Laboratory Experiments on Bentonite Samples: FY17 Progress

Spent Fuel and Waste Disposition

Revision 4
07/05/2017

APPENDIX E

NTRD DOCUMENT COVER SHEET [1]

Name/Title of Deliverable/Milestone/Revision No.	Laboratory Experiments on Bentonite Samples: FY17 Progress M4SF-17LB010302061
Work Package Title and Number	Crystalline Disposal R&D – LBNL SF-17LB01030206
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Quality Rigor Level for Deliverable/Milestone[2]	☐ QRL-1 ☐ Nuclear Data	☐ QRL-2	☐ QRL-3	X QRL 4 Lab-specific

This deliverable was prepared in accordance with   Lawrence Berkeley National Laboratory (LBNL)

(Participant/National Laboratory Name)

QA program which meets the requirements of

X DOE Order 414.1   ☐ NQA-1   ☐ Other

This Deliverable was subjected to:

☐ Technical Review   ☐ Peer Review

Technical Review (TR)	**Peer Review (PR)**
Review Documentation Provided	**Review Documentation Provided**
☐ Signed TR Report or,	☐ Signed PR Report or,
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X Signature of TR Reviewer(s) below	☐ Signature of PR Reviewer(s) below
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NOTE 1: Appendix E should be filled out and submitted with each deliverable. Or, if the PICS: NE system permits, completely enter all applicable information in the PICS: NE Deliverable Form. The requirement is to ensure that all applicable information is entered either in the PICS: NE system or by using the NTRD Document Cover Sheet.

- *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.*

NOTE 2: If QRL 1, 2, or 3 is not assigned, then the QRL 4 box must be checked, and the work is understood to be performed using laboratory specific QA requirements. This includes any deliverable developed in conformance with the respective National Laboratory Participant, DOE or NNSA-approved QA Program.

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SUMMARY

The viability of nuclear energy relies in large part on the creation of a long-term nuclear waste disposal repository capable of isolating high-level radioactive waste (HLW) over the time scales necessary for decay of long-lived radioactive isotopes ($> 10^6$ years). Most nuclear waste repositories currently under investigation use clay media (*i.e.*, bentonite or shale) as engineered barriers or as the host rock for geologic storage. Clays are good barriers for HLW due to their low hydraulic conductivity, which restricts contaminants to diffusion-based transport, and their high adsorption capacity for contaminants, which slows transport even further. Montmorillonite, a smectite mineral, is the dominant clay mineral found in bentonite and has a large specific surface area (~750 m^2/g) and cation exchange capacity (~1 mol$_c$/kg). However, other accessory minerals may also be present in bentonite, including quartz, feldspars, iron oxides, calcite, illite, and other minerals.

Radioactive decay of HLW can result in high temperatures (100-200 °C) near the waste canisters, and the effects of elevated temperature on the engineered barrier must be taken into account when designing a nuclear waste repository. In addition to changes in the hydrological and mechanical properties of clay, high temperatures may lead to changes in pore water chemical compositions and clay and accessory mineral composition or structure. The conversion of montmorillonite to illite, known as illitization, is one of the primary mineralogical changes that may occur during long-term exposure to high temperatures.

Because uranium is the primary constituent of spent nuclear fuel, and water-fuel chemical interactions could release soluble U(VI) into groundwater, a detailed understanding of the transport of U(VI) in clays is necessary to assess the safety and reliability of waste disposal facilities. U(VI) adsorption is highly dependent on aqueous geochemical conditions, in particular pH, bicarbonate concentrations, and calcium concentrations, due to the complex aqueous speciation of U(VI) and the different propensity for adsorption of these aqueous U(VI) species. The accessory minerals present in bentonite may play an important role in controlling aqueous geochemistry in pore waters through dissolution and precipitation reactions. For example, dissolved concentrations of Ca and bicarbonate are largely controlled by the solubility of calcite. Heat-induced changes in bentonite properties, including illitization, changes in pore water chemistry, and changes in accessory mineral compositions may affect the adsorption and transport of U(VI).

The primary goal of this study was to investigate the effects of bentonite heating on U(VI) adsorption behavior and to provide mechanistic insight into any observed differences in U(VI) adsorption. Bentonite samples from the FEBEX (Full-Scale Engineered Barriers Experiment) *in situ* experiment, which were subjected to temperatures up to 100 °C for 18 years, were tested for U(VI) adsorption. U(VI) adsorption on heat-treated bentonite was compared to adsorption on original FEBEX bentonite and *in situ* cold-zone (unheated) FEBEX bentonite. Batch kinetic and equilibrium U(VI) adsorption experiments were performed on both unpurified bentonite, which contained native accessory minerals and bentonite purified to remove accessory minerals.

Batch kinetic (1 week) U(VI) adsorption experiments were used to screen the FEBEX bentonite samples for differences in U(VI) adsorption at pH 7.5 in 0.05 M NaCl at a total U(VI) concentration of 8.4 x 10^{-7} M. Dissolved inorganic carbon (DIC), Ca, and Mg concentrations, and U(VI) adsorption in these experiments appeared to reach equilibrium in 48 hours. U(VI) adsorption onto FEBEX bentonite samples which experienced sustained temperatures of approximately 95 °C was ~10% lower than adsorption onto original unheated and cold-zone (20 °C) FEBEX bentonite (52% vs. 62% adsorbed, respectively). However, U(VI) adsorption onto FEBEX bentonite, which experienced more moderate temperatures (approximately 45 °C) was *not* lower than unheated FEBEX bentonite for the condition tested. Concentrations of dissolved Ca and DIC were very similar for all FEBEX bentonite samples, suggesting that aqueous chemical conditions, and thus aqueous U(VI) speciation, were *not* responsible for the lower U(VI) adsorption observed for the heat-treated sample.

Based on the results of the kinetics experiment, two samples were chosen for more detailed characterization and U(VI) adsorption experiments covering a range of chemical conditions (pH 7-8, Ca = 0.1 and 2.0 mM, 0.1 M NaCl, U(VI) total = 9.4 x 10^{-7} M) relevant for nuclear waste disposal scenarios. The two samples were the FEBEX bentonite subjected to 95 °C ("heated" bentonite) and the *in situ* cold zone (20 °C) FEBEX bentonite. U(VI) adsorption onto the heated bentonite was consistently lower than the cold-zone bentonite over the range of chemical conditions tested.

In order to determine whether the observed difference in U(VI) adsorption was due to the changes in the amount or type of accessory minerals or an alteration of the clay mineral structure (*e.g.*, illitization), the two selected bentonite samples were purified to remove accessory minerals and U(VI) adsorption experiments were conducted on the purified samples. U(VI) adsorption onto the purified bentonite was higher than on the unpurified bentonite for the same mass of bentonite. This result is expected and likely, due to the removal of non-adsorbing minerals (*e.g.*, quartz) which effectively dilute the highly sorptive clay minerals (montmorillonite) in the unpurified bentonite. The lower U(VI) adsorption onto heated (95 °C) FEBEX bentonite compared to cold-zone FEBEX bentonite persisted over the range of chemical conditions tested for the purified samples. This suggests that the observed decrease in U(VI) adsorption was due to alteration of the clay mineral structure, and *not* due to a change in the pore water chemistry or amount and type of accessory minerals. This may reflect illitization of the montmorillonite; however, further clay characterization is needed to verify this hypothesis.

The results of this study provide important information necessary for performance assessment of HLW disposal scenarios. The decreased adsorption observed in this study as a result of bentonite heating may impact the diffusion of U(VI) through engineered clay barriers. Structural changes in the clay mineral (*e.g.*, illitization) will likely also impact the adsorption of other radionuclides. Further investigation is needed to probe the structural changes that occurred as a result of heating and to better understand the mechanisms underpinning this behavior. Over the next fiscal year, we plan to characterize the heated and cold-zone bentonite samples and model the observed U(VI) adsorption behavior. The modeling work will build upon the U(VI) adsorption model developed for Na-montomorillonite in previous years.

ACKNOWLEDGEMENTS

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ACRONYMS

DIC	dissolved inorganic carbon
DOC	dissolved organic carbon
DOE	U.S. Department of Energy
ENRESA	Empresa Nacional de Residuos Radiactivos
FEBEX	Full-Scale Engineered Barriers Experiment
HLW	high-level radioactive waste
IC	inorganic carbon
ICP-MS	inductively coupled plasma mass spectrometry
LLW	low-level radioactive waste
OC	organic carbon
UMTRA	Uranium Mill Tailings Remedial Action

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LABORATORY EXPERIMENTS ON BENTONITE SAMPLES: FY17 PROGRESS

1.   Introduction and Research Motivation

Uranium (U) contamination in the subsurface is a part of the legacy of nuclear weapons and energy production, resulting from mining and milling activities, processing of nuclear materials, and nuclear waste disposal. The U.S. Department of Energy (DOE) is tasked with cleaning up U-contaminated aquifers at a number of sites, including the Uranium Mill Tailings Remedial Action (UMTRA) sites and the Savannah River, Oak Ridge, and Hanford sites where a variety of different radionuclides are present. In order for nuclear energy to be viable, a long-term nuclear waste disposal repository capable of isolating high-level (HLW) and low-level radioactive waste (LLW) over the time scales necessary for decay of long-lived radioactive isotopes ($> 10^6$ years) must be created. Most nuclear waste repositories currently under investigation use clay media (*i.e.*, bentonite or shale) as engineered barriers or as the host rock for geologic storage (Altmann, 2008; Altmann et al., 2012; Delay et al., 2007; Guyonnet et al., 2009; SKB, 2011; Tournassat et al., 2015). Clays are good barriers for HLW due to their low hydraulic conductivity, which restricts contaminants to diffusion-based transport, and their high adsorption capacity for contaminants, which slows transport even further. Montmorillonite, a smectite mineral, is the dominant clay mineral found in bentonite. It has a 2:1 layer-type phyllosilicate structure, with a large specific surface area ($\sim$750 m^2/g) and cation exchange capacity ($\sim$1 mol$_c$/kg).

Uranium can exist in both the tetravalent and hexavalent oxidation state, however, due to the limited solubility of U(IV), U(VI) is the most common oxidation state found in the dissolved phase. U(VI) adsorption varies as a function of pH, bicarbonate, and Ca concentrations due to changes in U(VI) aqueous speciation. At moderate bicarbonate concentrations (> 1 mM) above pH 7, U(VI) speciation is dominated by uranyl-carbonato complexes [$UO_2CO_3(aq)$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$] in the absence of Ca, and calcium-uranyl-carbonato ternary complexes [$Ca_2UO_2(CO_3)_3(aq)$, $CaUO_2(CO_3)_3^{2-}$] in the presence of typical groundwater Ca concentrations (> 1 mM) (Dong and Brooks, 2006; Fox et al., 2006; Guillaumont et al., 2003). These calcium-uranyl-carbonato complexes adsorb weakly or not at all to mineral surfaces, and thus changes in U(VI) speciation have a large impact on its sorption behavior and transport (Fox et al., 2012; Fox et al., 2006; Stewart et al., 2010). While U(VI) adsorption to purified Na-montmorillonite has been studied extensively over a range of chemical conditions (Marques Fernandes et al., 2012; Pabalan and Turner, 1996; Tournassat et al., 2017; Turner et al., 1996), the presence of mineral impurities and non-sodium forms of montmorillonite complicates U(VI) adsorption behavior and warrants further study.

Storage of HLW can result in high temperatures near the waste canisters resulting from radioactive decay. The effects of elevated temperature on the engineered barrier must be taken into account when designing a nuclear waste repository. Such effects may include changes in the hydrological and mechanical properties of clay, changes in pore water chemical compositions, and changes in the clay and accessory mineral composition (Cuadros and Linares, 1996; Wersin et al., 2007; Zheng et al., 2015). The conversion of montmorillonite to illite, known as illitization, is one of the primary mineralogical changes expected to occur during long-term exposure to high temperatures. Zheng et al. (2015) predicted the extent of illitization over a 1000-year simulation to be 1-8% (volume fraction) at 100 °C, and 1-27% at 200 °C in a modeling study. Concentrations of pore water potassium (K) and the abundance and dissolution rate of K-feldspar were the primary chemical factors controlling the extent of illitization in their study (Zheng et al., 2015). Intrusion of groundwater from the surrounding host rock may also have an effect on the clay properties. In order to investigate these combined effects on an engineered barrier, the FEBEX (Full-Scale Engineered Barriers Experiment) *in situ* heater test was conducted by Empresa Nacional de Residuos Radiactivos (ENRESA) under the auspices of the European Union at the Grimsel Test Site from 1997 to 2015. Highly compacted bentonite blocks, serving as the engineered test barrier, were placed in a radial

arrangement around two underground heaters and heated to a maximum of 100 °C in a crystalline host rock. Detailed information on the test can be found elsewhere (ENRESA, 2000). The clay selected for the FEBEX experiment was a bentonite from the Cortijo de Archidona deposit (Almería, SE Spain), which is primarily made up of smectite (93%), with minor amounts of quartz (2%), plagioclase (3%), cristobalite (2%), potassium feldspar, calcite, and trydimite as accessory minerals (Fernández et al., 2004).

The primary goal of this work was to study the effect of bentonite heating under realistic field conditions on U(VI) adsorption behavior. Furthermore, we aimed to provide mechanistic insight into observed differences in U(VI) adsorption as a result of heat treatment. Bentonite samples from the FEBEX *in situ* experiment, which experienced varying temperature and water saturation conditions, were tested for U(VI) adsorption. In this report, we first present results from an experiment comparing U(VI) adsorption kinetics at a single condition of temperature, pressure, and water composition onto FEBEX bentonite samples, which experienced a range of temperature and water saturation conditions. Following that, we present results from equilibrium U(VI) adsorption experiments conducted over a wider range of chemical conditions on both unpurified ("bulk") and purified FEBEX bentonite. A comparison of the U(VI) adsorption behavior on unpurified and purified bentonite can be used to determine whether the observed differences in U(VI) adsorption as a result of heating are due to (1) changes in the pore water chemistry and accessory mineral components, or (2) structural changes in the smectite clay structure. Lastly, we present a brief discussion of planned future work.

2.   Kinetics of Uranium(VI) Adsorption onto Heat-treated and Cold-zone FEBEX Bentonite

2.1   Materials and Methods

2.1.1   Bentonite Samples

Bentonite samples were obtained from the second dismantling of the FEBEX (Full-Scale Engineered Barriers Experiment) *in situ* heater test in 2015, after 18 years of heating. The FEBEX heater test was conducted by ENRESA under the auspices of the European Union at the Grimsel Test Site. Detailed information on the test can be found elsewhere (ENRESA, 2000). Briefly, bentonite was compacted into blocks ("bentonite rock") at 1650 kg/m^3 dry density, placed in a radial arrangement around two underground heaters and heated to a maximum of 100 °C. The degree of water saturation and temperature varied with radial distance, with water saturation greatest and temperature lowest at the furthest distance from the heater (Table 2-1). For this study, we studied bentonite samples from four locations, two locations in the heater test zone (BD-48) at radial distances of 50 and 108 cm from the center axis and two locations from a control non-heated zone (BD-59) at the same radial distances. The section layout during dismantling is described by Detzner and Kober (2015). Three replicate blocks were used from each location, with the exception of BD-59 at 108 cm, where only two blocks were used. The blocks were split open and approximately 200 g of bentonite was removed from the center of each block and dried in an oven at 60 °C for one week. The dried bentonite was then crushed by hand using a porcelain mortar and pestle, and sieved through a 0.063 mm sieve in order to remove sand particles and reduce sample heterogeneity. Equivalent weights of each replicate block were mixed together to form composite samples for the four locations. Average water contents and historical *in situ* temperatures are shown for each composite sample in Table 2-1. In addition to the heater test bentonite samples, a sample of the original untreated bentonite, which had not been compacted into bentonite rock or emplaced in the *in situ* experiment, was also obtained. This original bentonite was dried, crushed, and sieved in the same manner as the other bentonite samples. FEBEX bentonite contained primarily smectite (93%), with minor amounts of quartz (2%), plagioclase (3%), cristobalite (2%), potassium feldspar, calcite, and trydimite as accessory minerals (Fernández et al., 2004). Bentonite stock solutions were prepared at concentrations of 5 g/L for each sample and stored at 4 °C prior to starting experiments.

Table 2-1. Composite FEBEX heater test samples used for U(VI) adsorption experiments.

Test Section	Distance to axis (cm)	Replicate Blocks	Water Content (g water/g dry clay)	Average Temperature[b] (°C)
BD-48	50	BD-48-3, BD-48-6, BD-48-9	0.14	95
BD-48	108	BD-48-1, BD-48-4, BD-48-7	0.26	45
BD-59	50	BD-59-10, BD-59-11, BD-59-12	0.22	20
BD-59	108	BD-59-2, BD-59-3	0.26	20
Original[a]	-	-	0.09	-

(a) Unheated and uncompacted

(b) Average temperatures from ENRESA (2000) and L. Zheng, personal communication

2.1.2   Kinetic Adsorption Experiments

Batch kinetic U(VI) adsorption experiments were conducted on the four composite bentonite samples and the original bentonite at a single water chemical composition, in equilibrium with air at room temperature (22-24 °C). Chemical conditions were as follows: total U(VI) concentration = 8.4 x 10^{-7} M, pH = 7.5, NaCl concentration = 50 mM, and bentonite concentration = 0.5 g/L. The dissolved inorganic carbon (DIC) concentrations imposed by atmospheric CO_2 partial pressure under these conditions ranged between 0.18 and 0.28 mM. Experiments were conducted in 250 mL plastic (high-density polyethylene) bottles and subsamples were collected at various time points (4.8, 8.1, 24, 49, 75, and 168 hours) for up to one week. Samples were prepared by weighing appropriate volumes of stock solutions (1 M NaCl, 5 g/L bentonite stock) and MilliQ water to reach a total volume of 200 mL, then adjusting pH to 7.5 using 0.1 or 0.01 M HCl or NaOH. Duplicates were prepared for each bentonite sample. Samples were maintained under these conditions on an orbital shaker for 92 hours, adjusting pH 1-2 times a day as necessary to equilibrate the solids with the chemical conditions prior to spiking with U(VI). Samples were then spiked with U(VI) stock solution (3.15 x 10^{-4} M), and the pH was re-adjusted. At each sampling time, the samples were shaken to ensure the bentonite was fully suspended, then 15 mL was removed by pipet and transferred to 40 mL polycarbonate (Oak Ridge) centrifuge tubes and centrifuged at 39,000-x g for 20 minutes. This centrifuge speed and time was sufficient to remove all particles > 24 nm, as calculated from Stokes Law. After centrifuging, the supernatant was removed and analyzed for DIC and U, and metal concentrations (Ca, Mg, and K) by inductively coupled plasma mass spectrometry (ICP-MS). DIC was measured on a Shimadzu TOC-V analyzer, and metals on a Perkin Elmer Elan DRC II ICP-MS. ICP-MS samples were diluted with 0.15 M ultrex grade nitric acid and an internal standard was added prior to analysis. Solid-free control samples were also prepared and sampled in the same manner as the bentonite samples. All data are presented as the average and standard deviation of the duplicate samples.

2.2   Results and Discussion

2.2.1   Comparison of U(VI) Adsorption Kinetics across Bentonite Samples

Figure 2-1 shows U(VI) adsorption to FEBEX bentonite composite samples as a function of time. U(VI) adsorption was slightly higher for the first time point (4.8 hours) for all samples, with no clear kinetic trend after that, suggesting that U(VI) adsorption reached equilibrium very quickly. The magnitude of U(VI) adsorption was the same (61-62%) for all bentonite samples, except BD-48, 50 cm, which adsorbed 52%. The BD-48, 50 cm sample was located closest to the FEBEX heater, experiencing temperatures of approximately 95 °C for 18 years. The BD-48, 108 cm sample experienced temperatures closer to 45 °C, while the BD-59 samples and original bentonite samples served as *in situ* cold-zone (~20 °C) and un-heated controls, respectively. The water content also varied as a function of temperature and distance from the heater (Table 2-1). The fact that U(VI) adsorption was not significantly different across all other bentonite samples provides evidence that neither the mineralogical constituents nor the porewater chemical composition changed significantly enough to effect U(VI) sorption during the experiment for samples subjected to lower temperatures (≤ 45 °C) over this time scale.
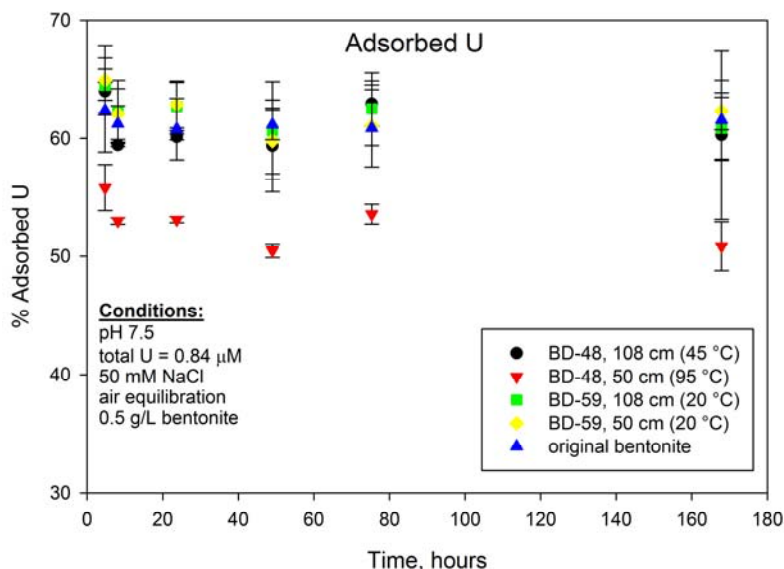
Figure 2-1. Kinetics of U(VI) adsorption onto FEBEX bentonite composite samples. Average historical temperatures experienced by each bentonite sample are shown in parentheses. Error bars represent standard deviations of replicate sorption experiments.

2.2.2   Chemical Composition during Kinetic U(VI) Adsorption Experiments

The chemical composition of the water in equilibrium with the bentonite samples was monitored throughout the experiment. Figure 2-2 shows measured pH, DIC, Mg, and Ca concentrations. These four parameters have a large effect on aqueous U(VI) speciation and consequently on U(VI) adsorption (Dong and Brooks, 2006; 2008; Fox et al., 2006; Guillaumont et al., 2003; Stewart et al., 2010) and thus are critical components of any U(VI) transport model. The pH was continuously adjusted throughout the experiment in order to maintain values close to the target pH (7.5). For the first two time points, pH values ranged from 7.30-7.42 then increased somewhat to values between 7.38-7.51 for the remainder of the experiment. The slightly lower initial pH is most likely due to the fact that the samples were initially spiked with an acidic (pH 2) U(VI) stock solution. DIC concentrations increased slightly over the first 48 hours of the experiment, seemingly reaching equilibrium after that. Ca and Mg concentrations decreased slightly over the first 48 hours, then either stayed the same (Ca) or increased slightly (Mg) for the duration of the experiment. Based on the observed small changes in U(VI) sorption and aqueous chemical conditions over time, it appears that 48-hour is sufficient time for U(VI) adsorption to reach equilibrium under these conditions and future experiments will be performed with a 48 hours reaction time.

All samples exhibited similar pH values, and DIC and Ca concentrations. However, the Mg concentrations for the BD-48, 108 cm sample were slightly lower than the other samples. The cause of this difference is unknown. Given the similarity in aqueous chemical conditions across bentonite samples, it is unlikely that the observed lower U(VI) adsorption for the BD-48, 50 cm sample was due to differences in aqueous U(VI) speciation. Instead, we hypothesize that the lower U(VI) adsorption resulted from either (1) structural changes in the clay mineralogy (*e.g.*, illitization of montmorillonite), or (2) changes in the amount or type of accessory minerals. Montmorillonite is the dominant clay mineral in FEBEX bentonite (Fernández et al., 2004), and illitization reactions (conversion of montmorillonite to illite) have been observed upon heating to temperatures of 100-200 °C (Cuadros and Linares, 1996; Wersin et al., 2007). Illitization may lead to a decrease in the specific surface area of bentonite (Macht et al., 2011) and consequently to a decrease in U(VI) adsorption capacity. Changes to the accessory mineral fraction may also occur because of heating, including dissolution of minerals (*e.g.*, calcite, K-feldspar) and precipitation of new mineral phases. Because montmorillonite is the most abundant and sorptive

phase, any changes in the mass fraction of montmorillonite (*i.e.*, dissolution or precipitation of accessory minerals) will result in changes in the bulk U(VI) adsorption when expressed in terms of mass of solid.
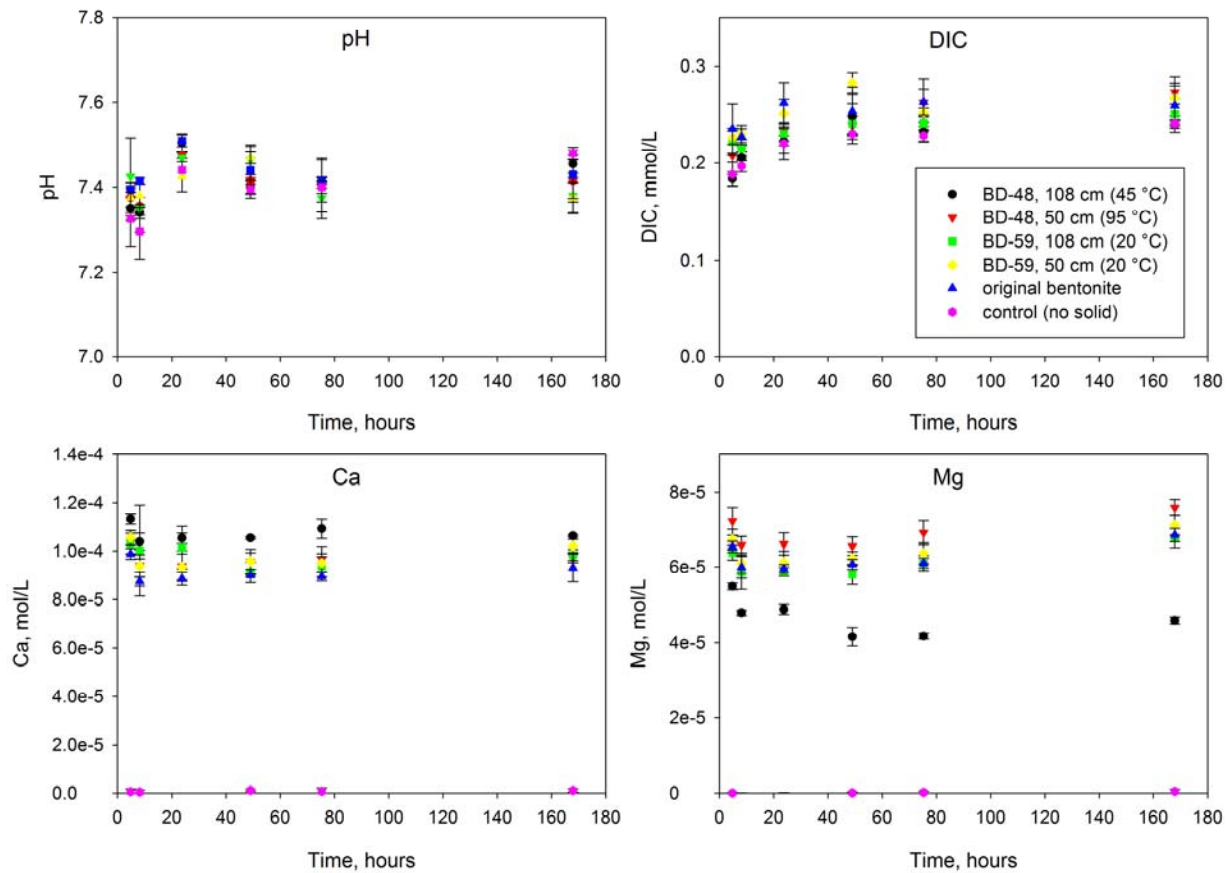

Figure 2-2. Aqueous chemical compositions over time for FEBEX bentonite U(VI) adsorption experiments. Average historical temperatures experienced by each bentonite sample are shown in parentheses. Error bars represent standard deviations of replicate sorption experiments.

3. Equilibrium Uranium(VI) Adsorption onto Purified and Un-Purified FEBEX Bentonite: Effect of Heat-Treatment

3.1 Materials and Methods

3.1.1 Bentonite Samples

Based on the similarity in U(VI) adsorption among all samples which were exposed to temperatures ≤ 45 °C in the kinetic experiments (Section 2), we chose to focus further experiments over a wider range of chemical conditions on two contrasting composite FEBEX bentonite samples: BD-48, 50 cm (sample heated to ~95 °C) and BD-59, 50 cm (cold zone sample experiencing ~20 °C). Experiments were performed with "bulk" composite samples (described in Section 2.1.1) and purified composite samples (described in Section 3.1.2). The comparison of U(VI) adsorption on purified and unpurified bentonite was then used to determine whether the observed difference in U(VI) adsorption on the heated sample was due to changes in the accessory mineral fraction or changes in the clay structure.

3.1.2 Bentonite Extraction and Purification

Composite FEBEX bentonite samples (BD-48, 50 cm and BD-59, 50 cm) were extracted and purified in order to compare extractable metal concentrations between the two samples and produce a purified clay sample for U(VI) adsorption experiments. The extraction and purification procedure was adapted from Tinnacher et al. (2016), allowing for the characterization of extracted metals. The procedure included the following major steps: (1) leaching of clay samples with water, (2) leaching with, and dialysis against, sodium acetate at pH 5 for carbonate mineral removal, (3) dialysis against NaCl to remove acetate and complete Na-saturation, (4) dialysis against water to remove excess salts, and (5) centrifugation to remove particles greater than 2 μm. Triplicate samples were extracted and purified for each composite sample, and extraction data are presented as the average and standard deviation of the replicates. Composite clay (2.5 g) was weighed into 40-mL polycarbonate centrifuge tubes and 25-mL of MilliQ water was added. Samples were placed on an end-over-end sample rotator and allowed to react for 5 hours, then centrifuged at 39,000-x *g* for 20 minutes. The supernatant was filtered through a 0.2 μm syringe filter polyvinylidene fluoride (PVDF) and retained for analysis of water soluble metals, dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and pH. Centrifuge tubes containing clay were weighed to determine the volume of entrained solution, then 25-mL of 1 M sodium acetate solution buffered at pH 5 with acetic acid was added. Samples were placed on the sample rotator and allowed to react for six days, then centrifuged, filtered, and retained for analysis of metals as described above. Clay samples were re-suspended in 15 mL of acetate buffer, transferred to pre-rinsed dialysis tubing (SpectraPor7, 8 kDa), and dialyzed against 900 mL of acetate buffer in a 1-L glass beaker for three days, changing dialysis solution daily. The acetate buffer dialysis solution was then exchanged with 1 M NaCl (dialyzed for one week), then with MilliQ water (dialyzed for two weeks), again changing dialysis solution daily. The purified clay suspensions were then transferred into plastic bottles and diluted and dispersed in MilliQ water to reach a clay concentration of approximately 15 g/L, and centrifuged at 1000-x *g* for 7 minutes. This centrifugation speed and time was deemed sufficient to remove all particles > 2 μm as calculated from Stoke's Law. The replicate < 2 μm clay fractions were then combined into a single bottle and diluted to reach a final clay stock concentration of 10 g/L. The exact clay stock concentration was determined by drying a subsample in a porcelain crucible at 85 °C. Clay stock solutions were stored at 4 °C prior to starting experiments.

3.1.3   Batch Adsorption Experiments

Equilibrium batch U(VI) adsorption experiments were conducted on purified and un-purified ("bulk") FEBEX bentonite composite samples at two Ca concentrations over the pH range 7 to 8 at an ionic strength of 0.1 M, using NaCl as the background electrolyte. Clay concentrations were 0.5 g/L and total initial U(VI) concentrations were 9.4 x 10^{-7} M. For purified bentonite samples, two separate experiments were conducted with Ca added to yield concentrations of 0.1 and 2.0 mM in solution, respectively. The 0.1 mM Ca concentration was chosen based on the concentrations of Ca released during kinetic batch experiments (Figure 2-2). In unpurified bentonite samples, some Ca was present in the clay, so two samples were prepared, one without added Ca, and another spiked with 2.0 mM Ca, achieving final dissolved Ca concentrations of approximately 0.14 and 2.17 mM, respectively.

Adsorption experiments were conducted in 40-mL polycarbonate centrifuge tubes. Clay samples were suspended in water and aliquots of 1 M NaCl, 0.1 M $CaCl_2$, and 0.1 M $NaHCO_3$ stock solutions were added to reach the desired final concentrations of Ca and HCO_3^- (to facilitate equilibration with atmospheric CO_2), and an ionic strength of 0.1 M. The pH was then adjusted to the desired pH using 0.1 M HCl or NaOH and samples were allowed to equilibrate for 24 hours on an end-over-end sample rotator. After equilibration, samples were spiked with U(VI), the pH was re-adjusted, and samples were placed on an end-over-end rotator for 48 hours to allow for U(VI) adsorption. Samples were then centrifuged at 39,000 x *g* for 20 minutes and the supernatant was removed for analysis by ICP-MS (U, Ca, and other metals), DIC, and pH. Adsorbed U(VI) was calculated by subtracting the final dissolved U(VI) concentration from the initial (total) U(VI) concentration. U(VI)-free control samples were prepared in the same manner as samples at pH 8, but without the addition of U(VI) to verify that samples were not contaminated with U(VI). No contamination was observed.

3.1.4   Analytical Techniques

DIC, DOC, and total carbon (on solid samples) were measured on a Shimadzu TOC-V analyzer. DOC was measured by non-purgeable organic carbon by acidifying with HCl and purging with N_2 in order to remove inorganic carbon prior to analysis. Total carbon was measured by catalytically aided combustion oxidation at 900 °C and a Nondispersive Infrared Detector (NDIR) on a Shimadzu TOC-V analyzer equipped with a solids module (SSM). Samples were analyzed for metal concentrations by ICP-MS (Perkin-Elmer Elan DRC II) after acidification and dilution with ultrapure (ultrex grade) 0.15 M nitric acid and internal standard addition.

3.2   Results and Discussion

3.2.1   Bentonite Characterization Results

Water extractions of unpurified FEBEX bentonite released greater concentrations of metals (Na, K, Ca, and Mg) and organic carbon (OC) for the heated sample (BD-48, 50 cm) compared to the unheated sample (BD-59, 50 cm), as shown in Table 3-1. The heated sample water leachates yielded lower inorganic carbon (IC) and pH values. It is possible that the soluble ion concentrations in both *in situ* samples have been altered compared to the original material due to intrusion of groundwater (cold-zone sample) and/or heat-caused alterations. For example, the lower concentrations of soluble metals and OC in the cold-zone sample may represent a loss due to groundwater leaching in this sample or an increase in the heated sample. While we did not perform extractions on the original bentonite sample, Fernández et al. (2004) reported concentrations of soluble salts during leaching experiments with the original FEBEX bentonite, although at a slightly higher solid to liquid ratio (0.15 kg/L compared to 0.1 kg/L in our study). In general, salt concentrations observed in the leachates of the original bentonite were in between the values observed in our study for the two samples (Na = 10.3 mM, K = 0.10, Mg = 0.12 mM, Ca = 0.10

mM), while pH (8.76) was closer to the pH in our cold-zone sample (Fernández et al., 2004). Because of the slightly higher solid to liquid ratio used in their study, it is very likely that the differences observed between the heated and cold-zone sample primarily represent a change in the heated sample. The change in pH and IC in particularly is noteworthy; suggesting that carbonate minerals may have been depleted from or altered in the heated sample. For example, a fraction of the calcite may have been converted to a lower-solubility carbonate mineral as a result of heating. Total carbon was measured in the unpurified clay solids, yielding slightly lower concentrations in the heated sample ($0.12 \pm 0.01\%$ by mass) compared to the unheated sample ($0.15 \pm 0.002\%$). However, we were unable to quantify total inorganic carbon concentrations in the clay solids due to methodological constraints, so it is unknown if differences in total carbon are due to differences in IC or OC. The pH 5 acetate extractions released very similar concentrations of K and Ca for the two samples, but slightly higher Mg concentrations in the heated sample. The acetate extractions are designed to dissolve carbonate minerals, but can also release adsorbed cations.

Table 3-1. Concentrations of extracted metals, inorganic carbon (IC), organic carbon (OC) and pH values for water extractions of unpurified FEBEX bentonite samples. Extracted metals only are shown for acetate (1 M acetate, pH 5) extracts. Concentrations of extracted constituents are expressed as the average and standard deviation of replicate extracts in mM.

	Water Extractions		Acetate Extractions	
	BD-48, 50cm (heated, 95 °C)	BD-59, 50cm (cold-zone, 20 °C)	BD-48, 50cm (heated, 95 °C)	BD-59, 50cm (cold-zone, 20 °C)
pH	7.96 ± 0.02	8.63 ± 0.12	--	--
IC (mM)	1.02 ± 0.04	2.07 ± 0.04	--	--
OC (mM)	0.786 ± 0.072	0.164 ± 0.007	--	--
Na (mM)	11.3 ± 0.1	7.69 ± 0.20	--	--
K (mM)	0.192 ± 0.008	0.077 ± 0.000	1.37 ± 0.03	1.34 ± 0.05
Ca (mM)	0.370 ± 0.004	0.069 ± 0.001	25.0 ± 0.6	24.2 ± 0.2
Mg (mM)	0.356 ± 0.002	0.088 ± 0.002	16.8 ± 0.1	15.3 ± 0.1

3.2.2   Comparison of Uranium(VI) Adsorption on Heated and Cold-Zone FEBEX Bentonite

U(VI) adsorption to purified and unpurified FEBEX bentonite was studied over a range of chemical conditions, which are considered relevant for waste disposal scenarios, including the pH range 7 to 8 and Ca concentrations of approximately 0.1 and 2.0 mM. We did not test pH values greater than 8 due to supersaturation with respect to calcite (at 2 mM Ca) and low U(VI) adsorption at alkaline pH. Results from these experiments are shown in Figure 3-1.

The pH measurements were performed on samples open to the atmosphere and it took a very long time for pH to stabilize. This effect was observed on both purified and unpurified bentonite, however, with unpurified bentonite, the pH was particularly unstable, continuing to drift upwards for over 15 minutes.

This pH drift made it difficult to obtain reliable pH measurements, particularly for the unpurified bentonite. We have plotted U(VI) adsorption as a function of both measured pH and measured DIC concentration; however, the plots with DIC may be more informative. As expected, U(VI) adsorption decreased with increasing pH and DIC concentration. U(VI) adsorption was also lower in the presence of high Ca (~2 mM) compared to low Ca (~0.1 mM), especially at higher pH and DIC values.

U(VI) adsorption onto unpurified (bulk) bentonite was higher on the cold zone sample (BD-59, 50 cm) compared to the heated sample (BD-49, 50 cm) over the entire DIC range at both low and high Ca. This is consistent with our observations in the U(VI) kinetic adsorption experiment (Section 2), which was performed at a single chemical condition (pH 7.5, low Ca, 0.05 M ionic strength).

U(VI) adsorption onto purified bentonite was also higher on the cold zone sample compared to heated sample over the entire range of DIC concentrations at both low and high Ca. This suggests that the difference in U(VI) adsorption between heated and cold zone samples is due to structural alteration of the smectite (montmorillonite) clay mineral, and not due simply to differences in pore water chemistry or the types and relative masses of accessory minerals. Further characterization, including cation exchange capacity, surface area, and x-ray diffraction, of the purified bentonite sample is needed to probe these structural changes.

In all cases, U(VI) adsorption was higher on purified bentonite compared to unpurified bentonite. This is expected and likely due to a 'dilution' effect from accessory minerals that have a much lower adsorption capacity compared to montmorillonite in the unpurified bentonite. These minerals may include silica and feldspar minerals as well as carbonate minerals (*e.g.*, calcite).
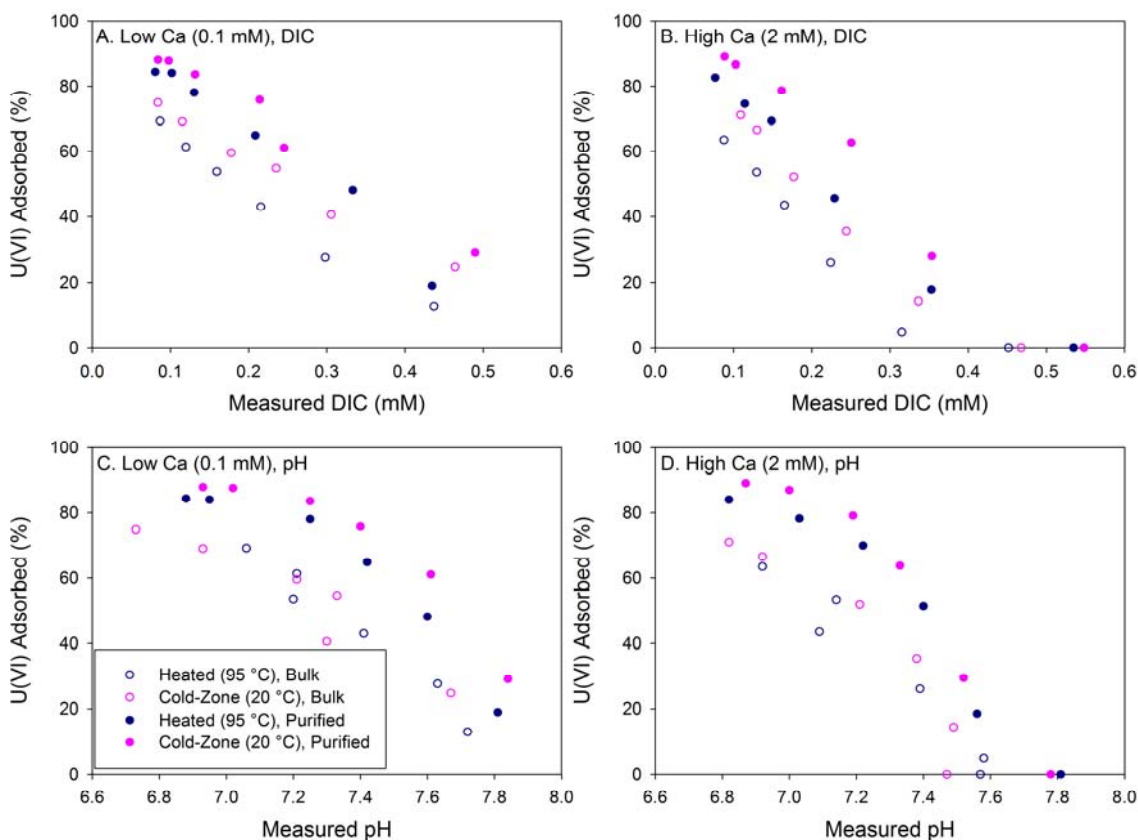
Figure 3-1. U(VI) adsorption as a function of DIC (A, B) and pH (C, D) onto bulk (unpurified) and purified FEBEX bentonite samples from the heated zone (BD-48, 50 cm, 95 °C) and cold zone (BD-59, 50 cm, 20 °C). A) and C) show experiments conducted at low Ca concentrations (approximately 0.1-0.14 mM); B) and D) show experiments conducted at high Ca concentrations (2.0-2.2 mM). All experiments were conducted at an ionic strength of 0.1 M using NaCl as the background electrolyte, with total U(VI) = 9.4 x 10^{-7} M and 0.5 g/L bentonite, and under open atmosphere at room temperature (22-24 °C).

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4.   Summary and Conclusions

This report detailed the results from a series of experiments conducted in FY17 designed to test the effect of bentonite heating on U(VI) adsorption. U(VI) adsorption onto bentonite samples from the FEBEX *in situ* experiment, which were subjected to 18 years of heating at temperatures of 45-100 °C, was compared to adsorption onto original FEBEX bentonite and cold-zone FEBEX bentonite from the *in situ* experiment. The major conclusions to date are as follows:

1) Kinetics of U(VI) adsorption appear to be very fast, reaching equilibrium in less than 8 hours, while DIC concentrations reach equilibrium in 48 hours. Small fluctuations in pH and DIC concentrations over the 1-week experiment seem to coincide with small fluctuations in U(VI) adsorption observed over this period.

2) Although water and acetate extractions revealed small differences in the leachate compositions of heated and cold-zone FEBEX bentonite, the measured DIC, Ca, and Mg concentrations in solution during U(VI) adsorption kinetic experiments were similar for all FEBEX bentonite samples. This suggested that differences in aqueous U(VI) speciation were not responsible for differences in U(VI) adsorption.

3) U(VI) adsorption onto unpurified FEBEX bentonite samples which experienced sustained temperatures of approximately 95 °C was lower than adsorption onto original unheated and cold-zone (20 °C) FEBEX bentonite over a range of chemical conditions (pH 7-8, Ca = 0.1 and 2.0 mM) relevant to nuclear waste disposal.

4) U(VI) adsorption onto unpurified FEBEX bentonite which experienced more moderate temperatures (approximately 45 °C) was *not* lower than unheated FEBEX bentonite for the single chemical condition tested (0.05 M NaCl, pH 7.5, 0.1 mM Ca).

5) The difference in U(VI) adsorption between heated (95 °C) and cold-zone (20 °C) FEBEX bentonite persisted over the range of chemical conditions tested when the bentonite samples were purified to remove mineral impurities such as calcite, quartz, and feldspars. This suggests that the decrease in U(VI) adsorption was due to alteration of the clay mineral structure, and *not* due to a change in the pore water chemistry or amount and type of accessory minerals. This may reflect illitization of the montomorillonite; however, further clay characterization is needed to verify this hypothesis.

These results provide key information necessary for performance assessment of HLW disposal scenarios. The decreased adsorption observed in this study as a result of bentonite heating may impact the diffusion of U(VI) through engineered clay barriers. Because the decreased U(VI) adsorption was due to changes in the clay mineral structure and *not* to aqueous U(VI) speciation, other radionuclides may be similarly affected. Further investigation is needed to probe the structural changes, which occurred as a result of heating and to better understand the mechanisms underpinning this behavior.

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5.   Outlook on Future Work

During the remaining time in this fiscal year (FY17), we plan to complete aqueous geochemical analysis for U(VI) adsorption experiments – specifically measurement of aqueous Ca, Mg, K, Al and Si concentrations. This will allow us to calculate the aqueous chemical speciation of U(VI) and saturation state for minerals (*i.e.*, clays and carbonates) during the experiments.

For the upcoming fiscal year (FY18), we plan to:

1) Characterize purified bentonite clay, including measurements of specific surface area, cation exchange capacity, x-ray diffraction (XRD) analysis, and other analyses as necessary. This information is necessary not only to gain a better understanding of the structural changes occurring in the bentonite as a result of heat treatment, but also to provide a basis for surface complexation modeling.

2) Model U(VI) adsorption behavior onto purified and unpurified bentonite. This work will build upon the U(VI) adsorption model developed for Na-montmorillonite in previous years (Tournassat et al., 2017).

3) Conduct U(VI) adsorption experiments with FEBEX bentonite samples exposed to 'intermediate' heat (~60 °C) to explore the threshold temperature necessary to affect U(VI) adsorption.

4) Begin U(VI) diffusion experiments with compacted, purified FEBEX bentonite. This will provide information on U(VI) transport under physical conditions relevant for waste disposal scenarios.

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