed TR Report or,
☐ Signed TR Concurrence Sheet or,
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☐ Peer Review

Peer Review (PR)

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Name and Signature of Reviewers

MARK SUTTON, LLNL 9/8/16

*Note: In some cases there may be a milestone where an item is being fabricated, maintenance is being performed on a facility, or a document is being issued through a formal document control process where it specifically calls out a formal review of the document. In these cases, documentation (e.g., inspection report, maintenance request, work planning package documentation or the documented review of the issued document through the document control process) of the completion of the activity along with the Document Cover Sheet is sufficient to demonstrate achieving the milestone. QRL for such milestones may be also be marked N/A in the work package provided the work package clearly specifies the requirement to use the Document Cover Sheet and provide supporting documentation.

August 16, 2016

M4FT-16LL080303052-State of Knowledge for Colloid Facilitated Radionuclide Transport and Update on Actinide Diffusion in Bentonite Backfill

M. Zavarin and C. Joseph

Glenn T. Seaborg Institute, Physical & Life Sciences, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550, USA.

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Contents

1. Introduction

This progress report (Level 4 Milestone Number M4FT-16LL080303052) summarizes research conducted at Lawrence Livermore National Laboratory (LLNL) within the Crystalline Disposal R&D Activity Number FT-16LL080303051 and Crystalline International Collaborations Activity Number FT-16LL080303061. The focus of this research is the interaction of radionuclides with Engineered Barrier System (EBS) and host rock materials at various physico-chemical conditions relevant to subsurface repository environments. They include both chemical and physical processes such as solubility, sorption, and diffusion. The scope of the FY16 effort included the following:

- Summarizing the state of knowledge for colloid-facilitated transport and parameterizing our data and conceptual model for use in reactive transport and Performance Assessment models
- Supporting Np(IV) diffusion experiments through bentonite backfill material. The result of this effort will provide sorption/diffusion data for the Np oxidation state most likely to be present in repository scenarios and least studied in the literature.
- Publication of a longterm U(VI) diffusion experiments. These data provide unique information on the longterm performance of bentonite backfill material.
- Supporting the involvement of the Used Fuel Disposition campaign in the Nuclear Energy Agency Thermodynamic Database Development (NEA-TDB, supported through the International Work Package Number FT-16LL08030306)

The colloid facilitated transport effort focused on preparation of a draft manuscript summarizing the state of knowledge and parameterization of colloid facilitated transport mechanisms in support of reactive transport and performance assessment models for generic crystalline repositories. This draft manuscript is being submitted as a level 3 milestone with LANL as the primary author. LLNL's contribution to that effort is summarized only briefly in the present report. A manuscript summarizing longterm U(VI) diffusion experiments through bentonite backfill material was recently accepted for publication; the contents of that manuscript are summarized in the present report. The Np(IV) diffusion experiments were started mid-year and are ongoing. The completion of these experiments is planned for early FY17. Our progress in quantifying Np(IV) diffusion in bentonite backfill is summarized in the present report. Our involvement with the NEA TDB project was summarized in a recent Argillite Disposal activity report. It is not included in this report.

2. Colloid Facilitated Transport

Due to their importance as backfill material and repository host rock, the interaction of radionuclides with aluminosilicate clay minerals has been the subject of intense study. Recent efforts at LLNL have focused on the potential role of montmorillonite colloids in facilitating Pu migration. In these studies, the focus has been on understanding both the mechanisms and rates of Pu sorption and desorption from montmorillonite clay (Begg et al., 2014; Begg et al., Submitted; Begg et al., 2015; Begg et al., 2013; Benedicto et al., 2014; Zavarin et al., 2008). In our contribution to the report co-authored with Paul Reimus (LANL) "Colloid-Facilitated Radionuclide Transport: Current State of Knowledge from a Nuclear Waste Repository Risk Assessment Perspective" (referred to as the LANL report), we summarized the experimental results and numerical modeling approach used to quantify the observed Pu interaction behavior with aluminosilicate clays. Importantly, these experiments were focused on adsorption and desorption processes rather than transport behavior. Thus, the numerical approach did not include processes associated with colloid transport or filtration. However, the adsorption and desorption processes were based on the same simple first order reaction equations that were employed to describe radionuclide behavior in field and column flowthrough experiments summarized in the LANL report. As a result, values determined in LLNL experiments could be applied and compared to the values determined from field and column flowthrough experiments summarized in the LANL report. Based on these comparisons, it appears that the numerical approaches and the associated constants reported in the LANL report provide a consistent roadmap for incorporation of colloid-facilitated transport processes into nuclear waste repository performance assessment.

Colloid-facilitated transport may occur via intrinsic or pseudocolloid transport processes. The majority of the discussion in the LANL report was focused in pseudocolloid transport. However, we did include some insight into the behavior of intrinsic Pu colloids as well. From a transport modeling perspective, the numerical approach to simulating the behavior of intrinsic and pseudocolloids is quite similar. The ability of radionuclides to migrate downgradient will still be a function of the colloid filtration rate and the chemical stability of the radionuclide. For pseudocolloids, this chemical stability is governed by the rate of radionuclide desorption. For intrinsic colloids, the chemical stability is principally governed by the rate of intrinsic colloid dissolution.

Based on our Pu intrinsic colloid experiments, it appears that the conditions of Pu nanoparticle formation will have a significant impact on their stability over time. Pu precipitation under mild temperature and solution conditions will lead to unstable Pu nanoparticle formation while higher heat loads and/or acidic conditions may produce more stable nanoparticles. The results suggest that nuclear repository scenarios that include higher heat loading may result in stabilization of Pu oxide phases, which can lead to greater migration of intrinsic Pu nanoparticles.

The repository temperature history, combined with the predicted timing of canister failure, re-saturation of the repository near field, presence of natural and anthropogenic colloids, and other factors will all play a role in the evolution of any specific repository scenario and the potential for colloid facilitated radionuclide mobilization. While uncertainties associated with each of the mechanisms that affect colloid facilitated transport remain, numerical approaches and the associated constants are sufficiently well developed to provide a roadmap for incorporation of colloid-facilitated transport processes into nuclear waste repository performance assessment.

3. Np(IV) Diffusion through Bentonite

In FY16, we continued our efforts in the determination of actinide diffusion coefficients under repository conditions. We began our investigation of ^{237}Np diffusion, which represents a highly radiotoxic component in high-level nuclear waste with a long half-live of 2.144×10^{6} a.

In the case of the rupture of waste containers, Np can be mobilized by inflowing water. Under the reducing repository conditions, it will be mainly present as Np(IV). In addition, due to the radioactive decay of the waste, elevated temperatures are expected in this near-field of the waste container (between 50-280°C in the first 1,000 years (Jové Colón et al., 2014)). This will influence the radionuclides' mobility further.

One potential barrier to limit the radionuclides' entry to the biosphere is the clay-rich rock bentonite which is proposed as backfill material between host rock and waste containers. Bentonite will acquire bulk densities ranging from 1.5 to 1.8 g/cm^3 depending on the design of confinement (Keto et al., 2007). Under these conditions, molecular diffusion is expected to be the main transport process for waste-released radionuclides such as Np(IV). The bentonite pore water composition varies based on the pH and redox potential ranges expected under repository conditions. This affects the partial pressure of CO_2. Conservative modeling results assume partial pressures of up to $10^{-1.5}$ bar (Curti and Wersin, 2002) to be present in the repository.

To mimic repository conditions as close as feasible in the laboratory, we are studying the ^{237}Np(IV) diffusion through compacted MX-80 bentonite (1.6 g/cm^3) at room and elevated temperatures (25, 65, 85°C) under controlled atmosphere conditions ($pO_2 < 10$ ppm, $pCO_2 = 3.2$ vol.% $= 10^{-1.5}$ bar).

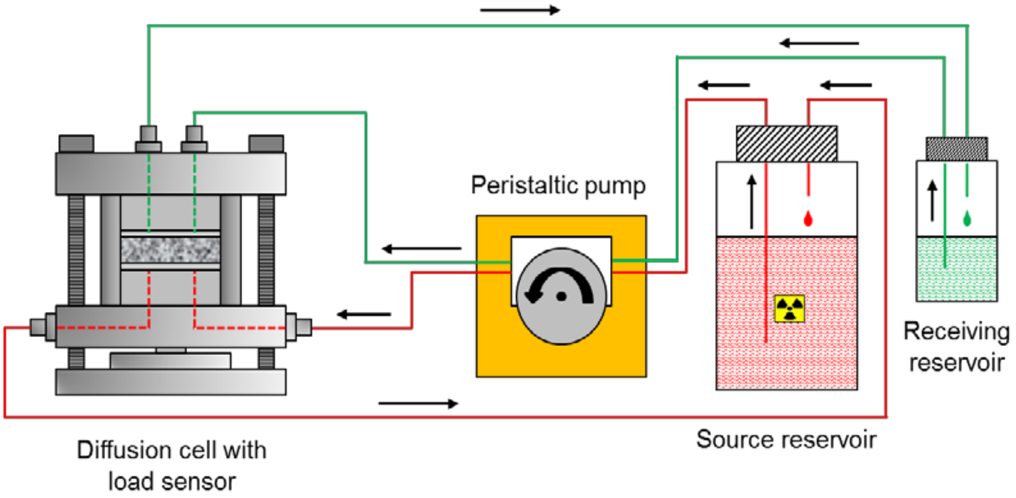

Figure 3-1. Experimental set-up of the diffusion experiments (taken from Joseph et al., 2016).

In Figure 3-1, the general set-up of the experiment at room temperature is given, consisting of a stainless steel diffusion cell containing compacted bentonite (Ø = 0.73'', *L* = 0.39'') and equipped with a load sensor, a peristaltic pump, and two reservoirs: the source reservoir, which contains the radioactive tracer, and the tracer-free receiving reservoir, each of them connected to one end plate of the diffusion cell. For the experiments at elevated temperature, the diffusion cells are placed in aluminum beads baths, which are put on a hot plate together with the reservoirs.

As mobile phase, synthetic bentonite pore water is used in the diffusion experiments (cf. Table 3-1). Its composition is based on the modeling results found in (Van Loon et al., 2007) for a MX-80 bentonite density of 1.6 g/cm^3. However, the salt load needed to be adjusted to hinder carbonate precipitation.

Before the actual diffusion experiment started, the bentonite was equilibrated with the synthetic pore water. This guaranteed the presence of a pore-water-saturated clay. To monitor the saturation of the clay, the swelling pressures were measured daily using the attached load cells. After about 25 days, the three samples (at 25, 65, and 85°C) were regarded to be fully saturated.

Table 3-1. Composition of synthetic MX-80 bentonite pore water.

Cation	***c* / mol/L**	**Anion**	***c* / mol/L**
Na^+	2.9×10^{-1}	Cl^-	1.8×10^{-2}
K^+	3.1×10^{-3}	SO_4^{2-}	9.6×10^{-2}
Mg^{2+}	1.2×10^{-4}	F^-	2.2×10^{-4}
Ca^{2+}	9.8×10^{-5}	CO_3^{2-}	8.0×10^{-2}
I	0.51 mol/L		
pH	8		

To characterize the clay samples porosity under the applied conditions, HTO through- and out-diffusion experiments were performed. The diffusive flux and accumulated HTO activity in the receiving reservoir solution was measured at distinct time steps. Figure 3-2 depicts the measured diffusive flux as a function of time and temperature for the through- and out-diffusion experiments. With increasing temperature, the diffusive flux increased in the HTO through-diffusion experiments. In the case of the HTO out-diffusion experiments, the diffusive flux at 65°C was slightly higher than at 85°C. However, both fluxes were increased compared to the flux for the experiment performed at room temperature.

Based on a slope analysis (Van Loon and Soler, 2004), first values for the effective diffusion coefficient and effective porosity could be estimated. The results are summarized in Table 3-2. The results reflect the findings for the flux, with increasing temperature the effective diffusion coefficient increases. The slope analysis reveals that the accessible porosity of the clay for diffusing HTO decreases with increasing temperature.

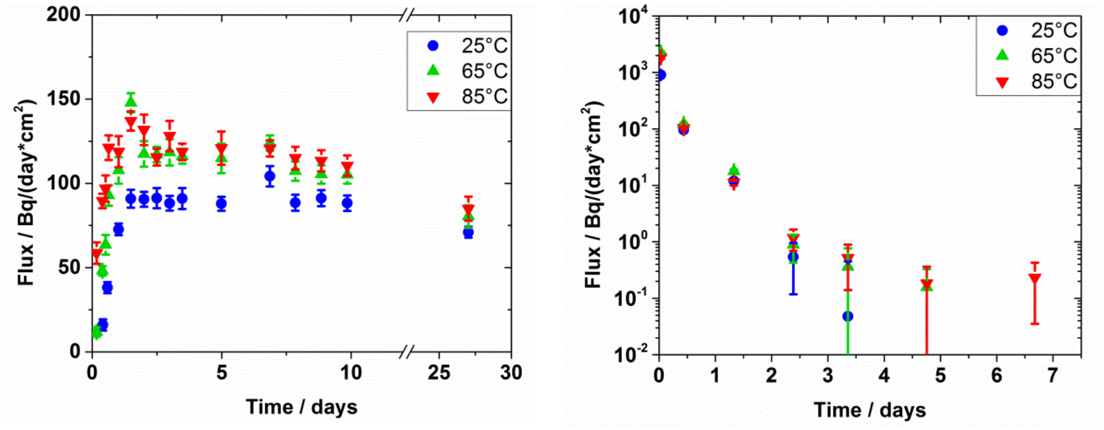

Figure 3- 1. Diffusive flux as a function of time and temperature for the HTO (left) through-diffusion and (right) out-diffusion. Activities were measured in the receiving reservoir solution.

Currently, a ^{237}Np(IV)-carbonate stock solution has been prepared via electrolysis under controlled atmosphere. The oxidation state was checked by UV/vis spectroscopy to be Np(IV); solvent extraction is underway (Bertrand and Choppin, 1982). A total of 3 Np(IV) diffusion experiments (25, 65, and 85 ºC) are underway. The Np(IV) diffusion experiment will continue for about two months at an initial concentration of 1×10^{-6} mol/L. Under our conditions, the aqueous complexes $Np(OH)_3CO_3^-$ (59.8%) and $Np(OH)_2(CO_3)_2^{2-}$ (38.6%) (calculated with EQ3/6, Wolery, 1992) should be the dominant diffusing species in solution. Characterization of the bentonite material will be performed at the end of the diffusion experiments (early FY17) to quantify Np(IV) diffusion rates.

Table 3-2. First estimates of the effective porosity $\varepsilon_{\mathrm{eff}}$, and the effective diffusion coefficient, D_e, obtained via slope analysis (Van Loon and Soler, 2004).

Temperature	c_0 **/ Bq/g**	$\varepsilon_{\mathrm{eff}}$ **/ –**	D_e **/ m²/s**
25°C	884 ± 18	0.44 ± 0.02	$(1.19 \pm 0.03) \times10^{-10}$
65°C	882 ± 18	0.30 ± 0.03	$(1.51 \pm 0.04) \times10^{-10}$
85°C	906 ± 18	0.11 ± 0.03	$(1.53 \pm 0.04) \times10^{-10}$

4. A New View of Uranium Diffusion through Compacted Bentonite: Revelations from a 6-Year Study

The manuscript by Joseph, C., Mibus, J., Trepte, P., Müller, Ch., Brendler, V., Park, D.M., Jiao, Y., Kersting, A.B., and Zavarin, M., entitled “Long-term diffusion of U(VI) in bentonite: Dependence on density” was recently accepted for publication in Science of the Total Environment. This work summarizes a multi-year study of the longterm diffusion behavior of U(VI) in bentonite. Importantly, the results suggest that radionuclide diffusion rates will tend to decrease with time which could substantially reduce the longterm risk of radionuclide diffusion through bentonite backfill material and release into the environment.

To protect the environment and people from the ecological and health risks of high-level nuclear waste, one internationally accepted concept is to safely isolate the waste in deep geologic formations. This manuscript, resulting from an international collaboration between the LLNL Glenn T. Seaborg Institute, USA, and the Institute of Resource Ecology at Helmholtz-Zentrum Dresden-Rossendorf, Germany, represents an important contribution to the risk assessment of long-term storage of high-level nuclear waste. The clay, bentonite, is considered as potential buffer material in most of the nuclear waste repository concepts regardless of the surrounding host rock. Our results of a unique 6-year laboratory study on uranium (U) diffusion through MX-80 bentonite as a function of clay dry density suggest that long-term diffusion of U(VI) through clay will be significantly slower than most short-term diffusion experiments have indicated (Figure 4-1). Our long-term diffusion experiments yield diffusivities that are about two orders of magnitude lower than previously reported (the majority of published studies were conducted for less than one year). We propose that the bentonite porosity and pore connectivity decreases with time and hinders U(VI) diffusion through the bentonite. The results of these experiments improve our understanding of long-term performance of proposed nuclear waste repositories and may significantly change the long-term outlook for safety assessment of nuclear waste storage worldwide.

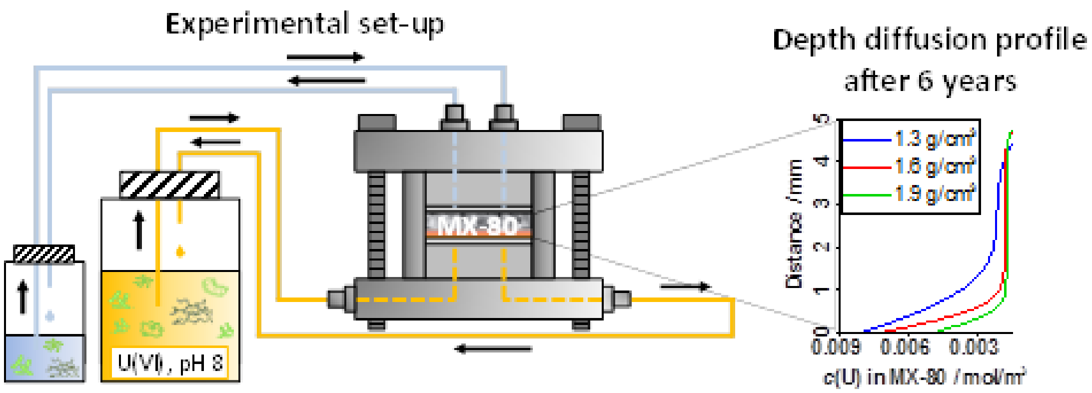

Figure 4-1. Diagram of the diffusion cell used to determine longterm U diffusion rates and a simplified plot of the observed density-dependent diffusion profiles.

5. Planned FY17 Efforts

In FY17, we plan to continue our efforts in data collection and model development in support of the UFD program. In particular, our research will focus on identification, quantification, and parameterization of processes relevant for the evaluation of the performance of various repository scenarios under investigation by the UFD program. Our specific FY17 goals for the crystalline and international work pages are the following:

- Completion of the Np(IV) diffusion experiments and quantification of the diffusion rates.
- Evaluation of the radionuclide sequestration potential of corrosion products produced during canister breaching and radionuclide release (described below)
- Continued engagement with the NEA TDB project through the support of Dr. Atkins-Duffin as the UFD representative for international thermodynamic database development effort.
- Continued collaboration with HZDR thermodynamic and sorption database development groups in support of the database needs of the UFD program

Our interest in radionuclide sequestration by corrosion products stems from (1) the potential for this process to significant inhibit radionuclide release during canister breaching and (2) from the absence of such processes in most repository performance assessments. Discussions with James Jerden (Argonne National Laboratory) suggest that a model of radionuclide incorporation can be added to the waste package cell of the GDSA model and may lead to a reduction in the source term of mobile radionuclides. Steel corrosion rates have been implemented within the used fuel matrix degradation process model but have not yet been implemented into GDSA. Results from an experimental and modeling study of radionuclide partitioning into steel corrosion products will facilitate the incorporation of this process into the GDSA as the steel corrosion model is implemented.

We will evaluate this process from both an experimental and modeling perspective. Experimentally, LLNL has been in the process of developing methodologies to grow various iron oxides phases (goethite, hematite, magnetite) in the presence of radionuclides. We will perform a small number of binary (RN-mineral) coprecipitation experiments to test radionuclide (Pu, Am, Np, and U) partitioning. Experiment will quantify coprecipitation partitioning and also examine the effects of aging and the potential iron oxide recrystallization effects associated with the presence of aqueous phase Fe(II). These data will form the basis for testing our modeling approach, described below.

Several parameters can be used to quantify metal sorption to surfaces and coprecipitation into solid phases. A distribution coefficient, D, relates the solution concentration to the solid concentration (Mn sorption/coprecipitation used as an example):

$$D = (\mathrm{Fe})/(\mathrm{Mn}) \times X_{MnOx}/X_{FeOx}$$

where (Fe) and (Mn) are the solution activities and X_{MnOx} and X_{FeOx} are the solid solution concentrations. The value D is appropriate for measuring partitioning in coprecipitation experiments but not for adsorption experiments since partitioning in adsorption samples is a function of the surface area and not the mass of the bulk solid. For adsorption experiments, the results can be related to surface partitioning ratios. A surface partitioning coefficient can be described by:

$$D^* = (\mathrm{Fe})/(\mathrm{Mn}) \times Q_{Mn}/Q_{Fe}$$

where Q_{Mn} and Q_{fe} are the surface concentrations of those elements. A comparison between D and D* values can be used to determine if sorption and coprecipitation results follow the Doerner-Hoskins rule in which partitioning by coprecipitation is assumed to behave as a continuum of surface sorption partitioning due to the constant formation of new surface sites. If the Doerner-Hoskins rule applies, a model of radionuclide partitioning into corrosion products can be, at least qualitatively, developed based on the relatively rich radionuclide adsorption data already available in the literature. The efficacy of this approach will be evaluated in FY17.

6. Acknowledgments

This work was supported by the Used Fuel Disposition Campaign of the Department of Energy's Nuclear Energy Program. Prepared by LLNL under Contract DE-AC52-07NA27344.

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