

STUDENT SUMMER INTERNSHIP TECHNICAL REPORT

Neptunium (IV) Diffusion through Bentonite Clay

DOE-FIU SCIENCE & TECHNOLOGY WORKFORCE DEVELOPMENT PROGRAM

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ABSTRACT

DOE Fellow, Silvina A. Di Pietro, completed a 10-week internship at Lawrence Livermore National Laboratory (LLNL) in Livermore, California. The objective of the study was to determine the diffusion profile of neptunium (Np) in bentonite clay (potential geo-engineered barrier for nuclear waste repositories). Under the mentorship of Drs. Claudia Joseph (Karlsruhe Institute of Technology, Germany) and Mavrik Zavarin, she prepared a series of core abrasion peeling samples. This procedure was a continuation of a Np diffusion experiment conducted by Dr. Joseph during her post-doc residency at LLNL in the year 2016. The second part of the experiment (from now on will be referred as *abrasive peeling*) focuses on understanding (1) the Np movement through the clay core and (2) the influence of temperature (25°C, 65°C, and 85°C) for the Np transport across the clay core under anaerobic conditions. End of 2016, the diffusion core samples were embedded in epoxy resin to stabilize them for long-term. The abraded core powder samples vary in material (epoxy vs. clay), Np activity and concentration, temperature exposed during the diffusion experiment, and mass, or amount of clay peeled off. Throughout the course of the 10-week internship program at LLNL, the experiments implemented and discussed in this report aimed to answer the questions: (1) How is the Np(IV) diffusion profile through bentonite influenced by the temperature? and (2) Will Np(IV) migrate through the geo-engineered barrier of a nuclear waste repository? In addition, Ph.D. candidate Di Pietro received invaluable guidance in experimental design and development that will benefit her ongoing research endeavors.

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1. INTRODUCTION

Neptunium (Np, $Z = 93$) was discovered in 1940 by scientists Edwin M. McMillan and Phillip Abelson (Katz et al., 1986). They bombarded low-energy neutrons on a thin uranium (U) foil and showed that the radionuclide formed with a 2.3-day activity was an isotope of element 93. A year later, it was shown that the decay product of ^{239}Np was ^{239}Pu . In 1942, Arthur C. Wahl and Glenn T. Seaborg discovered the long-lived isotope ^{237}Np and later in 1944, Lawrence B. Magnusson and T.J. LaChapelle were able to isolate and obtain a weighable quantity of $\sim 45 \mu\text{g}$ of NpO_2 . Np is produced in moderate quantities in nuclear reactors fueled with natural U (Burney and Harbour, 1974).

Currently, radiotoxic and manmade element Np has four main sources: (1) fallout from nuclear weapons, (2) effluent cooling water from fission reactors, (3) industrial processing of ^{237}Np produced in fission reactors, and (4) presence of ^{237}Np as a long-lived component of high-level nuclear waste (HLW) (Thompson, 1982). The latter source will be the focus of this report.

HLW results from nuclear weapons production and spent nuclear fuel used in nuclear power plants. High-level nuclear waste is highly radioactive ($5 \times 10^{16} - 5 \times 10^{17} \text{ Bq/m}^3$) and releases high decay heat in the range of $2\text{--}20 \text{ kW/m}^3$. It has a diverse and complex transuranic elements composition (Ewing et al., 1995). Although the amount of ^{237}Np present in HLW is small compared to other radionuclides (Cohen, 1977), based on its long half-life (2.14×10^6 years) it will be the most hazardous isotope upon disposal for up to 3×10^7 years (Cohen, 1982; Lowles et al., 1992).

HLW shall be disposed in deep ($> 500 \text{ m}$) geological formations (Figure 1). For this, three host rocks are investigated internationally, salt domes, crystalline rock and clay rock. To prevent HLW from exiting the waste containers and entering the biosphere, a multiple barrier system shall be installed (Figure 2).

A material of particular interest is bentonite clay rock, as it has been proposed as backfill material (geo-engineered barrier) in HLW repositories. Ultimately used as a buffer to surround and protect individual waste packages, clay-rich bentonite rock demonstrates several advantages. Bentonite has a low permeability when saturated, ensuring diffusion as main transport process for waste-released radionuclides. In addition, bentonite has a high swelling pressure, ensuring a self-sealing ability and gaps closure. Lastly, bentonite is a cost-effective natural material that is stable for millions of years.

For safety assessment of nuclear waste repositories, the transport parameters through bentonite and the retardation strength of bentonite towards waste-released radionuclides, such as Np-237 , need to be known.

The objective of this internship was to develop an understanding of prior research related to the diffusion of the radioactive element Np through the potential geo-engineered barrier, bentonite clay. The presented report aims to contribute to our understanding of the transport of the contaminant ^{237}Np .

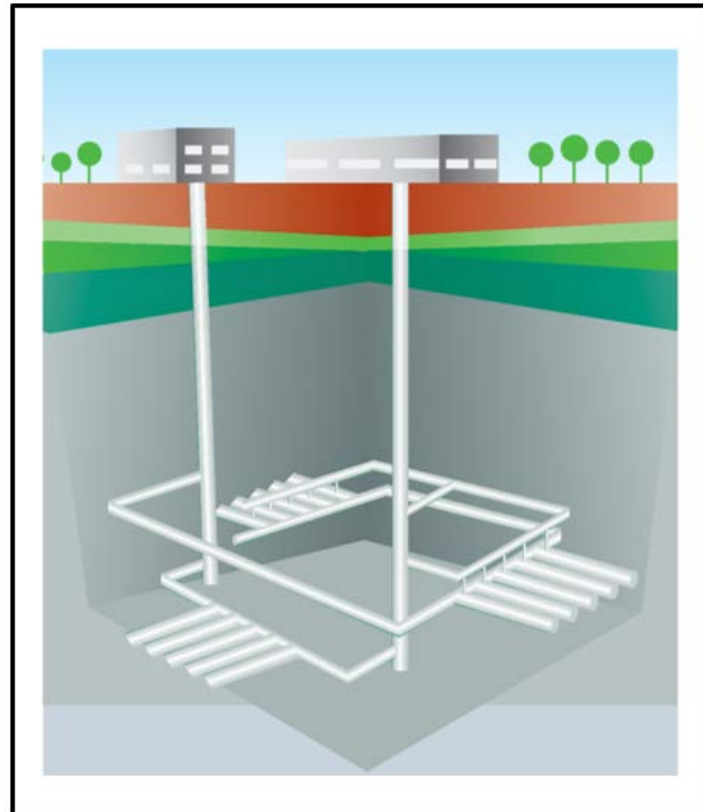


Figure 1. Schema of a repository for final disposal of nuclear waste in deep geological formations (Sachs et al., 2009).

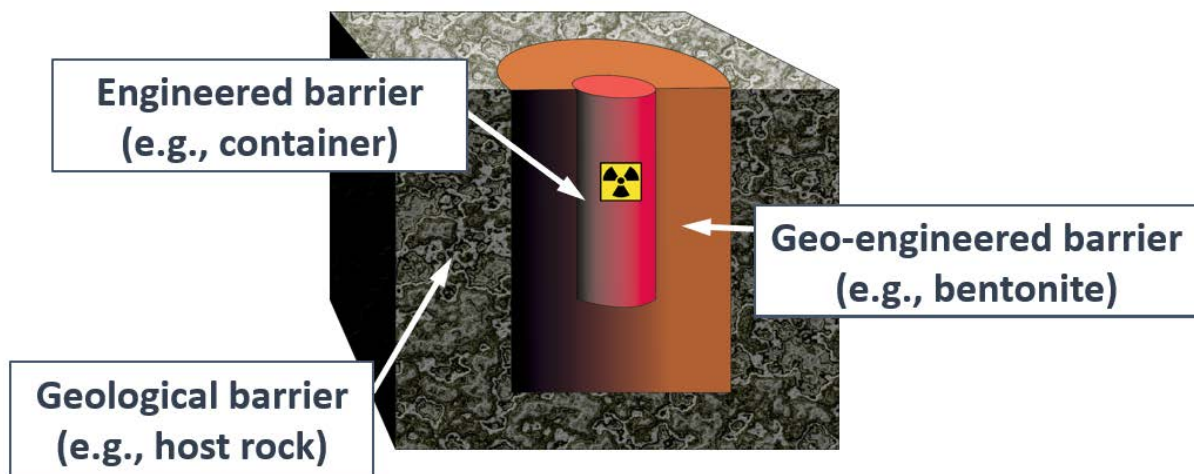


Figure 2. Multiple barrier system of a nuclear waste repository (Joseph, 2013).

2. EXECUTIVE SUMMARY

This research work has been supported by the DOE-FIU Science & Technology Workforce Initiative, an innovative program developed by the US Department of Energy's Environmental Management (DOE-EM) and Florida International University's Applied Research Center (FIU-ARC). During the summer of 2019, DOE Fellow intern Silvina Di Pietro spent 10 weeks doing a summer internship at Lawrence Livermore National Laboratory (LLNL) in Livermore, California under the supervision and guidance of Dr. Mavrik Zavarin, director of the Glenn T. Seaborg Institute. The intern's project was initiated on June 3rd, 2019 and continued through August 10th, 2019 with the objective of performing research and assisting with experiments related to the understanding of the neptunium diffusion through bentonite clay.

3. MATERIALS AND METHODS

The purpose of this research was to contribute to the safety assessment of nuclear waste repositories. After the completion of the first part of the experiment (*diffusion*), Np was quantified within the second part of the experiment by *abrasive peeling*. The principle is described in detail in Van Loon and Eikenberg (Van Loon and Eikenberg, 2005). To reiterate, the *abrasive peeling* is used to determine (1) the Np movement through the clay core as a function of depth (in millimeters) and (2) the influence of temperature (25°C, 65°C, and 85°C) on the Np transport across the clay core under anaerobic conditions.

3.1 The Diffusion Experiment

Briefly, the *diffusion* experiment (completed in 2016 by LLNL post-doc Dr. Claudia Joseph) was conducted with ^{237}Np diffusing through bentonite clay (Figure 3). As Figure 4 shows, Np was spiked in a synthetic bentonite pore water solution (ionic strength: 0.51 mol/L; pH = 9.65) filled in a source reservoir. With the aid of a peristaltic pump, the spiked radioactive solution ($c_0(\text{Np-237}) = 1 \cdot 10^{-6}$ mol/L) was transferred to the diffusion cells kept at three different temperatures, 25°C, 65°C and 85°C, respectively. After an experimental time of 59 days, the diffusion experiment was stopped. Each source and receiving reservoir solution were analyzed (Figure 4). It is important to note that this process was performed inside an anaerobic chamber to maintain low-oxygen levels ($p\text{O}_2 < 10$ ppm) and high CO_2 pressures ($p\text{CO}_2 = 10^{-1.5}$ bar). These conditions resulted in the dominant formation of a mobile Np(IV)-carbonate species in the source reservoirs, which should be relevant to geological repositories conditions.

3.2 The Abrasive Peeling

Prior to part II of the experiment, several steps were needed to be executed. First, as shown in Figure 5, the three diffusion cells were dismantled and the bentonite-containing plugs extruded (Np-spiked at 25°C, 65°C and 85°C). The clay was dried in an oven overnight to remove attached water. The next day after cooling, the three clay plugs and an additional bentonite blank were embedded in an epoxy resin to stabilize the Np profiles in the clay on a long-term. Thereby, a stainless steel plunger was glued to each clay plug sample with the help of the resin (Figure 5). In 2019, a bench drill press (RYOBI® 10 inch-Exactline laser alignment) was placed inside the fume hood (Figure 6) to drill out a 6.7 mm in diameter hole in each clay core (Figure 7). This is needed for an even abrasion of the clay cores. Care was taken to contain any radioactive dust particles that may have been dispersed within the fume hood. It is important to note that the fume hood was monitored with an alpha detector prior to, during and after using the drill press.

In preparation to the abrasive peeling, punched out circles of sandpaper (3M Prograde Precision® 22.8 x 27.9 cm) of approximately 1.0 inch in diameter were glued (Gorilla Superglue®) into plastic jars. Allowing approximately 24 hours for the glue to harden and dry, the jars (with lids and glued-sandpaper) were weighed and masses were recorded. Depending on the segmenting step, different grit/particle size sandpaper and number of jars were needed (Table 1). Note that the 400-grit size sandpaper was used only for the blank core abrasive peeling process as its thickness (25.8 μm) was determined to be too thin.

With the sandpaper pre-weighed jars and the resin-embedded clay samples, the abrasive peeling process was started. The stainless-steel sample holder with the clay plug sample was mounted into the bench drill. Each sample was abraded in three steps depending on the sandpaper particle size (Figure 8, left). For each clay plug (i.e., blank and 25°C, 65°C and 85°C), serie-step #1 consisted of abrading 22 jars containing 60-grit sandpaper. It is important to note that the first 0.5–1 mm of the abraded material in each clay plug consisted of epoxy material and sand. Thus, the material was abraded with the rougher sandpaper. For serie-step #2, 44 jars containing 320-grit sandpaper were used resulting in a smaller step size, important for determining the Np diffusion profile. Lastly, for serie-step #3, 22 jars containing 60-grit sandpaper were used, since Np should be present only in low concentrations at farer distances. The goal of the aforementioned step-series sequence was to (1) obtain approximately 1–3 mm of clay core abraded and (2) have the part of the clay sample abraded where the Np(IV) activity is potentially the highest as hypothesized in section 3.1 of the experiment (*diffusion*). The drill press' rotation speed was set to the lowest (~ 600 rpm). The sandpaper contact time with the sample was 1–2 seconds. To determine the amount of clay abraded, the sample holder was dismounted from the bench drill and the thickness was measured with an electronic digital caliper at three points around the core's circumference (Figure 9). For the 60-grit sandpaper jars, data were recorded every 5th sample. For the 320-grit sandpaper jars, thickness was recorded every 10th sample. Once the abrasive peeling process was terminated, the 88 sample jars were left inside the photo-tray inside the fume hood (Figure 8, right). The following day the jars containing the clay abraded segments were weighed again. Due to problems with sandpaper ungluing from the jar's surface or low abraded-clay masses, 30 jar-samples were selected out of the 88 samples abraded. Preference was given to those jars that contained the most bentonite clay. Samples were then acidified in 1.0 mL of 4.0 mol/L nitric acid (HNO₃, 67-70% IQ Ultrapure Grade Seastar®) to form a small clay suspension. Jar samples were weighed, and the post-acidification step masses were recorded. After 48 hours of equilibration on a horizontal shaker (mod. 3527 Environ Orbital Incubator Shaker, Lab-Line Instruments, Melrose Park, IL, USA), the suspensions were pipetted into 1.5-mL-microcentrifuge tubes and centrifuged (MiniSpin Eppendorf®) for 10 minutes at 10,000 rpm. For ²³⁷Np α -emitter activity and concentration quantification, liquid scintillation counting (LSC, Perkin Elmer®TriCarb 2900TR) and inductively coupled plasma–mass spectrometry (ICP-MS) analysis were performed at the supernatants after centrifugation. For LSC tracer activity analysis, a 1.0 mL aliquot of the acidic supernatant was pipetted in 7-mL-liquid scintillation vials. Then, 5.0 mL of scintillation cocktail (Ultima Gold®) were added to each vial. For ICP-MS (iCAP-Q), a 1.0 mL aliquot of the acidic supernatant was pipetted into 5 mL sterile transport tubes (Axygen Scientific®). Sample-containing tubes were given to the Center for Accelerator Mass Spectrometry (CAMS) in the Chemical Sciences Division group for Np concentration analysis.

Table 1. Three types of sandpaper used for abrasive peeling with its respective particle size and jar quantity for each clay sample (Joseph, 2019)

Standard grit	Average particle size (µm)	Jar Quantity
60	250	2×22
320	40.5	44
400	25.8	22*

*Note: 400-grit size was used for blank clay core only.

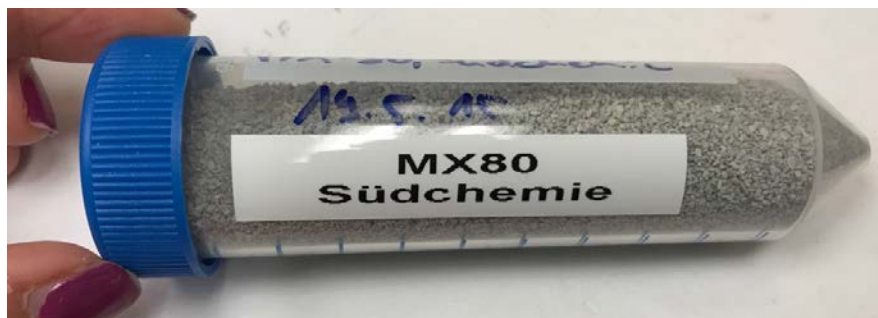


Figure 3. Na-bentonite clay (commercial name *MX-80*, from Wyoming, USA and provided as granulate by Süd-Chemie AG Munich, Germany) consists of ~90% montmorillonite, 4% quartz, 2% muscovite, 2% calcite, 2% cristobalite, and 1% pyrite, used in the diffusion experiments.

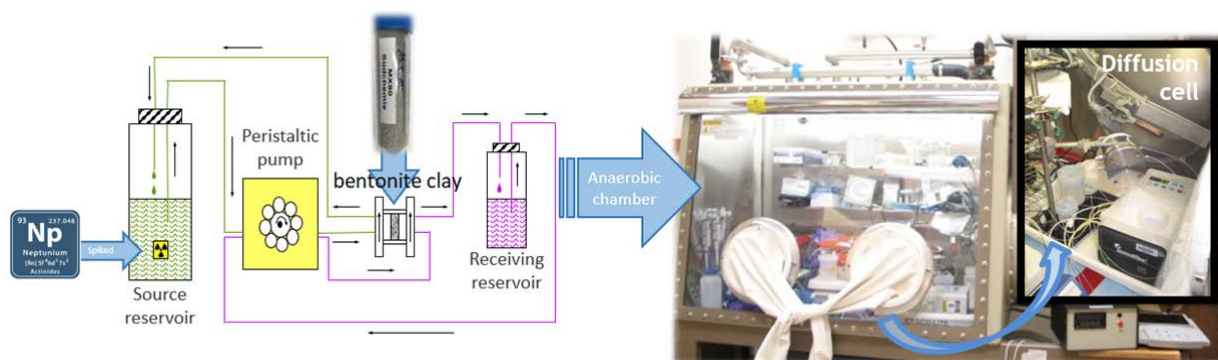


Figure 4. Set-up of the diffusion experiment (section 3.1) performed by Dr. Claudia Joseph.

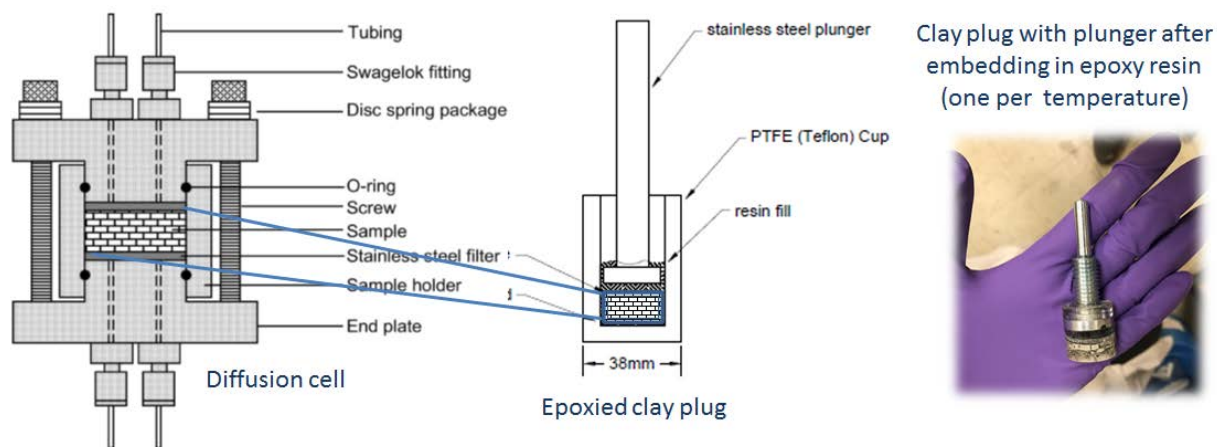


Figure 5. Diffusion cell drawing (left, Van Loon and Soler, 2004). Bentonite clay plug epoxied and combined with plunger (center). Example of a bentonite-clay plug with plunger prior to abrasive peeling (right).



Figure 6. RYOBI-10 inch with exactline laser alignment bench drill press placed inside the fume hood of the Glenn T. Seaborg laboratory at LLNL.

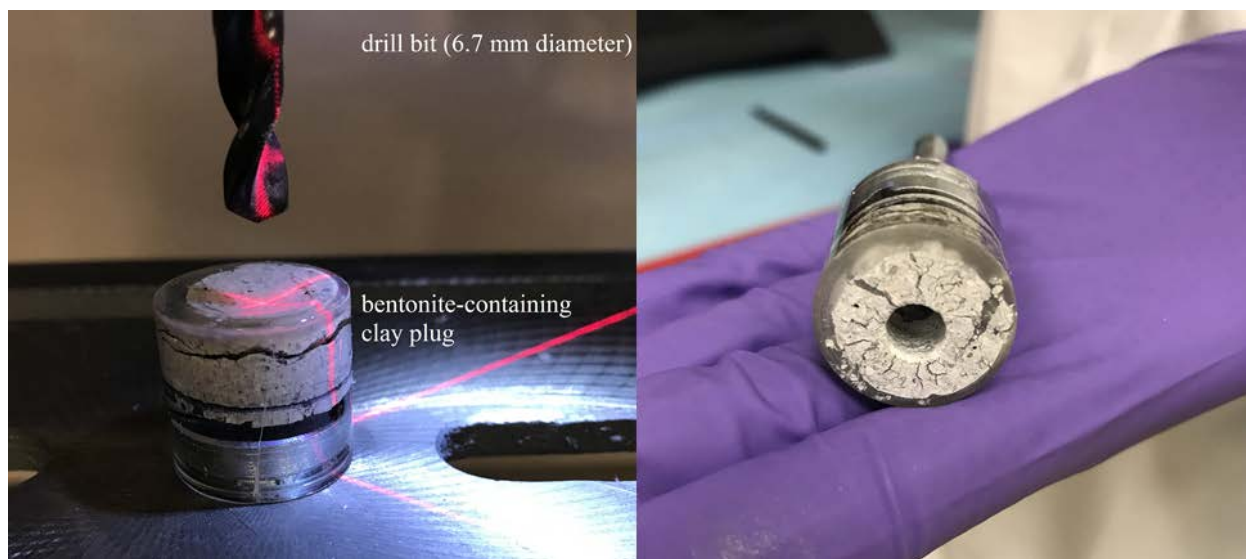


Figure 7. 6.7-mm diameter drill bit from the bench drill press (left). Post-drill out image of the blank clay core (right).

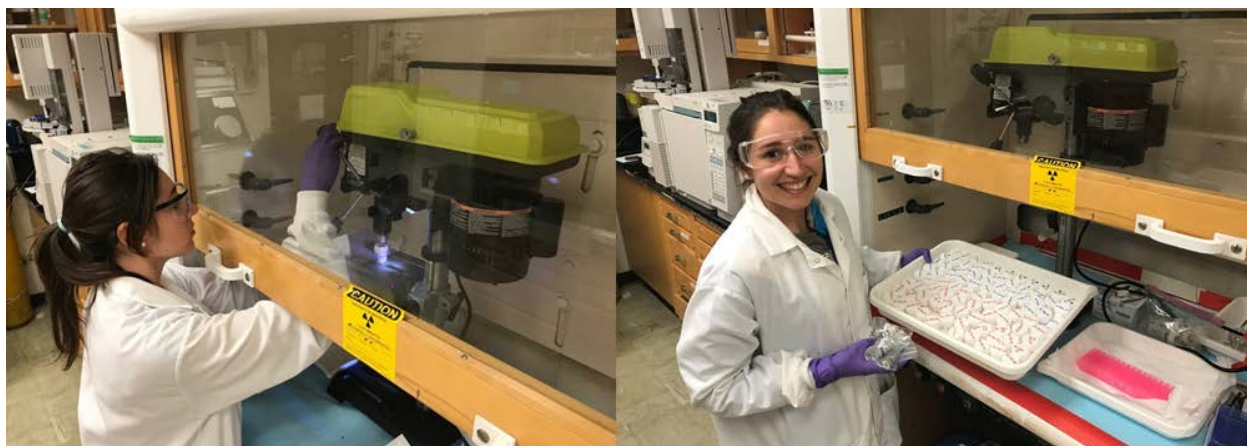


Figure 8. DOE Fellow Silvina Di Pietro performing abrasive peeling onto the 85°C clay plug (left). Di Pietro holds a photo tray containing the 88 jars bentonite-abraded samples to be acidified (right).



Figure 9. 150-mm stainless-steel caliper was used to measure the thickness of the bentonite clay plug throughout the abrasive peeling process.

4. RESULTS AND DISCUSSION

4.1 Acid Extraction Efficiency

Prior to performing abrasive peeling on the blank (i.e., no spiked Np) clay sample, a series of preliminary experiments were completed in order to optimize the acid extraction recovery of Np from the abraded bentonite clay. The goal was to adjust the ^{237}Np LSC-protocol and to evaluate if it was an effective quantitative technique to determine the ^{237}Np α -emitter activity in the clay samples (Figure 5, right). In addition, there was a need to test which HNO_3 concentration was most efficient at extracting Np from the clay.

Table 2 shows a summary of four experiments performed varying the (1) type of bentonite clay source and (2) HNO_3 concentration. For the first experiment, *MX-80*, a simple batch-sorption experiment was conducted where fresh bentonite clay granulate (Figure 3) was contacted with Np-spiked synthetic groundwater (pH = 9.65), which was the remaining source reservoir solution of the diffusion experiment conducted at 25°C (The Diffusion Experiment). The recoveries were consistent (average: 64%) showing that the recovery is very reproducible using 1.0 mol/L HNO_3 . However, in the case of the 25°C -clay core (the second experiment), after addition of Np source reservoir solution and extraction with 1.0 mol/L HNO_3 , the Np recoveries varied and were very low, in particular, when the Np had diffused deeper into the clay core. For this reason, a third set of acid extraction experiments was performed varying the HNO_3 concentration from 4.0 to 9.0 mol/L. Using three different 25°C -abraded clay samples, the Np recoveries were consistently high and promising. The LSC-protocol demonstrated that higher HNO_3 concentrations were able to extract higher Np loadings from the bentonite samples in comparison to 1.0 mol/L HNO_3 . For 25-320-5 and 25-320-16 samples (sample ID nomenclature corresponds to: *core name-sandpaper grit size-sample # abraded*), the percent recovery is greater than 100%. These bentonite samples originated from the Np diffusion experiment and contained already Np of unknown concentration. It was concluded that regardless of HNO_3 concentration (4.0, 8.0, or 9.0 mol/L), (1) the recoveries were similar among the different acid concentrations and (2) a higher HNO_3 concentration resulted in higher acid extraction. For cost-saving and precaution handling reasons, 4.0 mol/L HNO_3 was chosen for further extraction experiments (see data in Table 2: 25°C core, 4.0 mol/L HNO_3 experiment).

A recovery analysis was also executed with LSC. A set of 25°C -abraded clay samples were analyzed by ICP-MS and LSC in parallel. Upon comparing LSC data to ICP-MS data, it was decided that ICP-MS results have a better selectivity and sensitivity.

Table 2. Neptunium recovery after acid extraction (%) using Np-spiked bentonite samples detection via liquid scintillation counting (LSC). Note sample ID nomenclature: *core name-sandpaper grit size-sample # abraded*.

Experiment	Sample ID	Liquid:Solid, mL/g	HNO ₃ , mol/L	Recovery, %
MX-80 bentonite clay	1	140	1.0	64%
	2	181	1.0	66%
	3	216	1.0	62%
25°C core, 1.0 mol/L HNO₃	25-60-15	9.00	1.0	64%
	25-400-22	181	1.0	43%
	25-320-21	158	1.0	24%
	25-320-43	134	1.0	21%
25°C core as f(HNO₃)	25-320-1	234	4.0	99%
	25-320-5	328	8.0	110%
	25-320-16	388	9.0	104%
25°C core, 4.0 mol/L HNO₃	25-60-17	27.8	4.0	81%
	25-400-21	401	4.0	90%
	25-320-27	403	4.0	70%
	25-320-28	206	4.0	70%
	25-320-39	320	4.0	71%

4.2 Correlation mass vs. thickness

Figure 10 shows the abraded masses for all four bentonite clay plug segmentation sets versus their respective abraded thickness. Overall, the abraded masses and thickness are strongly correlated. This is indicative that the abraded mass represented well the clay position within the clay plug. From Figure 10, it can be concluded that the blank and 65°C clay cores were the least and best correlated, respectively. This may, in part, be due to the fact that the blank core was the first to be processed as a test of the abrasive peeling protocol. As more practice was acquired with the drill bench press (Figure 6) and the protocol was optimized, the later clay plugs (e.g., 65°C) were processed more consistently. Lastly, the total thickness abraded was different for all four core plugs. It followed: 65°C > 85° > 25° > blank. While in the case of the 65°C clay plug 3.0 mm were abraded, only 1.5 mm were abraded from the blank clay sample. It is for this reason that the 400-grit sandpaper was not applied in the final abrasive peeling protocol.

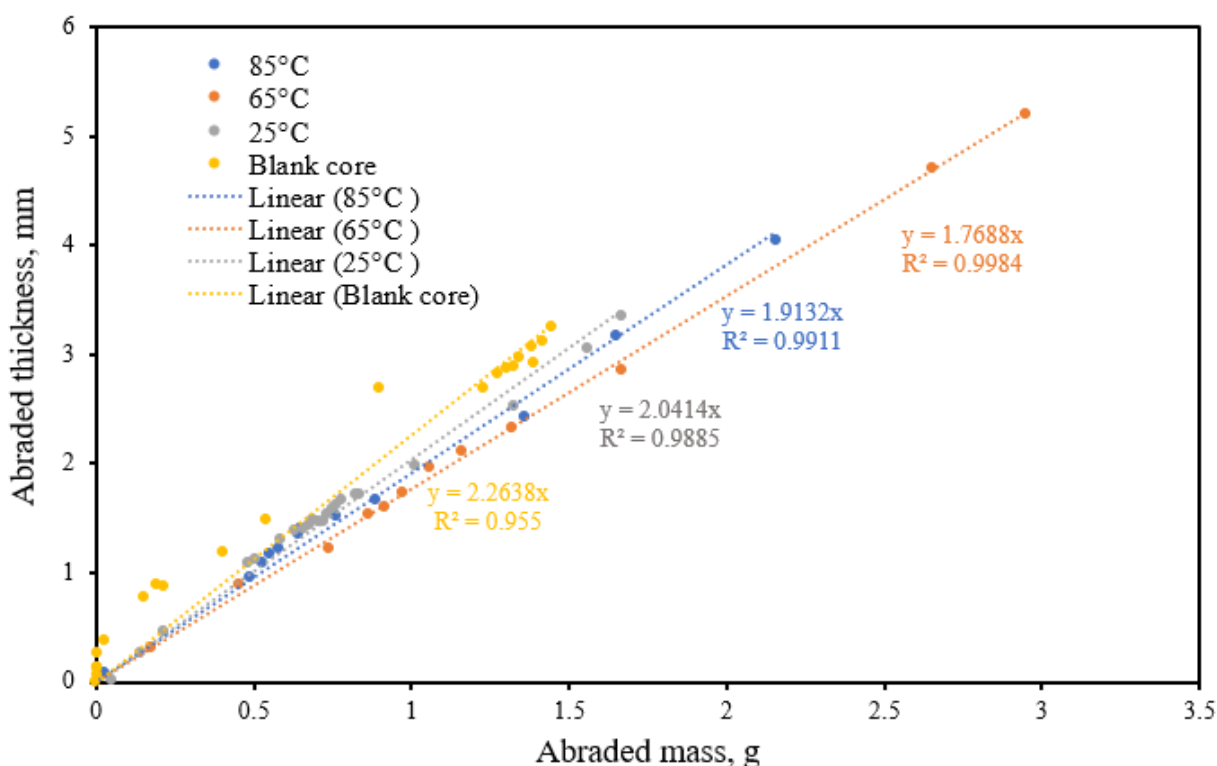


Figure 10. Correlation between the abraded mass to the abraded thickness for the blank (yellow), 25 °C (gray), 65 °C (orange), and 85 °C (blue) clay cell cores.

4.3 *Np* diffusion profile of the 25°C clay plug

The goal of this section was to clarify how the Np(IV) diffusion profile through bentonite is influenced by the temperature. Via abrasive peeling, the Np diffusion through the clay core (diffusion profile) was obtained. Prior to employing the abrasion protocol, a series of model calculations were conducted in order to optimize the experimental procedure. For brevity, the calculations are not shown. However, Figure 11, left depicts the calculations by graphing the calculated Np diffusion profile for the 25°C clay plug. The estimated data demonstrates that the maximum Np activity is expected to be found at the interface between epoxy/sand and bentonite clay. The estimated diffusion profile also shows that the Np activity decreases as a function of depth. The α -emitting activity ceases at approximately 3.5 mm depth. For comparison, Figures 11, right shows the experimentally determined Np diffusion profile of the 25°C clay plug. The Np activity increased in the first 1.0 mm of the abraded clay plug and reached its maximum at 1.5 mm. With increasing depth, the Np activity decreases from 1.5 mm to 3.5 mm. When comparing experiment to model, it can be seen, that the Np profile ceased at the same depth (3.5 mm). Np activity was detected in the epoxy part of the clay plug. This is probably due to the bentonite clay being lopsided (i.e., not in parallel position to the epoxy) as it was embedded in the epoxy resin. In addition, the maximum Np activity for the investigated clay plug was one order of magnitude lower in the experiment compared to the modeled maximal Np activity, indicating that the Np activity was less than expected. One explanation could be that the Np has sorbed to the diffusion cell equipment (reservoir jars, tubing, filters) during the diffusion experiment.

Although this experiment focuses on Np diffusion and the effect of temperature on it (i.e., 25°C, 65°C, and 85°C), here only data of the Np diffusion profile at 25°C is presented. The bentonite-clay plugs of the diffusion experiments at 65°C and 85°C were also abraded and the segments were extracted. The Np-containing supernatants are waiting to be analyzed by ICP-MS. Therefore, these data will not be presented in this report.

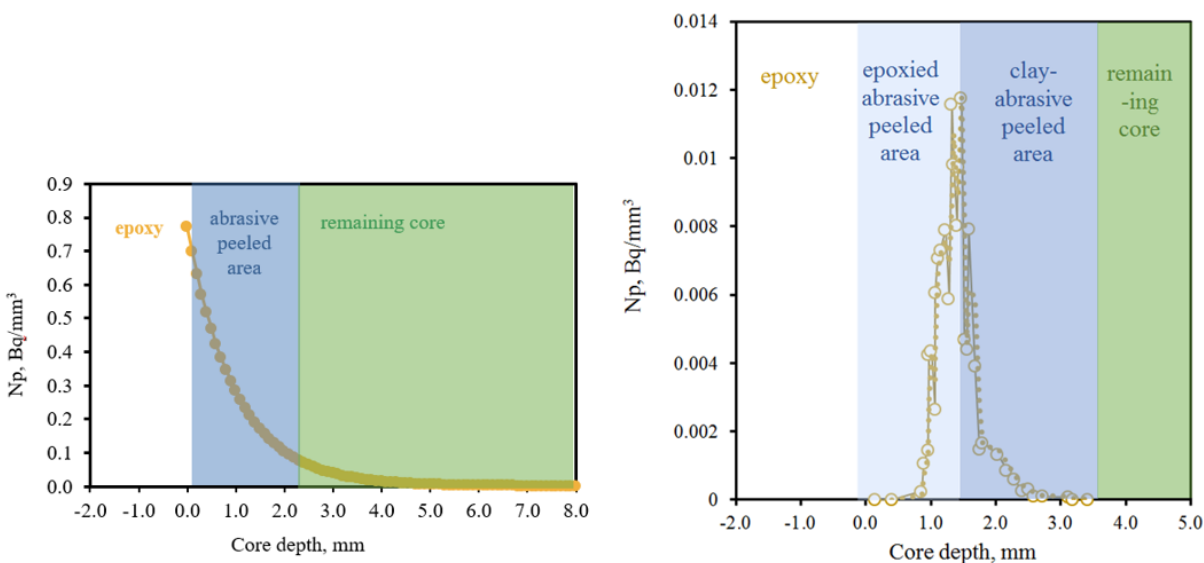


Figure 11. Estimated Np diffusion profile (left) and measured Np diffusion profile (right) for the 25°C clay plug.

5. CONCLUSIONS

Although the amount of ^{237}Np present in HLW is small compared to other radionuclides (Cohen, 1977), due its long half-life (2.14×10^6 years) it will determine the radiotoxicity of HLW > 1000 y after waste emplacement. Np is considered to be the most problematic of the actinide elements (5f group) for waste storage because of its high solubility [$\text{Np(V)} = (5.50 \pm 1.97) \times 10^{-6}$, pH = 8.5] in groundwater (Antonio et al., 2001; Efurud et al., 1998). In order to prevent Np transport and entry into the biosphere, bentonite clay is proposed as geo-engineered barrier, backfill material, in nuclear waste repositories. The material shall act as a buffer between the host rock and the waste containers (Figure 2) in deep geological formations.

In order to assess the migration of $^{237}\text{Np(IV)}$ through bentonite clay, laboratory diffusion experiments were performed at three different temperatures (25, 65, and 85°C) at low-oxygen and high CO_2 levels ($p\text{O}_2 < 10$ ppm and $p\text{CO}_2 = 10^{-1.5}$ bar). To determine the diffusion profile of the sorbing tracer Np in the clay samples, abrasion peeling was conducted. For the 25°C clay plug, the maximum Np(IV) activity was determined with 0.012 Bq/mm^3 at a depth of 1.5 mm. This activity was one order of magnitude lower than the estimated maximal Np activity. While the reason for the Np loss is still under investigation, Np sorbing to the equipment during the diffusion experiment is proposed as hypothesis.

Np was detected up to a diffusion distance of 3.5 mm. When comparing the abraded bentonite-clay masses and abraded thicknesses, all investigated clay plugs (blank, 25°C, 65°C, and 85°C) demonstrated a strong correlation ($R^2 > 0.955$).

The Np recovery by acid extraction was optimized. It was concluded that 4.0 mol/L HNO_3 has the highest Np recovery after acid extraction ($> 70\%$). However, due to samples containing low Np activities, analytical methods were shifted from LSC to high sensitivity and selectivity ICP-MS quantitative analysis.

While the presented work is promising, further analysis of the data is necessary. The abraded and extracted samples of the clay plugs where Np diffused through bentonite at 65°C and 85°C are still under analysis. The goal is to compare the obtained 25°C-Np-bentonite diffusion profile with the Np profiles at 65 and 85°C in order to understand the influence of temperature on Np diffusion. Based on the Np profiles and Np reservoir concentrations, transport parameter values such as diffusion coefficients shall be modeled. These data shall contribute to the safety assessment of nuclear waste repositories.

6. ACKNOWLEDGEMENT

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APPENDIX A.

Each summer, LLNL hosts students from all over the world for the opportunity to engage them in work-study employment opportunities in science, technology, engineering, and mathematics (STEM). At the end of the summer, the Laboratory's Strategic Human Resources Management (SHRM) department and the Institutional Education Committee sponsor a student poster symposium as a forum for students to showcase their summer research projects and communicate their work with others. Representing her work at the Glenn T. Seaborg Institute for the Nuclear and Chemical Sciences Division (NACS) and Physical and Life Sciences Division, DOE Fellow Di Pietro communicated her 10-week findings at the LLNL Student Poster Symposium. Figure 12 shows an image of her poster. Figure 13 shows Di Pietro with her mentor, Dr. Mavrik Zavarin, whose help and mentorship was invaluable throughout the 10-week internship program.

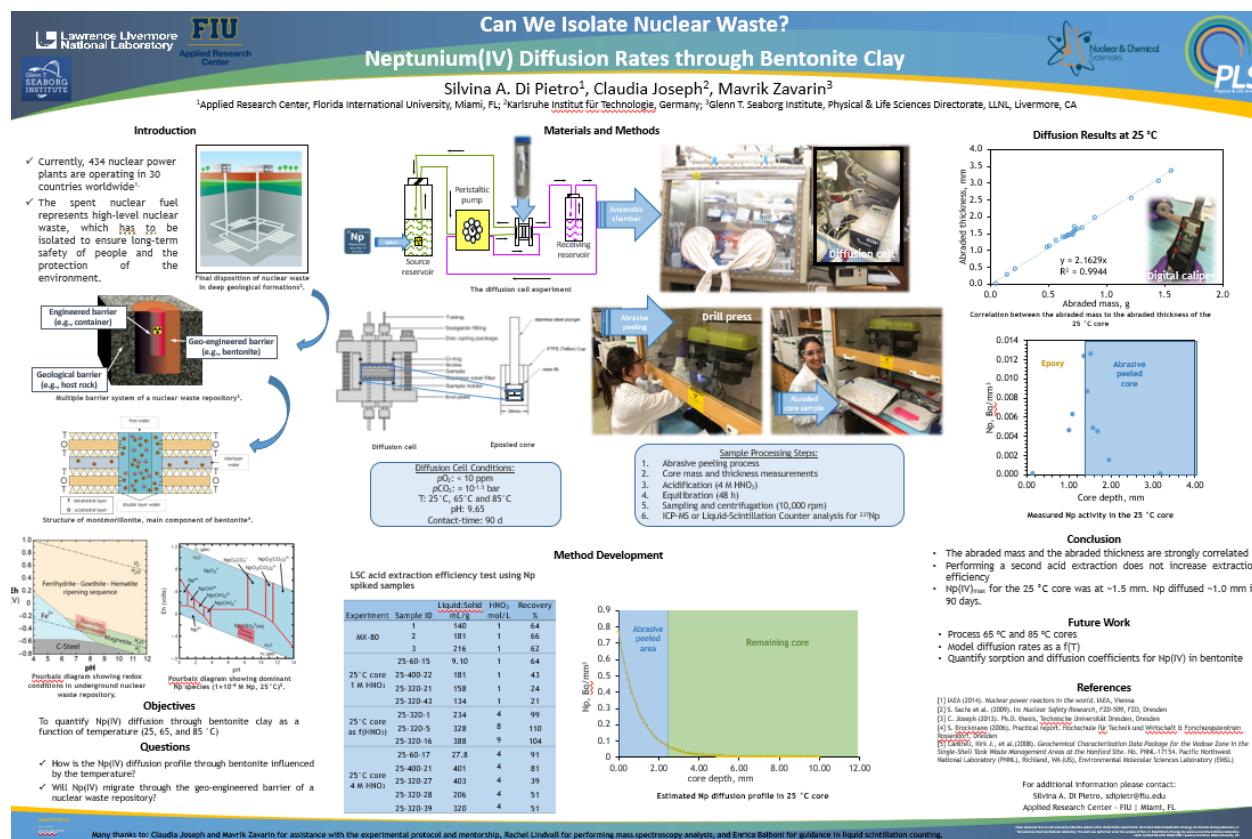


Figure 12. Di Pietro's summer internship poster titled "Can We Isolate Nuclear Waste? Neptunium(IV) Diffusion Rates through Bentonite Clay" presented at the 2019 LLNL Student Poster Symposium.

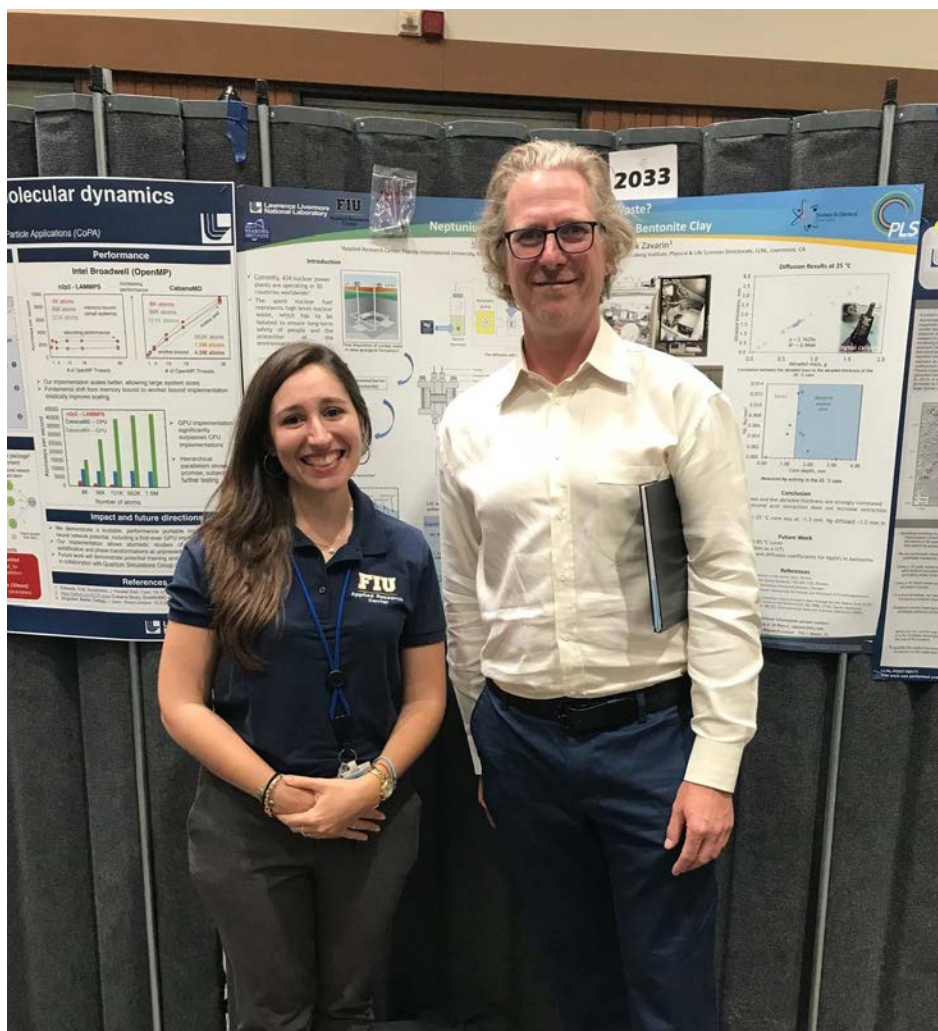


Figure 13. DOE Fellow Silvina Di Pietro with her summer mentor and Glenn T. Seaborg Institute's director Dr. Mavrik Zavarin at the 2019 LLNL Student Poster Symposium.