Determination of Sorption Properties for Sedimentary Rocks Under Saline, Reducing Conditions – Key Radionuclides

NWMO-TR-2016-08 June 2016

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Southwest Research Institute

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ABSTRACT

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Abstract

This report summarizes the results of an experimental project designed to measure sorption values for the key redox-sensitive radioelements uranium (U), selenium (Se), arsenic (As), technetium (Tc), neptunium (Np), and plutonium (Pu). The experiments investigated sorption of the elements on three substrates—two Canadian sedimentary rock types (exemplified by samples of Queenston Shale and Cobourg Limestone) and a bentonite—and were conducted in synthetic brine solutions (SR-270-PW) and dilute solutions under low-O_2, reducing conditions.

Protocols were developed to (i) ensure repeatable generation of brine solutions meeting target compositions; (ii) ensure accurate pH and Eh measurements in the brines; and (iii) establish an appropriate reducing environment for the experiments. Kinetics and batch sorption tests were conducted.

Results of the sorption experiments indicated that the highest distribution coefficients (K_ds) in brine and dilute solutions were associated with Pu and U. Sorption of Se and As was moderate in the brine and dilute solutions. Tc and Np showed variable sorption behaviour. In a long-running batch test, Tc showed strong sorption to limestone and MX-80, but low sorption on shale. Measured Np sorption was low in brine solutions but strong (equivalent to that of U) in dilute solutions. Experimental solution conditions were confirmed to be significantly reducing and targeted Eh values were met in most cases. Where Eh values were higher than desired, the experimental results did not indicate changes in behaviour of the elements being tested.

For some elements such as Np, Pu, and U, multiple experiments demonstrated consistent sorption results over various conditions. Sorption in brines was lower for Np, Pu, and U than in dilute solutions. Sorption in brine and dilute solutions was similar for As, Se, and Tc. There was typically no significant difference in measured sorption for the different substrates examined in these tests. With the exception of Np, it is likely that the experiments adequately evaluated the targeted valence state for the radioelements tested [As(III), Pu(III/IV), Se(−II), Tc(IV), and U(IV)]. Although not confirmed by direct measurement, support for these valence states includes preparation of stock solutions in the expected form (As), preparation based on previously known techniques to generate reduced valence state (Pu, Se, and U), comparative evidence for sorption of oxidized and reduced forms (Tc, U, and Pu), and comparisons of the results to sorption values presented in the literature.

The results of the sorption experiments will be used to update the NWMO's database of sorption values for Canadian sedimentary rocks and bentonite for use in the evaluation of potential deep geological repository (DGR) sites.

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1. INTRODUCTION

Radionuclide transport and retardation are modelled in performance assessments for deep geological repositories (DGRs) for used nuclear fuel. Radionuclide retardation is commonly represented by sorption processes and, in turn, sorption is typically represented in models by the empirically derived distribution coefficient (K_d). Commonly, K_d values are determined through laboratory-based sorption experiments. Measured K_d values are dependent upon several factors including properties of the element of interest, geochemistry of the groundwater, and properties of the sorbing materials. Some of the most important factors to consider in the development and selection of K_d values include pH and carbonate content of groundwater, oxidizing or reducing (redox) conditions of the system and susceptibility of radionuclides to changes in redox, specific surface area of minerals, variation of mineralogy of sorbent surfaces, and the ionic strength of the groundwater, which may impact ion-exchange potential of elements and interfere with the number of available sorption sites on mineral surfaces. These important factors may also interact in complex ways to influence sorption. Thus, development of K_d values using conditions relevant to site-specific groundwater chemistry and mineralogy is important. Establishing reasonable K_d data for a particular element requires experimental results that not only mimic site-relevant conditions, but also cover a range of conditions that account for expected variations in site characteristics.

The Nuclear Waste Management Organization (NWMO) initiated the development of a Canadian sorption database for highly saline groundwaters by conducting a review of the open literature and international sorption databases to find the available data relevant to Canadian sedimentary rocks and bentonite for the elements of interest for safety assessment (Vilks, 2011). This initial database is being augmented with sorption data measured experimentally for Canadian sedimentary rocks (shale and limestone) and bentonite in saline solutions. The sorption database supports the preparation of safety assessments and safety cases for a deep geological repository in a Canadian sedimentary environment.

The NWMO engaged the Center for Nuclear Waste Regulatory Analyses (CNWRA®) at Southwest Research Institute® (SwRI®) to extend a number of previous sorption tests in highly saline waters (Vilks et al., 2011; Vilks and Miller, 2014) and address data gaps identified in reviews of relevant sorption literature (Vilks, 2009, 2011). Project GS-301, Determination of Sorption Properties for Sedimentary Rocks Under Saline, Reducing Conditions – Key Radionuclides, was designed to measure sorption values for the key redox-sensitive radioelements uranium (U), selenium (Se), arsenic (As), technetium (Tc), neptunium (Np), and plutonium (Pu). The project plan specified that sorption values were to be measured for three substrates—two Canadian sedimentary rock types (exemplified by samples of Queenston Shale and Cobourg Limestone) and a bentonite—in a brine solution under reducing conditions. The results of the experiments conducted will be used to update the NWMO's database of sorption values for Canadian sedimentary rocks and bentonite for use in the evaluation of potential DGR sites.

This report provides a detailed description of the technical approaches and methods used during the course of the project. The overall experimental approach is summarized, followed by presentation and discussion of sorption results.

1.1 GENERAL REQUIREMENTS AND GOALS OF THE PROJECT

As designed, the project goals included development of sorption data suitable for use in the NWMO's sorption database for redox sensitive elements. The sorption data were to be determined by conducting a series of batch sorption and sorption-kinetics tests to measure sorption values for the specified elements (As, Se, U, Np, Pu, and Tc). The sorption tests would be conducted under reducing conditions (a target of −200 mV SHE) in a synthetic brine solution (specified as SR-270-PW). The brine sorption tests were to be complemented by characterization and analysis of the sorbent solids and a series of sorption tests using dilute solutions.

An important aspect of the proposed project plan was to not only establish an experimental setup meeting the environmental requirements for the sorption tests, but in doing so, to attempt to conduct the experiments without the need for added reductants, which had been used extensively in previous experiments at low-Eh conditions. The majority of potential DGRs under study in various countries are sited in settings with groundwater/porewater compositions that are anoxic and reducing (e.g., Andra, 2005a; Nagra, 2002; Ota et al., 2011; SKB, 2011). Experimental studies designed to develop sorption data to support DGR safety analyses typically include controlled-atmosphere experimental apparatuses and utilize additions of reducing agents, not typical of the natural geologic environment, to establish low-Eh conditions (e.g., Berry et al., 2007; Andra, 2005b).

Difficulties in establishing and maintaining a low-Eh experimental environment have been reported (Berry et al., 2007). However, review of available literature indicated that although low-O_2 gases were utilized, direct measurement of O_2(g) in the experimental environment was typically not reported (Selnert et al., 2008, 2009; Berry et al., 2007; Huitti et al., 1996). It seems possible that the difficulties in maintaining a low-Eh environment could be related to a lack of accurate information regarding the actual O_2(g) content of the experimental system (e.g., Huitti et al., 1996; Selnert et al., 2008, 2009). Moreover, addition of reducing agents typically results in significant increases in pH, and the resulting experimental solution conditions are often quite different from the groundwater conditions of the proposed DGR environment (Berry et al., 2007).

Thus, for this study, efforts were made to develop an experimental design that incorporated quantifiable measurements of O_2(g) and eliminated addition of reducing agents. Once an appropriate low-O_2(g) and low-Eh environment was established, the target elemental valence states would be achieved through exposure to the reducing conditions. Ultimately, this experimental approach was not entirely successful, but the methodology does provide a basis for alternative approaches to sorption experiments conducted under reducing conditions.

2. EXPERIMENTAL APPROACH

2.1 MATERIALS

Project materials include the solid substrates, solutions, and radioelements used in the sorption experiments. These are described in detail in the following subsections.

2.1.1 Solids

2.1.1.1 Acquisition and Sources

Samples of the three solid substrates used in the experiments were acquired early in the project. Sodium-bentonite commercially known as Volclay MX-80 was purchased (two packs of ~5 kg each) from the American Colloids Co. (Colony East, Wyoming). Core samples representative of the Queenston Shale (sample DGR5-511.15 m) and the Cobourg Limestone (sample DGR6-758.01 m) were provided by the NWMO. Both core samples were about 30 cm in length and 8 cm in diameter, and weighed ~4 kg.

2.1.1.2 Characterization and Preparation of Solids

Each solid substrate used in the experiments was characterized to assess mineral content, general elemental composition, and surface area. Mineralogy was assessed using X-ray powder diffraction (XRD; Siemens Kristalloflex 805 with a D500 Goniometer). General elemental composition was assessed using scanning electron microscopy energy dispersive X-ray microanalysis (SEM-EDS; FEI Quanta 650 SEM with IXRF Systems model 550i EDS). Surface areas of samples were measured using the N_2-BET method (ASAP 2020, Micromeritics). Some preliminary particle settling tests were also conducted on the bentonite to evaluate the ability to remove solids prior to sampling.

2.1.1.2.1 MX-80 Bentonite

The two separate packages of MX-80 bentonite were labelled “A” and “B” upon receipt. Prior to use, samples of both A and B were characterized separately to evaluate the material.

The MX-80 was analyzed using XRD and SEM-EDS to verify its composition and assess the potential for any contamination. Both bulk and oriented clay samples were prepared for analysis. The bulk fraction included a small aliquot of each sample loaded into an aluminum mount without additional preparation. Oriented samples were prepared by mixing aliquots of the clay samples with a 5% solution of sodium hexametaphosphate [$(NaPO_3)_6$] and doubly-deionized water (ddH_2O, 18.1 MΩ) in a glass beaker. The ~300-mL clay mixture was stirred, placed in an ultrasonic bath for 20 min to separate particles, and then further diluted by adding 150 mL of the mixture to an additional 100 mL of 5% sodium metaphosphate in a graduated cylinder. The solution in the graduated cylinder was stirred and allowed to settle for 2 hours. A 2-mL aliquot of clay and solution was withdrawn from the 10-cm settling line to gather a known size fraction of the clay. The clay solution was vacuum-filtered onto a 0.45-μm membrane filter and laid face down on a glass slide. After drying, the filter was carefully removed to produce an oriented sample for XRD analysis. Some air-dried clay slides were equilibrated with ethylene glycol vapour in a sealed flask at 60°C for 24 hours to produce ethylene glycol solvated samples. Air-dried and ethylene glycol samples for MX-80 samples A and B were analyzed by XRD.

In conjunction with the XRD analyses, the bulk samples of MX-80 A and B were analyzed using SEM-EDS. After results of the XRD and SEM-EDS analyses (discussed in Section 2.1.1.3) indicated that there were no significant differences in the two MX-80 packages, sample A was selected for use in the experiments. Approximately 250 g of MX-80 A were transferred in a glass jar to a low-O_2 atmosphere glove box for storage. An aliquot of MX-80 A was also collected and analyzed for surface area. The MX-80 sample A was minimally processed prior to use in the experiments. Other than storage in the controlled low-O_2 atmosphere, no pretreatment or size fractionation of the MX-80 A was employed.

Prior to starting sorption experiments a settling test was conducted to confirm that preliminary size fractionation of the MX-80 was not required. It was expected that the clay would flocculate readily in the brine solutions to be used in the experiments, but clay settling behaviour in the dilute solution was undetermined. Small aliquots (~2 g) of MX-80 were transferred to 50-mL polycarbonate (PC) Oak Ridge-type centrifuge tubes into which ~30 mL of dilute SR-270-PW brine (same concentrations as expected for use in the experiments) were added. The test tubes were centrifuged (Thermo Scientific Sorvall^{TM} Legend^{TM} X1) at 10,000 rpm for 10 min to remove all particles with an effective diameter greater than 0.1 μm. After centrifugation, the solution was clear and free of any visible clay particles. Based on these results, there was no need for separation of very fine clay particles from the bulk MX-80 prior to its use in experiments.

2.1.1.2.2 Queenston Shale

The core samples of shale and limestone were received from the NWMO in sealed aluminum-Mylar® bags and kept under refrigeration at 4°C until further processed for use in characterization and the experiments. To minimize exposure of the core to O_2 during early processing, portable temporary-use glove bags (Fisher Scientific) were purchased and used during the physical separation and processing of the core samples.

The plan for processing the cores into fragments suitable for use in the sorption experiments was to break each core into several, approximately equal length, segments along the length of the core. Each of the segments was then broken into smaller fragments and split. The split samples were separated into two groups, one of which was archived and another that was further processed.

The cores were expected to be well-indurated and difficult to break into smaller sizes. To facilitate core splitting, a hydraulic core sample splitter (CM-10 Coremaster, Park Industries, St. Cloud, MN) was used. The core, splitter, and expected equipment and transfer bags were placed in a temporary glove bag filled with N_2 gas before opening the Mylar bag.

Upon opening the sealed aluminum-Mylar packaging, the Queenston Shale sample core was found to have been broken into two large pieces. The break appeared fresh on visual inspection and no evidence of mineralization or other chemical marks were found on the fracture surface. The two pieces of the core remained closely fit together, and there was no evidence of fine particles or residue due to rubbing of the pieces. It seems likely that the break occurred after the sample was packed (possibly during shipping). The core samples were carefully and minimally handled after their arrival at SwRI, and there were no events that were obvious candidates for causing the break. The break did not have an impact in processing and did not impact the core's use in experiments.

The reddish brown shale sample was unpacked and split into nine segments using the hydraulic core splitter. Because of scatter of very small fragments and the possible flaking of paint from the core jaws, some the core residual was left in the glove bag to prevent the potential carryover of contaminants. The separated core segments were packed in plastic bags, sealed, and transferred to another N_2-filled glove bag where they were further broken using hammer and chisel into smaller pieces. The largest pieces generated had edge dimensions (on the order of

3-cm) to facilitate the next segment of crushing. The core was very well indurated. Even when using a large hammer and chisel, the shale core was extremely difficult to fragment (especially when striking perpendicular to laminations).

The broken core fragments were separated according to their original nine-segment splits and were separately bagged accordingly. The broken core fragments were split into archival and experimental components. Approximately 60% (slightly more than half by visual estimate) of each segment-fraction was archived by transferring the material to an aluminum-Mylar bag that was temporarily closed, transferred out of the glove bag, and heat-sealed with a roto-sealer. Oxygen scavenging packets were also placed inside each aluminum-Mylar bag prior to sealing to minimize any O_2 contamination during transfer. The sealed archival bags were labelled, weighed, and again stored at 4°C. The remainder of the broken sample segments to be used in the sorption experiments were transferred to plastic bags (double-bagged), sealed, weighed, and placed in a low-O_2 atmosphere glove box to await crushing. These samples were labelled QS-1 through QS-9.

During the next processing step, the samples were transferred to lab atmosphere and crushed using a mechanical jaw crusher (Sepor Mini-Jaw Crusher with Tungsten Carbide jaw and cheek plates). Operation of the rock crusher was not practical inside the temporary glove bags. The goal of the crushing was to produce a sample composed of coarse sand-sized particles. During initial crushing, one carbide steel jaw fractured. This required a halt of the sample crushing while a replacement component was ordered and installed. Examination of the crushed sample revealed the possibility of some steel contamination, but the sample grain size was adequate. The initial crushed sample was discarded, and the remaining samples were processed using the new carbide steel jaw. The crushed samples were packaged separately by original segment number (QS-1 through QS-9) and each was analyzed by XRD and SEM-EDS. Prior to the analyses, aliquots of each sand-size fraction were further crushed to a powder using a synthetic sapphire mortar and pestle (Diamonite™, Fisher Scientific).

Following crushing and XRD analyses, the core samples were consolidated into one large aliquot and sieved using a rotary sieve shaker (Ro-Tap®, W.S. Tyler) and stainless steel sieves to create four size fractions: >0.5 mm (retained on a No. 35 sieve); 0.5 to 0.25 mm (passing through a No. 35 and retained on a No. 60 sieve); 0.25 to 0.074 mm (passing through a No. 60 sieve and retained on a No. 200 sieve); and a fine fraction < 0.074 mm (passing through the No. 200 sieve). The specific surface areas of the three smallest (all but the >0.5-mm) size fractions were measured using N_2-BET analysis. The size fractions were placed in glass jars, and the target fraction for the experiments, the consolidated 0.074–0.25 mm fraction, was transferred and stored in the low-O_2 atmosphere of the glove box.

2.1.1.2.3 Cobourg Limestone

The Cobourg Limestone core and samples were processed in a manner similar to the shale core. The Cobourg Limestone core was split into 10 segments initially. Sample splitting, archiving, crushing, sieving, and preparation for XRD and SEM-EDS analyses were conducted in the same way as was done for the shale. One primary difference was that the core splitter was used to disaggregate the core segments into smaller pieces prior to use of hammer and chisel. This made breaking the core segments into smaller pieces easier and minimized the required use of hammer and chisel. The final 0.074–0.25 mm size fraction was stored in a low-O_2 atmosphere glove box prior to use.

2.1.1.3 Results of Solids Characterization Analyses

2.1.1.3.1 MX-80 Bentonite

The results of XRD and SEM-EDS analyses confirmed the presence of sodium montmorillonite along with trace amounts of quartz and illite in the MX-80. There were no significant differences in the mineralogy and general elemental make-up of the two samples. Bulk XRD results (Figure 1) of both the MX-80 A and B samples indicate a montmorillonite-dominated mineralogy and very similar diffraction patterns. The patterns were also consistent with previous XRD analyses of the MX-80 (e.g., Vilks et al., 2011). The associated SEM-EDS results (Figure 2) are consistent with the minerals observed in the XRD pattern.

The air-dried and ethylene glycol-solvated oriented sample results (Figure 3) are indicative of Na-montmorillonite and reveal the characteristic changes in interlayer spacing resulting from the ethylene glycol saturation observed for MX-80 in previous studies (e.g., Carlson, 2004).

The N_2-BET measured specific surface area of the MX-80 A sample was 26.2 ± 0.2 m^2/g. Preheating of the bentonite sample was limited to 200°C for all samples to minimize any potential effects on the mineral structure. Although some changes may have occurred even at that temperature, some studies have indicated that changes are minimal for some bentonite up to 250° C (Macht et al., 2011) and the measured value was consistent with other MX-80 surface area measurements (e.g., Bradbury and Baeyens, 2011; Vilks et al., 2011).

2.1.1.3.2 Queenston Shale

Results of the XRD and SEM-EDS analyses indicated that the sample fractions were all extremely similar, and the mineral makeup of the fractions was consistent with previous investigations (e.g., Skowron and Hoffman, 2009). The shale XRD patterns exhibited peaks associated with calcite, ankerite, quartz, dolomite, clinochlore, and illite, as exemplified by the results of analyses for sample QS-8 (Figure 4). SEM-EDS analyses produced results of elemental concentrations (as weight percent) consistent with the mineralogy revealed by the XRD analyses. A summary of the SEM-EDS analysis for all Queenston Shale samples is shown in Table 1. The variance in elemental composition between the samples is small with the exception of sulphur, which has a relatively high standard deviation (σ). This value is biased by samples QS-3 and QS-4, which have a measured weight percent of sulphur of 1.42 and 2.98, respectively, while the other samples average 0.22 ± 0.1 weight percent sulphur. A comparison of the XRD patterns of QS-4 (Figure 5) and QS-8 (Figure 4) shows an additional peak at ~25.5° 2θ in the QS-4 sample that does not exist in the QS-8 sample pattern. This peak is consistent

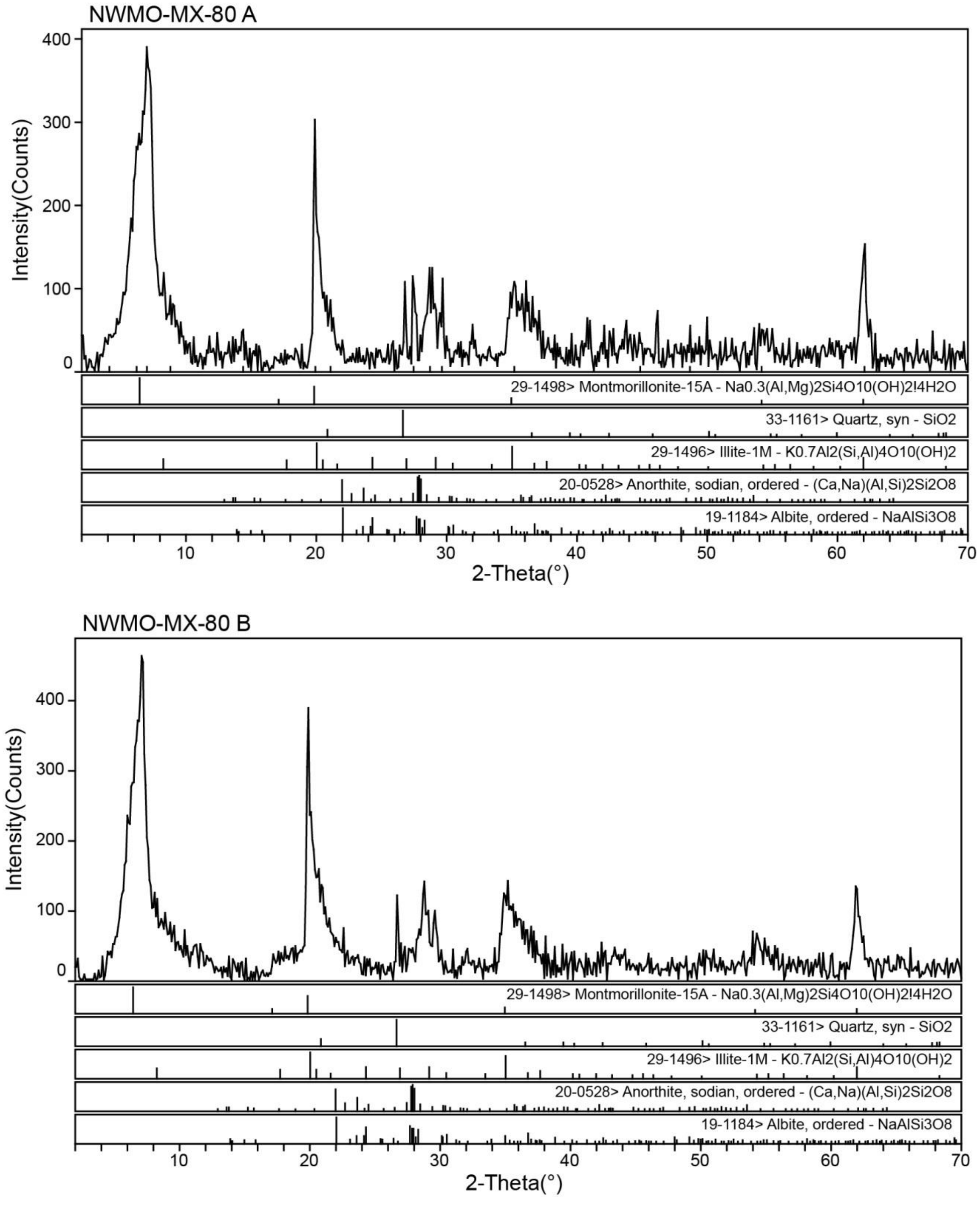
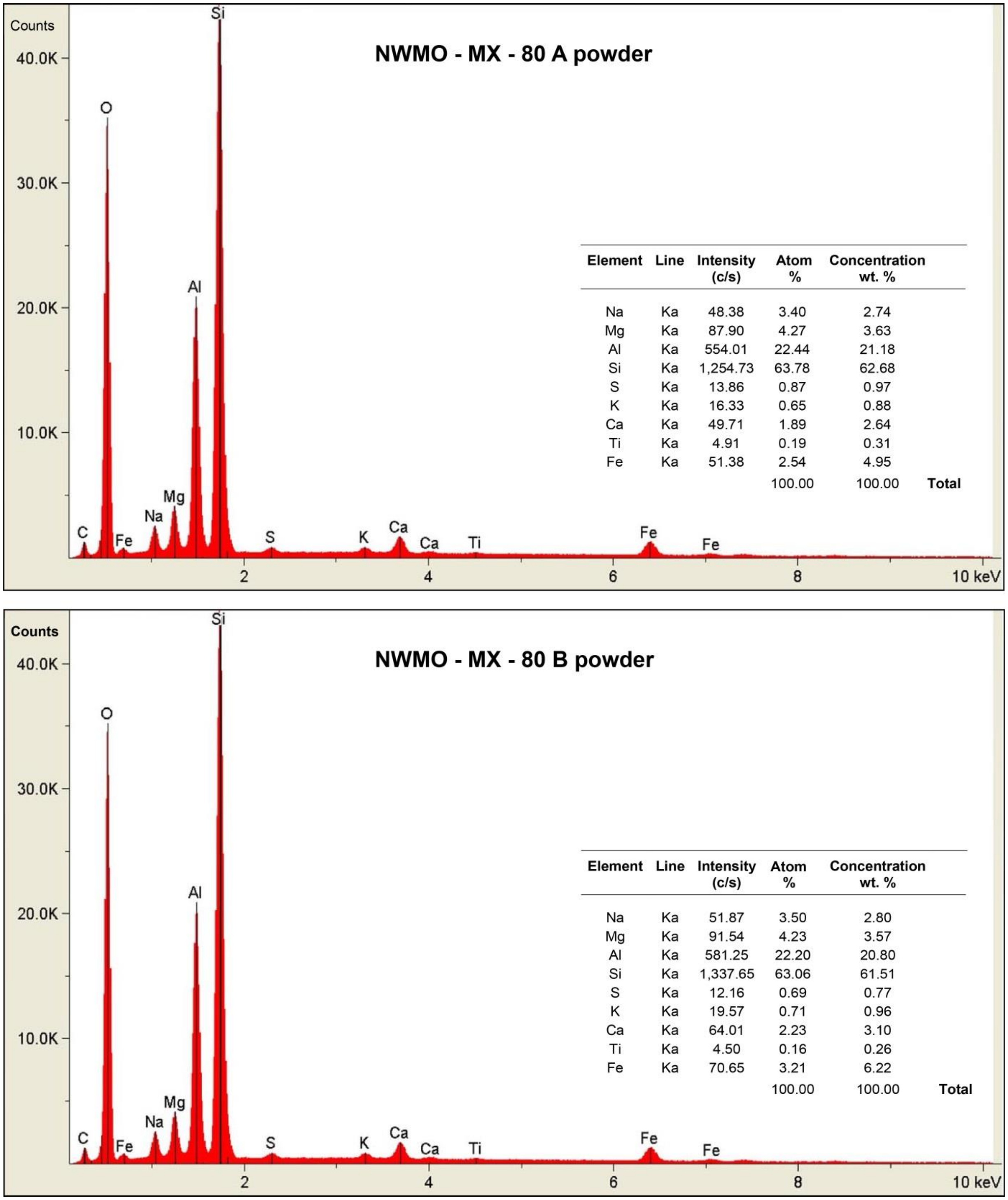


Figure 1: Bulk XRD Patterns for MX-80 A and B Samples (NWMO-MX-80 A and NWMO-MX-80 B). The Patterns are Consistent with Na-montmorillonite with Minor to Trace Amounts of Illite and Quartz. Both Samples Have Very Similar Patterns



NWMO - MX - 80 A powder

Element	Line	Intensity (c/s)	Atom %	Concentration wt. %	
Na	Ka	48.38	3.40	2.74	
Mg	Ka	87.90	4.27	3.63	
Al	Ka	554.01	22.44	21.18	
Si	Ka	1,254.73	63.78	62.68	
S	Ka	13.86	0.87	0.97	
K	Ka	16.33	0.65	0.88	
Ca	Ka	49.71	1.89	2.64	
Ti	Ka	4.91	0.19	0.31	
Fe	Ka	51.38	2.54	4.95	
			100.00	100.00	**Total**

NWMO - MX - 80 B powder

Element	Line	Intensity (c/s)	Atom %	Concentration wt. %	
Na	Ka	51.87	3.50	2.80	
Mg	Ka	91.54	4.23	3.57	
Al	Ka	581.25	22.20	20.80	
Si	Ka	1,337.65	63.06	61.51	
S	Ka	12.16	0.69	0.77	
K	Ka	19.57	0.71	0.96	
Ca	Ka	64.01	2.23	3.10	
Ti	Ka	4.50	0.16	0.26	
Fe	Ka	70.65	3.21	6.22	
			100.00	100.00	**Total**

Figure 2: SEM-EDS Spectra for Bulk NWMO-MX-80 Samples A and B. The Elemental Composition is Consistent with Na-montmorillonite, and the Spectra are Similar for both Samples

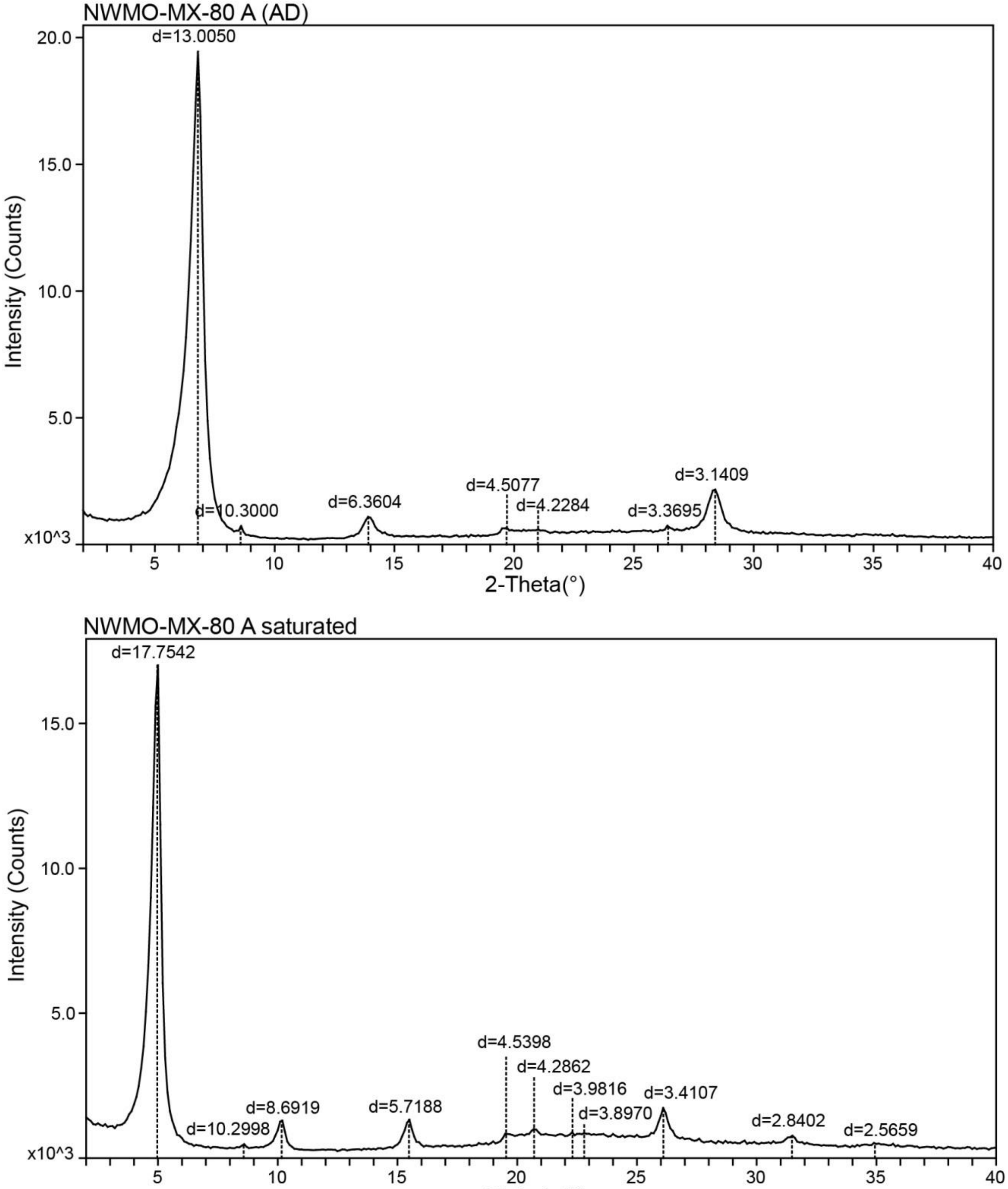


Figure 3: Air-dried [NWMO-MX-80 A (AD)] (top) and Ethylene Glycol Solvated (NWMO-MX-80 A saturated) (Bottom) XRD Patterns for MX-80 Sample A. The Shift in d Spacing for the 001-peak is Consistent with that Observed for MX-80 in Other Investigations (e.g., Carlson, 2004)

Table 1: Summary of the Elemental Composition of Queenston Shale Samples

Element	Average weight percent (wt%) (n=9)	1σ (wt%)	Average weight percent (wt%) with QS-3 and QS-4 excluded (n=7)
Na	0.71	0.07	0.83
Mg	4.03	0.15	4.61
Al	14.28	0.26	15.70
Si	39.29	0.83	42.31
S	0.71	1.01	0.22
Cl	1.77	0.09	1.67
K	7.32	0.16	6.70
Ca	23.32	1.33	20.97
Ti	0.77	0.05	0.65
Fe	7.81	0.66	6.35

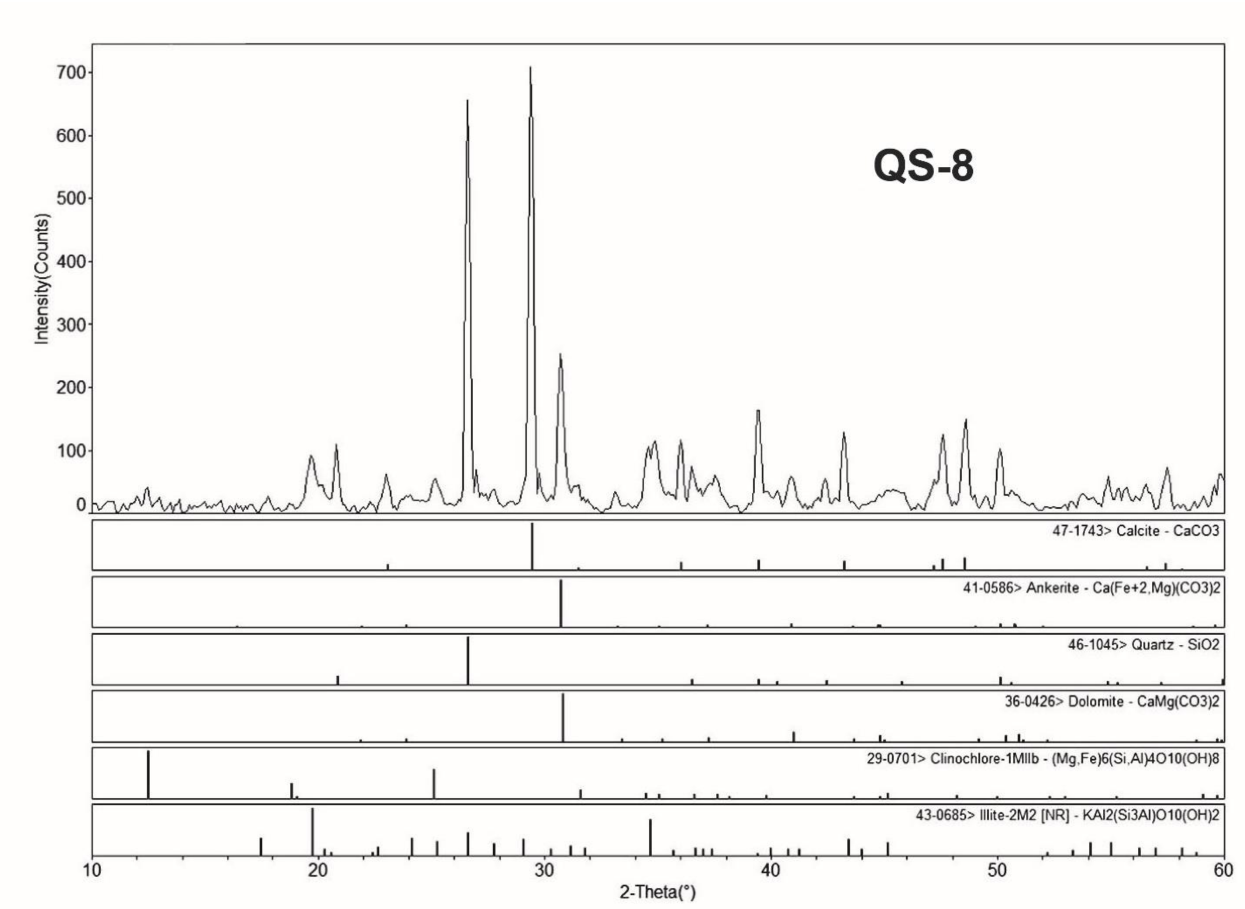


Figure 4: XRD Pattern of Queenston Shale Sample QS-8. The Results Indicate the Shale is Composed Primarily of Quartz, Calcite, Ankerite, Dolomite, Clinochlore, and Illite. With Minor Exceptions (See Text for Discussion), XRD Patterns for Other Samples are Similar

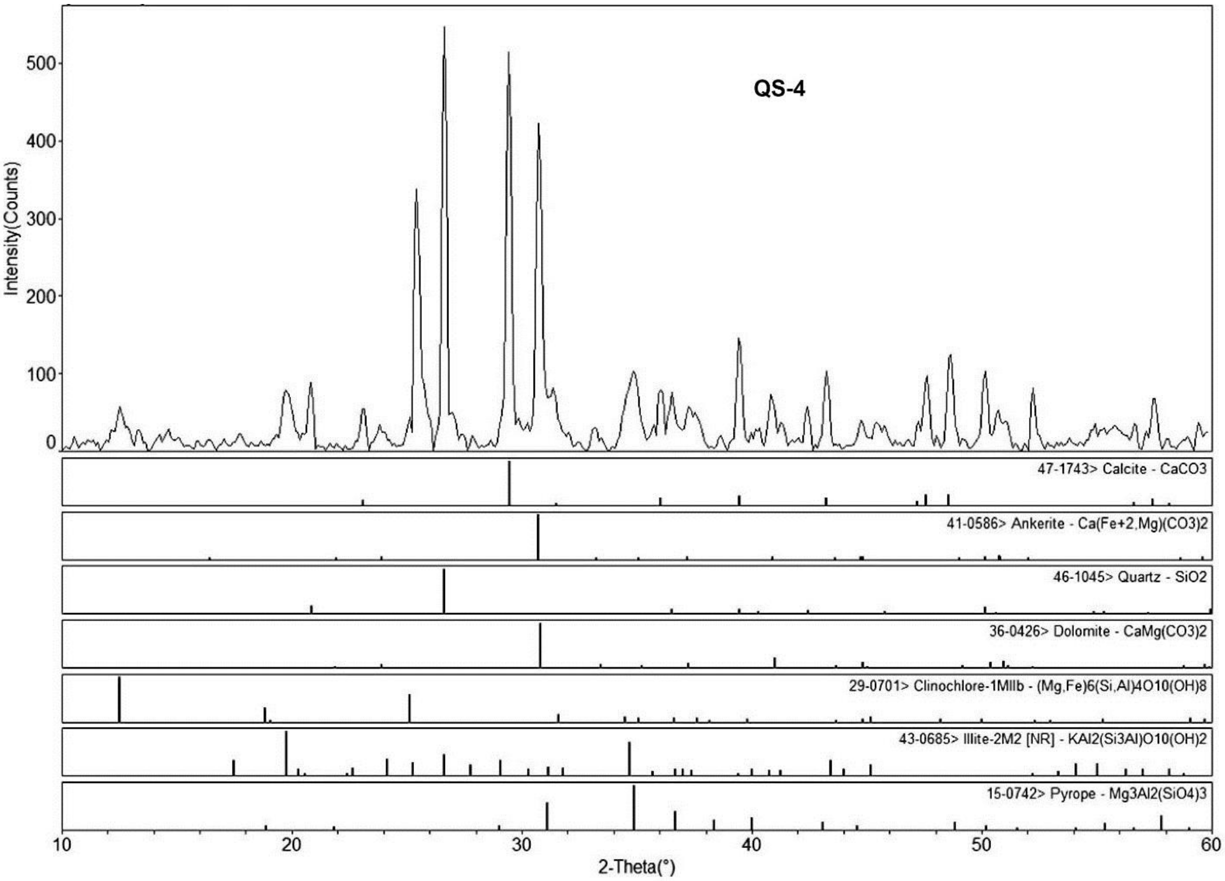


Figure 5: XRD Pattern of Queenston Shale Sample QS-4. Higher Measured Concentration of Sulphur in Sample QS-4 is Likely a Result of the Presence of Minor Anhydrite in These Samples. Peak of Anhydrite (at ~25.5° 2θ) is Shown by the A in the Figure. Anhydrite was not Identified as a Constituent in the Original XRD Analysis in Sample QS-8

with that of anhydrite (not identified in the original XRD analysis), which has been previously identified in analyses of the Queenston Shale from other DRG cores (Hobbs et al., 2011).

Measured N_2-BET surface area for the composite Queenston Shale sample used in the experiments (0.074–0.25 mm fraction) was 10.3±0.05 m^2/g, which is consistent with the value of 11.5 m^2/g reported by Vilks et al. (2011).

2.1.1.3.3 Cobourg Limestone

Like the shale, results of the XRD and SEM-EDS analyses of the samples from the Cobourg Limestone indicated that the fractions were all extremely similar, and the mineral makeup of the fractions was consistent with previous investigations (e.g., Skowron and Hoffman, 2009; Vilks et al., 2011). As the XRD pattern from sample CL-1 indicates, the limestone is primarily composed of calcite with minor amounts of dolomite and quartz (Figure 6). Elemental compositions produced by the SEM-EDS analysis are consistent with the mineralogy. A summary of elemental composition (in weight percent) for all analyzed samples is shown in Table 2.

Table 2: Summary of the Elemental Composition of Cobourg Limestone Samples

Element	Average weight percent (wt%) (n=6)	1σ (wt%)
Na	0.32	0.01
Mg	2.40	0.31
Al	3.02	0.99
Si	8.29	2.81
S	0.34	0.18
Cl	0.43	0.07
K	1.57	0.53
Ca	82.16	4.63
Ti	0.25	0.05
Fe	1.54	0.19

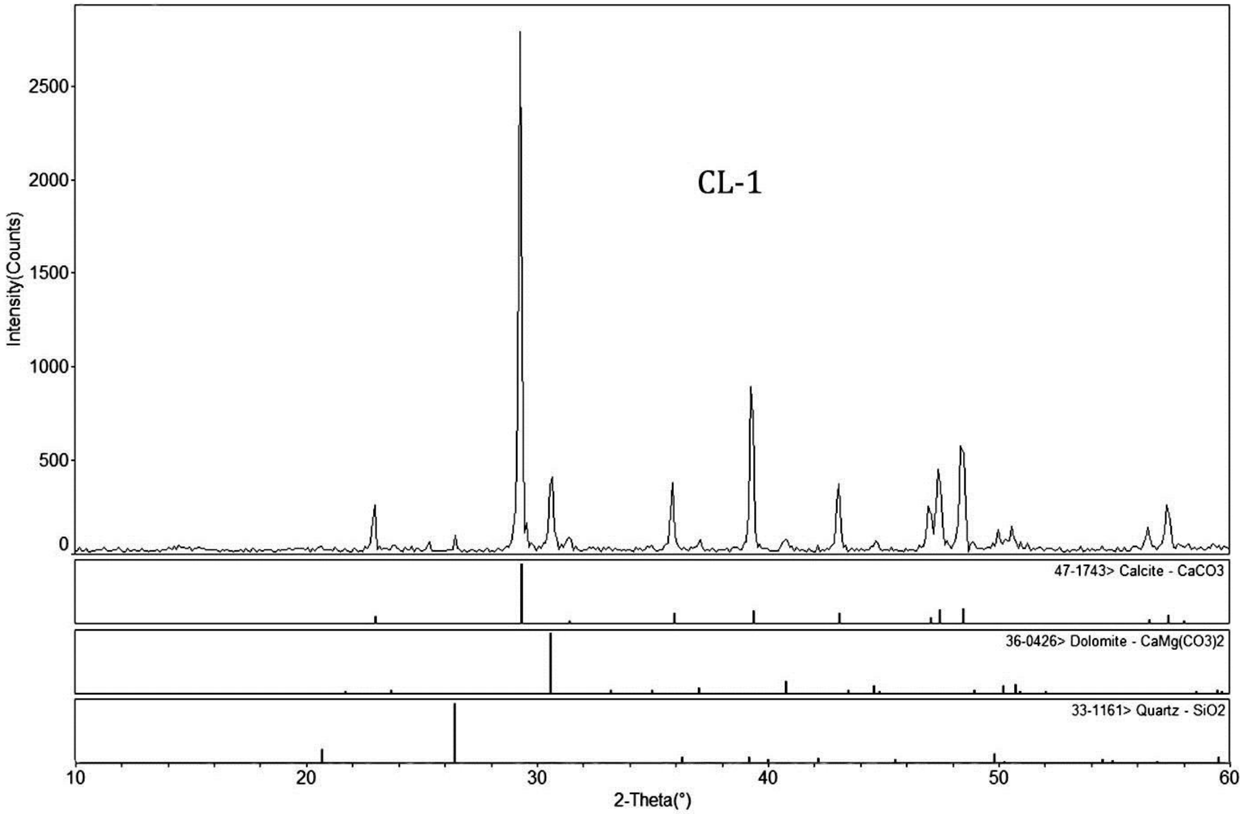


Figure 6: XRD Pattern of Cobourg Limestone Sample CL-1. The Limestone is Primarily Composed of Calcite with Minor Dolomite and Quartz. Although not Identified in this Analysis, Other Minor Peaks are Likely Associated with the Presence of Trace Illite (Skowron and Hoffman, 2009)

The measured N_2-BET surface area for the composite Cobourg Limestone sample used in the experiments (0.074–0.25 mm fraction) was 2.6±0.01 m^2/g, which is consistent with the value of 2.9 m^2/g reported by Vilks et al. (2011).

2.1.2 Brine Solutions

The experimental solutions to be used in the sorption tests were specified by the NWMO in the project guidelines. The target brine composition was that of SR-270-PW, a synthetic brine calculated to mimic pore water compositions in deep boreholes and representing the sedimentary rock environment of a potential waste repository. A summary of the SR-270-PW composition is provided in Table 3.

Table 3: SR-270-PW Chemical Composition

Water Type: SR-270-PW		
Solute	**Concentration (mg/L)**	**Concentration (mg/L) as targeted for the project**
Na	50100	50100
K	12500	12500
Ca	32000	32000
Mg	8200	8200
HCO_3	110	110*
SO_4	440	440
Cl	168500	168500
Br	1700	1700
Sr	1200	1200
Li	5	0†
F	2	0†
I	3	0†
Br	80	0†
Si	4	0†
Fe	30	30
NO_3	<10	0†
PO_4	low	0†
TDS (mg/L)	275000	275000
Nominal pH	6	6*
Nominal Eh (mV)	-200	-200

*HCO_3 concentration is understood to be variable and dependent on the partial pressure of CO_2(g) in equilibrium with the solution. Likewise, the equilibrium pH is dependent in part on the HCO_3 concentration.

†The NWMO project guidance noted that minor ions (in the shaded cells) could be excluded from the experiments.

For the project, target concentrations of solutes were based on the provided composition of the SR-270-PW water. Minor solutes such as Br and NO_3 were not required to be included in the experimental solution preparation. As a result, several solutes were purposefully omitted from consideration (as listed in the shaded cells of Table 3) for project purposes. A recipe consisting of several chemical compounds was developed to meet the target concentration goal for each solute. The goal was to achieve a concentration for each solute within 10% of the solute's SR-270-PW value. Although the mass of $NaHCO_3$ required to achieve the target HCO_3 concentration was included in subsequent recipes, it is well known that the final HCO_3 concentration is/would be determined by the partial pressure of CO_2(g) in equilibrium with the solution. For the pH and HCO_3 concentrations provided by the NWMO, the calculated equilibrium atmospheric concentration of CO_2(g) required is ~1% by volume (10,000 ppm). The initial project plans included concentrations well below that level (~400 ppm), but it was anticipated that additional experiments would include tests at higher concentrations. As will be discussed later, the experimental design and apparatus setup unexpectedly resulted in very low CO_2(g) concentrations.

A matrix was developed to calculate the recipe and the appropriate mass of compounds required to achieve the target concentrations of solutes. First, using the target concentrations and gram formula weights for each element, the required number of moles of each element was determined. Several water soluble compounds (primarily salts) containing the required elements were identified, and these were paired with the required moles for each element to calculate the mass of each compound required to make 1 L of the brine solution. A summary of the recipe types used during the project is provided in Table 4.

Table 4: Mass of Compounds Used to Prepare Brine Solutions

Compound	Mass (g) required to make 1 L of stock brine solution		Final order of addition
	Initial Recipe	Modified Recipe	
KCl	22.2485	22.2485	1
NaCl	126.7194	126.7194	8
$CaCl_2$•$2H_2O$	117.3828	117.3828	7
$MgCl_2$•$6H_2O$	68.5901	68.5901	6
$SrCl_2$•$6H_2O$	3.6515	3.6515	4
$NaHCO_3$	0.1514	0.1514	3
Na_2SO_4	0.6506	0.3253	5
KBr	2.5318	2.5318	2
Na_2S•$9H_2O$		0.5500	9[‡]
$FeCl_3$•$6H_2O$[†]	0.1453[†]	0.1453[†]	

[†] Iron was not added to early solutions and was added to only a few solutions during the project. When added, the quantity and form were as listed here.

[‡] A combination of sulphate and sulphide was added to some solutions. When used, the sulphide was added last.

To prepare the brine (SR-270-PW equivalent) solutions, certified ACS reagent-grade chemicals were purchased from quality assurance-approved suppliers and mixed with Type I reagent-grade, double deionized water (ddH_2O, 18.2 MΩ, Barnstead Nanopure). In general, chemical compounds were added in quantities sufficient to make 1 L of brine solution (using the Table 4 recipes). When greater amounts of brine stock solution were required for experiments, several 1 L batches were prepared and combined to make a large batch.

Part of the project requirements also included conducting some sorption experiments under similar reducing and low-O_2 conditions but using a dilute solution. To prepare dilute solutions, approximately 4 mL of brine were diluted to 2 L using ddH_2O. The resulting dilute solution was estimated to be about 550 ppm TDS.

A series of test solutions was prepared to evaluate the recipe efficacy and to establish a repeatable procedure for generating the brine solution. During the preparation of each solution, care was taken to note possible precipitation, behaviour of the solutions after addition of each component, and difficulty in dissolving each compound. Following the preparation of each brine or dilute solution, samples were collected for chemical analysis to verify the composition and concentration of solutes. Solids or other precipitates were also sampled and analyzed as needed to assess and potentially modify the preparation process. As solution preparations progressed during the course of the project, the methodology was altered several times to determine the most reasonable and repeatable preparation process. Some examples of method tests and changes include modification of the order of chemical additions, altering the form of compounds used, preparing solutions under different atmospheric conditions, evaluating effects of heating, and gas sparging of the water prior to mixing. A summary of brine solutions prepared during the project is provided in Table 5.

The initial brine solutions (1 and 2) were prepared to evaluate in detail the success of achieving target solute concentrations. During the mixing of Solution 1, solubility problems were observed and there was some residual precipitate or undissolved salt even after a few days. A second brine was immediately prepared using a different sequence of addition for the chemical compounds. Precipitates were again observed. Each solution was filtered using a qualitative P5-grade cellulose filter (Fisher Scientific). The solids from both Solutions 1 and 2 were collected and analyzed chemically and by XRD. Aliquots of both solutions were also collected for chemical analysis.

Chemical analyses of the brine solutions indicated that concentration targets for all solutes with the exception of sulphate and bicarbonate were achieved within 10% (average of 97% and 95% of the desired concentrations for Solutions 1 and 2, respectively). Sulphate concentrations were about 70% of the target, while HCO_3 concentrations were about 15% of the target. As mentioned previously, the HCO_3 values were expected to be driven by $CO_2(g)$ in the atmosphere. Geochemical equilibrium modelling using PHREEQCi (Parkhurst and Appelo, 2013) and the PITZER database calculated an HCO_3 concentration equivalent to that measured in the chemical analyses for Solutions 1 and 2 (measurements were 90% of calculated value). Subsequent chemical testing following brine preparations indicated consistent results for HCO_3 (e.g., the measured values were as predicted by modelling, and dilute and brine values were the same, as expected for equivalent atmospheric exposure); thus, this parameter was not tracked in analyses for later solutions. The low sulphate concentrations were more problematic, although sulphate is a relatively minor component (0.16% by mass) of the overall composition of the brine. Results of the chemical analyses of the precipitates from Solutions 1 and 2 were dominated by sodium, calcium, chloride, and sulphate and indicated there was a relatively large percentage (~12% by mass) of sulphate in the precipitates. Additional mass balance calculations indicated that 90-96% of the sulphate mass was accounted for when combining brine solution and precipitate values.

Analyses of the Solution 2 precipitate by XRD proved difficult because of the highly deliquescent nature of the salt solids. However, the results indicated the presence of halite and sodium and calcium sulphate minerals (Figure 7). The loss of sulphate through precipitation improved only moderately despite the modification of the addition of sulphur to include sulphide (50% of S mass through sulphate and the remainder as sulphide). During preparation of subsequent brine solutions, additional methods such as sparging the ddH_2O prior to mixing and modifying the order of compounds improved the recovery of sulphur in solution to near 90%.

Table 5: Summary of SR-270-PW Preparations

Solution	Type	Notes
1	Initial test solution to evaluate recipe and mixing process	Lab atmosphere, ddH_2O (distilled deionized water, 18 MΩ), precipitate noted and analyzed
2	Second test solution to evaluate order of chemical addition, mixing method	Lab atmosphere, ddH_2O, precipitate analyzed chemically and by XRD
3	Evaluation of using reduced form of sulphur in recipe	Higher initial pH as expected, analysis of sulphide difficult. No impact observed.
4	Evaluation of mixing atmosphere, use of reduced sulphur, addition of iron	ddH_2O N_2-sparged, mixed in glove box under low O_2, black precipitate when iron incorporated, chemically analyzed precipitate by XRD, pH 8.26
5	Evaluation of iron addition with sulphate only	ddH_2O N_2-sparged, glove box, orange precipitate, Eh† 440 mV after 3 weeks in glove box, pH 7.66
6	Sodium sulphide and sulphate (prepared the same as solution 4). Dilute solution also made. No iron.	ddH_2O N_2-sparged, filtered, first scoping experiments. Modification of glove box atmosphere to include H_2. Eh −80 mV, pH 9.04.
7	Sulphate only. Dilute solution also made. Order of ingredients adjusted. No iron.	Lab atmosphere, N_2-sparging, glove box and bench top versions used in experiments. Continued scoping experiments. First element samples.
8	Sodium sulphide and sulphate. Dilute solution also made.	Lab atmosphere, N_2-sparging. Equilibration and initial sorption experiments (Tc-kinetics). Eh brine −100 mV, pH 7.6
9	Sulphate only	Lab atmosphere, N_2-sparging. White flaky precipitate noted. SEM-EDS analyses revealed Teflon contamination from stir bar erosion. Method adjusted. Analyzed but discarded.
10	Sodium sulphide and sulphate	Lab atmosphere, N_2-sparging. Greenish precipitate. Analyzed but discarded.
11	Sulphate only. Dilute version made.	Lab atmosphere, N_2-sparging. Filtered. Extended experiments.
12	Sodium sulphide and sulphate. Dilute version made.	Lab atmosphere, N_2-sparging. Filtered. Extended experiments.
13	Brine and dilute versions. Sulphate only. Larger volume made (4L).	Lab atmosphere, N_2-sparging. Filtered. Used for bulk of initial experiments.
14	Brine and dilute versions. Sulphate only. Larger volume made (4L).	Lab atmosphere, N_2-sparging. Filtered. Used in batch experiments.

† Oxidation-reduction potential (ORP) measurements were made using a HACH 5048 (Ag/AgCl) electrode. The observed ORP (mV) values at time of measurement have been converted to Eh (mV) relative to the standard hydrogen electrode (SHE).

Preparation of brine Solutions 3 through 5 evaluated additional components of the solutions such as pH and oxidation-reduction potential (ORP, or redox) and the addition of iron. Unfortunately, the selection of $FeCl_3•6H_2O$ as a source of iron resulted in some form of iron precipitation. A dark-coloured precipitate that formed during mixing of brine Solution 4 was collected and dried, then analyzed by XRD. The results revealed the presence of significant calcium carbonate phases along with possible evidence of an iron sulphide phase (Figure 8). Results of chemical analyses of brine Solutions 4 and 5 indicated recovery of about 50% of the added iron. Based on the difficulties of iron mixing and loss, iron was excluded from subsequent brine preparation. Although the lack of iron in solution could impact the redox behaviour of the experimental system, it was noted that each substrate contained some measureable concentration of iron. Thus, the exclusion of added iron in solution was determined to be acceptable.

Measurements of pH and ORP for Solutions 3 through 5 indicated higher than expected redox conditions even after significant solution equilibration time in the low-O_2 glove box atmosphere. Measurements of Eh[1] were consistently on the order of +440 mV even when sulphide solid was added as part of the recipe. Measurements of pH reflected the higher pH values caused by the addition of sodium sulphide, but ORP values did not respond accordingly. Some scoping tests were conducted (discussed later in the experimental section) to evaluate the addition of $Na_2S•9H_2O$ solution following brine preparation under low-O_2 conditions, but the reduction of ORP values was less than optimal. Only after modifying the glove box gas mixture to include H_2 did measured ORP values for the brine solutions decrease to acceptable values.

Brine Solutions 6 through 14 were prepared to support experimental work. Both sulphate-only and sulphate-sulphide solutions continued to be prepared to evaluate any potential impacts those compositions might have on experiments. Results of sorption tests indicated no discernable differences resulting from the sulphate-only or sulphate-sulphide solution preparation. Sulphide species in solution, either formed by the reduction of sulphate or added via sodium sulphide, can react with iron present in the solid substrates or iron in solution to form iron sulphides, which might enhance the measured sorption (Berry et al., 2007). For the sorption experiments in this study, iron was not added to either the brine or the dilute solutions. Furthermore, Berry et al. (2007) indicated that the presence of sulphide did not have a significant impact on their sorption results. In general, solutions were prepared using N_2-sparged ddH_2O to remove as much O_2 as possible before transfer into the low-O_2 glove box atmosphere and were filtered to remove any potential precipitates (although the presence of precipitates diminished in subsequent preparations). Using a standard dissolved oxygen probe (Oakton DO6+ meter and probe), dissolved oxygen was not detectable (0.0 mg/L) in the N_2-sparged solutions prior to addition of chemicals. Once prepared, the brine solutions were transferred to a glove box and sparged with gas from within the glove box to equilibrate the solutions. Chemical analyses of the solutions indicated consistent achievement of target solute concentrations (typically on the order of 95-102% of targets). An example of chemical analytical results for a brine solution (Solution 11) is provided in Table 6.

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[1] Measurements of ORP were conducted using a HACH 5048 (Ag/AgCl) electrode. The observed ORP (mV) values were converted to Eh (mV) values relative to the standard hydrogen electrode (SHE). All ORP or Eh values presented in this report are given as Eh (mV SHE).

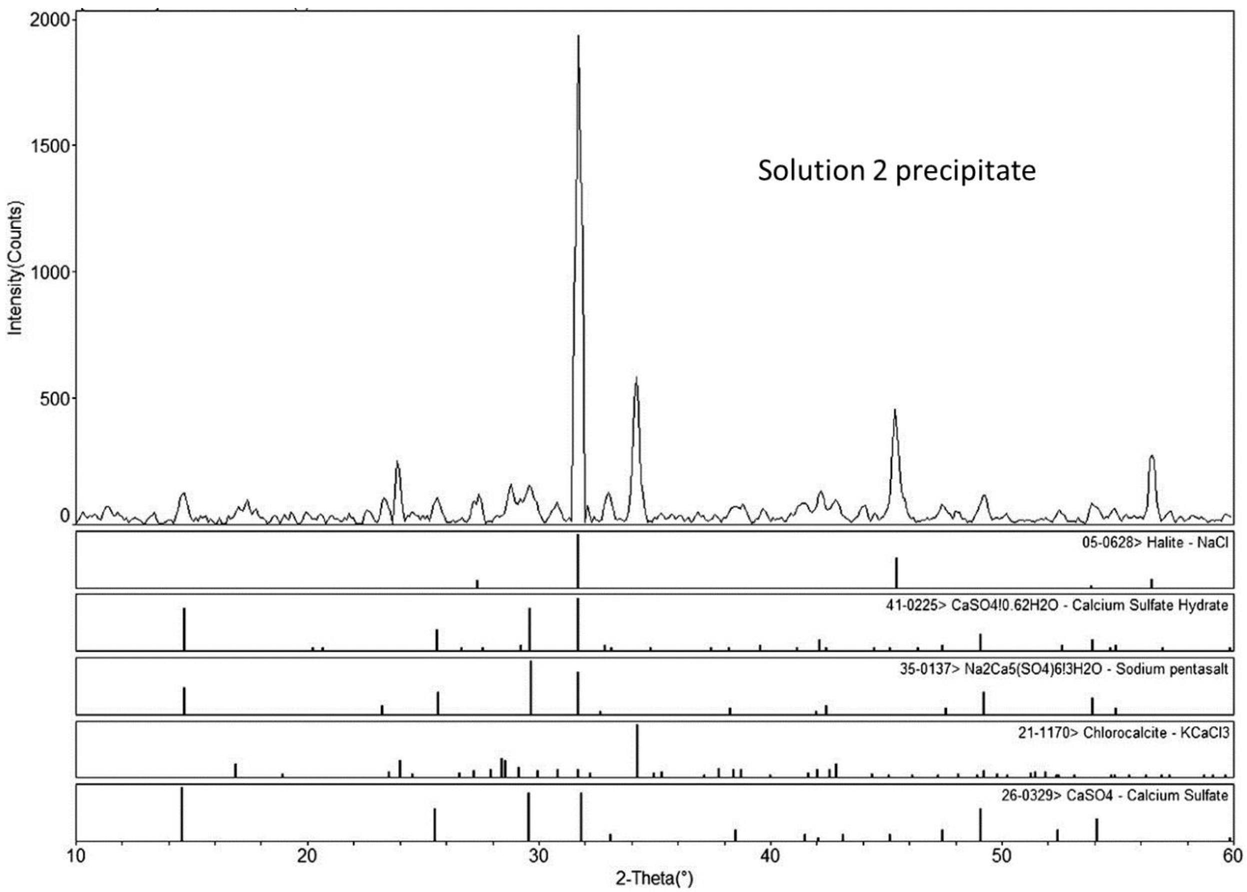

Figure 7: XRD Analysis Results for Precipitate Solids Collected during Preparation of Brine Solution 2. The Presence of Sulphate Mineral Forms is Consistent with the Low Recovery of Sulphate in the Initial Solutions

Table 6: Chemical Analyses Results for Solution 11 Brine (11B) and Dilute (11D) Mixtures

Compound	Calculated brine ppm based on mass added	Calculated dilute ppm	11B Brine results (ppm)	11D Diluted results (ppm)	% Recovery for dilute solution	% Recovery brine using mass added	% SR-270-PW target for brine
Na	50096.3	100.2	48800	98.5	98.3	97.4	97.4
Cl	168939.5	337.9	167000	335	97.1	98.9	99.1
Mg	8197.6	16.4	7670	15.7	95.8	93.6	93.5
K	12498.8	25.0	12100	24.3	97.2	96.8	96.8
Sr	1200.0	2.4	1150	2.39	99.6	95.8	95.8
Br	1699.9	3.4	1660	3.55	102.6	97.6	97.6
Ca	31996.5	64.0	30100	62.5	97.7	94.1	94.1
SO_4	440.1	0.9	409	0.794	88.7	92.9	93.0
HCO_3	109.9	0.2	12.8	<1.02		11.6	11.8†
S	146.9	0.3	137	0.304	103.5	93.3	93.3

†HCO_3 concentration determined by atmosphere. Target not applicable.

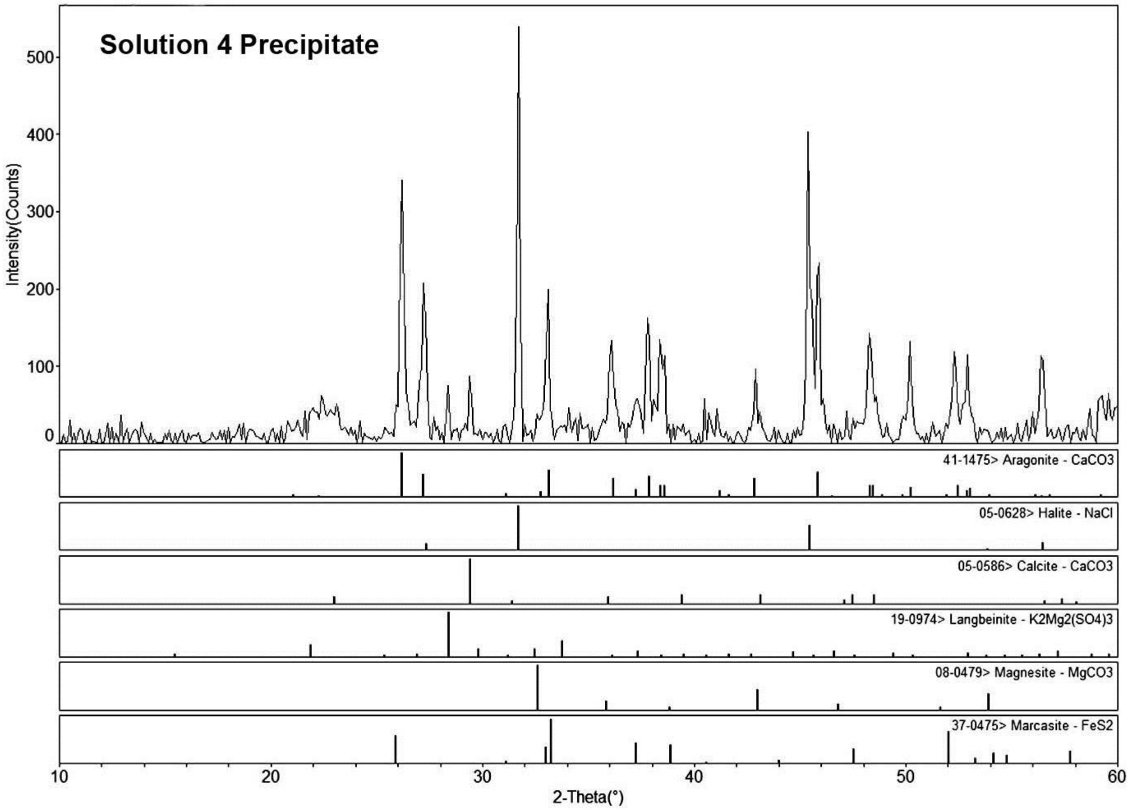

Figure 8: XRD Analytical Results for Dark-Coloured Precipitate from Preparation of Brine Solution 4. Along with the Presence of Calcium Carbonate Phases, there is Some Evidence of Trace Iron Sulphide

Exceptions to general success in solution preparation were Solutions 9 and 10. In the case of Solution 9, a white precipitate (in the form of flakes) was observed during preparation. Subsequent SEM-EDS analysis of the flakes from Solution 9 indicated they were composed primarily of fluorine. Inspection of the stir bars and beakers used to prepare the solution revealed evidence of erosion. The flakes were likely derived from the Teflon stir bars during solution mixing. A stir bar assembly designed to maintain the bar above the beaker bottom was used in subsequent preparations. Solution 9 was discarded after chemical analyses were conducted. Solution 10 produced an unknown precipitate. Chemical analyses for Solution 10 indicated most solute targets were met, but sulphur recovery was relatively low (~70%). Solution 10 was also discarded and not used in experiments.

2.1.3 Gases

Many types of gas mixtures can be used to establish appropriate low-oxygen environmental conditions for sorption experiments. Gas mixtures predominately composed of high-purity argon or nitrogen with O_2 excluded/removed are typically used for experimental work in which a low-O_2 environment is required. While argon provides a more inert atmosphere than N_2, there were no chemical constituents planned for use in the sorption experiments that were sensitive to N_2. Moreover, since N_2 makes up the bulk of atmospheric gases in the natural environment, and thus, diffusion of the gas into or out of experimental containers would not be a concern, N_2 was selected for use as the bulk component of the gas mix.

Because actinide sorption is known to be sensitive to carbonate complexation in solution, and because the carbonate concentration in solution is primarily controlled by the presence and concentration of CO_2(g) in contact with the solution, a gas mixture containing CO_2(g) was chosen for use in the experiments. Review of sorption experimental results conducted in low-O_2 environments indicated that a lack of CO_2(g) or a lack of CO_2(g)-concentration control in the experimental environment atmosphere may have influenced results in unexpected ways (Selnert et al., 2008; 2009). Furthermore, the specified solution composition of SR-270-PW brine and equilibration calculations of groundwater/porewater indicated solution equilibration with CO_2(g) concentrations as high as 1%. Thus, a more realistic evaluation of sorption in the tests would include the presence of CO_2(g). The initial experimental design was based on use of CO_2(g) at a concentration equivalent to atmosphere, and the gas mixture was specified to include 400 ppm CO_2(g). The experimental plan included the acquisition of additional gas mixtures with varying levels of CO_2(g) to influence experimental solution pH and evaluate the potential effects of higher CO_2(g) concentrations on sorption.

Gas mixtures were acquired in batches from Matheson Tri-gas (an SwRI approved supplier) with a certified composition of <1.0 ppm O_2, 400 ppm CO_2, and the balance as N_2.

Initial evaluation of the glove box system and solution response was conducted in early 2014. Although the glove box systems reached the low-O_2 conditions required (consistent measured atmospheric O_2 concentrations of 2.0 ppm or less), the measured Eh values in test solutions equilibrated with the glove box atmosphere remained higher than desired. The minimum measured Eh values for dilute solutions were 0 to −100 mV instead of the target value of −200 mV. The brine solution measurements indicated Eh values were much higher (typically in the range of +100 mV).

After reporting these issues at the NWMO Geoscience seminar in the summer of 2014, use of a gas mixture incorporating H_2 was suggested by other attendees. Although this was an optional gas included in the original project proposal, it had not been included in the experimental process. A new O_2-free gas mixture comprising 4% H_2, 400 ppm CO_2, <1.0 ppm O_2, and the balance N_2 was used for the glove box atmosphere. After equilibrating test solutions in the new H_2-bearing atmosphere, measured dilute solution Eh values decreased to −300 mV while measured brine solution values decreased to −100 mV.

Active monitoring of O_2(g) and CO_2(g) concentrations was conducted as part of the experimental setup. Initially, CO_2(g) measurements were collected with the detectors physically located outside of the glove boxes and connected via tubing to access ports. However, initial measurements revealed inconsistent CO_2(g) values or episodes in which no CO_2(g) was detected. After evaluating the tubing connections, confirming the CO_2 content of the supplied gas mixture, and verifying detector operation, measurement of CO_2(g) continued to be problematic. As a result, the CO_2(g) detectors were moved into glove boxes in order to sample the glove box atmospheres directly. CO_2(g) measurements were again sporadic or failed to detect CO_2(g) (i.e., continued to give very low concentration readings). Subsequent tests showed that CO_2(g) was being removed by the O_2 scrubbing system, a process not advertised or known by the manufacturer, according to discussions with Labconco technical staff.

The effective removal of CO_2(g) by the O_2-scrubber meant that CO_2(g) concentrations diminished rapidly (change from 400 ppm to 0 ppm) within a few hours even after large volume purges with fresh gas mixture. Thus, use of the O_2-scrubber, required for maintenance of very low O_2(g) concentrations, would result in very low CO_2(g) concentrations. This was a significant disadvantage because varying the levels of CO_2(g) can be important in assessment of sorption of actinides and for controlling pH of experimental solutions.

Effort was made to evaluate other options for controlling gas concentrations within the glove boxes. Options for controlling the CO_2(g) content of the glove box atmospheres included (1) conducting purge and fill cycles to introduce CO_2 and reduce O_2 without running the gas purifier, and (2) running a continuous gas bleed through the glove boxes to maintain a desired atmosphere. Because the gas bleed would require significant quantities of the certified mix, we concluded that the bleed would not be cost or time effective. We conducted a small experiment to assess the purge and fill method (Figure 9). Results of the three-day experiment indicated that the pH of solutions was influenced by varying the CO_2(g) concentration in the glove box, and the O_2(g) concentrations increased significantly without the O_2(g) scavenging system in operation. For both brine and dilute solutions, adequate solution Eh values could be maintained (−150 to −250 mV) while influencing solution pH with increased CO_2(g). However, the purge and fill method was quite labour intensive, and it was determined that making progress in the sorption experiments was more important than addressing the CO_2(g) issue. Thus, the final testing conditions included variable low to very low CO_2(g) concentrations within each glove box.

Evaluation of results from sorption kinetics tests later in the course of the project indicated some unexplained increases in measured ORP (see section 3.1.2.1). Further evaluation of the changes suggested that the H_2 levels within the glove boxes may also have been reduced over time by the O_2 scrubber. To minimize the impact of loss of H_2, the operation of the glove boxes was modified to incorporate periodic (twice weekly) gas purging to replenish H_2.

2.1.4 Radionuclides and Elements

The project requirements included evaluating the sorption of six redox sensitive elements present in nuclear waste. These elements included As, Np, Pu, Se, Tc, and U. Only radioactive forms of Np, Pu, Tc, and U are available, while As and Se are available in stable form in many common chemical compounds.

The proposed experimental plan for the project was based on several factors associated with the unique features of the elements to be tested. Some of the considerations included method of measurement and quantification of the elements in the high TDS brines, isotopic forms available, half-life and specific activity of the isotopes, possible solubility limit constraints for the reduced forms of the elements, and handling of the chemical form of the elements.

Because As and Se were available in standard chemical forms, they were acquired as high-purity (ACS reagent-grade) chemicals with the intention of analyzing experimental results using inductively coupled plasma mass spectrometry (ICP-MS). Later in the project, it was determined that effective measurement of Se would require a radioactive form, and a standard solution of Se-75 was acquired. Technetium was acquired as a Tc-99 standard solution with the intention of analyzing results using liquid scintillation analysis (LSA) and/or ICP-MS.

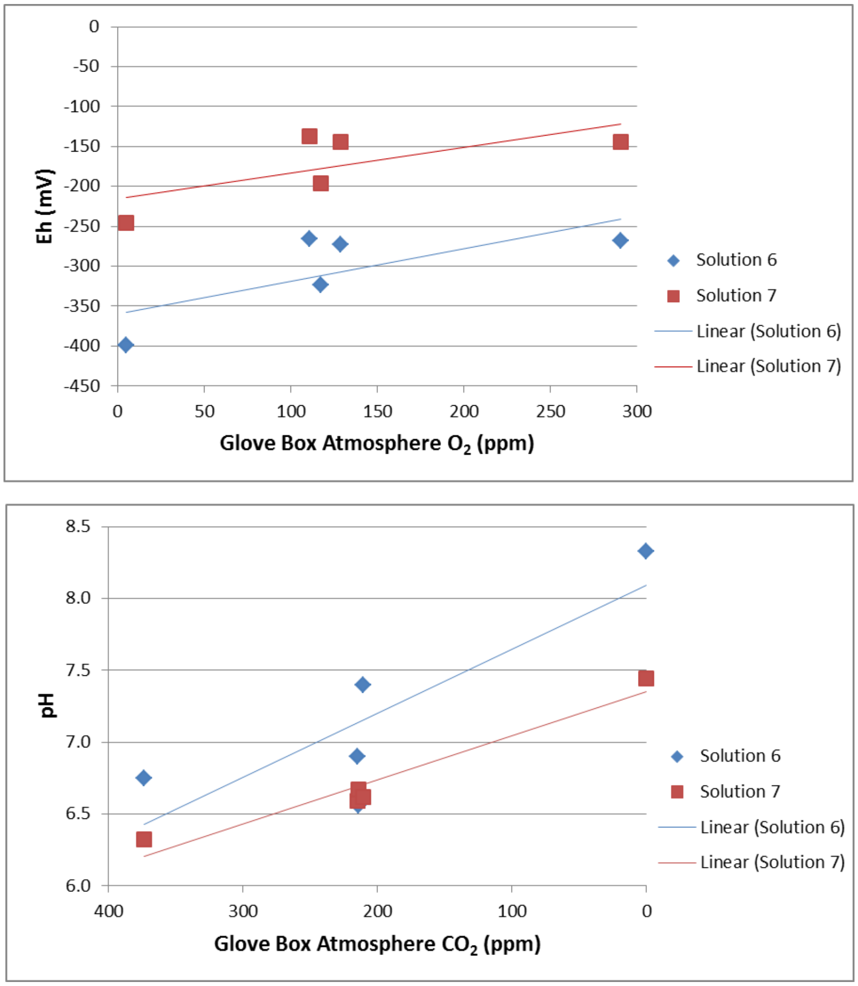

Figure 9: Results of Purge and Fill Test to Evaluate Effects of Increases in O_2 and CO_2 within the Glove Boxes. Maintaining Higher CO_2 Concentrations Resulted in Elevated O_2 Levels in the Glove Box and Measured Eh in the Brine Solutions. Linear Trends Are Shown as a Guide Only

The actinides Np, Pu, and U were acquired as specific isotopes (Np-237, Pu-239, Pu-238, and U-233) in the form of NIST-traceable standard solutions. The experimental plan was to measure the concentrations of these isotopes using a mix of LSA and alpha spectrometry (α-spectrometry). Use of LSA offered the advantages of minimal sample preparation and manipulation prior to analysis. Use of α-spectrometry offered two potential advantages. First, the sensitivity of detection was lower for Np-237 than could be achieved in the LSA. Second, because of the distinct separation in energy levels between the isotopes, we could potentially evaluate more than one nuclide in the same experimental solution. Although some testing of α-spectrometry was conducted, it was limited to single nuclide measurement and was not effective for the purpose of the project. The radionuclide counting was accomplished using LSA for all radioactive elements.

All radioisotopes were acquired from Eckert & Ziegler Isotope Products Laboratories (Valencia, CA). The isotopes were provided as NIST-certified reference standard solutions. The chemical form of the solutions varied and was dependent on the specific isotope (Table 7).

Table 7: A Summary of the Radioisotopes Used in the Project

Isotope	Form	Activity (MBq)	Assessment Method(s)
Tc-99	NH_4TcO_4 in water	0.372	LSA, ICP-MS
Tc-99	NH_4TcO_4 in water	3.752	LSA
U-233	$UO_2(NO_3)_2$ in water	0.891	LSA, α-spectrometry
U-233	$UO_2(NO_3)_2$ in water	1.190	LSA
Pu-239	$Pu(NO_3)_4$ in 4M HNO_3	1.897	LSA, α-spectrometry
Pu-238	$Pu(NO_3)_4$ in 4M HNO_3	0.199	LSA
Np-237	$Np(NO3)_4$ in 4M HNO_3	0.189	LSA, α-spectrometry
Se-75	H_2SeO_3 in 0.1M HCl	4.192	LSA

Arsenic stock solutions were prepared by diluting reagent-grade $AsCl_3$ in N_2-purged double deionized water (ddH_2O) in a 100-mL volumetric flask. After mixing, the As(III) stock solution was transferred to a 125 mL polypropylene (PP) bottle and stored in an atmosphere-controlled glove box. Transfers of As(III) stock solution to experiments were conducted in the glove box atmosphere. The target As concentration of the stock solution was 2000 μg/L, and results of chemical analyses of the stock solution indicated a final concentration of 1983 μg/L As(III).

The Se-75 standard solution (4.192 MBq Se-75 as H_2SeO_3 in 0.1M HCL, 100 μg/g Se carrier) was processed using the methods outlined in Iida et al. (2011) to produce a stock solution of Se(−II) for use in the sorption experiments. Approximately 2 g of the Se-75 standard solution was mixed with 2 mL of reagent-grade, 98% hydrazine monohydrate ($N_2H_4 \bullet H_2O$) in a polypropylene centrifuge tube, and the mixture was stored for 4 days (within the atmosphere-controlled glove box) to reduce the Se. The mixture was filtered using a 10,000 molecular weight cutoff (MWCO) centrifuge filter device (Amicon® Ultra-15 10K, Millipore) and diluted with ddH_2O to generate a 6×10^{-5} M Se(−II) stock solution. Based on differences in calculated expected and measured Se-75 activities of the stock solution, there was 48% recovery of Se during the reduction and filtration process. Approximately 0.1 g of the stock solution was added to each experimental container (~30 g solution) to produce an initial Se(−II) experimental concentration of $\sim2\times10^{-7}$ M.

Technetium stock solutions were prepared by diluting the Tc-99 standard reference solution in ddH_2O. The final solution composition consisted of 500 ppm Tc-99 as measured by LSA. The Tc-99 stock solution was stored in a 125-mL PP bottle under laboratory atmosphere [as Tc(VII)]. Experimental solutions were spiked with Tc-99 under laboratory atmosphere conditions. A second reference solution of Tc-99 was prepared using the method employed for Se. Use of hydrazine as a reducing agent for Tc is not uncommon (e.g., Marchenko et al., 2008). Approximately 2 g of the Tc standard solution were mixed with 2 mL of hydrazine solution and allowed to react for 4 days. A noticeable brown colour developed in the solution upon addition of the hydrazine. After 4 days the solution was diluted to ~20 mL by adding ddH_2O (previously sparged with glove box atmosphere and stored in the glove box) and filtered using the 10,000 MWCO filter device. The resulting filtered Tc-hydrazine solution was transferred to a 30-mL PP bottle and stored in the glove box. The reduced Tc-99 solution was used to test analysis of Tc(IV) using UV-VIS spectroscopy, but was not used in the sorption experiments.

Np-237, Pu-239, and U-233 stock solutions were prepared by diluting their standard reference solutions in ddH_2O. The target stock solution concentrations were based on addition of 0.5 mL to experimental containers. That is, the concentrations were based on achieving an effective count rate within the experiments to adequately quantify changes in element concentrations due to sorption.

Additional Pu-238 and U-233 stock solutions were prepared by adding hydrazine to an aliquot of the reference solution. Hydrazine has previously been used for the reduction of actinides in solution (e.g., Marchenko et al., 2008; Ganesh et al., 2010; Karraker, 1981). Again, the method of Iida et al. (2011) was modified for use with the U and Pu. Approximately 2 g each of the Pu-238 and U-233 solutions were combined with 4 mL and 2 mL of hydrazine, respectively. A larger quantity of hydrazine was used for the Pu to ensure complete oxidation of its HNO_3 carrier solution. The mixtures were allowed to reduce for 4 days and then diluted with N_2-sparged ddH_2O and filtered using a 10,000 MWCO centrifugal filter. The reduced Pu and U stock solutions were used in the second set of brine and dilute sorption experiments.

2.1.5 Equipment

2.1.5.1 Atmosphere Control

Two working controlled-atmosphere glove boxes were required to accommodate the number of solutions and experiments planned for the project. A new Labconco® Protector® Model 50800 fiberglass glove box with an automated pressure control system was purchased. Also, an existing Labconco Model 50600 glove box was upgraded with a new pressure control regulator (equivalent to that of the 50800) so that both boxes would have equivalent capabilities and operation. Both boxes were also equipped with a Labconco AtmosPure™ Re-Gen Gas Purifier that uses a molecular sieve and copper catalyst to remove O_2 (and H_2O).

The O_2(g) content of each glove box atmosphere was monitored using an Alpha Omega® Instruments Series 3000 trace oxygen analyzer [operating in the range 0-100 ppm (v/v) O_2(g)]. A separate analyzer was installed in each glove box. The analyzers continuously measured O_2(g) concentrations (displayed on instrument panel) and logged data at 15-min intervals. Data logs were download approximately weekly and reviewed to assess any potential unattended O_2(g) excursions (Figure 10). The O_2 monitors were paired with a LI-COR® Model LI-840A and Model 810 CO_2 gas analyzers for monitoring of CO_2(g). During the project, the Model 810 analyzer failed (October 2014) and was replaced with a new Model LI-820 CO_2 gas analyzer. The CO_2(g) analyzers were linked to an external computer and monitor for continuous readout and logging of data. Data were collected at 1-min intervals (primarily as a result of troubleshooting efforts early in the project) (Figure 11).

The final laboratory setup included two glove boxes that maintained O_2(g) levels at ~2 ppm or less (or ~3.5 ppm or less for the older box) for the bulk of the operation time. Exceptions include minor increases in O_2 levels during equipment and solution transfers into the glove boxes (Figure 10) and during gas purifier catalyst regeneration periods. Transient O_2 increases due to transfers were controlled within an hour by the gas purification system (Figure 10).

2.1.5.2 Redox and pH Probes

Initial redox and pH measurements for solutions in the laboratory were made using an Orion 920A Bench-top meter and Model 9179BNMD (ORP) and Orion 810BNUWP (pH) electrodes. Redox conditions (ORP) and pH of the solutions in the glove boxes and after start of sorption experiments were measured using combination pH/ORP electrodes and their associated meters

(Hach SensION+ MM150 meter with Hach 5048 electrode). The portable meters were better suited for the space-restricted environment of the glove boxes. The Hach 5048 electrode has a plastic body, non-refillable gel reference electrolyte (equivalent to Ag/AgCl, 4M KCl), built-in Pt1000 temperature sensor, glass pH sensor, platinum ORP sensor, and a ceramic pin reference junction. This electrode and meter combination has a nominal potential reading of −202 mV (ORP) relative the SHE at 25° C (ASTM International, 2014). In this report, all redox values are reported as Eh (mV) relative to SHE. Electrodes were calibrated on each use with NIST-traceable pH buffers or standards. After extended use, the electrode response appeared to degrade, and it took longer to reach stable readings during pH/ORP measurements of experimental solutions. As a result, electrodes were replaced periodically (approximately every 4 months).

The ionic strength of the brine solutions seemed to interfere with the operation of our standard flow-through ceramic-frit electrodes (the ionic strength of the brine exceeds the ionic strength of the internal fill reference solution). In the transition to the gel-type electrodes, it took several weeks to identify the best measurement process to collect stable readings. The electrodes are calibrated for pH and ORP prior to use. Because the ORP standard is oxidized (Zobell's solution, ORP ~+230 mV, +432 mV SHE), a low-ORP conditioning solution was used to prepare/clean the electrode before measuring low-ORP solutions. Measurements of pH are affected by high ionic strength solutions (Wiesner et al., 2006; Marvin, 2013; Nir et al., 2014; Schnurr et al., 2015). In an effort to assess the impact of the brine solutions on measured pH, buffers were modified by adding an aliquot of 2.25 M NaCl solution to each buffer. The higher ionic strength pH buffers were also used as a quality assurance check before and after measurements of brine solutions to verify that no significant drift in probe performance occurred. Figure 12 shows the results of the pH measurement of the buffers after addition of NaCl. The measured pH of the brine is approximately 0.6 units lower for all values and the trend remains linear through the calibrated range of the probe. Measurement of brine Solution 11 produces a pH value of 7.5 (Figure 12). Using the modified buffers as a guide, the value of measured brine pH (or $-\log m_{H+}$) reported here should be adjusted by adding approximately 0.6 units (or more depending on the correction method applied) (e.g., Nir et al., 2014; Schnurr et al., 2015). In this report, the measured pH values are provided without correction so that direct comparisons can be made to field measured pH values. Finally, because there is a distinct memory effect, separate probes were used for brine and dilute solutions. In practice, each pH/ORP measurement typically took an hour or more for each experimental solution.

2.1.5.3 Radionuclide Counting

Radionuclide concentrations were measured primarily using LSA with a Perkin Elmer TriCarb 3100TR liquid scintillation counter (LSC). Samples of radioactive solutions were placed in 7- or 20-mL glass scintillation vials, into which 0.5 mL of 0.02 N HNO_3 had been added, and an aliquot of scintillation cocktail (the volume of which varied from 5 to 20 mL based on vials size and type of sample matrix) was added. The type of cocktail used varied depending on the matrix of the solutions. Initially, Perkin Elmer Ultima Gold® AB was used for all solutions, and later was used in the analyses of dilute solution samples. Perkin Elmer Ultima Gold® LLT, which has better performance with high ionic strength aqueous samples, was used later in the project for analysis of brine solutions.

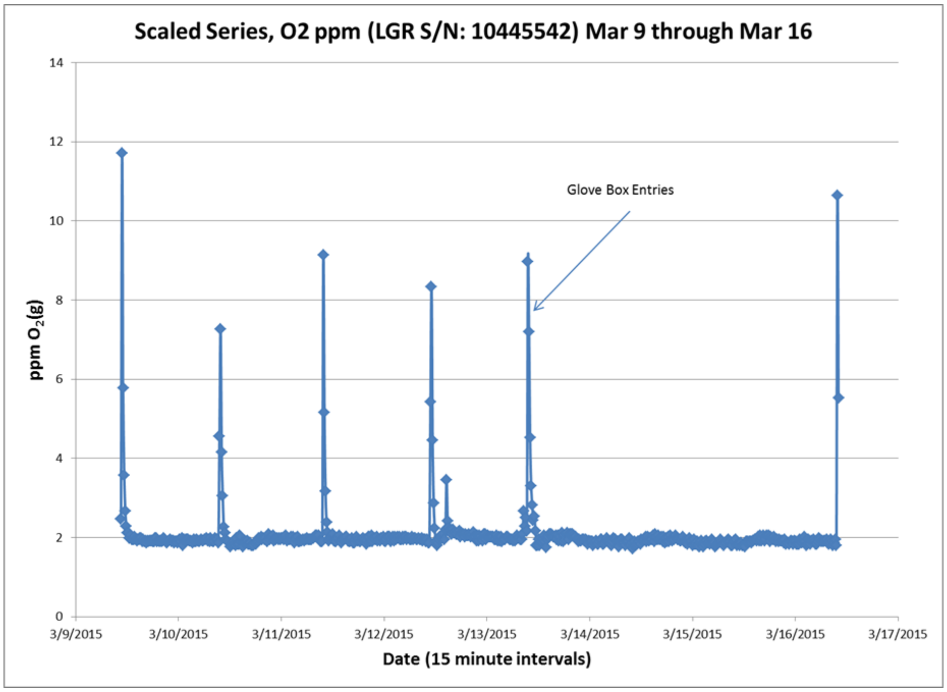

Figure 10: Example of Measured O_2 Gas Concentrations in One of the Atmosphere-Controlled Glove Boxes. O_2 Concentrations Remain just under 2 ppm. Peaks are Associated with O_2 Level Increase Resulting from Glove Box Entries to Transfer Materials and Supplies

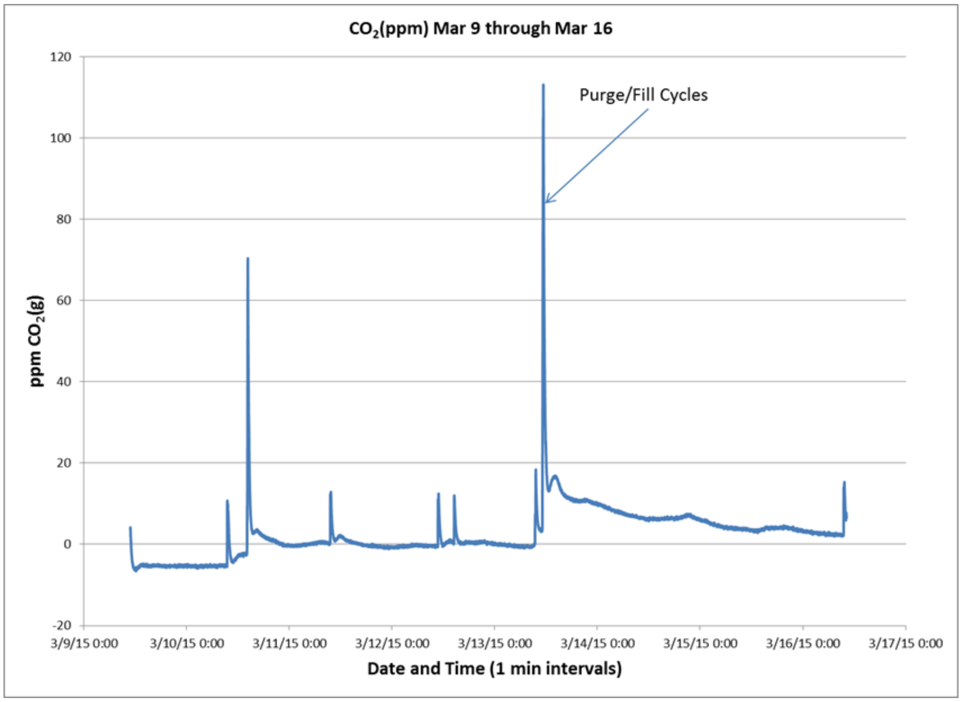

Figure 11: Example Record of CO_2 Gas Concentration (ppm) in One of the Glove Boxes. Peaks are Associated with Purge and Fill Cycles to Ensure Sufficient H_2 Levels. The Fast Removal of CO_2 by the Gas Purifier is Apparent

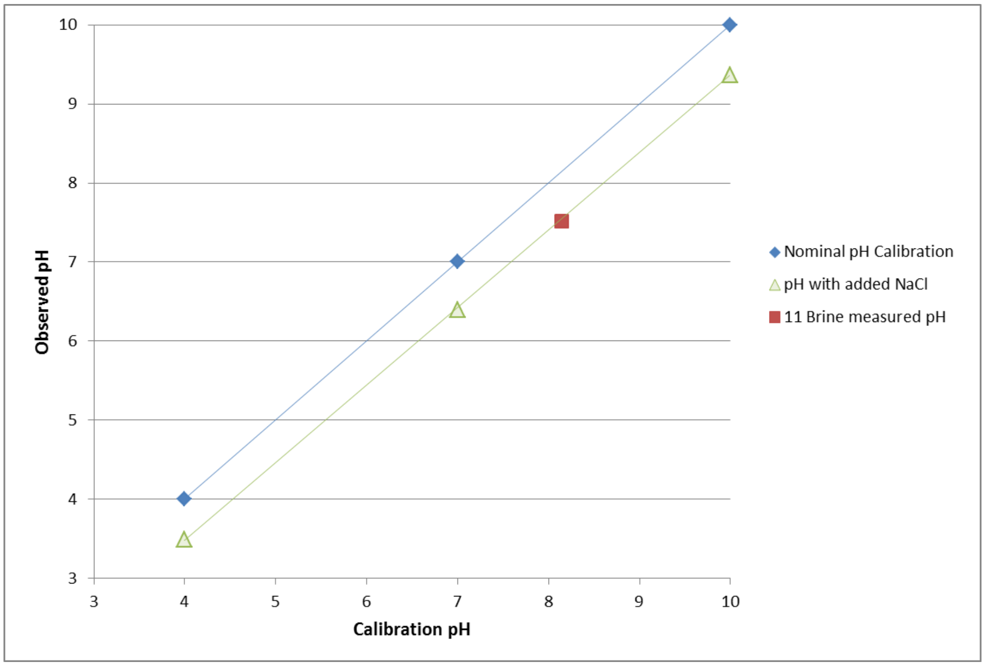

Figure 12: Calibration and Measurement of pH in Solution 11 Brine. Observed Brine pH of 7.52 is Equivalent to a Value of ~8.15 in Dilute Solution

Counting of the radionuclides was achieved using a blank solution representative of brine or dilute matrix and known samples containing a measured mass of the nuclide of interest in brine or dilute matrix. Quantification of samples included automatic subtraction of background and collection of total counts over an energy range suited to the particular nuclide. Duplicate samples from each experimental container were collected and the measured activities were corrected for mass of the sample and efficiency of counting for the nuclide based on the known samples. Samples were counted for various lengths of time designed to meet particular statistical counting uncertainty targets and to balance analytical time with available resources.

With the exception of Np-237, the counts per minute (cpm) method was used for all radionuclides. In the cpm method, all counts (minus background) in a given energy range are collected. For Np-237, alpha-beta discrimination was used to separate the Np-237 alpha counts from high energy beta counts from its immediate daughter Pa-233. For Se-75, which has a relatively short half-life of 119.7 d, the counting results were automatically adjusted for decay. Because the total counting time was only a couple of days for the Se-75 samples, the corrections were minor.

2.1.5.4 Chemical Analyses Methods and Equipment

The general composition of brine and dilute solutions was determined using inductively coupled plasma (ICP) spectroscopy for cations/metals and ion chromatography (IC) for anions. ICP-MS was used to quantify As and Tc in some solutions. Measurements of Np-237, U-233, and Pu-239 were verified by conducting duplicate analyses of selected samples using α-spectrometry. UV-VIS-NIR spectroscopy (Perkin Elmer Lambda 900) was used to test measurements of oxidation states of some elements.

2.2 EXPERIMENTAL METHODS

2.2.1 Scoping Tests

Once adequate preparation of brine and dilute solutions was verified, several small scoping experiments were conducted to assess behaviour of solutions upon exposure to low-O_2 atmospheres and/or the solid substrates and to assess the efficacy of methods planned for use in the sorption experiments.

Early measurements of brine and dilute solutions equilibrated with the low-O_2 atmosphere within the glove boxes indicated that modest reducing (Eh values of about −70 mV) conditions could be established for dilute solutions. A preliminary test was conducted to evaluate the effects of adding MX-80 to dilute Solution 6 (Figure 13). The MX-80 and dilute solution mixtures were agitated daily to enhance exchange of gas and allow for equilibration. Results of the two-week test indicated that addition of the MX-80 resulted in an increase in measured Eh (up to +450 mV) while the control solution without MX-80 added remained at an Eh of approximately −70 mV. Although the MX-80 had been stored in a low-O_2 atmosphere, it may have carried adsorbed O_2 that caused the increase in Eh; however, an explanation for the inability to lower Eh over the remaining test period was not found. A second important outcome of the ORP scoping test was that measurement of ORP was sensitive to the order of measurement. When low-ORP solutions were measured first, the low ORP value carried over to measurement of solutions at higher redox. The ORP electrode readings would eventually stabilize at a correct value, but the memory effect resulted in long equilibration times. As a result of this behaviour, ORP measurements were taken in order from expected high values to expected low values, and probes were preconditioned in low-Eh solutions after calibration under oxidizing solutions (as previously discussed in Section 2.1.5.2).

A second scoping test was conducted to assess whether addition of a reductant might facilitate lowering of the solution Eh. In the second test, brine and dilute mixtures of Solution 6 were used in conjunction with added MX-80 (Figure 14). The added reducing agent was a solution of 0.01 M $Na_2S{\bullet}9H_2O$ (prepared with N_2-sparged ddH_2O). The sodium sulphide solution was added in specific volume increments approximately daily over a period of two weeks, and pH and ORP were measured. The results indicated that ORP was reduced to about −250 mV (Eh −50 mV) after cumulative addition of 60-80 µL of the sodium sulphide. Interestingly, the ORP of the control brine (with no sulphide added) increased during the test. As a result of information derived from this test, some later sorption experimental solutions were spiked with sodium sulphide to facilitate initial ORP reduction of the solutions.

As discussed in Section 2.1.3, following discussions with NWMO staff and contractors at the Geoscience Seminar in 2014, the gas mixture for the glove boxes was changed to include added H_2. Following the receipt of the new gas mixture and re-establishment of atmosphere in the glove boxes, another batch equilibration test was conducted to evaluate changes in ORP with added MX-80 (Figure 15). Brine and dilute version of Solution 6 with added MX-80 substrate were equilibrated with the new glove box atmosphere, and pH and ORP were measured over a period of 10 days. In contrast to the previous test (Figure 13), results of this scoping experiment indicated successful reduction of the solutions could be achieved and maintained without addition of an external reducing agent.

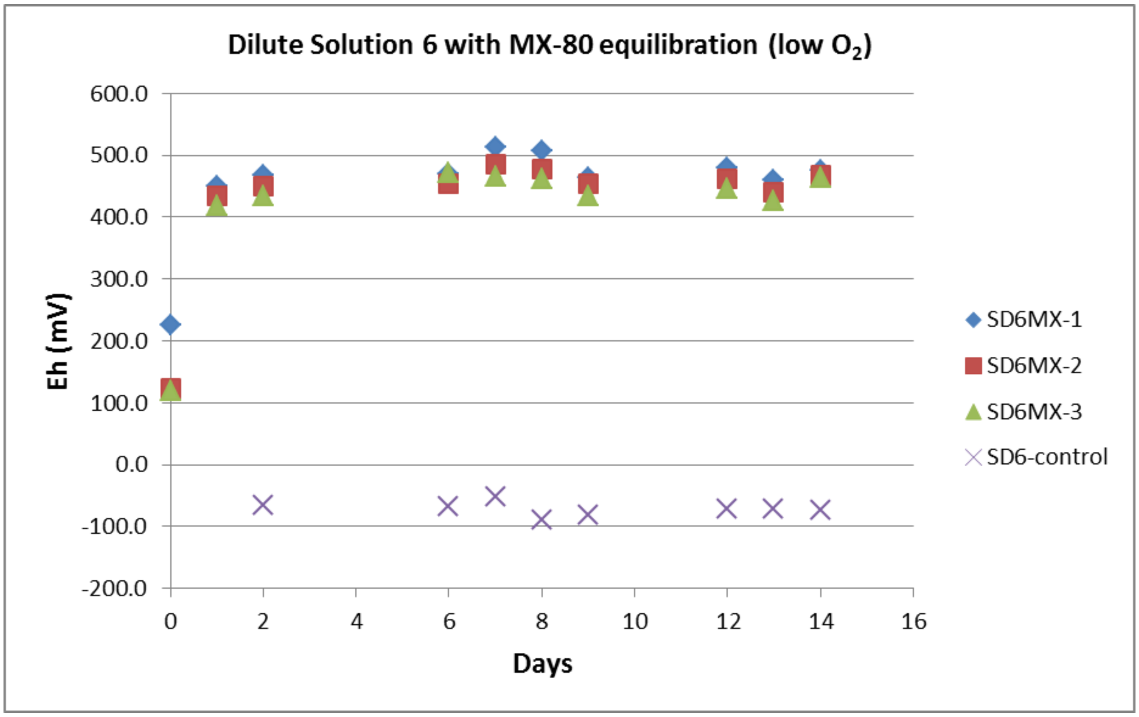

Figure 13: Results of Testing Conducted to Evaluate the Potential Change in EH when MX-80 was Added to Dilute Solution 6. Under the Glove Box Conditions Tested (no H_2), the Eh Values did not Decrease over Time

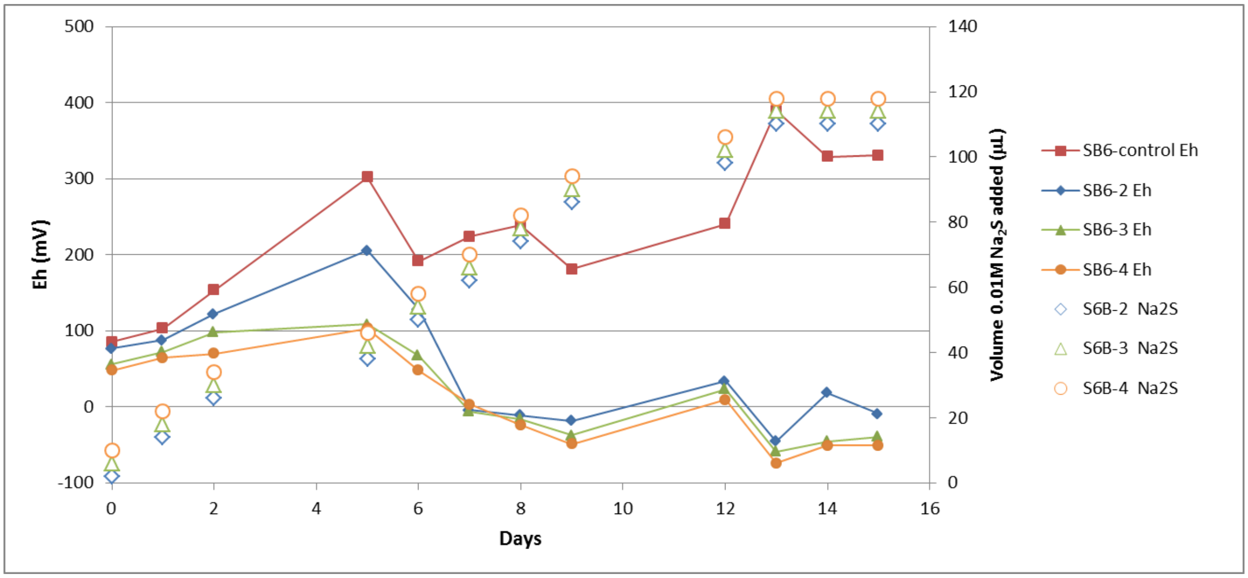

Figure 14: $Na_2S·9H_2O$ (0.01 M) was Added Incrementally to Different Test Samples (SB6-control, 2, 3, and 4) of Brine Solution 6. Both Brine and Dilute Versions of Solution 6 were Tested (only Brines are Shown). The Results Indicated that Addition of $Na_2S·9H_2O$ would Reduce the Eh. Additionally, the Brine Control Solution (with no Sulphide Added) Exhibited an Increase in Eh over Time

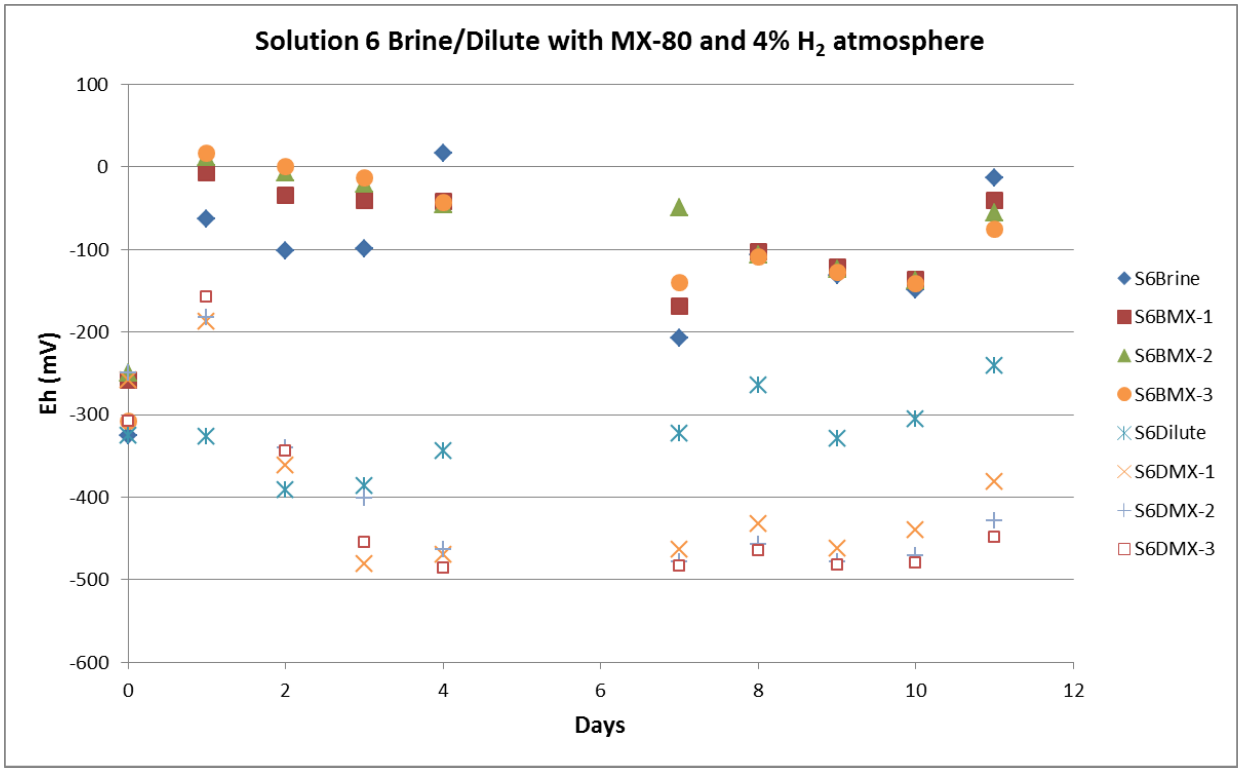

Figure 15: Results of Equilibration Testing with 4% H_2 Added to Glove Box Gas Mixture. Without the Addition of Any External Reductant, Measured Eh Values Decreased to −100 mV for Brines and −400 mV for Dilute Solutions Containing MX-80

For the dilute solutions, the presence of MX-80 resulted in lower measured ORP values. This was completely opposite of the results observed in the previous test (Figure 13). The Eh values measured (less than −400 mV) for the dilute solutions were promising. The measured Eh values for the brine were higher (about −100 mV). Subsequent experience during the project indicated that without addition of an external reducing agent, an Eh of approximately −150 mV was the lowest consistently achievable value for the brines.

2.2.2 Batch and Kinetics Sorption Experiments

2.2.2.1 Sorption Experiment Scoping Tests

Although a general outline of the batch experiment design and methodology existed at the start of the project, initial scoping experiments and testing work were required to develop a final experimental procedure. The initial plan for the batch sorption experiments was to (1) prepare suitable solid phases and experimental solutions; (2) add both to sorption vessels; (3) allow the system to equilibrate; (4) add the radionuclide or element to be tested; (5) allow the system to re-equilibrate; and (6) sample the solution to measure the amount of element lost.

Because of the various behaviours exhibited with respect to ORP by brine and dilute solutions thought to be equilibrated with the low-O_2 atmosphere in the glove boxes, an additional scoping test was conducted to quickly evaluate methods and results for an actual batch sorption experiment. To conduct the test, 25 mL of brine and dilute versions of Solution 7 were combined with 0.5 g of MX-80 solids and spiked with Tc-99 in 50-mL PC Oak Ridge-type centrifuge tubes. The test was conducted using two replicate brine and dilute experiments both in the glove box atmosphere and out of the glove box in laboratory atmosphere. Two individual dilute solution experiments without MX-80, but with Tc-99 added, were also included (one in the glove box and one on the lab benchtop). The goal of the experiment was to test the sorption of Tc-99 under clearly different ORP conditions. By conducting some of the tests in lab atmosphere, it was assured that an oxidizing system would be established. The sorption results of the oxidized and reduced systems could be compared to check the effects of the reducing environment. Tc-99 was selected because Tc had been used in previous low-O_2 experiments as a check for establishment of reducing conditions (e.g., Kulmala et al., 1996; Huitti et al., 1996). Moreover, based on past experience with sorption testing of Tc in our laboratory, it was expected that oxidized Tc(VII) would not sorb. Thus, there would be no issues in trying to compare different magnitudes of sorption—measureable Tc sorption would indicate successful reduction to Tc(IV). The experiment was meant to be a quick test and was conducted over 10 days (sampled 5 days after experiments were spiked with Tc-99).

Results of the batch sorption scoping test indicated that, as expected, no sorption occurred in the experiments conducted in oxidizing conditions (Figure 16). Despite maintenance of low-$O_2(g)$ conditions and measured Eh values of −150 mV and −300 mV for the brine and dilute solutions in the glove box experimental tubes, no sorption of Tc-99 on MX-80 was observed (Figure 17). The quick sorption test demonstrated that significant kinetics testing would be required and that the behaviour of Tc in low-ORP solutions was not simple.

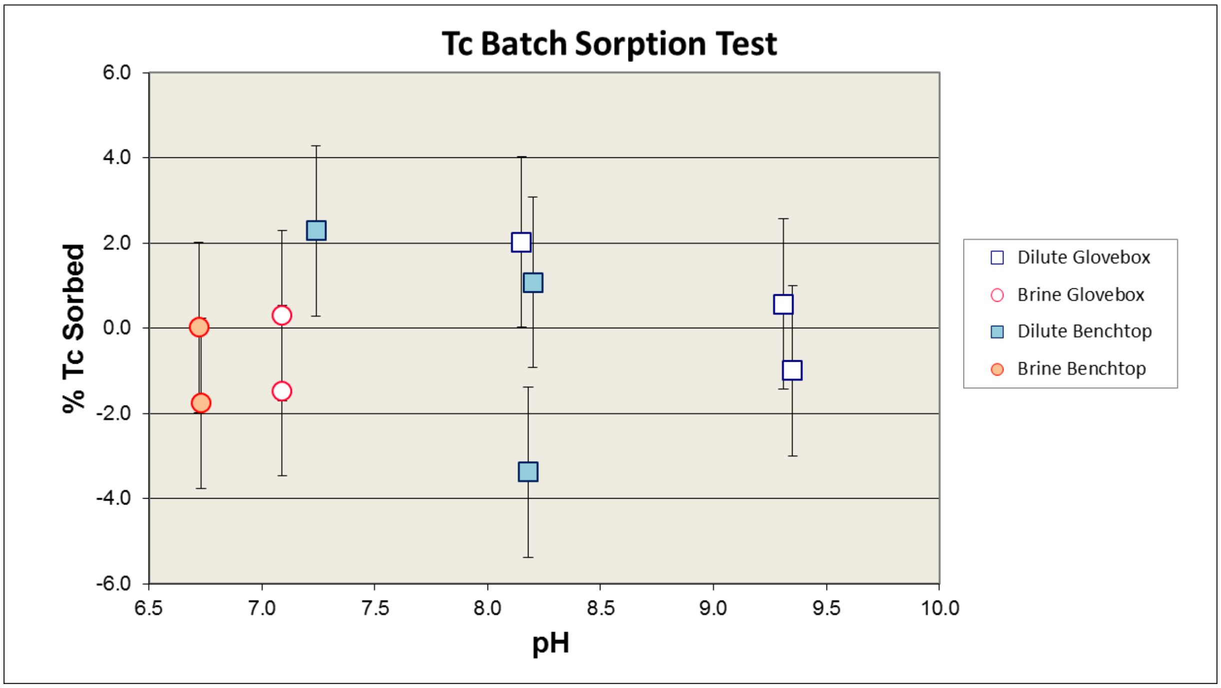

Figure 16: Results of Initial Tc-99 Sorption Test. Brine and Dilute Solutions with MX-80 Added were Equilibrated in Glove Box and Laboratory Atmospheres. Despite Clear Differences in Eh Conditions (Low Eh in Glove Box), no Sorption was Observed for the Glove Box Experiments over 10 Days. All Replicates are Shown and Error Bars Represent Estimated Uncertainty in Counting Tc-99 Activity

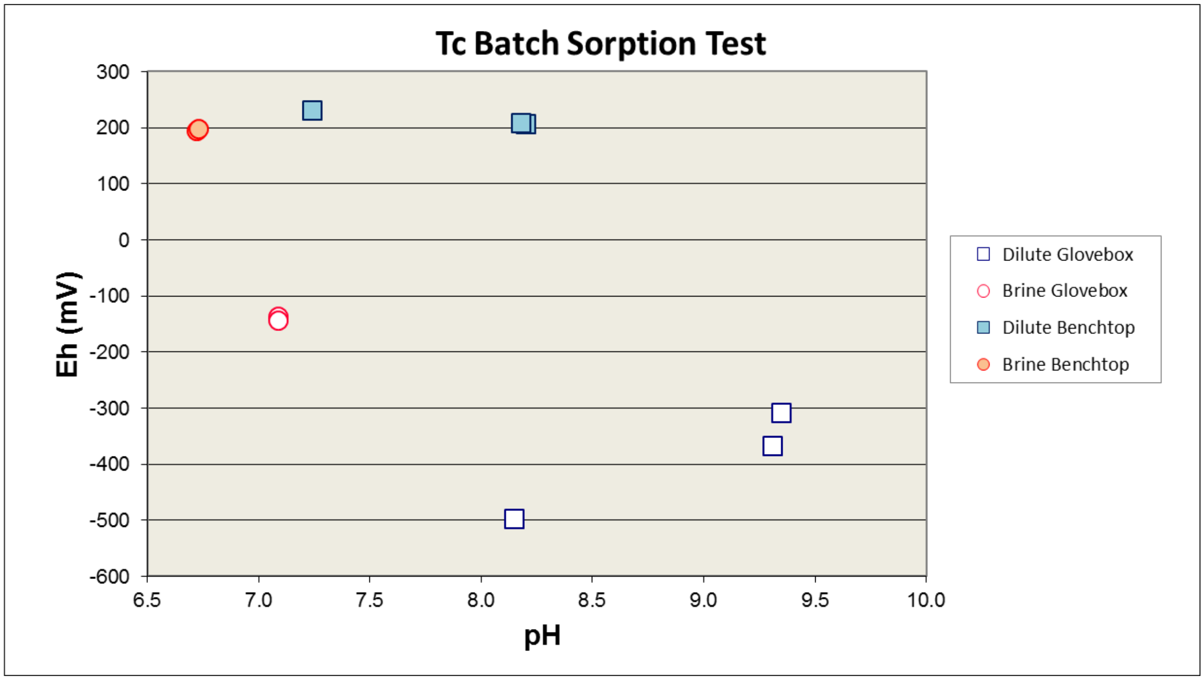

Figure 17: Measured Eh (mV) Values for Brine and Dilute Experimental Solutions Equilibrated in the Controlled Atmosphere Glove Box and under Lab Atmosphere

This first sorption test also provided information needed to adjust sampling protocols for LSA. The ionic strength of the brine solutions was too high to enable proper mixing in the Ultima Gold AB scintillation cocktail at the loading ratio (0.5-mL sample and 5-mL cocktail) used for the 7-mL sample vials (7-mL vials are preferred to minimize radioactive waste generation). The brines required larger volumes of scintillation cocktail and acceptable mixing was achieved using 0.5-mL samples and 15-mL of scintillation cocktail in 20-mL sample vials. An additional cocktail type, Ultima Gold LLT, which features improved loading characteristics for high ionic strength aqueous solutions, was acquired and subsequently used for brine sample analysis in the 20-mL vials.

At the end of the sorption scoping test, brine and dilute experimental solutions were sampled for chemical analysis. Results of chemical analyses for the major constituents of the brine and dilute solutions indicated the brine composition did not change substantially during the course of the experiment (Table 8). Slight increases in concentrations for both the brine and dilute (blanks) solutions were consistent with evaporation of water (~5% loss) from the experimental solutions. Because of the lower humidity and additional mixing of solutions in the glove box, slightly more evaporation was observed for those samples. Results for the dilute solutions with MX-80 added revealed an exchange of cations consistent with the ion-exchange capability of the MX-80 (CEC of ~0.8 meq/g) (e.g., Muurinen, 2011). A mass balance for the cation changes indicated that excess Na (+0.06 meq) was present in the dilute solutions (presumably released from the bentonite). The additional Na was calculated (using a PHREEQCi model simulation) to be consistent with the amount required to produce the observed change in dilute solution pH (from ~6.2 to ~8.2) after the addition of the bentonite. Results of analyses of Tc-99 by ICP-MS corroborated the concentration values determined using LSA for both the brine and dilute solutions.

Table 8: Summary of Results from Chemical Analyses of Experimental and Stock Solutions for the Tc-99 Scoping Sorption Test

	Measured concentration of solute (ppm)						(ppb)
Solution	**Na**	**Mg**	**K**	**Sr**	**Ca**	**Tc-99**	**Tc (LSA)**
Dilute Lab 1	253.2[†]	1.692	13.8	0.174	4.962	0.114	109
Dilute Lab 2	255.6	1.698	14.04	0.177	4.974	0.116	114
Dilute Glovebox 1	270	1.632	15.48	0.1932	5.424	0.118	115
Dilute Glovebox 2	271.8	1.584	15.12	0.1854	5.13	0.117	114
Dilute Blank Lab	99	15.96	23.76	2.478	64.8	0.123	117
Dilute Blank Glovebox	112.2	17.64	26.94	2.79	73.2	0.113	110
Average Dilute 7 stock	100.2	16.4	25.0	2.4	64.0		
Brine Lab 1	51420	7980	12240	1182	34380	0.112	91.4
Brine Lab 2	50100	7980	11940	1176	34200	0.111	93.4
Brine Glovebox 1	51240	8100	12180	1200	34500	0.112	96.1
Brine Glovebox 2	51600	8100	12180	1200	35340	0.115	95.4
Average Brine 7 stock	49033	7677	12267	1213	31300		
Brine 7 stock with calculated 5% evaporation	51485	8061	12880	1274	32865		

[†] After exposure of dilute solutions to MX-80, the average difference in Na concentration was +0.17 meq and the difference in total concentration of other cations was -0.11 meq, leaving an excess of +0.06 meq Na (or ~50 ppm), which is calculated to produce a change in pH from 6.3 to 8.3 for solutions in lab air. The measured change in pH was from 6.22 to 8.20.

2.2.2.2 Batch Experiments

The batch sorption experimental design incorporated several considerations, including (i) a need to match space limitations in the glove boxes with the number of experiments planned, (ii) a need to transfer solutions to and from the glove boxes for mass measurement, (iii) a desire to sample solutions without filtration, and (iv) large enough openings in experimental containers to measure pH and ORP directly. PC Oak Ridge-type 50-mL centrifuge tubes provided a means to address these experimental considerations. Additionally, the PC containers were known to perform well in a variety of sorption tests using various radionuclides (e.g., Bertetti et al., 2011).

The batch experiments were conducted as follows (with some variations as the experimental protocol was refined):

1. PC centrifuge tubes were labelled and weighed (including caps) and transferred into a working glove box under low-O_2 atmosphere. The design included triplicate experiments for each solid substrate–solution type combination. Thus, a batch sorption experiment for one element and a brine solution would include 9 tubes total, three for each substrate.

2. An aliquot of the substrate was transferred to each labelled centrifuge tube. For the batch experiments, 0.5 g of substrate was added to each container. Since the actual mass of added solid could not be directly measured at time of addition, care was taken to deliver the same amount of solid to each tube. To accomplish this, a standard measuring spoon (1/8 teaspoon) was used. Preliminary testing indicated 1/8 teaspoon delivered approximately 0.5 g of each substrate (the slightly less dense MX-80 required a slight heap during measurement).

3. The tubes were recapped and transferred out of the glove box to measure and record the mass of solid added.

4. The experimental tubes were transferred back to the glove box where 30 mL of brine or dilute stock solution was added to each tube. Mechanical pipettes with disposable tips were used to deliver the solutions. Stock solutions were previously equilibrated with glove box atmosphere and stored in the glove boxes until used for experiments. Following addition of solutions, the experimental tubes were transferred out of the glove boxes and re-weighed to determine the amount of solution added.

5. Experimental containers were again transferred into the glove box where the solutions and solids were allowed to equilibrate for at least 14 days. During this time experimental containers were periodically uncapped and sparged with glove box air to facilitate development of low redox conditions. Sparging was accomplished by inserting a tube and ceramic diffuser into each experiment tube and pumping air with a small pump installed in the glove box. In practice, tube assemblies (or manifolds) were constructed to enable bubbling of several experimental tubes at once. As the project progressed, the periodicity and duration of bubbling applied were changed to reduce loss of water from the experiment tubes. The final established bubbling frequency and duration were once per week for 5 minutes per experimental tube.

6. During the equilibration process, measurements of pH and ORP were made on a small number of experimental tubes. These measurements allowed for monitoring of progress toward desired redox conditions.

7. Once desired equilibrium conditions were established and shortly prior to addition of the element of interest for the experiment, experimental tubes were transferred from the glove box and weighed. This weighing step ensured that mass lost due to evaporation and/or pH/ORP measurement was accounted for and minimized uncertainty in the amount of element added.

   Because of the length of time during solids–solution equilibration and the nature of bubbling to promote gas exchange, various amounts of water were lost from experiment containers. For batch sorption experiments conducted later in the project, an additional step was added. Equilibrated tubes were weighed and an average mass loss was calculated. Experimental tubes were transferred back to the glove box and a volume of ddH_2O equivalent to the average mass lost was added to each experimental container. The containers were then re-weighed prior to addition of the element.

   For most of the early batch sorption experiments, radionuclide solution aliquots (spikes) were added outside of the glove box. The maintenance, control, and location of radioactive solutions made this method of addition the most feasible. Aliquots of radionuclide solution were added using Eppendorf-type pipettes, and the solutions were capped and re-weighed to measure the mass of the spike. (Experimental solutions were capped except during actual addition of the spike to each tube.) For later sorption experiments, including those for As, Se, U, and Pu, newly prepared element stock solutions were added in the glove box, and experimental tubes were only transferred in and out of the glove box for weighing.

For some of the experiments, aliquots of 0.1 N NaOH (to neutralize some of the effects of HNO_3 included in the radionuclide solutions) and/or 0.01 M $Na_2S \bullet 9H_2O$ (to promote reducing conditions as observed in previous scoping tests), were added as appropriate following the addition of the radionuclide spike.

Following the addition of the element spike, experimental solutions were again allowed to equilibrate with glove box atmosphere. Periodic mixing and bubbling were conducted in a fashion similar to that done during the equilibration period prior to spiking. A few selected experimental tubes were measured for pH and ORP to assess progress toward and establishment of reducing conditions during the sorption phase.

As discussed previously (Step 7), the frequency and duration of bubbling were adjusted downward during the course of the project. Bubbler assemblies were built as dedicated units, so that the same apparatus was used for a given experiment tube and there was no cross contamination between experiments or individual tubes. A given assembly was used throughout the duration of an experiment and was not re-used. For the last two batch experiments, U and Pu with hydrazine added, bubbling was not employed.

8. After an equilibration period greater than the minimum equilibration period indicated by kinetics experiments, experimental tubes were prepared for sampling. Experimental tubes were removed from the glove box and weights were recorded. The tubes were then centrifuged at 10,000 rpm for 10 min. The time for centrifugation was confirmed in earlier tests and is effective at removing particles with an equivalent diameter $\geq 0.1\ \mu m$, but suspended particles were not visibly present even in dilute solutions prior to centrifugation. Following centrifugation, the experimental tubes were returned to the glove box.

   Pre-weighed, labelled borosilicate LSA vials with 0.5 mL of 0.02 N HNO_3 added (use of a small amount of acid minimizes the opportunity for sorption or precipitation of the sampled nuclide during sampling) were transferred into the glove box for sampling of the experiments. For dilute solutions 7-mL vials were used and 20-mL vials were used for brines. Duplicate 0.5-mL samples were collected from each experiment tube using a pipette and disposable tips. Once samples were collected for all tubes of a given experiment, the LSA vials were removed from the glove box and re-weighed to measure and record the actual mass of sample taken. Five or 15 mL (depending on LSA vial size) of scintillation cocktail was added to each vial, and the contents were thoroughly mixed.

   Mixed LSA vials were allowed to settle for a few hours to ensure the entire sample was dissolved and sample vials were clear. The vials were then placed into the LSA for counting along with appropriate blank and known standard samples. Separate counting protocols were established with appropriate energy range targets for counting individual nuclides. Although not required, separate protocol definitions were used to assess 7-mL and 20-mL samples to facilitate organization of results.

Following sampling and after LSA vials were removed from the glove box, ORP and pH measurements were conducted for all experimental solutions. Electrodes were calibrated prior to each day's use and separate electrodes and meters were used for brine and dilute solutions. ORP measurements in brine solutions often required significant time to reach a stable reading. Testing and evaluation of measurements indicated the ORP measurements could be terminated after a minimum of 10-min for equilibration and the recording of consecutive readings within ±10 mV (Eh) and stable pH over at least 5-min intervals, or after two hours if that criterion was not met.

9. Results of LSA counting and measurements of pH and ORP were recorded and transferred to spreadsheets for processing and calculation of distribution coefficient (K_d) values.

10. For batch and kinetics experiments, values of K_d were determined by calculating the ratio of equilibrium concentration of the element on the solid phase and the equilibrium concentration of the element in solution according to the equation:

$$Kd = \frac{concentration\ of\ element\ on\ solid}{concentration\ of\ element\ in\ solution} = \frac{(initial\ N_{soln} - final\ N_{soln})}{final\ N_{soln}} \times \frac{V_{soln,final}}{M_{solid\ phase}}$$

where,
K_d is the distribution or sorption coefficient;
initial N_{soln} is the initial mass of element in solution;
final N_{soln} is the final mass of element in solution;
$V_{soln,\ final}$ is the final equilibrium volume of the solution; and
$M_{solid\ phase}$ is the mass of the added solid phase.

The final equilibrium concentration in solution was calculated using the measured sample activity (or concentration) of the element of interest and the measured mass of the solution prior to sampling. The equilibrium mass of the element on the solid phase was determined by (i) calculating the initial mass of the element in solution using the measured mass and activity concentration of the added spike; and (ii) subtracting the equilibrium mass of the element in solution at time of sampling.

It is important to note that the units used for K_d can vary. Commonly, K_d is expressed in terms of mL/g, L/kg, and m^3/kg (equivalent to 1000 mL/g). In this report, we provide K_ds in terms of mL/g. Strictly speaking, however, this is incorrect, especially for the brine results. The values for critical parameters in the experiments reported herein are tied to measurements of mass. For dilute solutions, the mass is nearly equivalent to volume because the solution densities are very close to 1 g/mL. For the brine studied in this project, the solution density is on the order of 1.23 g/mL. The calculated K_ds are accurate in that they are determined on a mass basis and so are equivalent for the dilute and brine results. The units of mL/g are appropriate for the dilute solutions and are used here for familiarity, but a more correct unit would be g/g. However, use of this unit might be confusing to readers. It is unclear whether correction of the reported values for density is needed or even desired. Correcting for density would result in an increase in the K_d values for brines by a factor of 1.23, so the values reported here for brines are low. However, with experimental uncertainties included, there is little practical difference between reported K_ds of 100 and 123 mL/g or between 10,000 and 12,300 mL/g, for example. Thus, it was decided that units of mL/g would be used and, in an effort to enhance the transparency of the calculations, no internal density to volume conversions were applied.

2.2.2.3 Kinetics Experiments

Unlike the batch sorption experiments, the kinetics experiments were expected to be conducted over a longer period of time and require collection of numerous samples. Rather than have a series of small containers that were sampled at different times, the kinetics experiments utilized larger volume containers so that withdrawals of solution for sampling would not significantly alter the solution volume to solid mass ratio. Results of the kinetics tests would produce usable K_d values, but their main purpose was to ensure the batch experiment design included adequate reaction time to overcome any kinetic effects. The kinetics experiments used the same materials and general sampling methodology as described for the batch experiments, but the kinetics tests were limited to evaluation of MX-80 due to time and resource constraints.

The kinetics experiments were generally conducted as follows:

1. Pre-labelled square 250-mL PC bottles were weighed and the weights recorded. The bottles were transferred to the glove box where ~0.5 g of MX-80 was added. The bottles were transferred from the glove box for re-weighing to measure the mass of solid added.

2. Approximately 250 mL of the desired brine or dilute solution was added to each PC bottle by pouring directly from the stock solution in the glove box and add to the 250-mL marker on the bottle. PC bottles were removed from the glove box and re-weighed to measure the mass of solution added. Bottles were returned to the glove box to allow the MX-80 and the solutions to equilibrate. During the equilibration period, the bottles were frequently bubbled using plastic tubing and glove box air delivered via small pumps installed in the glove box. The kinetics test originally employed a simple capillary tube for delivery of air. Later the capillary tubes were replaced with the larger diameter tubing and attached diffusers used in the batch sorption experiments. Although the larger tubes were effective at ensuring gas exchange, their use resulted in greater amounts of water lost due to evaporation.

3. After an equilibration period of at least 14 days, the bottles were re-weighed and an aliquot of the element of interest was added to each bottle. Bottles were re-weighed to measure the mass of added element. For the second series of actinide kinetics tests, a predetermined aliquot of 0.1 N NaOH solution was added after spiking to neutralize some of the HNO_3 carried with the spike.

4. The experiment bottles were returned to the glove box and mixed. The solutions were allowed to settle overnight.

5. The day after spiking, duplicate 0.5-mL samples were withdrawn from each kinetics experiment bottle for subsequent analysis by LSA. Pre-labelled and pre-weighed LSA vials (7-mL for dilute solutions and 20-mL for brines), with 0.5 mL of 0.02 M HNO_3 solution added prior to weighing, were transferred into the glove box as needed for sampling. After samples were collected, the LSA vials were removed for re-weighing to determine the mass of added sample. Scintillation cocktail was added and the vials were mixed by vigorous shaking. Although the initial samples were analyzed without delay, as the experiment progressed, samples were often held to assemble samples from a number of days before counting. LSA samples were collected approximately daily for the first two weeks. Afterward, the interval between samples was lengthened.

6. Following collection of the LSA samples, the kinetics experimental bottles were measured for pH and ORP. The frequency of measurement for pH and ORP varies in the experiments. In some early tests, the measurements were conducted for all solutions approximately daily. In later tests, the kinetics solutions were measured at intervals of 2 to 4 days.
7. The kinetics tests were planned for durations of 30–60 days. In cases where the kinetics appeared slow, experiment durations were extended. Kinetics experiments were stopped when it was apparent that equilibrium conditions had been reached.
8. Results of LSA analyses and pH and ORP measurements were recorded and transferred to spreadsheets for processing and analysis. When practicable, K_ds were calculated as previously discussed for the batch experiments.

2.2.2.4 Testing of Valence States

Information to confirm the valence state of the elements during the sorption experiments is important in reducing the uncertainty of measured K_d values under reducing conditions. As originally proposed for this project, there were no planned analyses dedicated to Eh independent assessment of element valence state. Instead, it was planned that establishment of appropriate environmental conditions would drive the redox state of elements. As the project progressed it became clear that there was significant uncertainty in the kinetics and transition of elements from their likely oxidized state in the standard solutions to a reduced state in the experiments, despite clearly established reducing conditions in the experimental solutions. As alternatives were explored to modify the redox of the element prior to addition in the batch experiments, we also examined mechanisms to directly measure redox state for some elements.

Both UV-VIS spectroscopy and solvent extraction (e.g., Schramke et al., 1989) followed by LSA counting appeared to be promising candidates for exploration of valence states. However, low concentrations of elements in solution and recurrent apparatus failures limited the success of these efforts.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Batch sorption experiments were completed for all specified elements and substrates in both dilute and brine solutions. Kinetics experiments were completed for Tc, Np, Pu, and U on MX-80 for both brine and dilute solutions.

A summary of the significant experiments conducted and completed as part of the project is provided in Table 9. The table provides an outline of the experimental conditions and materials examined for each test. Each of these experiments is discussed in more detail in the Results sections that follow. A summary of the results of all experiments is provided in Table 10. The results table indicates the average equilibrium pH and Eh (mV relative to SHE) as well as representative K_d values when obtained.

Table 9: Summary of Conducted Experiments

Element	Experiment	Solution type	Solution number	Substrates†	Experiment type	Rep.‡	Experiment time (Days)	Conditions prior to start§
Tc	U7MX80-B	Brine	7 Brine	MX80	Batch	2	7	n.a.
Tc	U7MX80-G	Brine	7 Brine	MX80	Batch	2	7	n.a.
Tc	D7MX80-B	Dilute	7 Dilute	MX80	Batch	2	7	n.a.
Tc	D7MX80-G	Dilute	7 Dilute	MX80	Batch	2	7	n.a.
Tc	D7MX80-blank	Dilute	7 Dilute	n.a.	Batch	2	7	n.a.
Tc	8BMX	Brine	8 Brine	MX80	Kinetics	2	40	pH=7.3, Eh=−130 mV
Tc	8DMX	Dilute	8 Dilute	MX80	Kinetics	2	78	pH=8.9, Eh=−465 mV
Tc	Tc14B1	Brine	14 Brine	MX80, CL, QS	Batch	3	116	pH=6.8, Eh=−160 mV
Tc	Tc14B2	Brine	14 Brine	MX80, CL, QS	Batch	3	116	pH=6.8, Eh=−160 mV
Tc	Tc14D1	Dilute	14 Dilute	MX80, CL, QS	Batch	3	116	pH=8.5, Eh=−300 mV
As	As14B1	Brine	14 Brine	MX80, CL, QS	Batch	3	43	pH=6.8, Eh=−170 mV
As	As14B2	Brine	14 Brine	MX80, CL, QS	Batch	3	43	pH=6.8, Eh=−170 mV
As	As14D1	Dilute	14 Dilute	MX80, CL, QS	Batch	3	43	pH=8.7, Eh=−310 mV
Se	Se14B1	Brine	14 Brine	MX80, CL, QS	Batch	3	30	pH=6.9, Eh=−150 mV
Se	Se14B2	Brine	14 Brine	MX80, CL, QS	Batch	3	30	pH=6.9, Eh=−150 mV
Se	Se14D1	Dilute	14 Dilute	MX80, CL, QS	Batch	3	30	pH=8.8, Eh=−400mV
U	11D U	Dilute	11 Dilute	n.a.	Kinetics	1	26	n.a.
U	11DMX U	Dilute	11 Dilute	MX80	Kinetics	1	26	n.a.
U	12DMX U	Dilute	12 Dilute	MX80	Kinetics	1	26	n.a.
U	11-U2	Dilute	11 Dilute	n.a.	Kinetics	1	37	pH=7.6, Eh=−270 mV
U	11MX-U2	Dilute	11 Dilute	MX80	Kinetics	1	37	pH=8.8, Eh=−400 mV
U	13BM-U	Brine	13 Brine	MX80	Kinetics	1	37	pH=7.2, Eh=−240 mV
U	U13B1	Brine	13 Brine	MX80, CL, QS	Batch	3	33	pH=6.7, Eh=−130 mV
U	U14B1	Brine	14 Brine	MX80, CL, QS	Batch	3	17	pH=7.0, Eh=−130 mV
U	U14D1	Dilute	14 Dilute	MX80, CL, QS	Batch	3	17	pH=8.8, Eh=−400 mV

Table 9: Summary of Conducted Experiments (Continued)

Element	Experiment	Solution type	Solution number	Substrates[†]	Experiment type	Rep.[‡]	Experiment time (Days)	Conditions prior to start[§]
Np	11D Np	Dilute	11 Dilute	n.a.	Kinetics	1	26	n.a.
Np	11DMX Np	Dilute	11 Dilute	MX80	Kinetics	1	26	n.a.
Np	12DMX Np	Dilute	12 Dilute	MX80	Kinetics	1	26	n.a.
Np	11-Np2	Dilute	11 Dilute	n.a.	Kinetics	1	37	pH=6.8, Eh=−290 mV
Np	11MX-Np2	Dilute	11 Dilute	MX80	Kinetics	1	37	pH=8.8, Eh=−345 mV
Np	13BM-Np	Brine	13 Brine	MX80	Kinetics	1	37	pH=7.2, Eh=−235 mV
Np	Np13B1	Brine	13 Brine	MX80, CL, QS	Batch	3	33	pH=6.4, Eh=−120 mV
Np	Np14B1	Brine	14 Brine	MX80, CL, QS	Batch	3	57	pH=6.8, Eh=−180 mV
Np	Np14D1	Dilute	14 Dilute	MX80, CL, QS	Batch	3	57	pH=8.0, Eh=−310 mV
Np	Np14D2	Dilute	14 Dilute	MX80, CL, QS	Batch	3	57	pH=8.0, Eh=−310 mV
Pu	11D Pu	Dilute	11 Dilute	n.a.	Kinetics	1	26	n.a.
Pu	11DMX Pu	Dilute	11 Dilute	MX80	Kinetics	1	26	n.a.
Pu	12DMX Pu	Dilute	12 Dilute	MX80	Kinetics	1	26	n.a.
Pu	11-Pu2	Dilute	11 Dilute	n.a.	Kinetics	1	37	pH=6.7, Eh=−250 mV
Pu	11MX-Pu2	Dilute	11 Dilute	MX80	Kinetics	1	37	pH=8.8, Eh=−370 mV
Pu	13BM-Pu	Brine	13 Brine	MX80	Kinetics	1	37	pH=7.1, Eh=−215 mV
Pu	Pu13B1	Brine	13 Brine	MX80, CL, QS	Batch	3	33	pH=6.7, Eh=−130 mV
Pu	Pu14B1	Brine	14 Brine	MX80, CL, QS	Batch	3	17	pH=6.9, Eh=−135 mV
Pu	Pu14D1	Dilute	14 Dilute	MX80, CL, QS	Batch	3	17	pH=8.7, Eh=−320 mV

[†] Substrates used were: MX-80 – Voclay sodium bentonite, CL – Cobourg Limestone from core sample, QS – Queenston Shale from core sample. n.a. = no solid added

[‡] Rep. = Replicates. Three replicates per solid phase. Example: A total of nine tubes for Tc14B1.

[§] Typical solution conditions prior to adding target element stock solution, if measured and recorded. For experiments where those conditions were not explicitly quantified prior to start, n.a. is entered.

Table 10: Summary of Results of Sorption Experiments†

Element	Experiment	Solution type	Substrates	Days	pH	Eh (mV)	K_d (mL/g)	Notes
Tc	U7MX80	Brine	MX80	7	7	-325	0	No sorption for brine or dilute, same results for lab atmosphere
	D7MX80	Dilute	MX80	7	9.2	-125	0	
	8BMX	Brine	MX80	40	7.2	-140	0	No sorption for brine, but for dilute Tc conc. decrease by more than 80%
	8DMX	Dilute	MX80	78	8.8	-450	not determined	
	Tc14B1 & 2	Brine	MX80, CL§, QS§	116	7	-20	variable	Na_2S added to facilitate reduction of Tc to Tc(IV). K_d for shale=20 mL/g, limestone=10^4 mL/g, and MX-80=$5×10^3$ mL/g
	Tc14D1	Dilute	MX-80, CL, QS	116	8.5	-160	variable	Variable sorption: shale=10 mL/g, limestone=10^5 mL/g, and MX-80=10^4 mL/g
As	As14B1 & 2	Brine	MX80, CL, QS	43	7	-20	20	Brine and dilute have similar K_ds
	As14D1	Dilute	MX80, CL, QS	43	8.7	-120	20	
Se	Se14B1 & 2	Brine	MX80, CL, QS	30	8	-210	100	Se spike treated using hydrazine to generate Se(-II). Sorption similar for brine and dilute.
	Se14D1	Dilute	MX80, CL, QS	30	9.2	-360	80-100	
U	11DMX U & 12DMX U	Dilute	MX-80	26	6.7	-360	3400	Equilibration less than 5 days, K_d peaked then decreased slightly with time
	11MX-U2	Dilute	MX80	37	8.5	-400	1500	Equilibration slower ~14 days, K_d peaked then decreased slightly with time, same as 11DMX U
	13BM-U	Brine	MX80	37	7.1	-100	460	Slow change, may not have reached equilibrium, maximum K_d at the end of test provided
	U13B1	Brine	MX80, CL, QS	33	7	-40	2200	Similar K_ds for all three solids
	U14B1	Brine	MX80, CL, QS	17	8.4	-290	420	U-233 processed with hydrazine. Similar K_ds for all solids, K_d is like brine kinetics test 13BM-U
	U14D1	Dilute	MX80, CL, QS	17	9.7	-420	20000	Highest K_ds

Table 10: Summary of Results of Sorption Experiments[†] (Continued)

Element	Experiment	Solution type	Substrates	Days	pH	Eh (mV)	K_d (mL/g)	Notes
Np	11DMX Np & 12DMX Np	Dilute	MX80	26	6.2	-270	3000	Slow rate, equilibrium not reached, K_d are highest at end
	11MX-Np2	Dilute	MX80	37	6.4	-300	9000	Slow rate, equilibrium not reached, K_d are highest at end
	13BM-Np	Brine	MX80	37	7	-125	0	No sorption observed
	Np13B1	Brine	MX80, CL, QS	33	6.8	-50	20	Average value. Range of K_ds, 12-30 mL/g, is similar for all solids
	Np14B1	Brine	MX80, CL, QS	57	6.7	25	variable	Second test, also with low K_ds, shale=0 mL/g, limestone=10 mL/g, and MX-80=10 mL/g
	Np14D1 & D2	Dilute	MX80, CL, QS	57	8.8	-160	variable	Variable K_ds, averages for shale=500 mL/g, limestone=3.5×10^4 mL/g, and MX-80=1400 mL/g
Pu	11DMX Pu & 12DMX Pu	Dilute	MX80	26	6	-340	60000	Average K_d. Equilibration less than 10 days, plateau then variable K_d between 10^4 and 10^5 mL/g
	11MX-Pu2	Dilute	MX80	37	7	-350	78000	Equilibration less than 5 days, plateau then variable K_d above 10^5 mL/g at long times
	13BM-Pu	Brine	MX80	37	7.1	-150	10000	Slow kinetics, highest K_ds at end, K_d values at 25 days
	Pu13B1	Brine	MX80, CL, QS	33	6.6	-35	4000	Similar K_ds for all solids
	Pu14B1	Brine	MX80, CL, QS	17	8.2	-230	1500	Pu-238 processed with hydrazine, similar K_ds for all solids
	Pu14D1	Dilute	MX80, CL, QS	17	8.7	-380	12000	Variable K_ds, limestone high at 16000 mL/g, others lower at 8000 mL/g

[†]Only experiments with solids added are shown. Eh, pH, and K_d values are representative values for information, see the text and plots for data.
[§]CL=Cobourg Limestone, QS=Queenston Shale

3.1 RESULTS OF KINETICS EXPERIMENTS

Four major kinetics tests were conducted, each consisting of several components. In the first test, Tc-99 was added to brine and dilute solutions containing MX-80. In the second test, U, Pu, and Np were each added to two differently prepared dilute solutions containing MX-80. The third kinetics test again evaluated addition of U, Pu, and Np to dilute solutions containing MX-80. In the final kinetics test, U, Pu, and Np were added to brine solutions containing MX-80.

3.1.1 Technetium Sorption Kinetics on MX-80

The first kinetics tests were simplified experiments designed to examine more closely the behaviour of Tc in dilute and brine solutions containing MX-80. The tests were a direct result of the lack of Tc sorption observed in the scoping batch sorption experiment (e.g., Figure 16). In this experiment, 250 mL of dilute and brine Solution 8 (Table 5) were added to 250-mL PC bottles containing 0.5 g of MX-80. Duplicate experiments were prepared so that there were 2 dilute solution tests and 2 brine solution tests. This kinetics test was intended to be a qualitative inspection of Tc behaviour over time. As such, there were two shortcuts intentionally included in the experiments as time and labour saving measures. One shortcut was that the actual mass of solutions added to the experimental containers was not directly measured. Another shortcut was that the mass of LSA samples collected from the experimental solutions was not directly measured. Instead, the experiment relied on the repeatability of the mechanical pipette to deliver similarly sized samples. These uncertainties are somewhat mitigated by collection of duplicate samples and the analysis of duplicate experimental solutions. There were no attempts to calculate K_ds for this experiment. Instead, the results are reported as activity (or concentration) of Tc in the samples.

The results of measured Tc activity in the brine and dilute solutions over time are shown in Figure 18. While the brine solutions show no evidence of Tc sorption (sampling was stopped for the brines after 40 days), Tc concentrations in the dilute solutions continue to decrease nearly linearly over the 78 days of the primary test, suggesting the rate of change may have been limited by Tc reduction from (VII) to (IV). Differences in initial Tc concentrations are a result of the different masses of brine and dilute solutions added. A final sample collected from the dilute solutions after 146 days showed no further sorption. The change in Tc concentration for the dilute solution represents about 90% loss of initial Tc from solution and a final Tc-99 concentration of about 1×10^{-8} M. The Tc behaviour is nearly identical for both pairs of experiments. Figure 19 shows the changes in pH and Eh during the course of the kinetics experiments for both the dilute (upper) and brine (lower) experiments. As evidenced by the graphs, the tests were spiked after reducing conditions had been established and remained at low redox conditions for the duration of the tests (approximately −400 mV for the dilute tests and −130 mV for the brine tests). A final measurement of Eh and pH was taken for the solutions 146 days after spiking. These measurements indicated Eh values remained low (−310 mV for the dilute and −129 mV for the brine). Despite nearly ideal redox conditions for the tests, sorption of Tc in the brine was not observed more than 40 days after spiking. The Tc data in the brine also reveal some concentration effects (~6–10% increase), possibly from evaporation of the brine solution during the experiment. Results of these experiments suggested there was a fundamental difference in the behaviour of Tc in the brines versus the dilute solutions. These results did not address the possible causes: (i) higher brine redox was insufficient to reduce Tc (although that seems inconsistent with some literature); and/or (ii) the brine impacted sorption; and/or (iii) Tc kinetics were even slower in the conditions represented by the brine. Subsequent batch sorption tests included modifications of procedures to address some of these issues.

3.1.2 Uranium, Plutonium, and Neptunium Sorption Kinetics in Dilute Solutions

Another group of kinetics experiments investigated Np, Pu, and U in dilute solutions with added MX-80. These experiments also included duplicate solutions, but the duplicates were modified to include one dilute solution (Solution 11D) made with only sulphate and another dilute solution (Solution 12D) made using a combination of sulphate and sulphide. Besides examining the behaviour of the three actinides, the experiment was designed to test for differences in the redox behaviour of solutions from the differing brine recipes. In addition, a pair of solutions (one 11D and one 12D) were included but with no MX-80 added. These "blank" solutions without MX-80 were included to evaluate container sorption and/or solubility issues. Similar to the previous kinetics tests, 250 mL of the solutions were added to 250-mL PC bottles containing 0.5 g of MX-80 (except for the two blanks). Unlike the previous tests for Tc, the added mass of solutions, solids and radionuclides were directly measured. Similarly, masses of collected LSA samples were recorded at each sampling point. The experimental solutions equilibrated for about 21 days prior to spiking with the nuclides. Prior to spiking, the pH and Eh of the solutions (both 11D and 12D) were stable at approximately 8.8 and −460 mV.

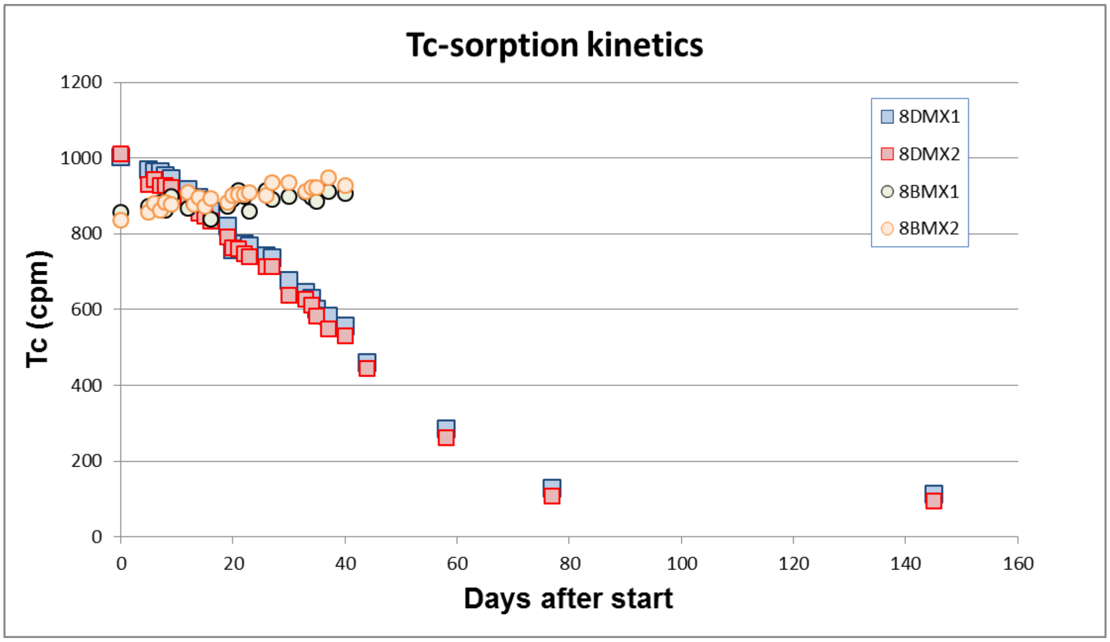

Figure 18: Measured Change in Tc-99 Concentration over Time for Dilute and Brine Solutions (Solutions 8 and 8D). No Sorption of Tc was Observed in the Brine Experiments

3.1.2.1 Uranium

For U (added as U-233), the results of the kinetics tests showed an initial decline in U concentration within the first few days and a sorption maximum reached between 5 and 7 days after spiking (Figure 20). This was followed by a steady increase in measured U concentration (and resulting lower calculated K_d) for the remainder of the experiment. The U concentration measured in the experiment without MX-80 (blank) added shows no evidence of U loss from solution. Based on the increase in U concentration in the blank, it is likely that the increase in U concentration observed in all the tests was due to concentration of the solution through evaporation of water over time (at least a 10% loss of mass through evaporation over 20 days) and/or due to some increase in pH of the solutions (Figure 21 and Figure 22). Calculated K_d values peaked at about 3400 mL/g. The sorption of U is relatively stable across the pH range from 6.5 to 8.0 (except for the early stages of the experiment when kinetics and oxidizing conditions impacted results) (Figure 21). Inspection of Figure 21 indicates that after the early oxidizing excursion caused by spiking, low redox condition were quickly re-established and remained low at about −400 mV. Sorption of U appears to closely follow the change in redox, so it is likely that kinetics for U sorption are much shorter than 5 days and the time to reach the sorption plateau observed was actually just the time for the solutions to re-establish their low redox conditions. In any case, the U system stabilizes within 5 days.

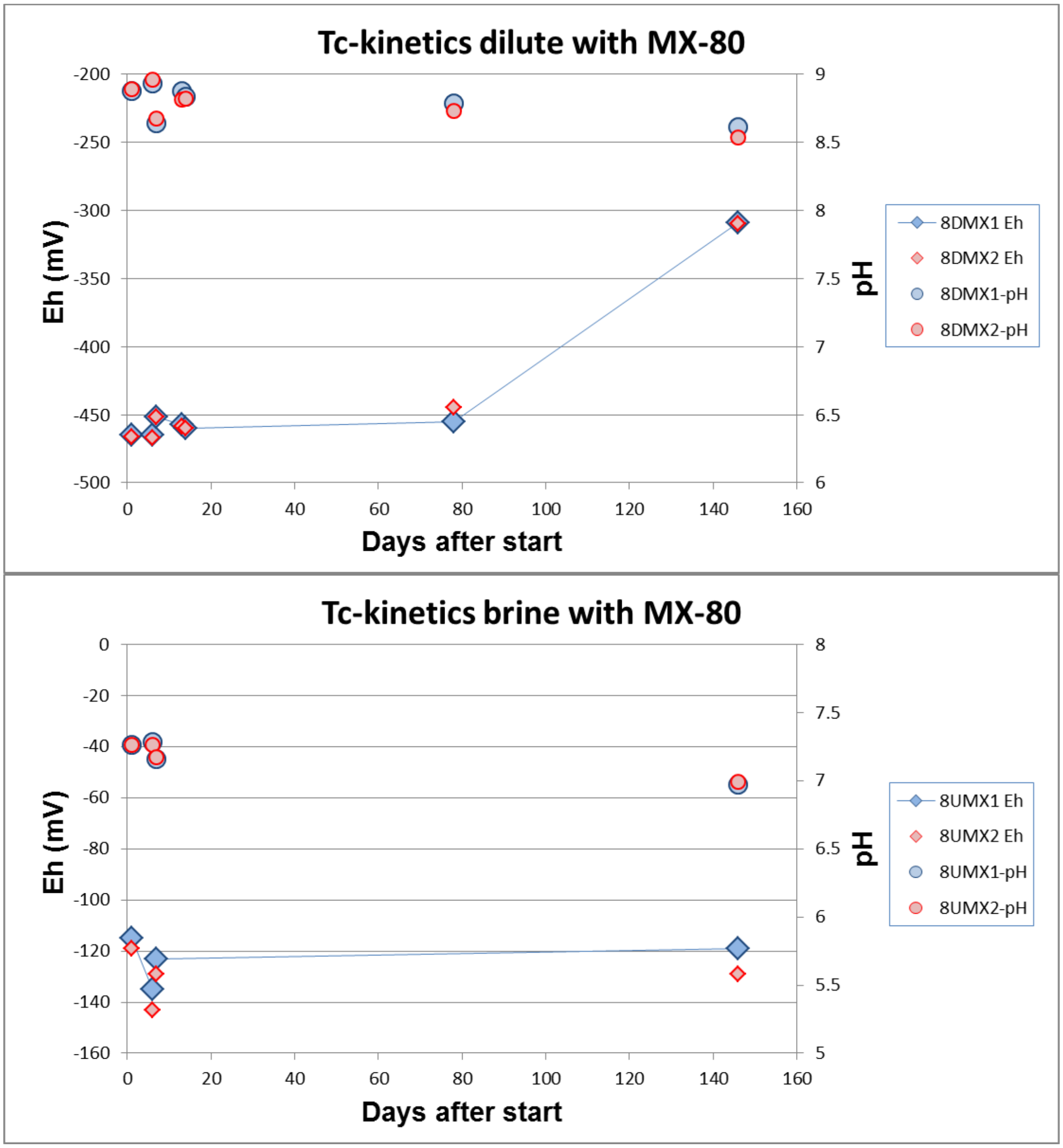

Figure 19: Change in Measured pH and Eh for Dilute (Top) and Brine (Bottom) Solutions Used in Initial Tc Kinetics Experiments (Note the Differences in Scales for Eh and pH)

Of note also are increases in measured Eh values occurring around days 9 and 23 (Figure 21). These Eh increases are unexplained, and they occur for all solutions. One possibility is the Eh readings are the result of probe “memory” effect or slow response time. In essence, the recorded Eh can be influenced by previous measurements, but previous testing suggested that the effect was biased toward low Eh readings, opposite of the issue in this test. However, the measurement procedure accounted for these processes, and there is no indication that measurements were incorrect on these days. After some consideration, it was determined that the lesser number of glove box entries during the experiments may have resulted in some depletion of H_2 in the glove box atmosphere. Because there were fewer gas fill cycles to replenish H_2 within the box, the H_2 concentration may have decreased substantially over time.

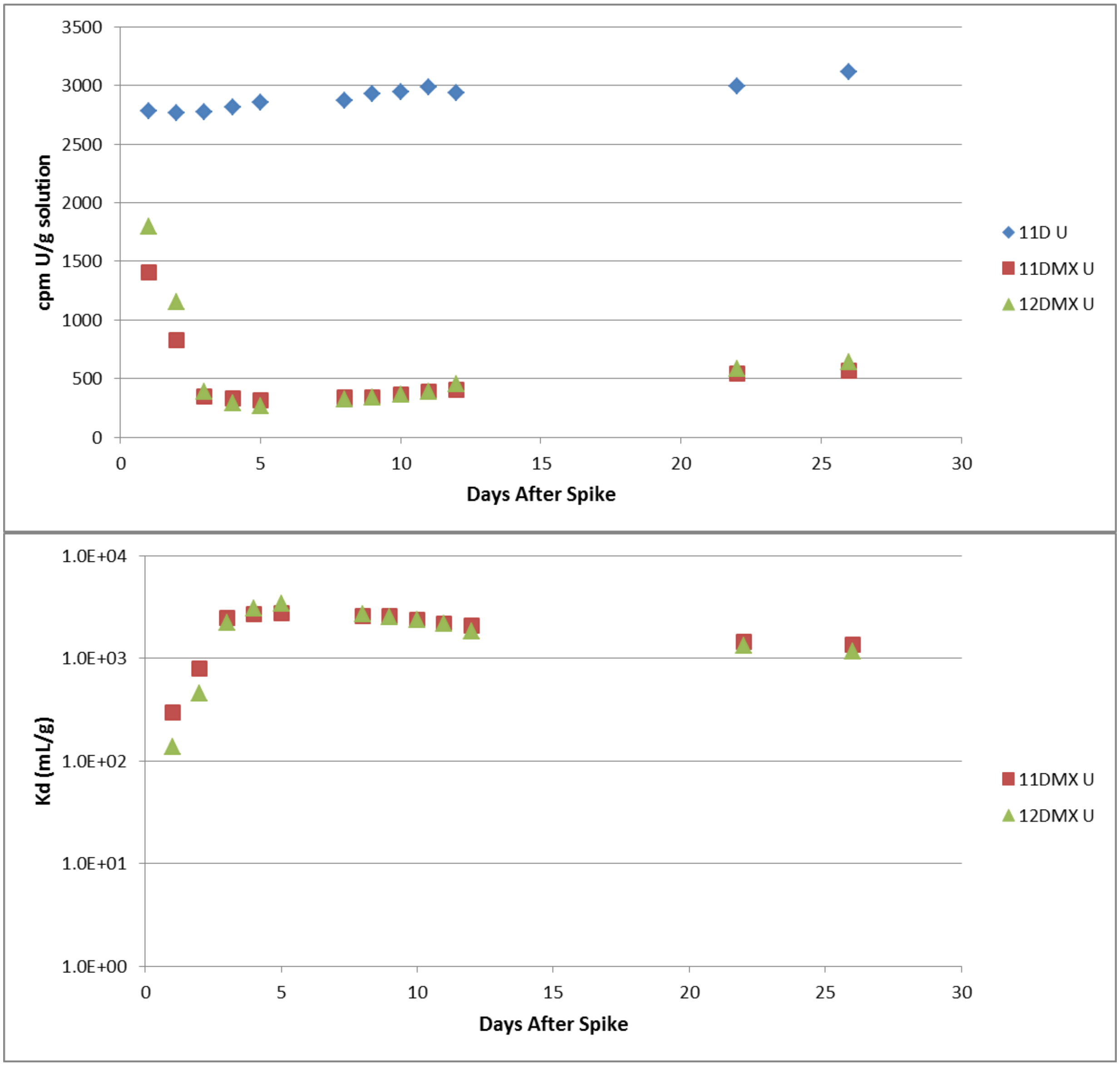

Figure 20: Measured Sorption over Time of U-233 on MX-80 in Dilute Solutions. Sorption Plateaus at about 5 days. The Observed Decrease in Calculated K_d may be Caused by Evaporation of the Experimental Solution (and Subsequent U Concentration), but may also be Influenced by an Increase in the pH of the Experimental Solutions

The possible loss of H_2 may also be a by-product of the O_2 scavenging system. To minimize effects of any H_2 depletion, the routine operation of the glove box system was modified to replenish H_2 by purging the glove box atmosphere twice weekly.

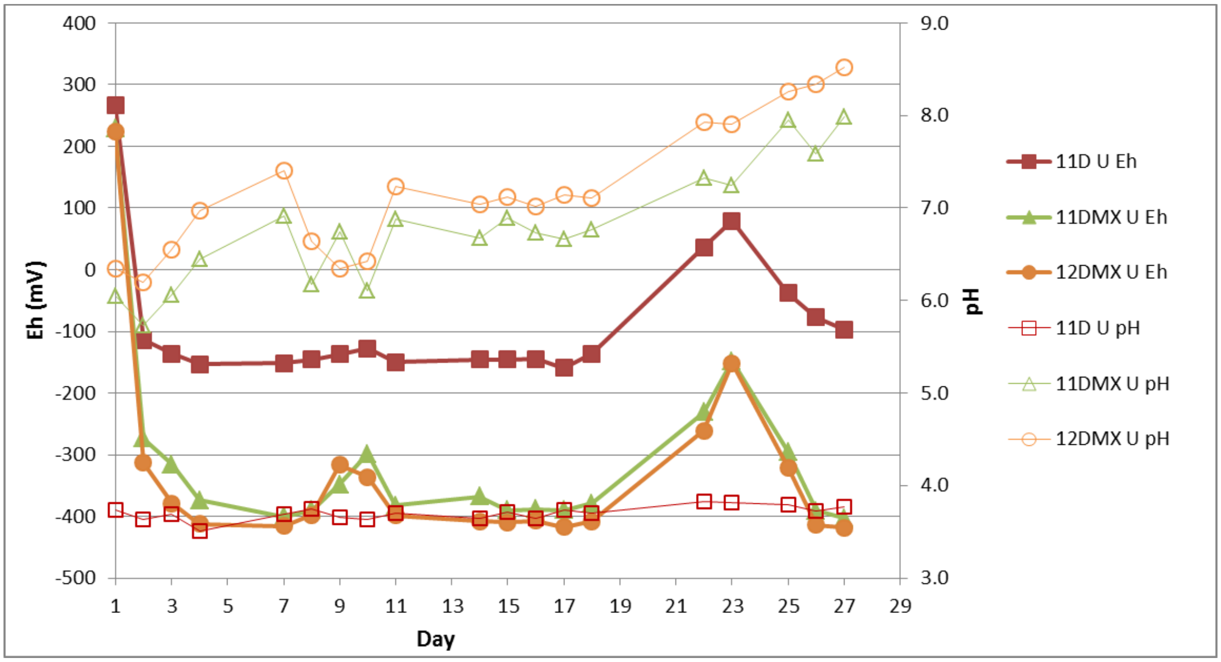

Figure 21: Change in Solution pH (Hollow Symbols) and Eh (Filled Symbols) over the Duration of the U-233 Sorption Kinetics Experiments Conducted in Dilute Solutions

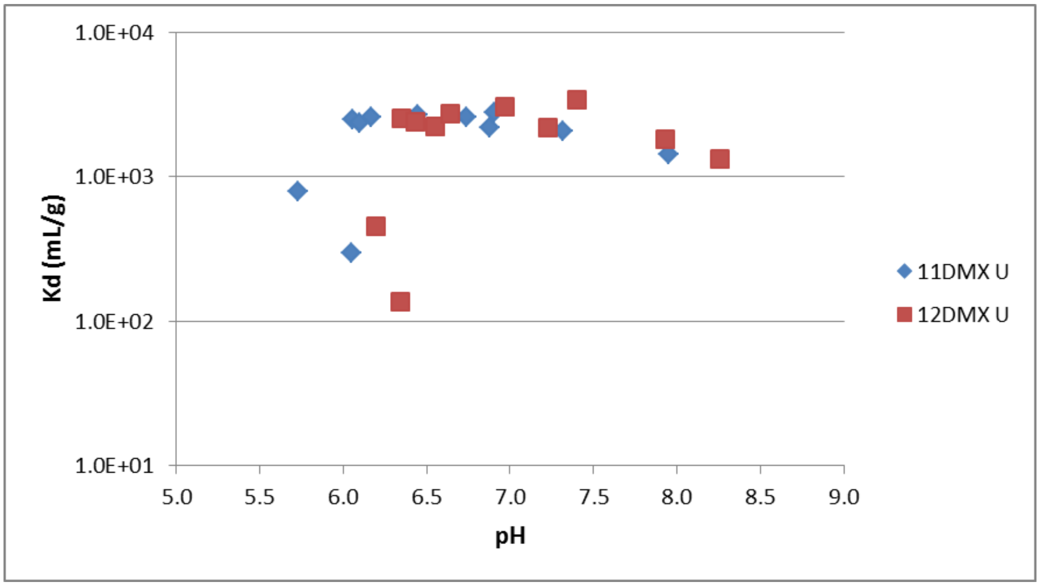

Figure 22: Calculated U K_d Values for Sorption onto MX-80 in Dilute Solution during the Kinetics Tests as a Function of pH. Changes in Calculated K_d may Result from Increases in pH over Time

3.1.2.2 Plutonium

Results of the kinetics tests with Pu (added as Pu-239) indicate that the Pu system reaches equilibrium after about 10 days (Figure 23). The effects of evaporation on pH and concentration that were evident in the U experiment are also seen with Pu, but are not as large. There is a small but steady increase in Pu concentration for the blank solution over the course of the experiment. The maximum calculated Pu K_d values are greater than 2×10^5 mL/g, but the average K_d value during the equilibrium period is 6×10^4 mL/g. The final concentrations of Pu are close to zero, so the calculated K_d values have a greater uncertainty and may be underestimated. The Pu K_ds stabilize through the end of the experiment, but there is significant variability in the results for Experiment 12DMX-Pu. For example, there is a large step change in Pu concentration for the 12DMX-Pu experiment for the sample collected on day 12 but later samples indicate a return to previous Pu concentrations. The cause of that excursion is unknown, but it may be that some of the solid phase was entrained during sampling (because of their size, the kinetics bottles were not centrifuged before sampling). The measured pH and Eh values (Figure 24) indicate that following the oxidizing excursion associated with spiking, solution Eh values returned to less than −300 mV in two days. The MX-80-bearing solutions remained between −300 and −500 mV with pH values between 6 and 6.5 throughout the remainder of the test, with the exception of a high Eh measurement on day 23 (same as observed in the U-bearing solutions). Because the Pu spike solution contained more HNO_3, the pH values for the Pu tests are generally lower than those for U. The slightly higher Eh values are consistent with the lower pH. The blank solution without MX-80 added had an average pH of 3.2 and an average Eh of −120 mV.

Both the U- and Pu-bearing kinetics experimental solutions exhibited a relatively rapid decrease in redox with a lowering of Eh to below −200 mV in about 2 days. The Pu results, however, indicate a slower approach to equilibrium sorption for Pu.

3.1.2.3 Neptunium

For Np (added as Np-237), results of the initial kinetics tests indicate that Np takes longer to reach sorption equilibrium than either U or Pu (Figure 25). The Np response in the solutions differs from U and Pu in several ways. First, the Np concentration in the blank experiment (without MX-80 added) increases steadily from the start of the test. While both U and Pu concentrations increased as their tests proceeded, the rate and relative magnitude of the change in Np is greater (e.g., the total U cpm/g increase was about 14% while Np cpm/g increased nearly 33%). Also, the sorption of Np onto the MX-80 proceeds relatively slowly along a near linear trend, similar to that observed for Tc. Both U and Np sorption increased rapidly as Eh decreased following spiking. Finally, there does not appear to be a clear plateau for the Np sorption—even at longer times when solute concentrations of the solutions were greater due to evaporative losses. Recall that in the U kinetics test, U sorption on MX-80 decreased during the time frame of U concentration increase in the blank solution. The behaviour of Np is different, and the magnitude of observed sorption of Np on MX-80 continues to increase for more than 21 days. The largest calculated K_d values are on the order of 3000 mL/g. Eh and pH of the solutions appear to stabilize in a similar time as observed for the U and Pu experiments (Figure 26). The Eh of the MX-80-bearing solutions stays below −300 mV for the majority of the test time frame. The pH for the MX-80 bearing solutions increases over time from approximately 6 early in the test to 7 near the end of the test. A plot of Np K_d versus pH suggests some of the Np sorption behaviour may be influenced by pH change (Figure 27). The slow sorption kinetics for Np are somewhat similar to those observed for Tc. It is unknown if the sorption rates observed are a result of redox limited processes or a function of pH change.

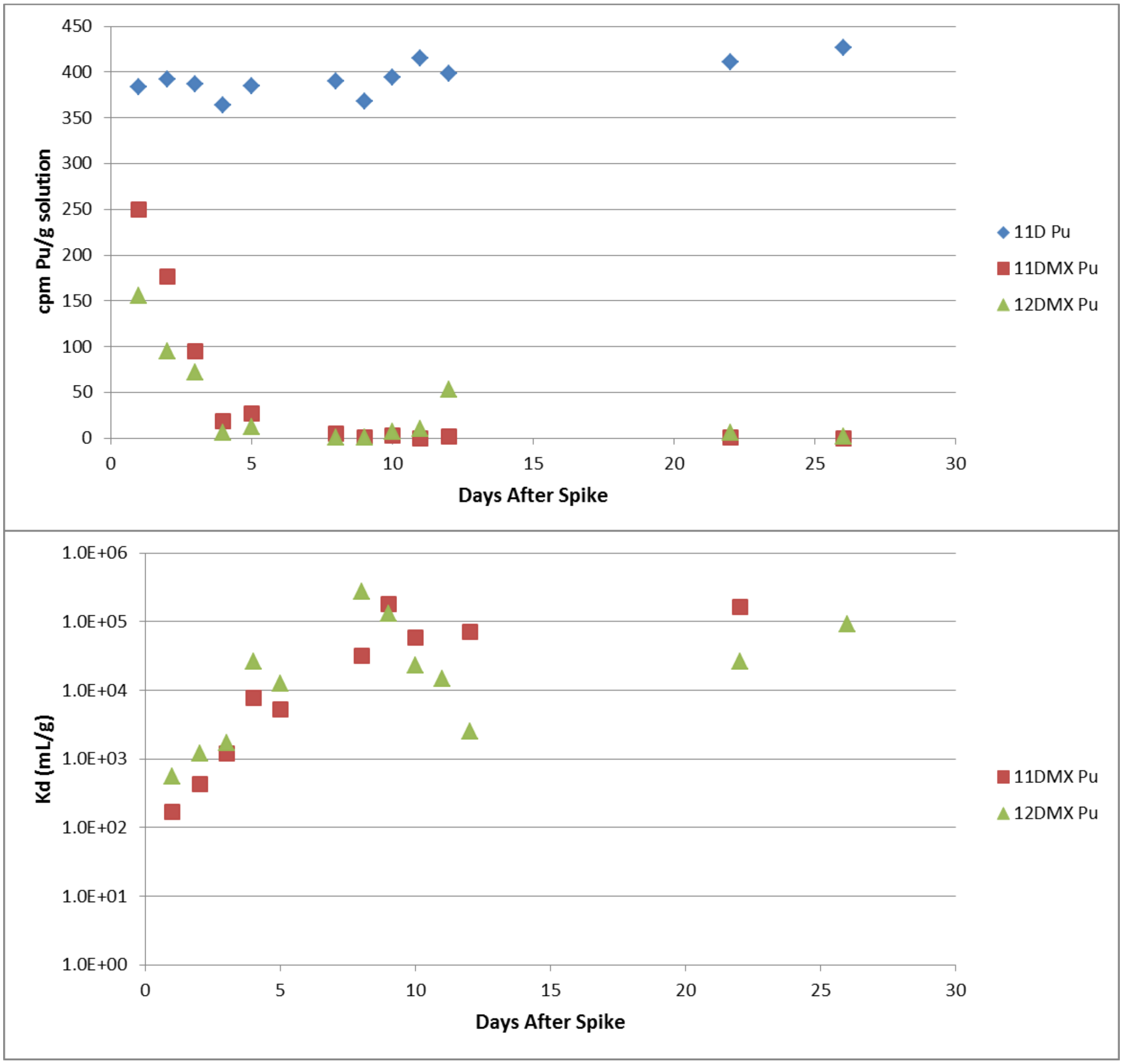

Figure 23: Measured Sorption over Time of Pu-239 on MX-80 in Dilute Solutions. Sorption Plateaus at about 10 Days

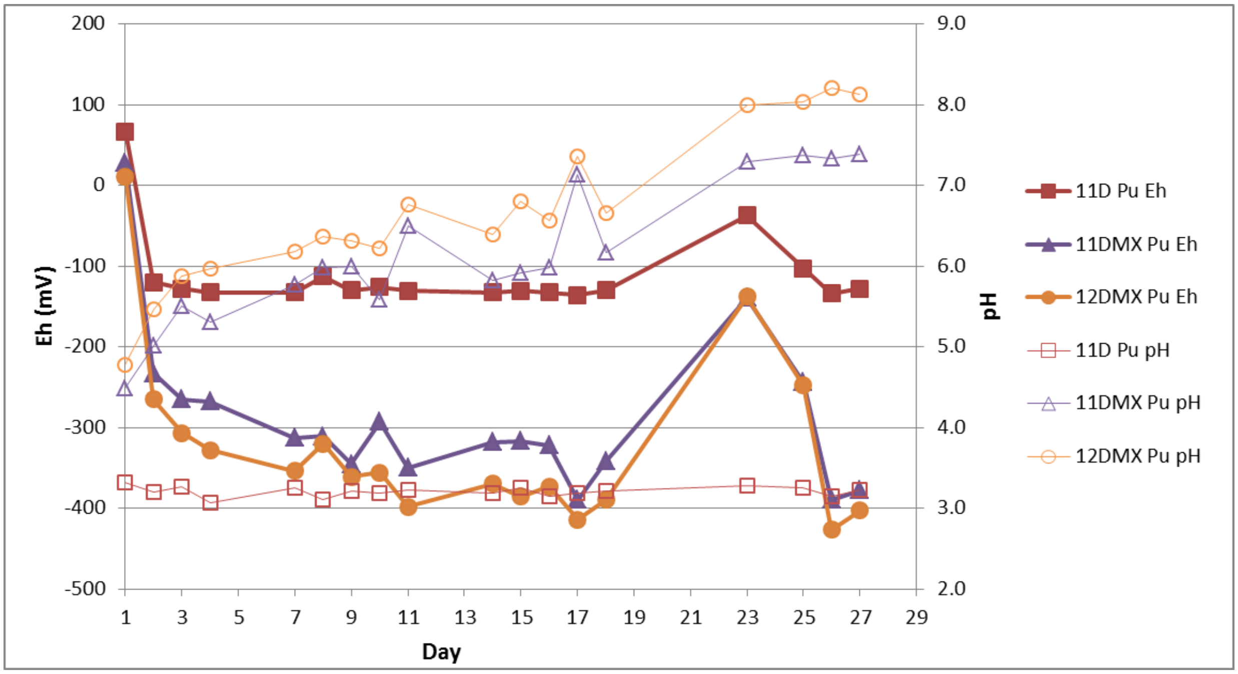

Figure 24: Change in Solution pH (Hollow Symbols) and Eh (Filled Symbols) over the Duration of the Pu-239 Sorption Kinetics Experiments in Dilute Solution

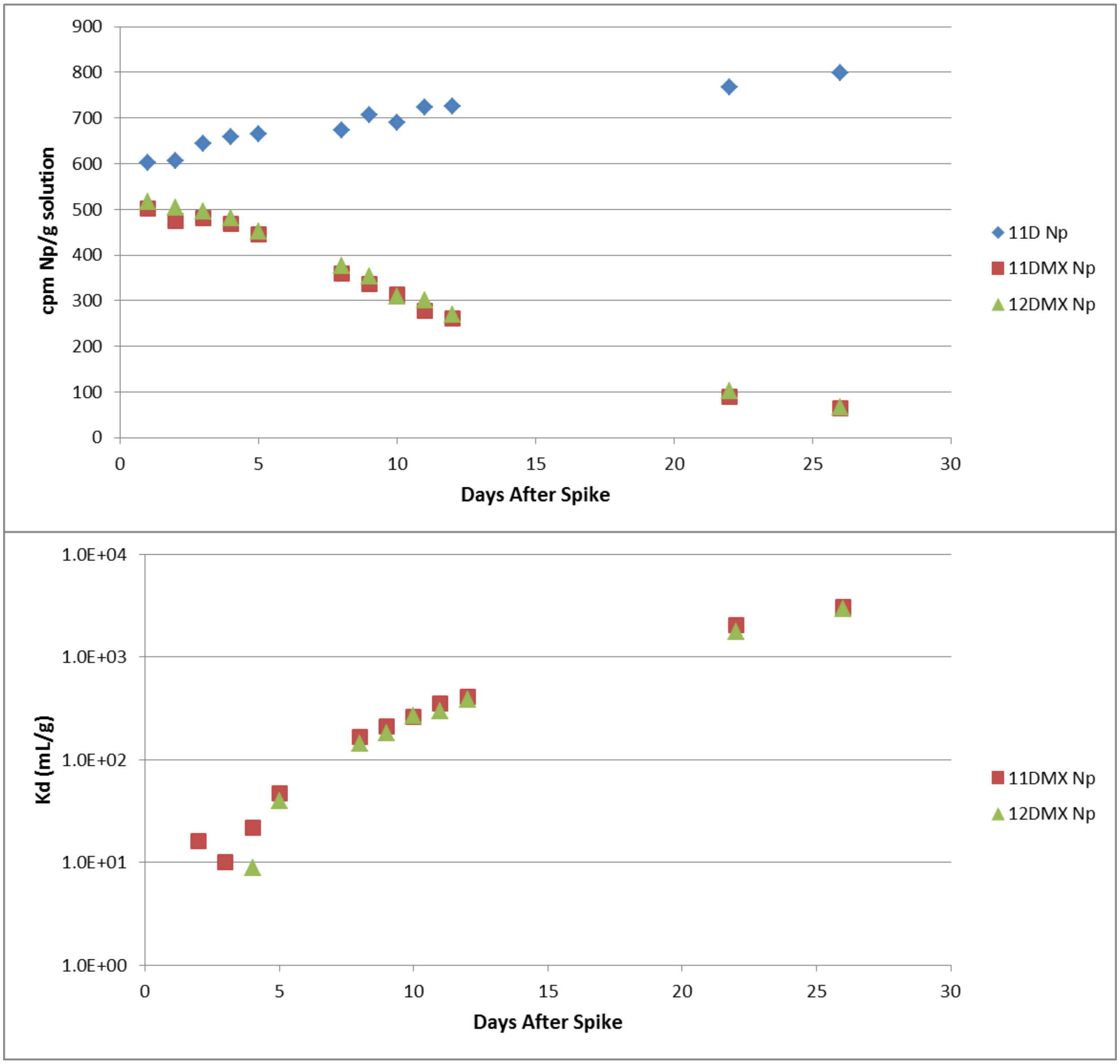

Figure 25: Measured Sorption over Time of Np-237 on MX-80 in Dilute Solutions. Sorption does not Plateau through the 27-day Test. The Observed Increase in Np Concentration in the Blank (11D-Np) may be Caused by Evaporation of the Experimental Solution

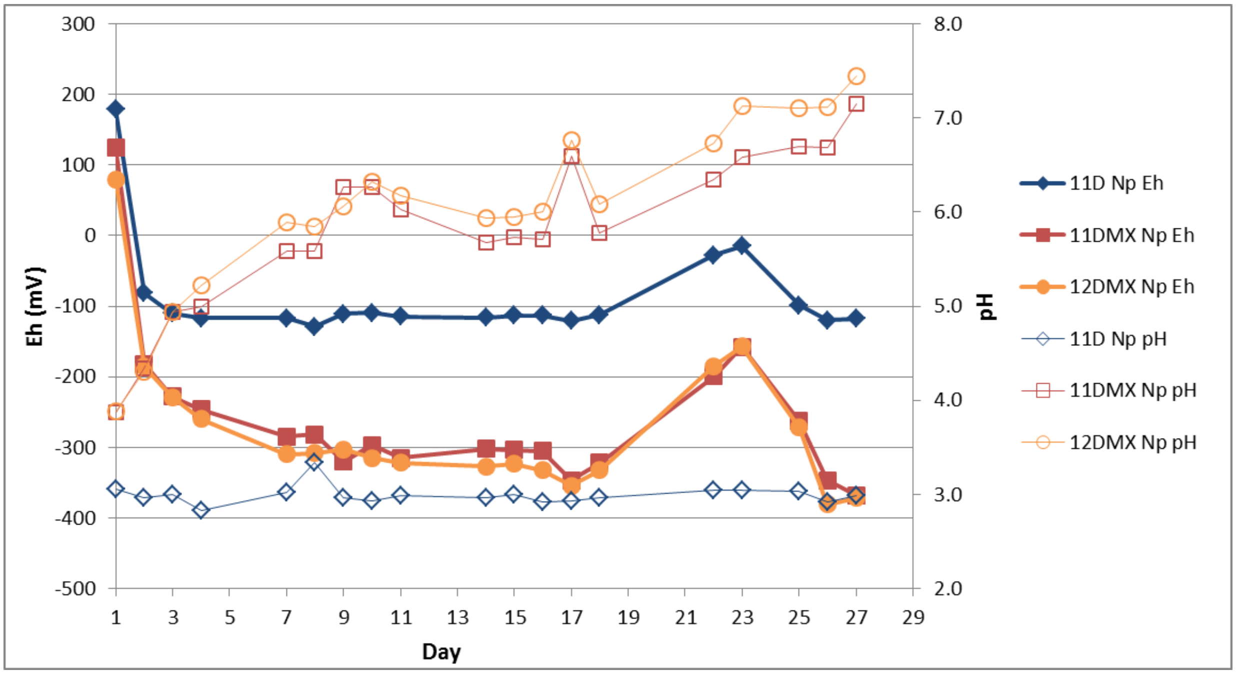

Figure 26: Change in Solution pH (Hollow Symbols) and Eh (Filled Symbols) over the Duration of the Np-237 Sorption Kinetics Experiments in Dilute Solution

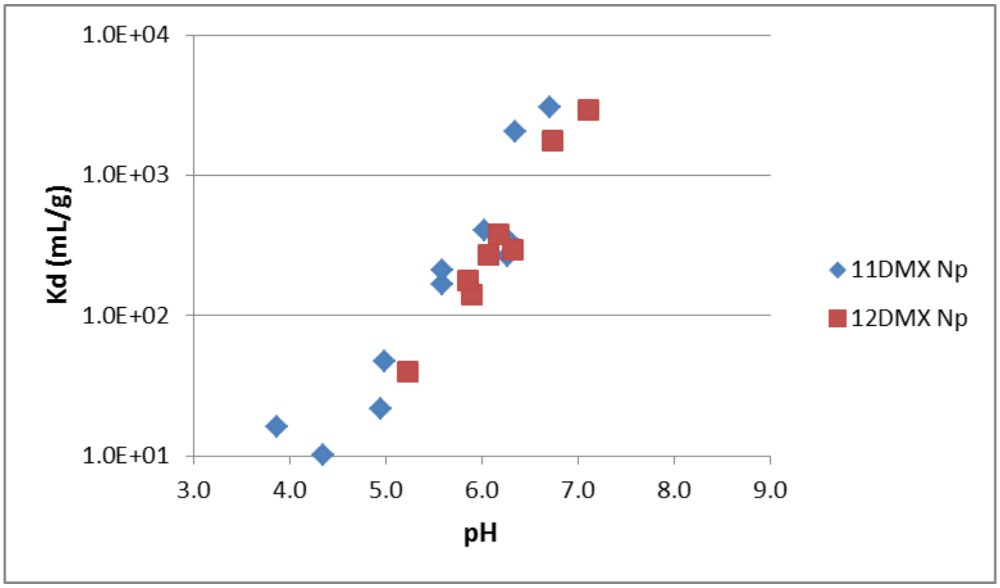

Figure 27: Calculated Np K_d Values for Sorption onto MX-80 in Dilute Solution during the Kinetics Tests. Changes in Calculated K_d may Result from Increases in pH over Time

3.1.3 Second Series Uranium, Plutonium, and Neptunium Sorption Kinetics on MX-80 in Dilute Solutions

A second series of kinetics experiments on U, Pu, and Np were conducted immediately following the first group of experiments. The second set of tests again used dilute solutions (11D) containing MX-80. The experimental containers again were 250-mL PC bottles to which 0.5 g of MX-80 were added followed by addition of ~250-mL of solution. Experiments equilibrated for 25 days prior to adding the radionuclides. Prior to nuclide addition the average pH and Eh of the solutions were 7.6 and −280 mV for the solutions without MX-80 and 8.5 and −382 mV for the solutions with added MX-80. Overall, the experimental setup was similar to the first actinide kinetics test. One significant difference included addition of a pH adjustment step following spiking of the experimental solutions. Because the pH values of blank solutions in the previous tests were significantly lower than that of the MX-80-bearing solutions, there were some questions as to whether the tests adequately evaluated the potential for precipitation or container sorption. Based on the compositions of the radionuclide stock solutions, estimates for the necessary aliquot volume of 0.1 M NaOH were made, and this aliquot was added immediately after quantifying the amount of added spike. Another difference was the number of experimental solutions used. This series of experiments included one blank solution and one solution with added MX-80 for each nuclide. There were no duplicate experiments. This second group of actinide experiments was also planned for a longer duration to evaluate whether an equilibrium or plateaus value of Np sorption could be reached. These tests ran for 62 days total and for 37 days after addition of the nuclides.

3.1.3.1 Uranium

Results of the second series of kinetics testing for U were very consistent with results from the first tests (Figure 28). Uranium sorption reached a maximum in about 5 days and plateaued at a K_d value of 1500 mL/g. Again, the blank solution showed an increase in U concentration with time, and calculated K_d values decreased after the initial peak. Addition of the NaOH as a neutralizing agent had mixed effects (Figure 29). The amount of added NaOH was more than was needed for the U solutions. The blank solution, which did not have a buffer, exhibited an increase in pH to 10. This pH increase appears to have had a significant impact on U concentrations in the blank solution. The initial concentration of U in the blank was about 25% low, and was measured at 1800 cpm/g instead of the 2400 cpm/g expected based on mass of U spike added (Figure 28). The U concentrations increased in the blank solution as the experiments progressed and reached the expected starting value after pH dropped below 9. The cause of the lower than expected U concentration may be precipitation of some U in the blank solution, but the initial U concentration of 4×10^{-7} M is below expected solubility limits. An alternative explanation is that the changes in U concentration are evidence of sorption onto the PC container at higher pH. Even as U(VI), U has been shown to sorb significantly onto containers in the absence of a competing substrate (Pabalan et al., 1998). As the pH returned to lower values—near 8.2 after 12 days—the U sorption on the PC container decreased to near 0. After a period of stable readings, U concentrations in the blank later increased as observed in the previous test, possibly due to evaporative effects.

The redox and pH conditions for the solution with added MX-80 remained fairly stable over the course of the test. For the 37 days following spiking, Eh remained near −400 mV. Although steps were taken to limit the amount of bubbling after starting the sorption test, an estimated 14% of solution mass was lost to evaporation from the 11MXU2 experiment.

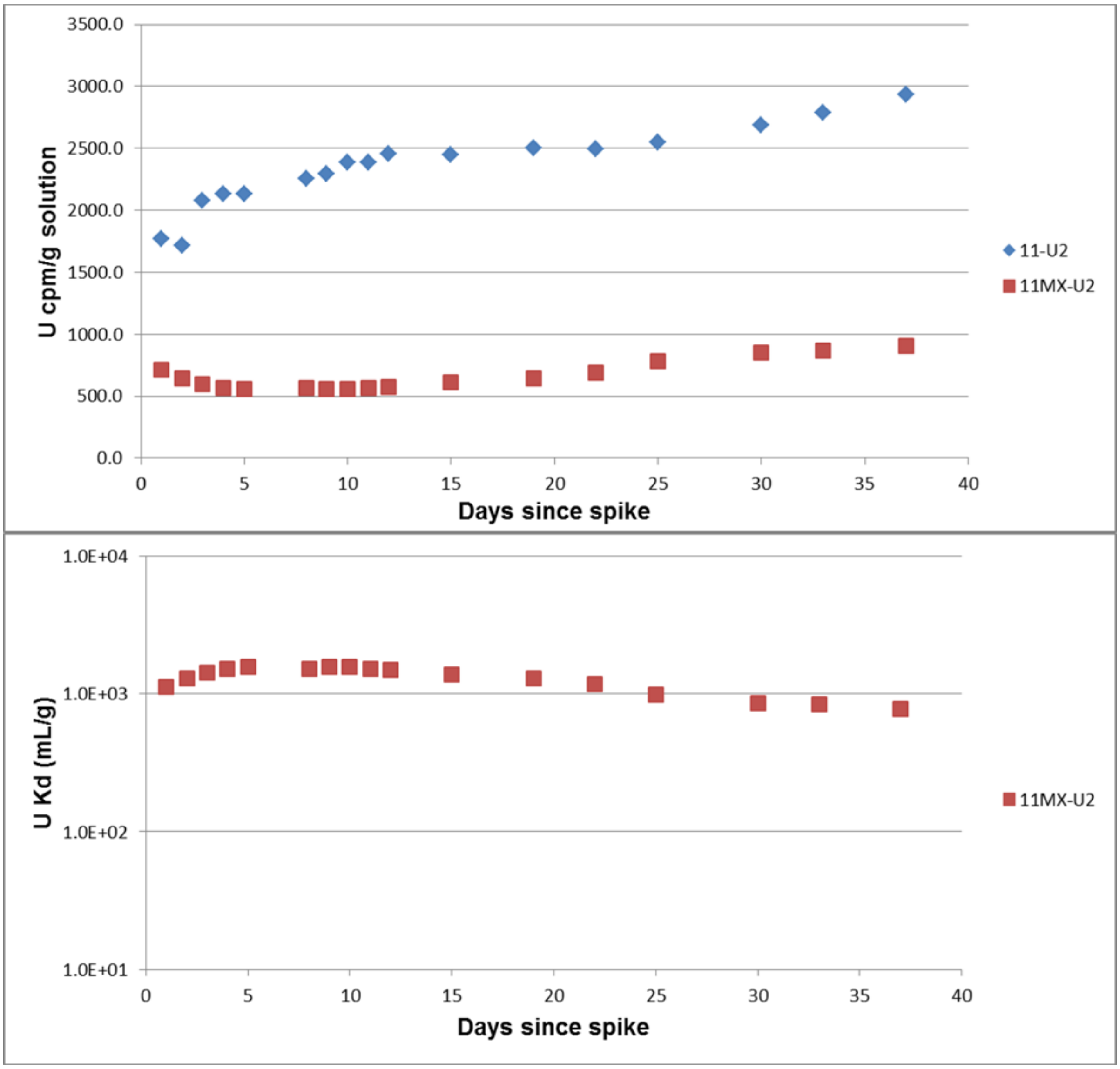

Figure 28: Results of Second Kinetics Test Using U and MX-80 in Dilute Solution. U Concentrations (cpm/g) in Solution (Top) and Calculated U K_d (mL/g) (Bottom) are Shown. The 11-U2 Experiments had no Added MX-80. Like the Previous Kinetics Test, U Sorption Equilibrium was Reached in 5 Days

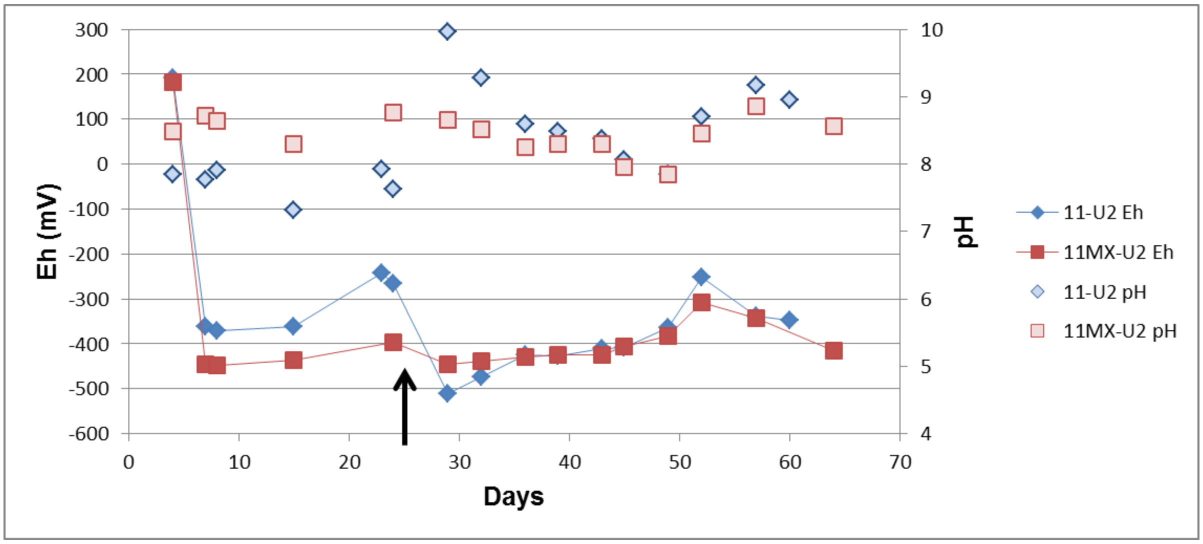

Figure 29: Results of pH and Eh Measurements for the Second U Kinetics Experiment in Dilute Solution. Data for Solutions before and after Spiking with U-233 are Shown (Spike Date Shown by Black Arrow). pH of the Blank Solution (11-U2) Increased to 10 after Spiking

3.1.3.2 Plutonium

Results for the second Pu sorption kinetics test were similar to those of the first experiment (Figure 30). The sorption of Pu reached an equilibrium K_d plateau of about 7.8×10^4 mL/g (as compared to about 6×10^4 mL/g previously) within 5 to 10 days. As the kinetics experiment progressed, Pu K_d values increased to as much as 1×10^5 mL/g, but the variation was high because of the low count rates measured for Pu in the MX-80 solution (nearly all the Pu was removed from solution). Unlike the U experiment, the Pu concentration in the blank solution remained constant. The experimental containers were handled similarly for both U and Pu, so it is difficult to discern or explain why Pu exhibits less change in concentration over time in the blank experiment. The initial concentration of Pu in the dilute system at pH of 4.7 was determined to be 8.4×10^{-9} M based on the measured activity, while the average Pu concentration in the MX-80-bearing solutions was 2×10^{-11} M after 10 days. The initial Pu concentration for the previous experiment, which did show increase in Pu in solution, was 1×10^{-8} M, thus it seems unlikely that the behaviour is solubility related. Like the second U kinetics experiment, addition of the NaOH as a neutralizer of the acidity added with the Pu spike was ineffective (Figure 31). Although no deleterious effects were observed, the blank solution pH dropped to below 5 after the spike and remained low, and the solution with added MX-80 dropped initially but ended with a similar pH at equilibrium as the initial Pu test. Eh of the MX-80-bearing solution was maintained between −300 and −400 mV for the duration of the test. Eh of the blank solution was higher (−220 mV), as would be expected for its lower pH.

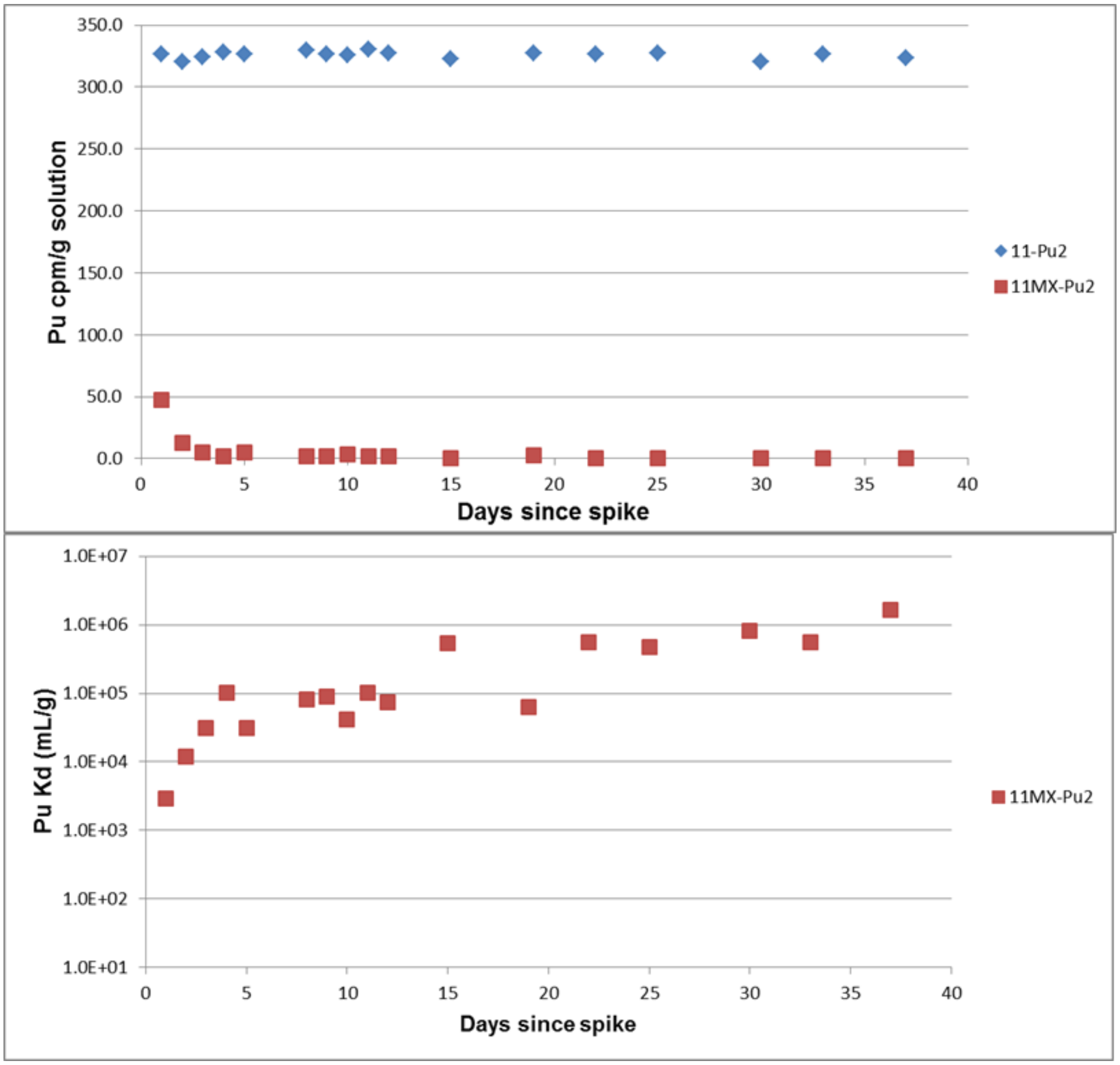

Figure 30: Results of Second Kinetics Test Using Pu and MX-80 in Dilute Solution. Pu Concentrations (cpm/g) in Solution (Top) and Calculated Pu K_d (mL/g) (Bottom) Values are Shown. The 11-Pu2 Experiment had no Added MX-80. Like the Previous Kinetics Test, Pu Sorption Equilibrium was Reached in within 10 Days

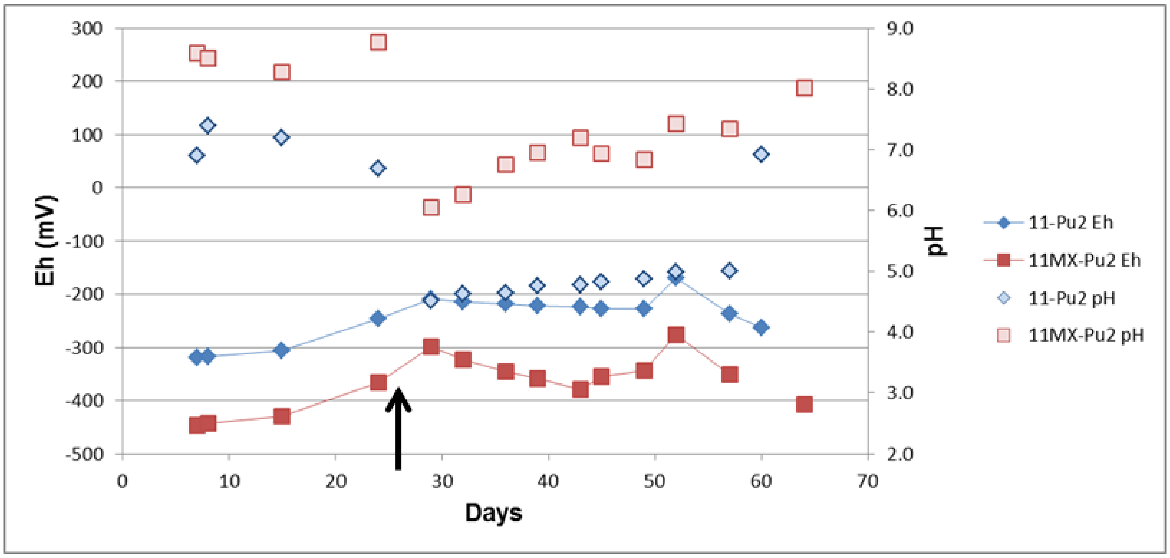

Figure 31: Results of Measurements for the Second Pu Kinetics Experiment in Dilute Solution. Data for Solutions (Eh as Squares, pH as Diamonds) before and after Spiking with Pu-239 are Shown (Spike Date Shown by Black Arrow)

3.1.3.3 Neptunium

The results of the second Np kinetics experiment mirrored the results of the first test (Figure 32). Sorption of Np increased (increasing K_d values) slowly over a longer period than observed for U or Pu. The rate of K_d increase was quite similar to the rate observed in the first kinetics test. For example, at 25 days following addition of Np, K_d values in the first test were approximately 2900 mL/g and were approximately 2800 mL/g in the second. The K_d values increased throughout the 37 days following addition of Np, but indicated some change toward equilibrium around 35 days. The final maximum measured K_d at the end of sampling was on the order of 9300 mL/g. Like previous tests, the concentration of Np in the solution without MX-80 increased slowly but steadily throughout the test. The total change of Np concentration in the blank solution was less than in the previous test (15% versus 33% previously), suggesting that there were fewer losses from evaporation and that efforts to minimize evaporation were impactful.

Addition of the Np spike produced an initial Np-237 concentration of 1×10^{-7} M and resulted in a decrease in pH for both experimental solutions (Figure 33), but redox conditions recovered rapidly after spiking and Eh values were maintained at −300 mV and −150 mV for the MX-80 and blank solutions, respectively.

The second series of kinetics experiments for U, Pu, and Np in dilute solutions, with and without MX-80 added, confirmed the results of the first set of tests. The magnitude and rate of sorption for all three nuclides were similar in both sets of tests. Changes in the amount of sparging used to ensure solutions remained at equilibrium with the low-O_2 glove box atmosphere resulted in fewer losses to evaporation, but significant losses over time still occurred. Eh and pH were adequately controlled and remained at or below the target value of −200 mV for all the tests containing MX-80. Attempts to neutralize the acid content of the radionuclide stock solutions were ineffectively applied, but in the case of U, did provide some evidence of what a precipitation or sorption transient would look like. The changes in Eh with changes in pH alone were consistent with expectations. In all the tests, the redox conditions recovered from the transient associated with spiking within 2–3 days. The tests indicated that, for dilute solutions, U and Pu reached equilibrium with respect to sorption between 5 and 10 days. The results indicated that Np, like Tc, was slow to reach equilibrium (more than 30 days). As expected for Tc, the slow kinetics observed seem to be a result of the transition from Np(V) to Np(IV), rather than sorption. Moreover, the solubility of Np(IV) at pH 6 is likely 10^{-8} to 10^{-9} M, so the changes in Np concentration could also be the result of precipitation of Np. The batch sorption experiments were designed with these observations in mind.

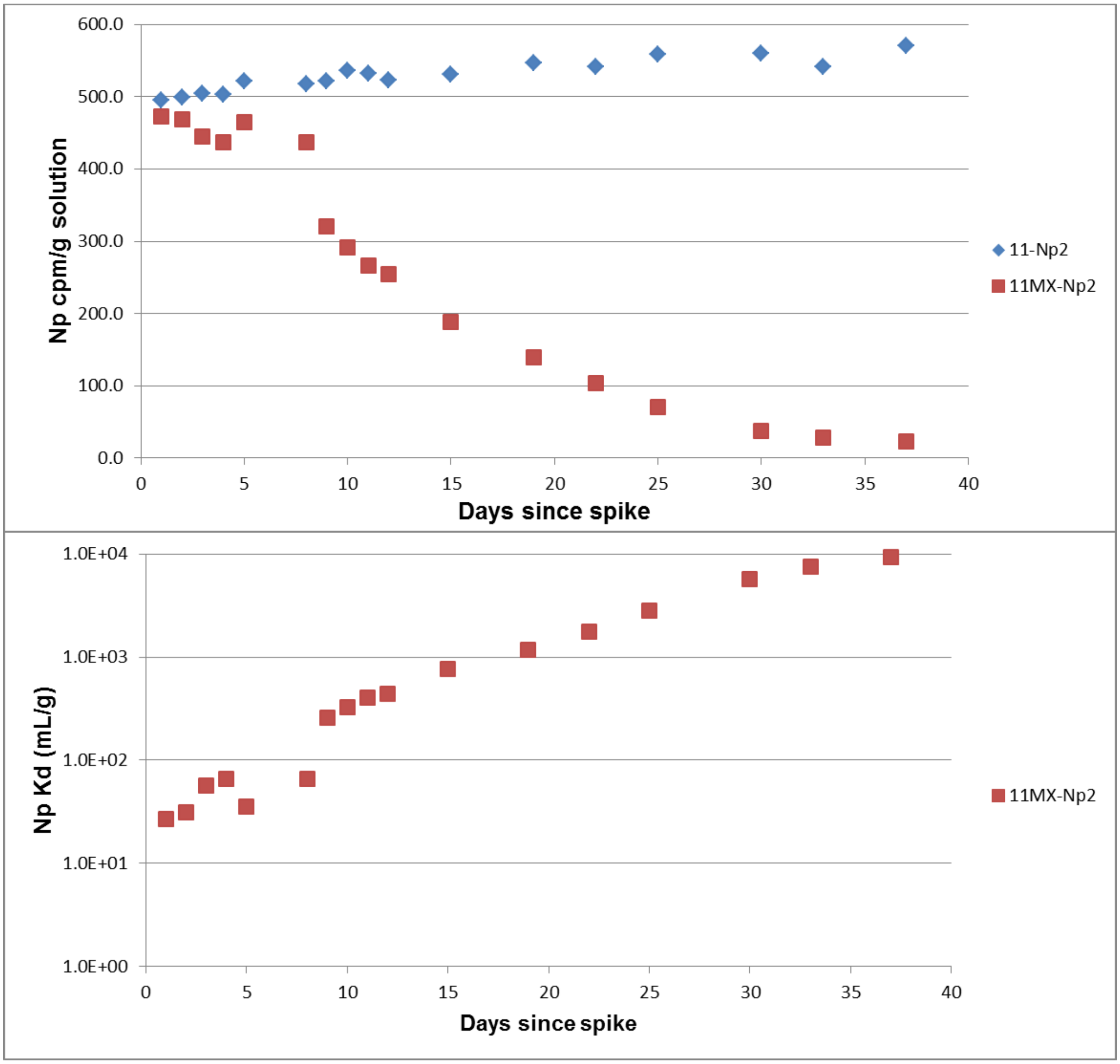

Figure 32: Results of Second Kinetics Test Using Np and MX-80 in Dilute Solution. Np Concentrations (cpm/g) in Solution (Top) and Calculated Np K_d (mL/g) Values (Bottom) are Shown. The 11-Np2 Experiment Had no Added MX-80. Like the Previous Kinetics Test, Np Sorption Equilibrium was not Reached during the Experiment

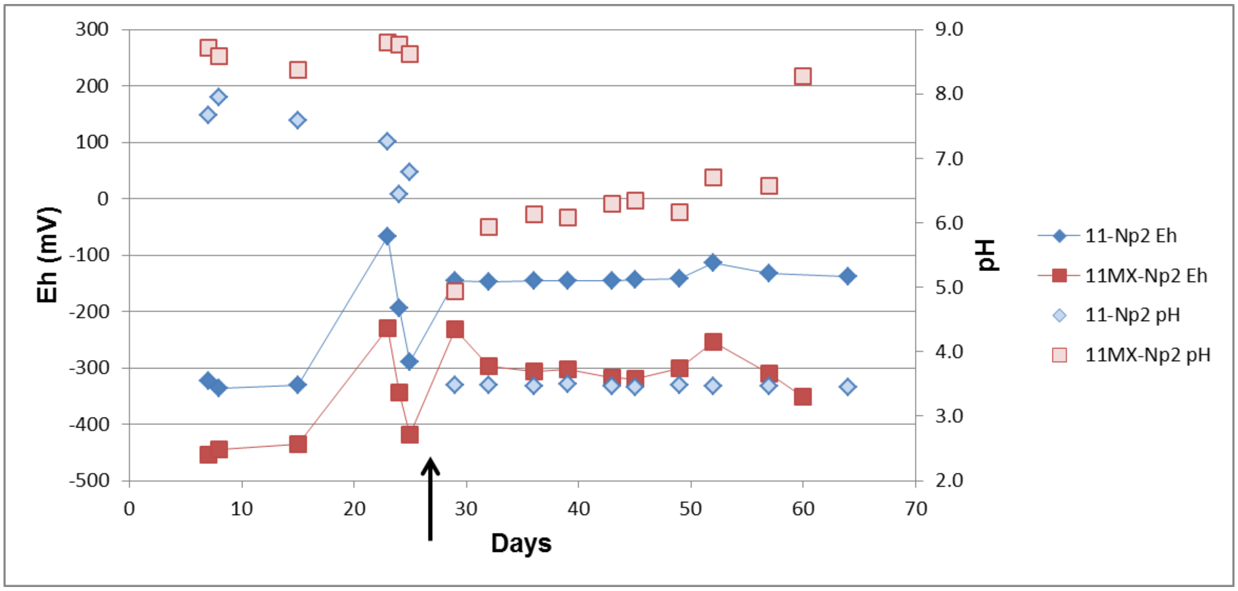

Figure 33: Results of Measurements for the Second Np Kinetics Experiment in Dilute Solution. Data for Solutions before and after Spiking with Np-237 are Shown (Spike Date Shown by Black Arrow)

3.1.4 Uranium, Plutonium, and Neptunium Sorption Kinetics in Brines

The final group of kinetics experiments evaluated the rates of sorption of U, Pu, and Np on MX-80 in brine solutions. The dilute experiments were conducted first because there were fewer uncertainties in measuring pH and Eh of the solutions, which provided opportunities to improve experimental protocols. Because the bulk of planned experiments would be conducted using brine solutions, kinetics tests using brine were required. The previous scoping test with Tc in brine solutions indicated that significantly different behaviour of the actinides might be expected relative to the results of the dilute solution experiments.

Like the previous kinetics experiments, 250-mL PC bottles were used for the brine solutions. Approximately 0.5 g of MX-80 was added to the PC bottles followed by 250 mL of brine solution (Solution 13). Unlike previous tests, only one experimental container per nuclide was used, and all solutions had MX-80 added. The experimental solutions and solids equilibrated for 12 days prior to addition of the radionuclide aliquots. The brine kinetics tests continued for 37 days after nuclides were added. Samples (0.5-mL) were collected in duplicate in 20-mL LSA vials approximately daily after the addition of nuclides, and the interval between samples was lengthened to 3-4 days near the end of the tests. Measurement of solution pH and Eh were made every 3-4 days during the experiments. Experimental solutions were bubbled to facilitate gas-exchange and redox stability, but bubbling times were kept to a minimum.

3.1.4.1 Uranium

The results of U sorption onto MX-80 in the brine kinetics test are summarized in Figure 34. The sorption behaviour of U over the course of the experiment was quite different from that observed in the dilute kinetics tests. Following addition of the U spike, which resulted in an initial U concentration of 3×10^{-7} M, U concentration in the brine solution decreased continuously over the duration of the experiment. Contrary to results of the dilute tests, there was no observed equilibrium or plateau of U sorption over the 37 days tested. The U behaviour in the brine test is reminiscent of the behaviour of Tc and Np in the dilute solutions and suggests that the rate of change is related to or controlled by the reduction of U(VI) to U(IV). Brine solution pH and Eh stabilized shortly after addition of the U spike. Eh values stabilized and were maintained at approximately −100 mV with a pH of ~7.1 for the sorption portion of the test.

The maximum U K_d values measured during the experiment ranged from 200 to 460 mL/g over the last two weeks of the test. These values are about an order of magnitude lower than observed for U in the dilute experiments and may be influenced by a mix of U(VI) and U(IV) in solution.

3.1.4.2 Plutonium

Results of the Pu-brine sorption kinetics experiments are shown in Figure 35. Of the three actinides, Pu sorption behaviour in brine was the most similar to its behaviour in dilute solutions. However, the rate of decrease of Pu concentration in the brine solution was slower than was observed for the dilute experiments. Although the rate of change in Pu sorption did slow after about 25 days, increases in sorption continued through the end of the test. The maximum Pu K_ds measured over the final 10 days of the test ranged from 1.0×10^4–1.7×10^4 mL/g. These values are also about an order of magnitude lower than those measured in the dilute solution tests. Similar to the U–brine kinetics experiment, pH and Eh values stabilized quickly after addition of the Pu spike and were maintained at approximately 7.1 and −120 mV for the sorption portion of the Pu experiment. Plutonium concentrations in solution ranged from 6.3×10^{-9} M at the test start to 2.1×10^{-10} M at the end of the test.

3.1.4.3 Neptunium

The results for the examination of Np sorption onto MX-80 in the brine solution are shown in Figure 36. No decrease in Np concentration was measured during the 37 days of the test, despite solution pH and Eh conditions equivalent to those established in the U and Pu tests. Solution redox recovered quickly after addition of the Np spike, and Eh and pH were stable at −100 mV (or less) and approximately 7.0 for the duration of the sorption portion of the test. The lack of sorption is similar to that observed for Tc in brine. In fact, Tc and Np had sorption responses similar to each other in both the dilute and brine kinetics tests. Thus, it is assumed that Np(V) was not reduced to Np(IV) and the lack of sorption is indicative of the Np(V) behaviour in solution.

The results of the experiments examining the kinetics of sorption for U, Pu, and Np in brine revealed several significant differences in their brine system behaviour relative to the dilute system results. U and Pu exhibited sorption in the brines, but the magnitude of the maximum sorption observed for both nuclides was about an order of magnitude less than observed in the dilute tests. Similarly, both U and Pu exhibited slower sorption kinetics in the brine tests, and neither appeared to reach a true equilibrium K_d or distinct plateau over the length of the experiments. On the other hand, Np showed a complete lack of sorption onto MX-80 in the brine test even though experimental solution conditions were equivalent for all three actinides. This behaviour was likely caused by the failure to reduce the Np to Np(IV). Assessment of solution losses during the tests showed that mass lost through evaporation (between 17 and

18%) was lessened through modification of experiment protocols that reduced the frequency and length of bubbling.

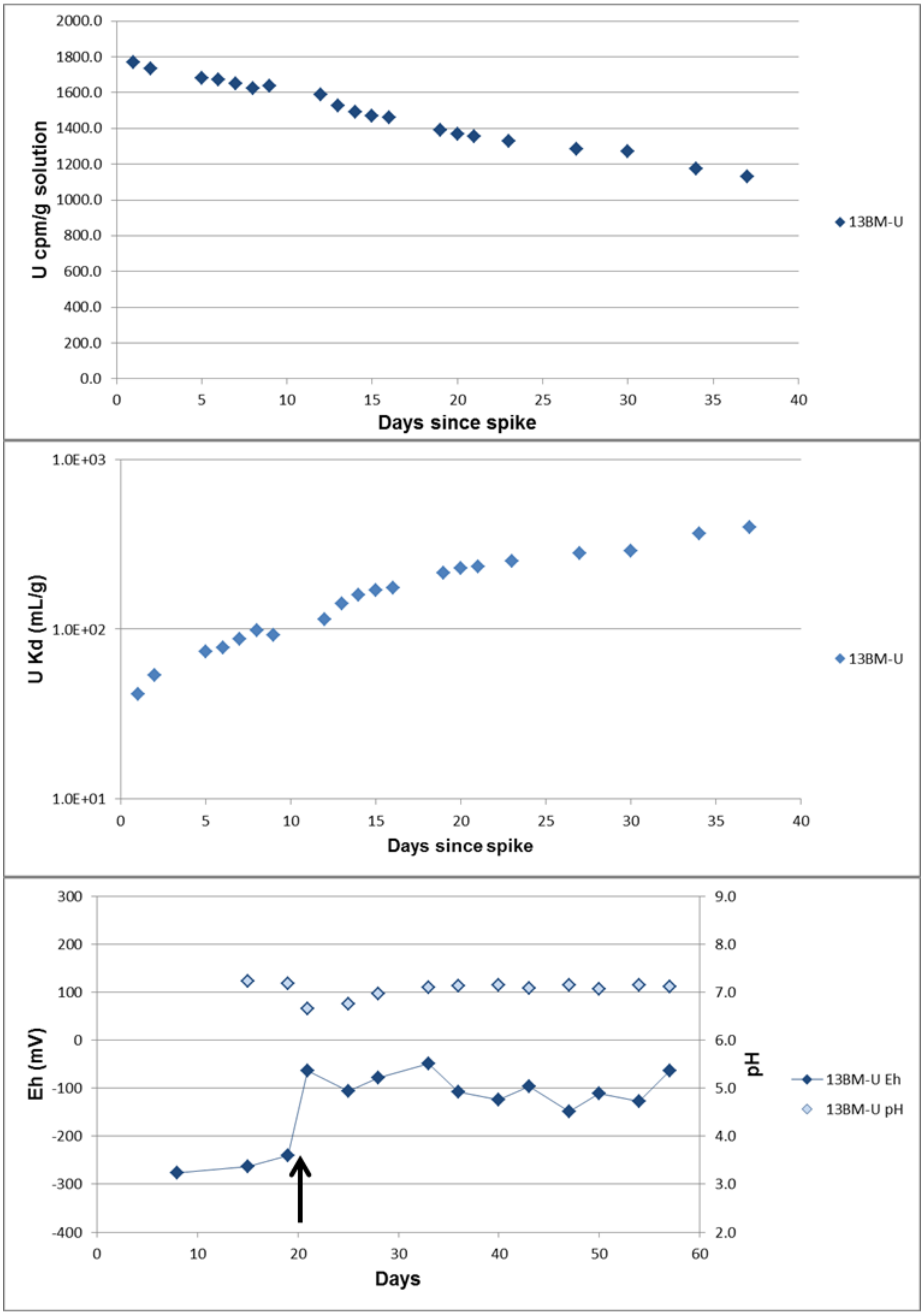

Figure 34: Results for Sorption Kinetics Experiments with U Added to Brine Solution Containing MX-80. Change in Concentration of U (Top), Calculated U K_d Values (Middle), and Variation in Measured pH and Eh (Bottom) are Shown. Arrow Indicates Time of Addition of U to Experimental Solution

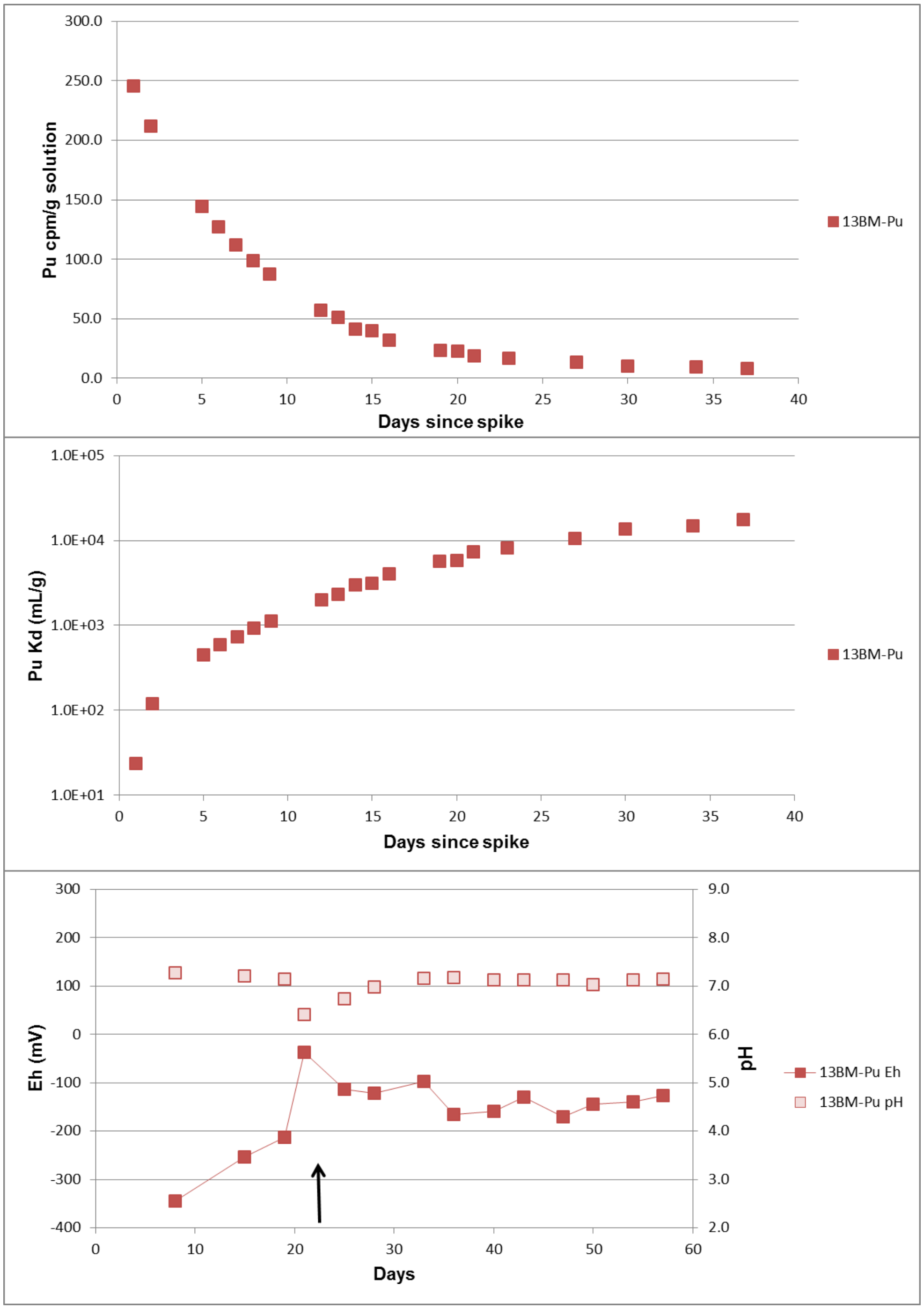

Figure 35: Results for Sorption Kinetics Experiments with Pu Added to Brine Solution Containing MX-80. Change in Concentration of Pu (Top), Calculated Pu K_d Values (Middle), and Variation in Measured pH and Eh (Bottom) are Shown. Arrow Indicates Time of Addition of Pu to Experimental Solution

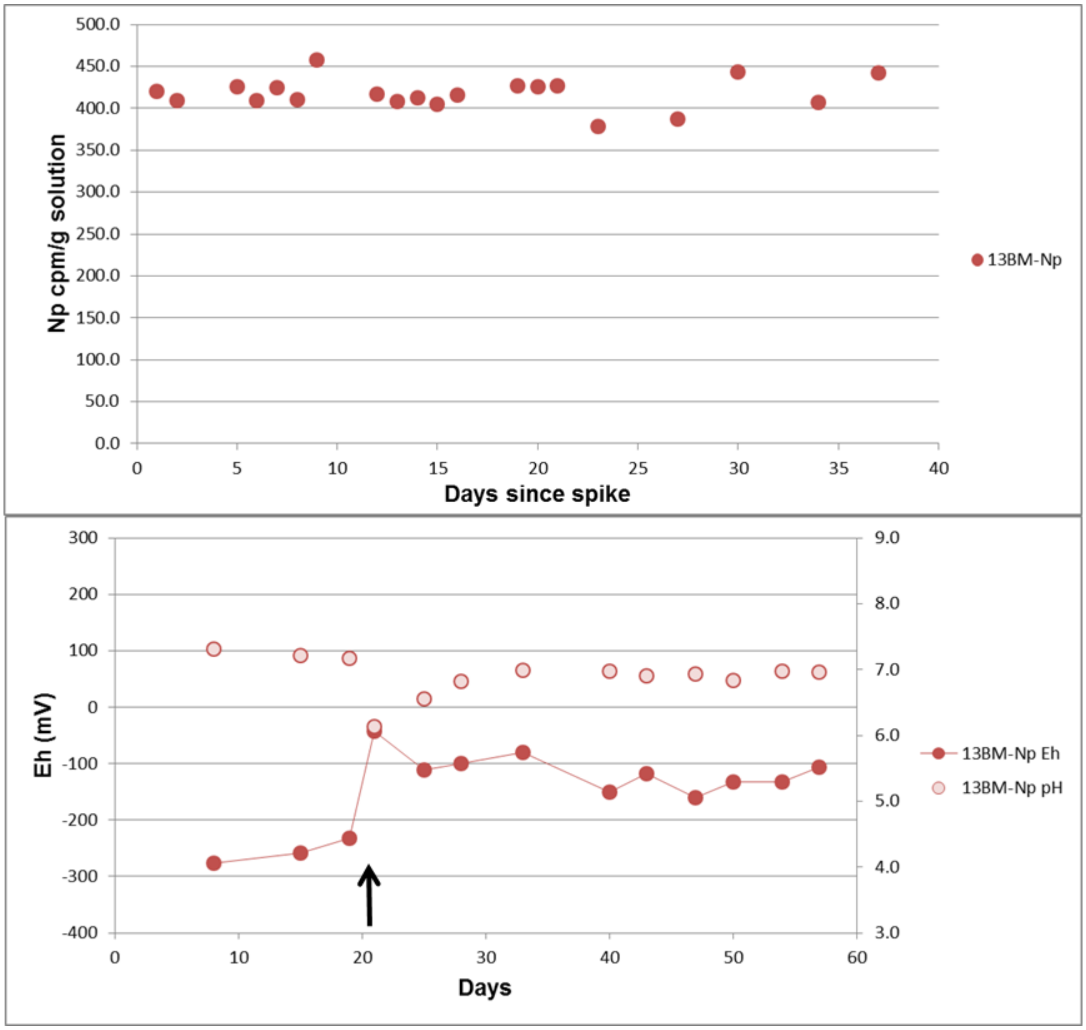

Figure 36: Results for Sorption Kinetics Experiments with Np Added to Brine Solution Containing MX-80. Change in Concentration of Np (top) and Variation in Measured pH and Eh (Bottom) are Shown. Arrow Indicates Time of Addition of Np to Experimental Solution. Np K_d Values were not Calculated as there was no Observed Decrease in Np Concentration

3.2 RESULTS OF BATCH EXPERIMENTS

Batch sorption experiments were conducted for all the elements of interest (As, Np, Pu, Se, Tc, and U) in both brine and dilute solutions. For each element and solution combination, at least one experiment was conducted for each of the three substrates (shale, limestone, and MX-80). The batch experiments were conducted in several series designed to optimize the available space and resources needed to conduct the tests. Generally, experiment groups would consist of one or two elements and their associated brine and dilute tests. For all batch experiments, three replicate (triplicate) experimental solutions were included for each element–solution type–substrate combination.

The batch experiment design was discussed in detail previously, but in general, 50-mL PC Oak Ridge-type centrifuge tubes containing 0.5 g of solid and 30 mL of solution were spiked with a solution of the element of interest to start the batch tests. Each group of experimental solutions was equilibrated with the solids prior to adding the element spike.

After a given equilibration time period, which varied over the course of the project, batch experimental tubes were centrifuged at 10,000 rpm (11,600 RCF) for 10 minutes and sampled for analysis of the element of interest. After collection of the sample, each experimental solution was measured for pH and Eh.

The results, organized by element, are detailed in the following sections.

3.2.1 Technetium Batch Sorption

The scoping tests investigating Tc sorption were discussed in Section 2.2.1. Three subsequent groups of Tc batch sorption experiments were conducted. Two of these used brine solutions (Solution 14) (Experiments Tc14B1 & 2) and the other used a dilute solution (Solution 14D) (Experiment Tc14D1). Based on the kinetics testing, the expected equilibration time for Tc was long (>60 days), so the Tc tests were planned for as long as possible given the resource and time constraints on project progress. The experiments were allowed to continue for 116 days following addition of the Tc-bearing solution. Also, because the previous scoping tests showed no evidence of Tc sorption in brine, a 500-μL aliquot of 0.01 M $Na_2S\bullet9H_2O$ was added to each experimental Tc solution at the time of spiking in an attempt to facilitate the potential reduction of Tc to Tc(IV).

Results of the Tc batch sorption experiments are summarized in Figures 37 and 38. Figure 37 shows the amount of Tc sorbed from solution onto the shale, limestone, and MX-80 solids in terms of percent sorbed. In the figure results of each experimental tube are provided to indicate the variation in values between replicates. In Figure 38, K_d, pH, and Eh values are averaged for all replicates, and error bars representing ±1 standard deviation ($\pm1\sigma$) of replicate sample K_d values are also shown (if larger than the symbol)[2]. Significant sorption is observed for both brine and dilute solution experiments. For MX-80 and limestone, more than 90% of the Tc initially placed in solution is sorbed and the calculated K_d ranges from 10^4 to 10^5 mL/g (Figures 37 and 38, Table 10). Results for the shale, however, are different. In both brine and dilute solutions about 20–30% of the Tc initially in solution is sorbed and the calculated K_d is about 10–20 mL/g (Table 10). The differences in magnitude are much greater than could be explained by the specific surface areas of the MX-80 (26.2 m^2/g) and shale (10.3 m^2/g), which differ by less than one order of magnitude, not three. An alternative explanation for the low Tc sorption on the shale is that entrainment of particles occurred during sampling. This appears unlikely, however, as the variability in sorption for the 9 different shale experimental solutions is small. If particle entrainment was occurring, a wide variation in sorption magnitude would be expected. The three sets of triplicates were also handled and centrifuged at different times (experiments were processed by experiment number, not substrate type), so there is little basis for a systematic error affecting only the shale experiments during sampling. Furthermore, shale experiments in batch sorption tests for the remaining elements do not exhibit any similar evidence of anomalously low sorption or particle entrainment. The difference in the measured magnitudes of Tc sorption between the shale and other substrates is perplexing. Vilks (2011)

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[2] Error bars are calculated for all data, but in some cases the range of error is smaller than the symbol size used in the plot. In these cases, the error bars are often not visible.

reports K_d values for Tc(IV) sorption on shale (based on a review of literature) of approximately 1 mL/g. Vilks (2011) notes the shale K_d seems low, but it is apparently consistent with the results observed in this test. As results of later experiments will show, there appears to be little influence of substrate type (with the possible exception of the limestone) on the measured sorption of the other radioelements.

The equilibrium pH of the dilute experiments is moderately impacted by the addition of the sodium sulphide and ends between 8.5 and 9.0. The pH of the brine solutions remained near neutral, but the final measured Eh values are higher than targeted (or anticipated given preliminary measurements and verified maintenance of the low-O_2 experimental environment) at about −5 mV for the shales and −20 mV for the MX-80 and limestones. The minor difference in Eh between the shale-bearing brine solutions and the limestone and MX-80-bearing solutions does not seem to be sufficient to explain the observed difference in sorption. Moreover, a similar difference between shale and limestone/MX-80 sorption behaviour is observed in the dilute solutions, which have Eh values ranging between −130 and −210 mV. The low Eh values for the dilute solutions are well within the range of conditions for Tc(IV).

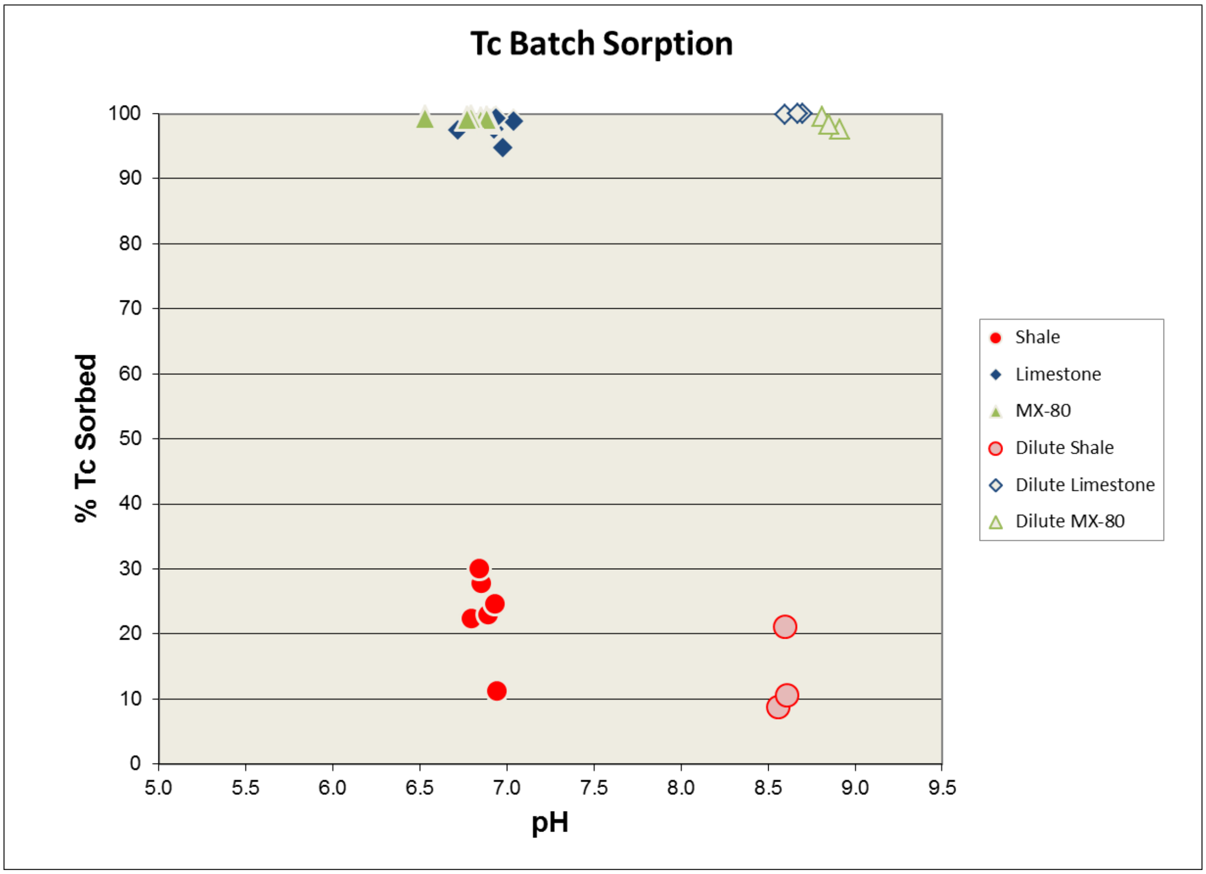

Figure 37: Percentage of Tc-99 Sorbed onto Shale, Limestone, and MX-80 Substrates in Brine and Dilute Solutions. Sorption onto Shale was Low for both the Brine and Dilute Experiments Despite pH and Eh Conditions Equivalent to the Limestone and MX-80 Experiments

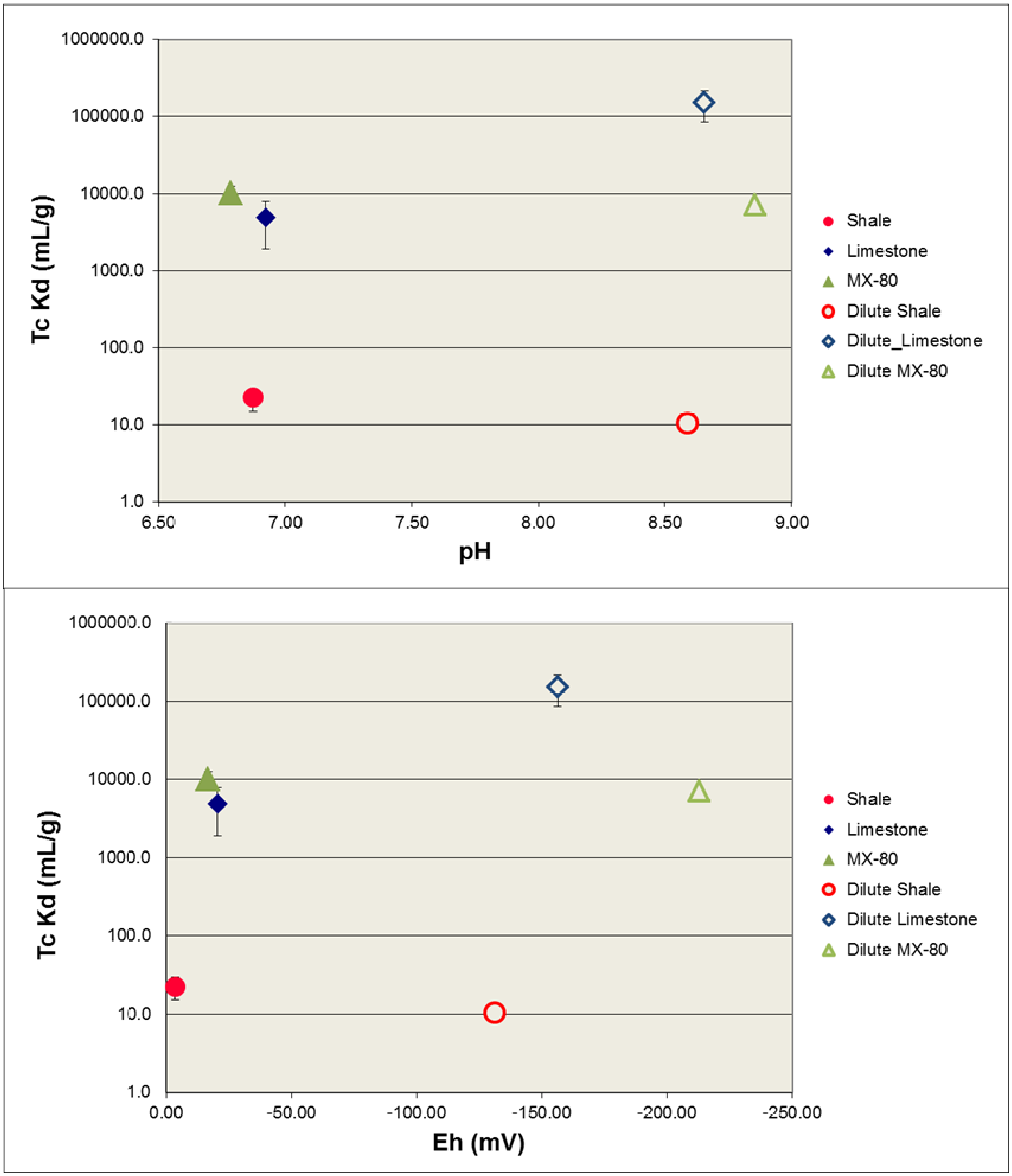

Figure 38: Sorption of Tc-99 Sorption onto Shale, Limestone, and MX-80 as a Function of pH and Eh. Points Represent Average Values of K_d, pH and Eh for all Replicates (6 for Each Phase in Brine and 3 for Dilute). Magnitude of Sorption on Each Phase for Brine and Dilute Solutions is Similar over the Range of Eh Values

Because the observed sorption in the brine and dilute solutions is similar despite their differences in measured Eh, we assume Tc is in the same oxidation state [Tc(IV)] in both sets of experiments. As we observed in previous experiments, Tc(VII) showed no evidence of sorption in either dilute or brine solutions. Thus, the positive sorption suggests strongly that the Tc is reduced. The measured Eh of the experimental solutions appeared to increase over the duration of the experiment. Figure 39 shows results of measurements of Eh over time for select experimental tubes (only a few were sampled during the course of the experiment). Comparison of Eh versus time indicates an increase in Eh for both brine and dilute samples and for all three substrates during the test. This increase occurred despite periodic re-equilibration of the solutions with the glove box atmosphere. The cause of the increase in Eh is not known, but previous studies have noted the degradation of added reductant over time (Berry et al., 2007). Despite the increase in Eh, which results in average Eh values near 0 mV for the brines, the magnitude of observed sorption is similar for both the brine and dilute solutions.

One concern regarding the Tc sorption test is that the initial concentration of Tc was on the order of 2×10^{-7} M, which is greater than some estimates of Tc(IV) solubility. However, the sorption results do not appear to be influenced by solubility limitations because the shale-bearing solutions have the same pH and Eh conditions yet show little or no loss of Tc. If Tc was precipitating, we would expect loss from all solutions. Final Tc concentrations for shale-bearing solutions, at the same environmental conditions and with final Tc concentrations of about 1.7×10^{-7} M, show no evidence of solubility issues.

Figure 40 presents the results of the Tc batch sorption experiments along with Tc(IV) sorption values taken from other literature sources (Berry et al., 2007; Andra, 2005b; Vilks, 2011) for comparison. Data from Berry et al. (2007) were collected under reducing conditions in both seawater and dilute solutions for bentonite, crushed tuff, and crushed granodiorite. These data are plotted as Sea-B, Sea-T, and Sea-G, respectively, with the dilute results at pH values above 9. The range of values reported by Berry et al. (2007) is similar to our results. The recommended ranges of values for Tc(IV) sorption onto Callovo-Oxfordian argillite (COx) from Andra (2005b), and for Tc(IV) sorption onto bentonite from Vilks (2011), are quite consistent with the results of the brine and dilute tests. Moreover, as previously discussed, the value of Tc(IV) sorption on shale reported by Vilks (2011) is very low, and is consistent with the low sorption of Tc on shale observed in these tests.

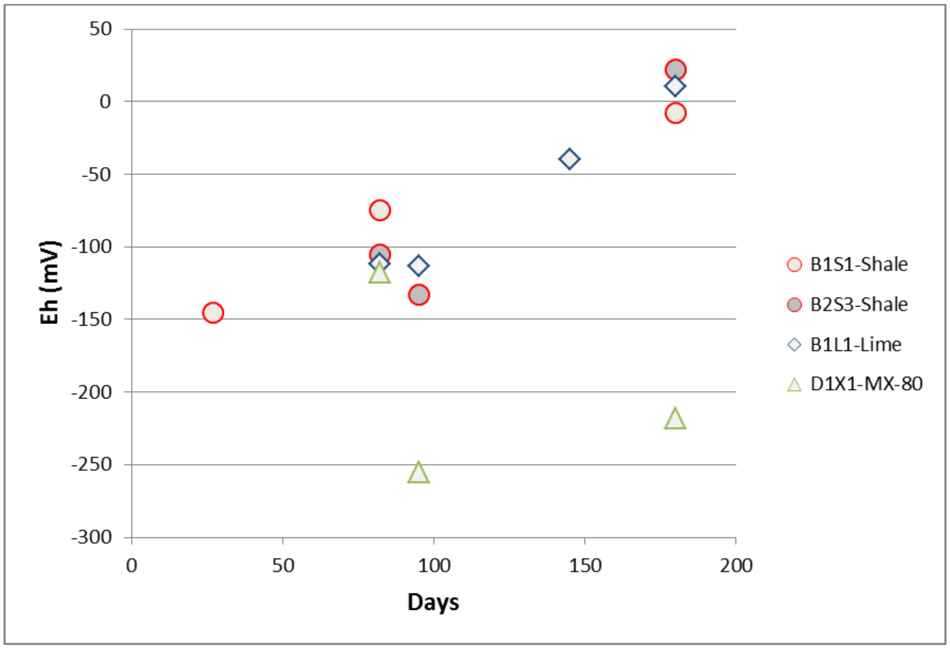

Figure 39: Changes in Measured Eh over Time for Selected Tc Sorption Experimental Solutions (B Denotes Brine, D Denotes Dilute). Solutions were Spiked at 80 Days

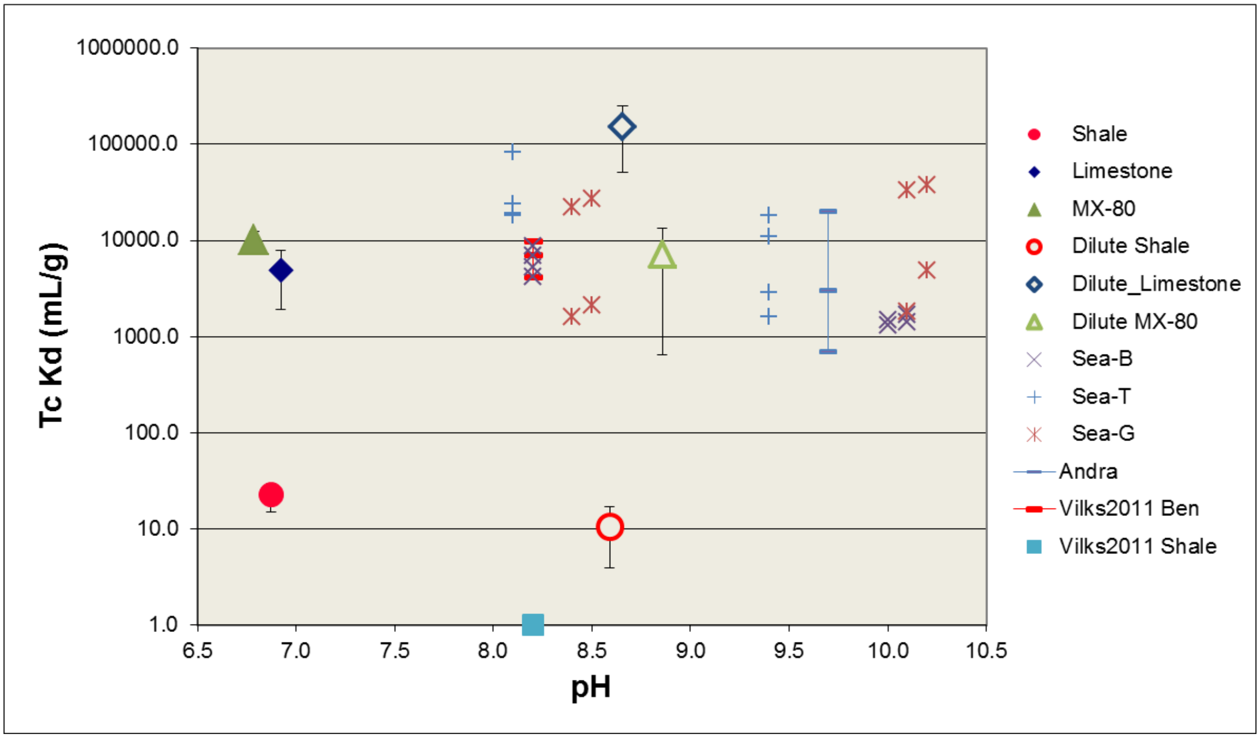

Figure 40: Summary of Results for all Tc Sorption Experiments. Also Included are Results from Berry et al. (2007) for Tc(IV) Sorption on Bentonite (Sea-B), Tuff (Sea-T), and Granodiorite (Sea-G) in Seawater and Dilute Solutions. Recommendations of Tc(IV) Sorption Values from Andra (2005b) (Argillite) and Vilks (2011) (Bentonite and Shale) are also Shown

3.2.2 Neptunium Batch Sorption

Like Tc, results of kinetics testing in brine and dilute solutions suggested there might be difficulties in measuring Np sorption in the batch experiments. Four sets of batch experiments were conducted with Np, two using brine solutions (Solution 13 and Solution 14) and two using dilute solutions (Solution 14D). The initial sorption experiment was conducted over a 30-day period while the second group of tests was conducted over 57-days. The dilute kinetics test results provided some indications that Np would sorb in the dilute solutions, but whether Np sorption would be measured in brines was unclear.

The first Np batch sorption experiment examined sorption using brines only and included shale, limestone, and MX-80 as substrates (Experiment Np13B1). An aliquot of 0.1 M NaOH was also added to each experimental container at time of spiking to neutralize some of the added HNO_3 in the Np stock solution. The initial Np concentration for this test was 2×10^{-7} M.

Results of the initial 30-day sorption test indicate some evidence of Np sorption in the brines (recall that no sorption was observed in the Np brine kinetics test), but the magnitude of sorption was low, ranging from ~20–30% or equivalently a K_d of 12–30 mL/g (Figures 41 and 42). Measured Eh values at time of sampling ranged from near 0 to −80 mV, and the solution pH values ranged from 5 to 7. Although sorption was evident in all experimental solutions, the magnitude of sorption was low. The K_d values measured are difficult to separate from K_d values measured for Np(V) in other experiments (e.g., Bertetti et al., 2011; Nagasaki et al. 2015). However, similar to what was observed for U and Pu in the brine and dilute kinetics tests, the magnitude of Np sorption in the brines was about an order of magnitude lower than the Np K_d values measured in the dilute kinetics tests at the same pH values. Thus, it is difficult to conclusively state using the sorption results alone that there was a failure to reduce Np(V) to Np(IV) in the brines (although the low K_ds do seem to favour an oxidized form of Np, calculations indicate the Eh-pH conditions were suitable for Np(IV)) (Hu et al., 2009; Takeno, 2005).

A second set of Np batch sorption experiments was conducted using brine and dilute experimental solutions and an initial Np concentration of 7.8×10^{-7} M (Experiments Np14B1, Np14D1 & D2). Results of the second Np batch sorption tests are provided in Figures 43 and 44. Figure 43 displays results in terms of percent Np sorbed on each substrate for all replicate solutions. Figure 44 presents results for replicate averaged values of K_d, pH, and Eh. Also shown are error bars indicating $\pm1\sigma$ of the K_d value measurements for replicates (if larger than the symbol).

Results of the second group of Np batch experiments are remarkably consistent with results obtained in the previous batch and kinetics tests. The Np K_d values for limestone and MX-80 in the brine solutions is ~12 mL/g, essentially the same as measured for all three substrates previously. The shale–brine experiments showed almost no sorption, and although K_ds can be calculated they likely are equivalent to 0 mL/g when considering uncertainties. The K_d values for shale and MX-80 in the dilute solutions bracket 1000 mL/g, and compare favourably to the Np K_ds of ~3000 mL/g observed in the first kinetics test for MX-80 (Np K_ds in the second kinetics test reached ~9000 mL/g). The dilute solutions with added limestone have higher Np K_ds, averaging of 3.5×10^4 mL/g; these values may be enhanced by favourable sorption and inclusion of Np into calcite (the solutions are at saturation with respect to calcite) (Heberling et al., 2008; Hu et al., 2008; Zavarin et al., 2005). Measured Eh values are high for the brines (0 to +40 mV), but are adequately reducing (less than −150 mV) for the dilute solutions.

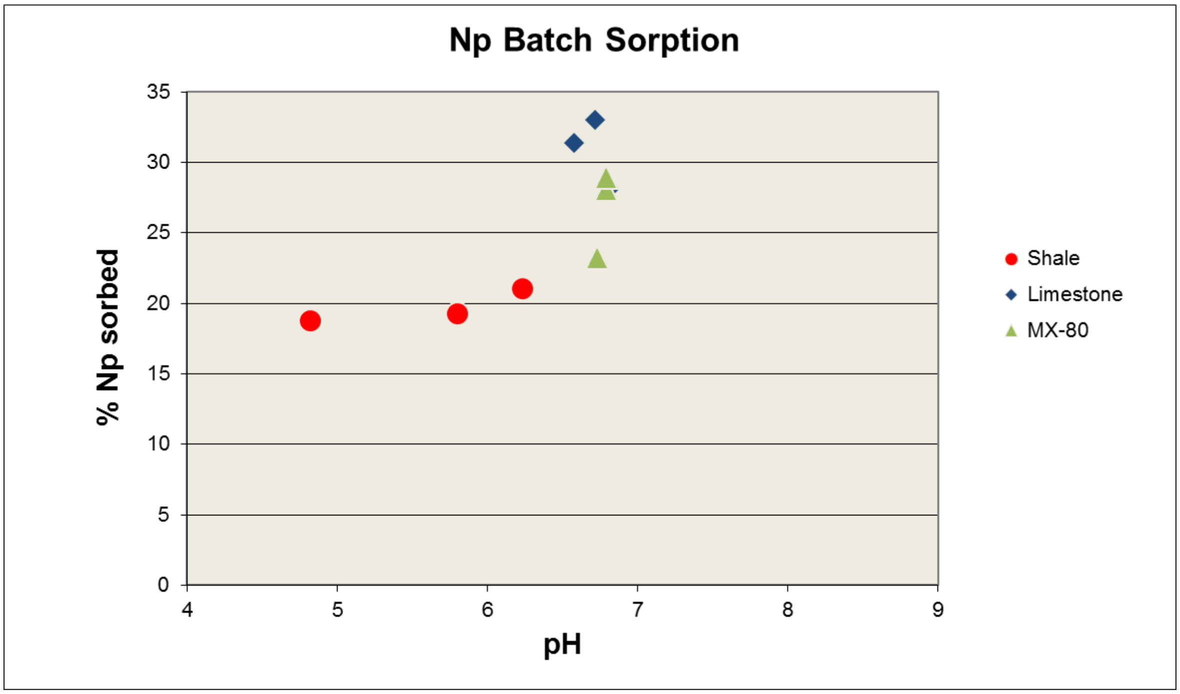

Figure 41: Sorption of Np onto Shale, Limestone, and MX-80 in Brine Solutions. Individual Results for Replicate Solutions are Shown

The Np batch sorption tests exhibit a mixed set of results. In dilute solutions over a range of pH from 6–9 and at Eh values of −150 mV and below, significant sorption of Np is observed. Kinetics tests using MX-80 suggest that even after 57 days the Np sorption may have not reached equilibrium (likely limited by rate of reduction from Np(V) to Np(IV)). The measured values of Np K_d in the reduced, dilute experiments are high at 10^3–10^4 mL/g but Np(V) sorption onto minerals is also significant at the same pH values in the absence of CO_2(g) (Turner et al., 1998). In the brine tests, Np did not sorb or sorbed minimally (Figure 44). Again, this may either be a function of the effects of the brine versus dilute solution composition or it may be indicative of oxidized Np. The rather high Eh values in the Np batch sorption tests in brines are not helpful.

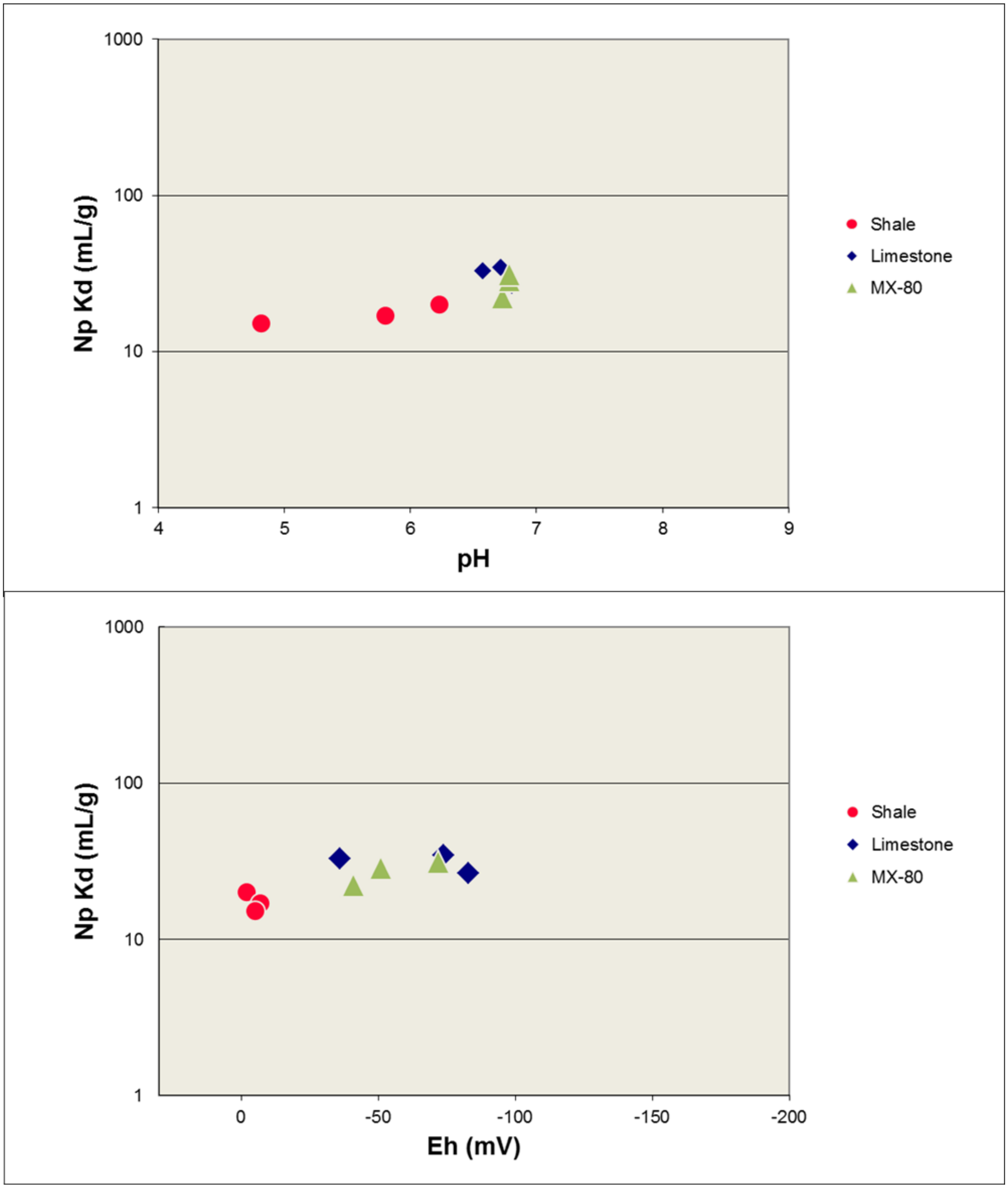

Figure 42: Results of Sorption of Np with Respect to pH (Top) and Eh (Bottom) onto Shale, Limestone, and MX-80 in Brine Solutions. The Observed K_d Values are Similar in Magnitude to those Measured for Np(V) Suggesting the Np was not Reduced to Np(IV) in the Experiments

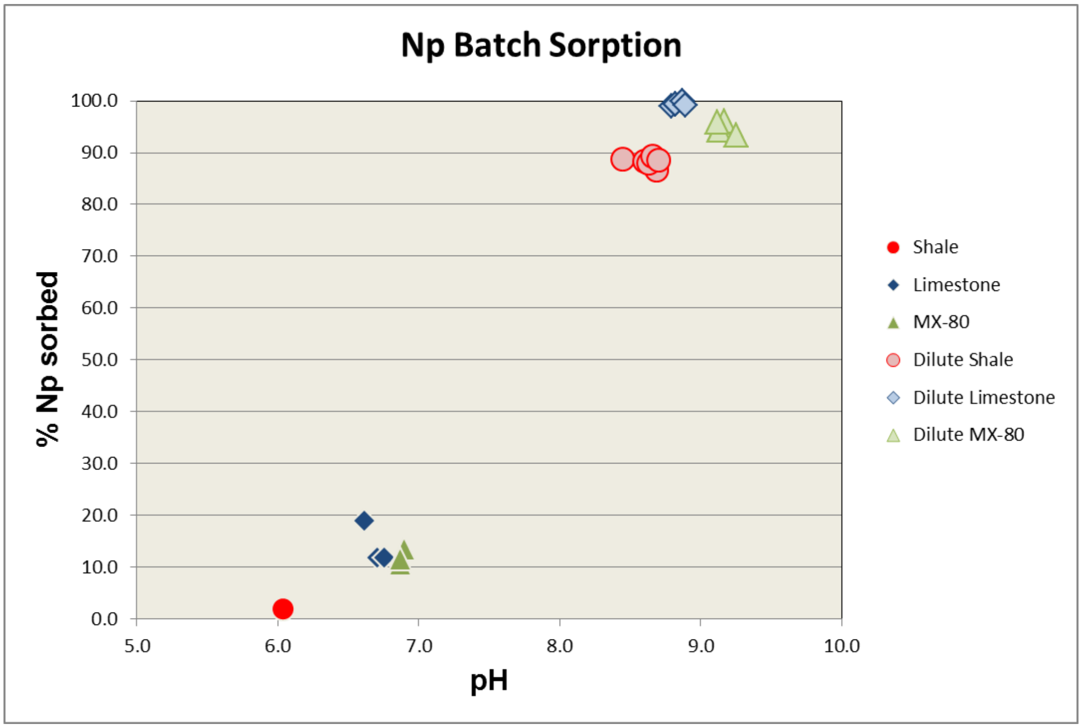

Figure 43: Sorption of Np onto Shale, Limestone, and MX-80 in Brine and Dilute Solutions. Individual Results for Replicate Solutions are Shown (3 Brine Replicates for Each Substrate, and 6 Dilute Replicates for Each Substrate)

A summary of all results from the Np sorption experiments is included in Figure 45. The Np data from this study are presented as averaged or representative Np K_d values for each substrate. For example, best estimates of equilibrium K_ds are taken from the kinetics data and averaged for inclusion in Figure 45. Figure 45 also presents some Np(IV) sorption values collected from other literature sources (Berry et al., 2007; Vilks, 2011). A comparison of this project's dilute solution sorption data to the Vilks (2011) recommended Np(IV) sorption value for bentonite (plotted as the geometric mean with standard deviation shown by the error bars) indicates that the dilute data are reasonable. The range and magnitude of the dilute results are also similar to the results of Berry et al. (2007) for Np(IV) sorption on bentonite (DI-B), crushed tuff (DI-T), and crushed granodiorite (DI-G) in dilute solutions and reducing conditions. Thus, the dilute batch and kinetics sorption data for Np are consistent with Np(IV) sorption behaviour.

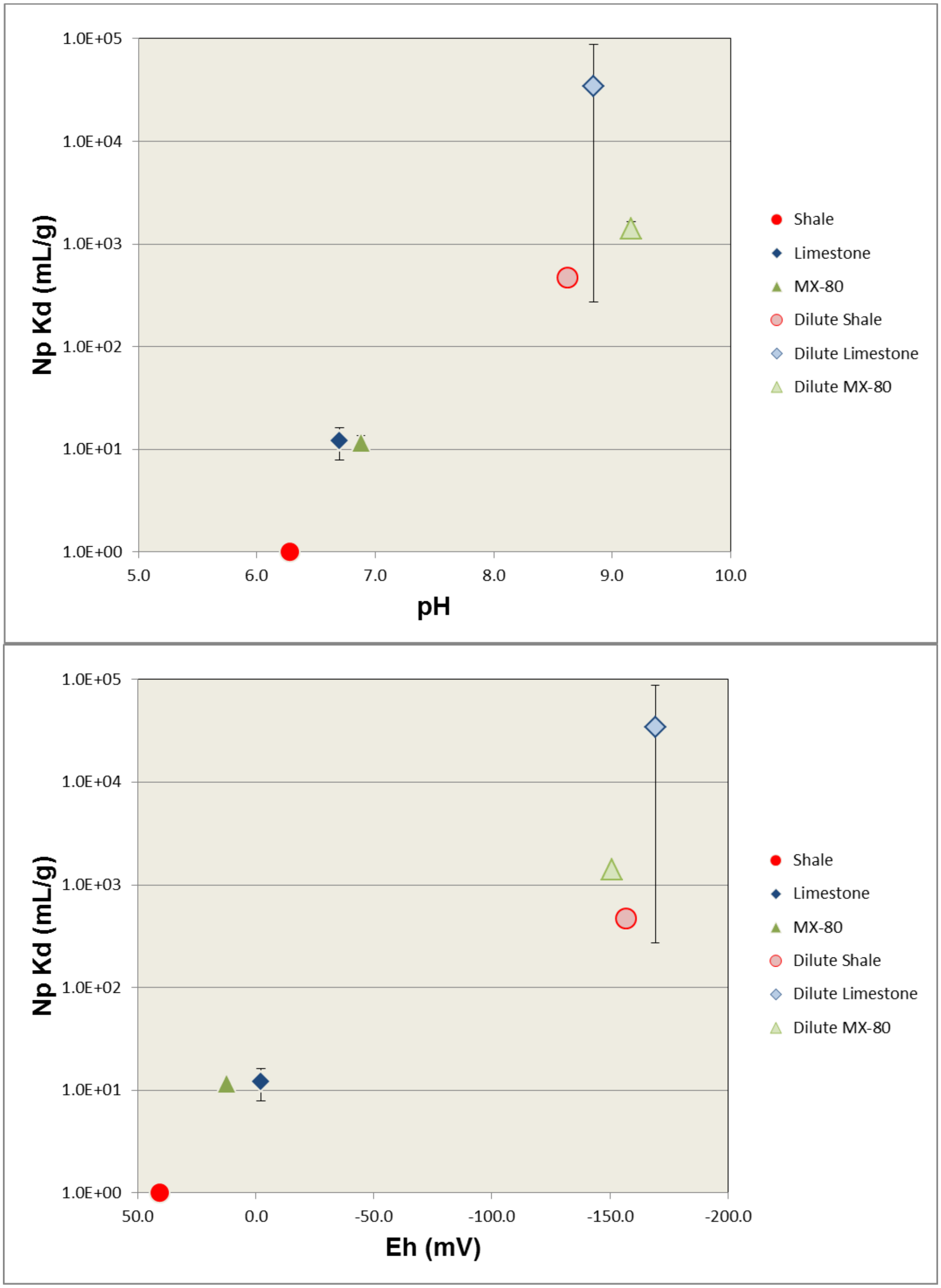

Figure 44: Results of Sorption of Np with Respect to pH (Top) and Eh (Bottom) onto Shale, Limestone, and MX-80 in Brine and Dilute Solutions. The Observed K_d Values are Similar in Magnitude to those Measured in the Previous Batch and Kinetics Tests

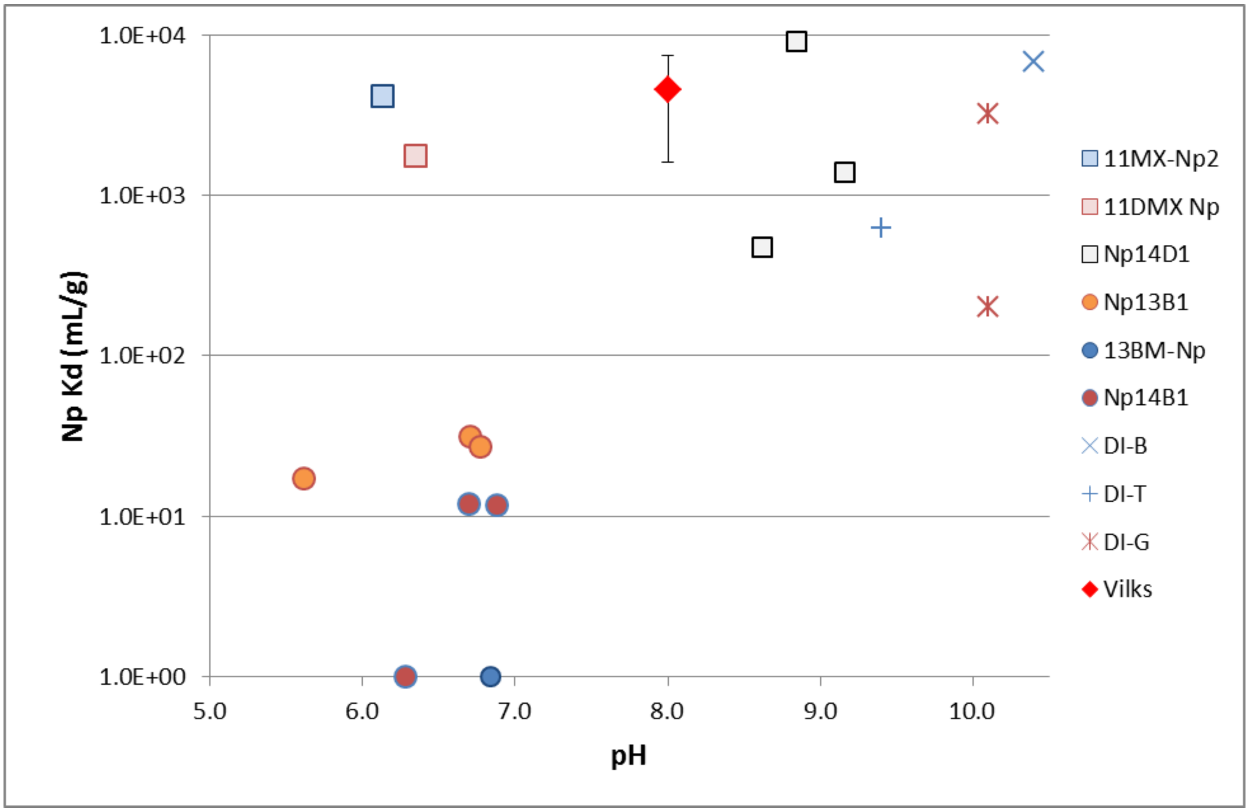

Figure 45: Summary of Results for all Np Sorption Experiments. Representative Values of Np K_d are Shown for Each Substrate in Each Experiment (Legend Codes are the Same as Used in Table 10). Also Included are Results from Berry et al. (2007) for Np(IV) Sorption on Bentonite (DI-B), Tuff (DI-T), and Granodiorite (DI-G) in Dilute Solutions, and Recommended Values of Np(IV) Sorption on Bentonite from Vilks (2011) (See Text for Discussion)

3.2.3 Uranium Batch Sorption

The sorption of U in batch solutions was examined in two groups of experiments. In the first group U was added to brine solutions (Solution 13) containing shale, limestone, and MX-80. The first experiment (Experiment U13B1) was conducted over 30 days using three replicates for each solid. A second test included U that was preprocessed using hydrazine (in the same manner as used for reduction of Se) and stored in the glove box prior to its addition to the experimental tubes. The reduction of U using hydrazine was employed as a mechanism to reduce U to the (IV) state prior to conducting the sorption test. Uranium was added to the experimental solution within the glove box, so there was no exposure to atmosphere during spiking. This second experiment (Experiments U14B1 and U14D1) utilized brine and dilute solutions (Solutions 14 and 14D) and included shale, limestone, and MX-80. This sorption experiment was conducted over 17 days following spiking with U and used three replicates for each solid–solution combination.

Results of the first U batch sorption study are shown in Figures 46 and 47. Figure 46 displays U sorption in terms of percent lost from solution, while Figure 47 displays measured K_d values relative to pH and Eh for each experimental solution (Solution 13). The initial concentration of U in this experiment was 3.5×10^{-7} M. There was substantial loss of U from solution in this first batch sorption test. Over 94% of U is lost from all solutions, irrespective of the substrate. The final measured pH values range from 6 to 8, with the shale samples having the lowest pH. Final measured Eh values ranged from −20 to −80 mV (with one shale solution at +20 mV, consistent with its low pH of 5.4). The measured U K_d values for this test were between 1230 and 3400 mL/g and the average K_d value was 2200 mL/g. The highest U K_d values were recorded for the shale samples. The U K_d values are higher than observed in the previous U kinetics test in brine, but similar to the results noted in the two dilute U sorption kinetics tests.

The second group of U batch sorption studies was conducted near the end of the project and was in response to continued uncertainty regarding the final oxidation state of U in the experimental systems. Results of this second U batch sorption experiment are provided in Figures 48 and 49. Figure 48 displays the percent U sorbed or lost from solution as a function of pH for all experimental solutions. Figure 49 shows the average measured U K_d, pH, and Eh values for each group of replicates, along with error bars (if larger than the symbol) representing the ±1σ uncertainty in the replicates' K_d values.

Addition of the hydrazine-bearing U spike had a significant effect on pH and Eh values for the experimental solutions. Final measured pH values for the brine and dilute solutions are ~8.5 and above 9.5, respectively, while measured Eh values are approximately −300 mV for the brines and −410 mV for the dilutes. Interestingly, the measured U K_d values for the brine solutions are on the order of 400 mL/g, substantially less than the previous U batch test but

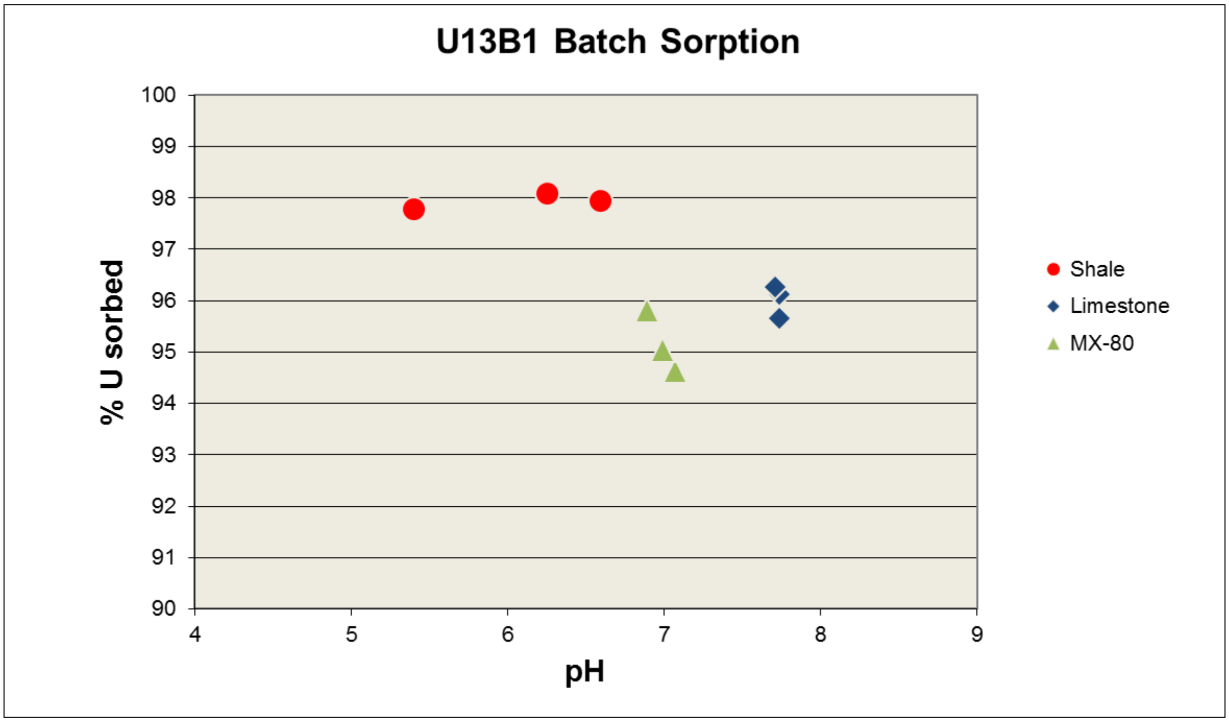

Figure 46: Sorption of U onto Shale, Limestone, and MX-80 in Brine Solution 13 Using an Initial U Concentration of 3.5×10^{-7} mol/L. Individual Results for Replicate Solutions are Shown. Note the Scale on the Figure

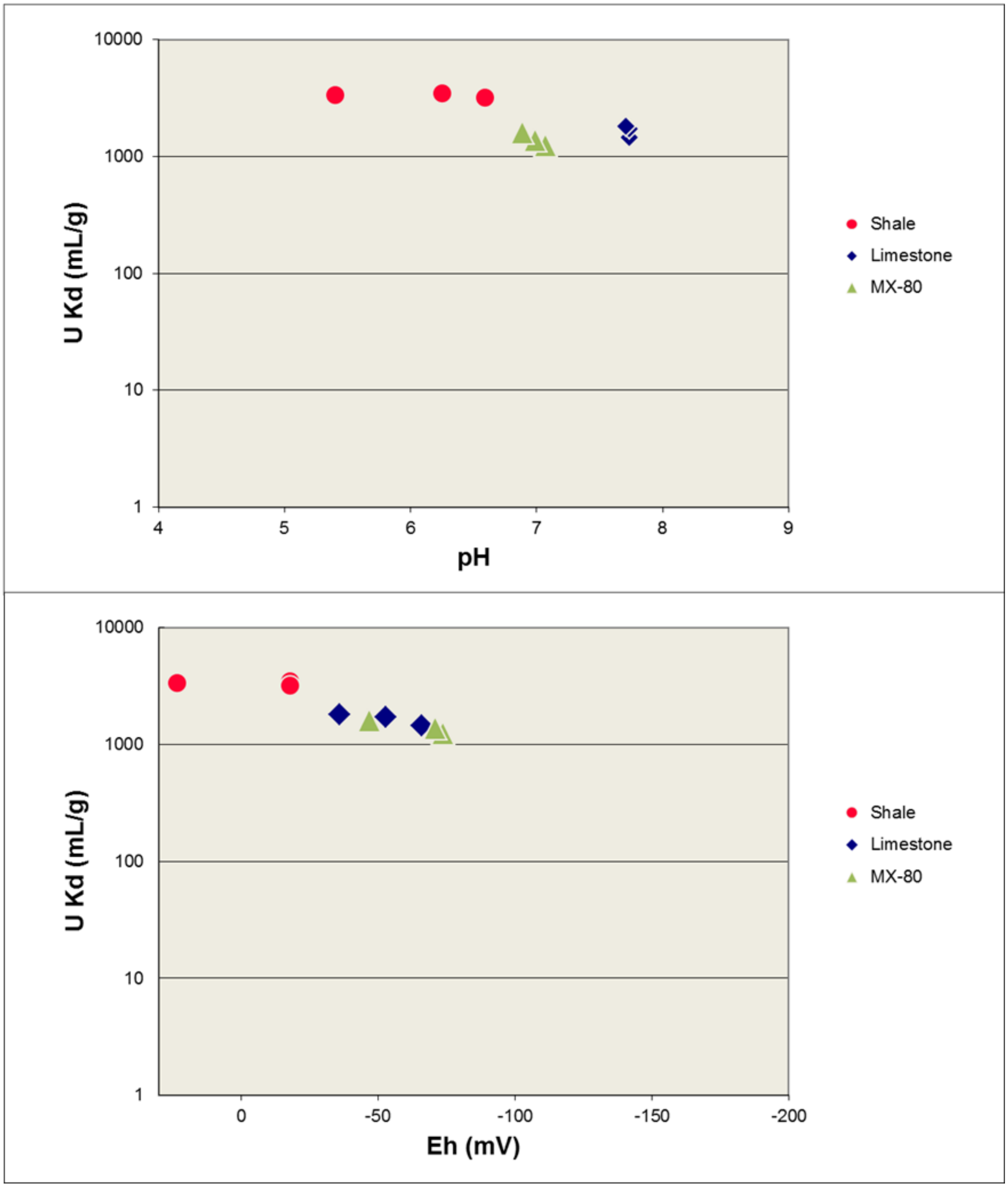

Figure 47: Results of Sorption of U with Respect to pH (Top) and Eh (Bottom) onto Shale, Limestone, and MX-80 in Brine Solution 13. The Batch Results are Consistent with U K_d Values Measured in the Initial Dilute Kinetics Tests

similar to the measured U K_d value (~460 mL/g) observed in the brine-bearing kinetics test for MX-80. The magnitude of U K_d for the dilute solutions is at least 2×10^4 mL/g, but that value is arbitrarily established because the final samples collected for these experiments showed no measureable U activity above background. As a result, LSA values were entered as 0.05 cpm, which results in the reported calculated K_ds. The actual K_d values may be higher but would contain considerable uncertainty. Recall from the second U sorption kinetics test that addition of NaOH, which drove U experimental solutions close to pH of 10, appeared to result in sorption of U (which later reversed as pH dropped). In the second kinetics test, the starting concentration of U was 4.6×10^{-7} M and did not fall below 3.5×10^{-7} M even after addition of NaOH. In this batch test, the starting U concentration was 3×10^{-9} M (with a final calculated value of less than 1×10^{-11} M). Thus, it appears unlikely that the loss of U is due to precipitation because U concentrations are below predicted solubility limits for U(IV) (Neck and Kim, 2001).

Figure 50 presents averaged or representative values for all tested substrates of the U kinetics and batch sorption experiments. Also included in Figure 50 are U(IV) sorption values collected from other literature sources (Berry et al., 2007; Andra, 2005b; Vilks, 2011). Berry et al. (2007) measured U(IV) sorption on bentonite (Sea-B), crushed tuff (Sea-T), and crushed granodiorite (Sea-G) in seawater (pH values less than 9) and dilute solutions under reducing conditions. Comparison of the Berry et al. (2007) data and the results for U sorption tests in this project indicate that the two data sets have similar magnitudes and ranges of U K_ds although the brine sorption results for this study are generally lower than those of Berry et al. (2007) in seawater. The Andra (2005b) recommended range of U(IV) K_ds for sorption onto Cox argillite brackets the dilute U sorption results, but is higher than results from the kinetics and brine tests form this study. The ranges of values for U(IV) sorption onto shale and bentonite reported in Vilks (2011) are also shown in Figure 50. While the Vilks (2011) bentonite range is higher than any of the measured results from this study, the shale U K_d values compare favourably.

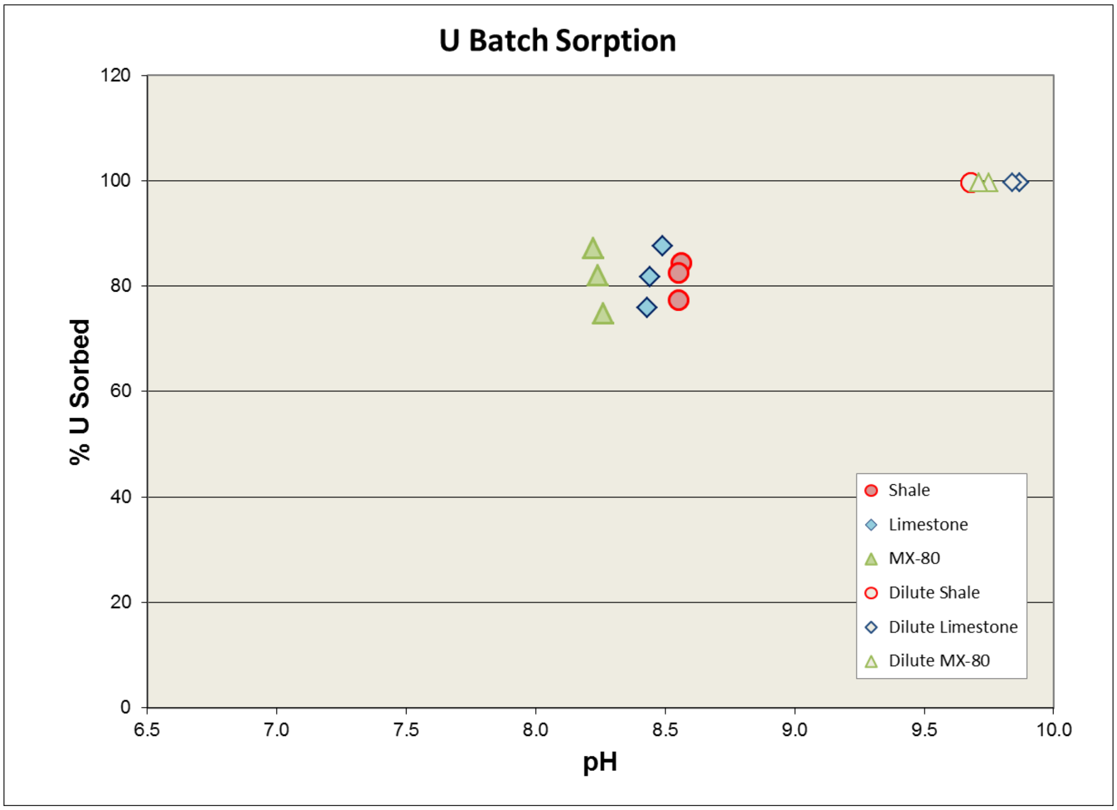

Figure 48: Sorption of U onto Shale, Limestone, and MX-80 in Brine and Dilute Solutions. U Stock Solution was Reduced Using Hydrazine Prior to Spiking. Individual Results for Replicate Solutions are Shown

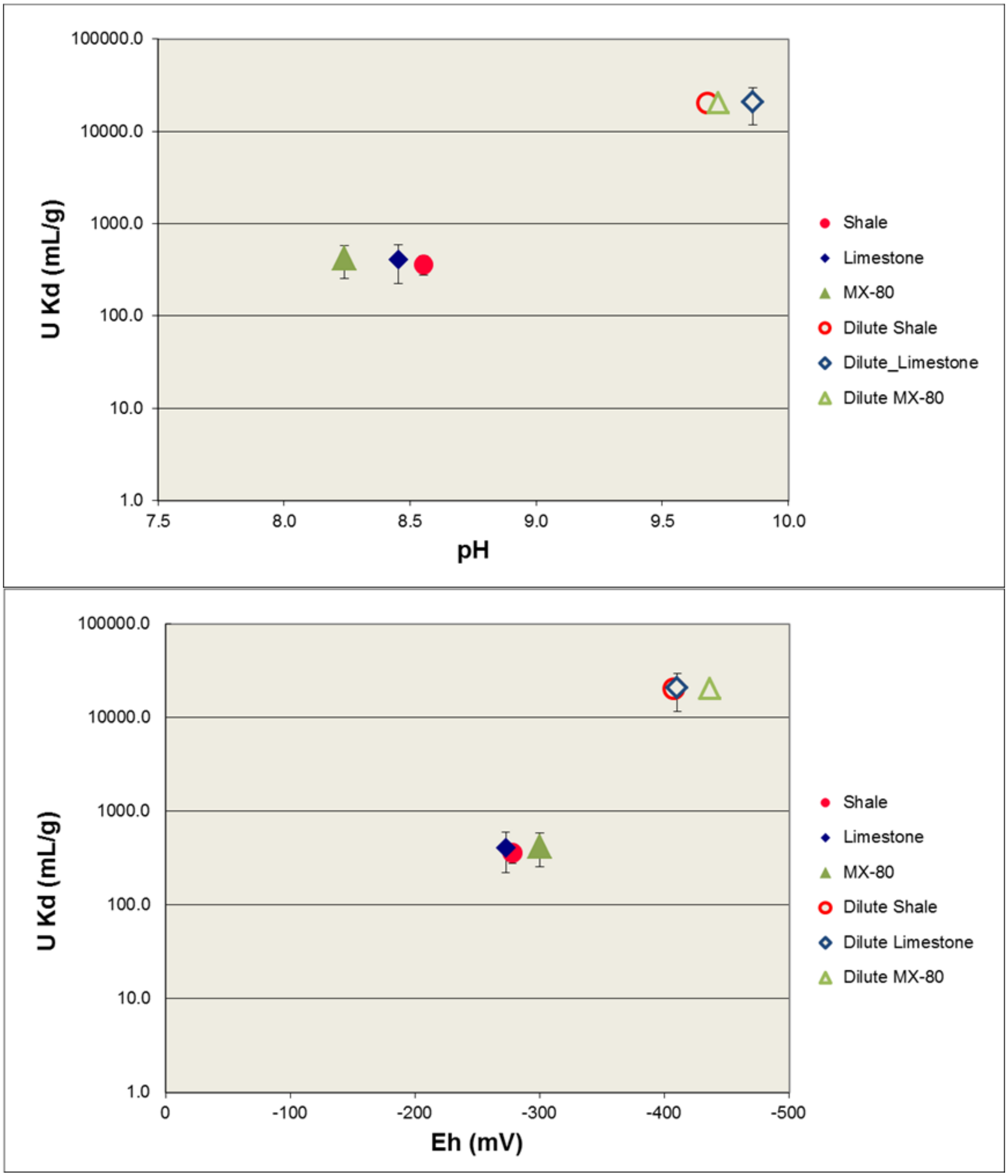

Figure 49: Results of Sorption of U with Respect to pH (Top) and Eh (Bottom) onto Shale, Limestone, and MX-80 in Brine and Dilute Solutions. The Batch Results Reflect Effects of Processing the U Using Hydrazine to Reduce to U(IV) Prior to the Experiment

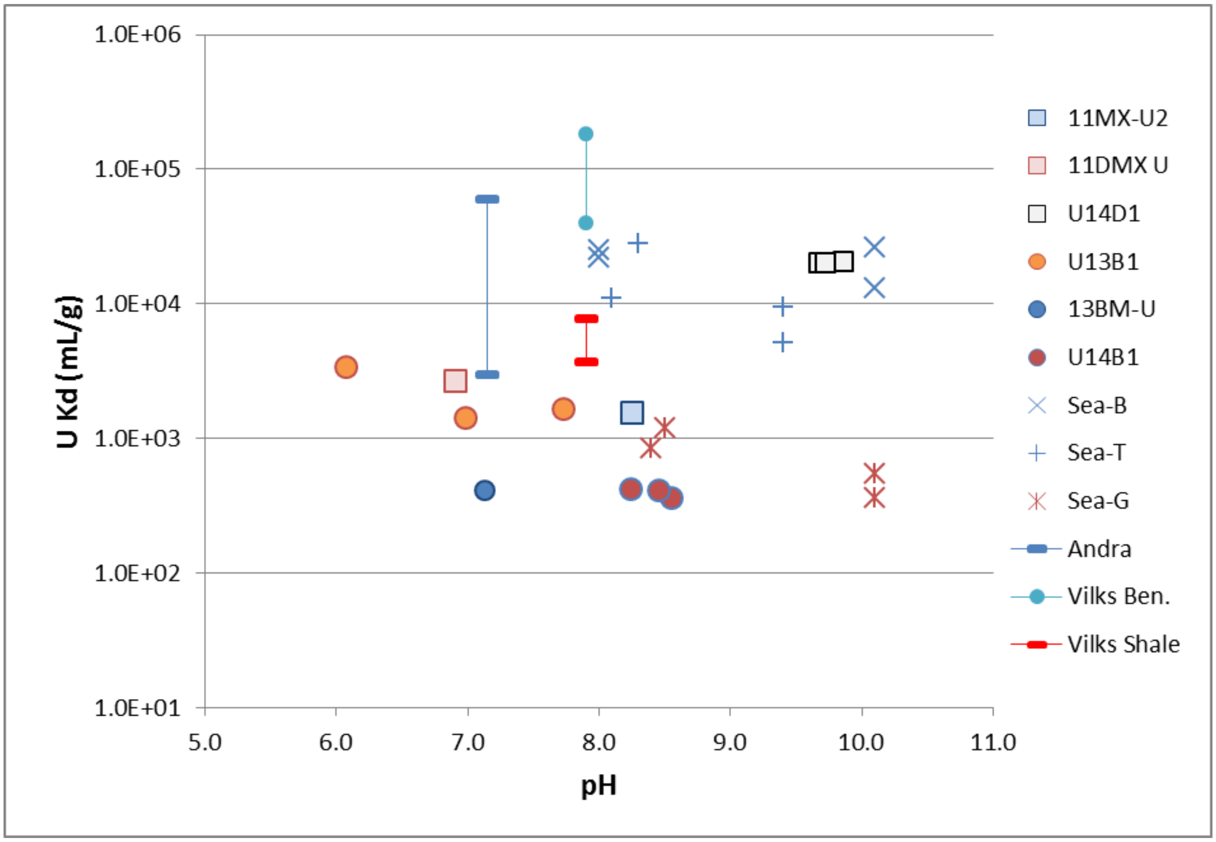

Figure 50: Summary of Results for all U Sorption Experiments. Representative Values of K$_d$ are Shown for Each Substrate in Each Experiment (Legend Codes are the Same as Used in Table 10). Also Included are Results from Berry et al. (2007) for U(IV) Sorption on Bentonite (Sea-B), Tuff (Sea-T), and Granodiorite (Sea-G) in Seawater and Dilute Solutions. Recommended U(IV) Sorption Values from Andra (2005b) (Argillite) and Vilks (2011) (Bentonite and Shale) are Also Provided

3.2.4 Plutonium Batch Sorption

Like U, Pu was explored in batch sorption experiments in two sequences of tests. In the first test, Pu was added to brine solutions (Solution 13) containing shale, limestone, and MX-80 using an initial Pu concentration of 6×10^{-9} M. This experiment (Experiment Pu13B1) was conducted over a period of 30 days following addition of Pu. The second Pu batch sorption test included Pu that was preprocessed using hydrazine to ensure production of a reduced form of Pu. Additionally, the Pu isotope was changed in the second test from Pu-239 to Pu-238 to provide better sensitivity for LSA counting while using a lower total concentration of Pu. The second batch sorption experiments were conducted over 17 days following spiking and included brine and dilute solutions (Solutions 14 and 14D) containing shale, limestone, and MX-80 using an initial Pu concentration of 8.4×10^{-12} M.

Results of the first Pu batch sorption experiments (Experiment Pu13B1) are presented in Figures 51 and 52. Figure 51 displays Pu sorption in terms of percent lost from solution, while Figure 52 displays measured K_d values relative to pH and Eh for each experimental solution. Inspection of the figures indicates that significant Pu (>94%) was removed from the brine solution for all three substrates. Measured Pu K_d values clustered at ~4.0×10^3 mL/g for all experiments (except for one limestone test exhibiting a K_d of ~1200 mL/g). Final measured pH values were between 6 and 7, and final measured Eh values were between −20 and −45 mV. The Pu K_d values for this test were lower than the values obtained in the Pu-brine kinetics test which had K_ds on the order of 1×10^4 mL/g. The Pu K_d values for this test were also about an order of magnitude lower than the Pu K_ds measured in the dilute kinetics experiments.

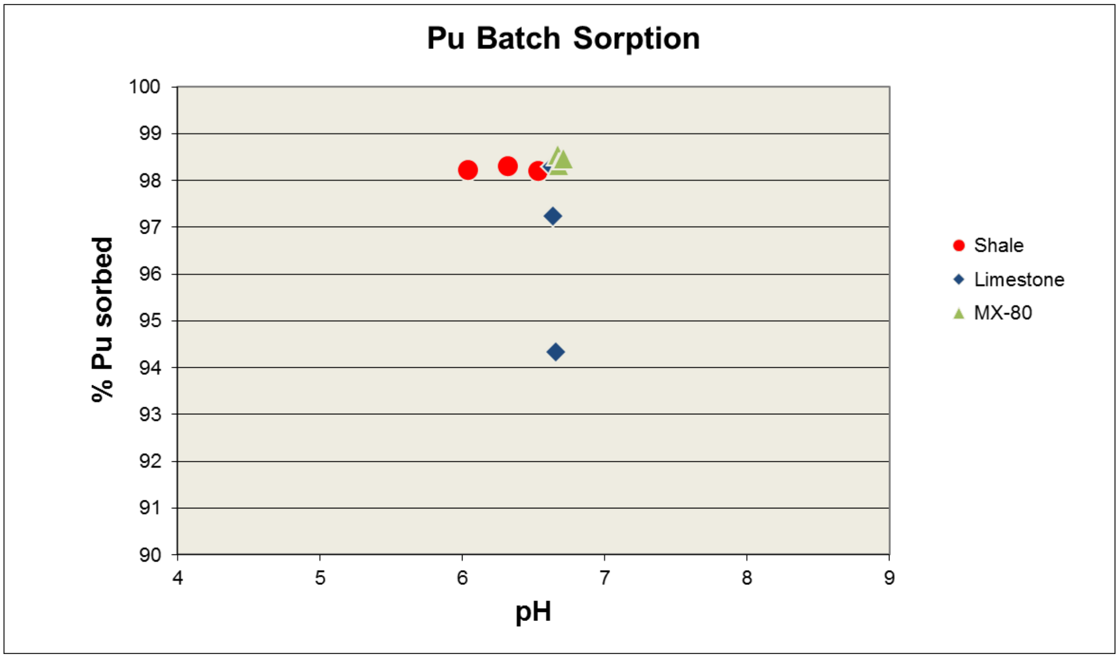

Figure 51: Sorption of Pu onto Shale, Limestone, and MX-80 in Brine Solutions. Individual Results for Replicate Solutions are Shown. Note all Results are >94% Sorbed

Results for the second group of Pu batch sorption experiments (Experiments Pu14B1 and Pu14D1) are shown in Figures 53 and 54. Figure 53 presents sorption results in terms of percent lost from solution for all replicate samples, and Figure 54 shows the sorption data as averaged values of Pu K_d, pH and Eh for each group of replicates, along with error bars (if larger than the symbol) showing the ±1σ uncertainty for the averaged Pu K_d values. Measured Pu K_d values for the brine solutions are similar for all substrates and are on the order of 1500 mL/g, which is less than measured in the previous Pu-brine batch experiments. For the dilute experiments, measured Pu K_d values ranged from $1\text{x}10^4$ to 2×10^4 mL/g, averaged as 1.2×10^4 mL/g. These dilute K_d values are lower (by an order of magnitude) than those measured for dilute solutions in the Pu kinetics studies. This may be a direct result of differences in sorption of Pu(IV) versus Pu(III) but is uncertain because of the lack of direct assessment of the Pu oxidation state. Within this experiment, the difference between the dilute solution K_d values and the brine solution K_d values is about an order of magnitude, similar to observations made when comparing the other brine versus dilute Pu sorption results from the kinetics tests.

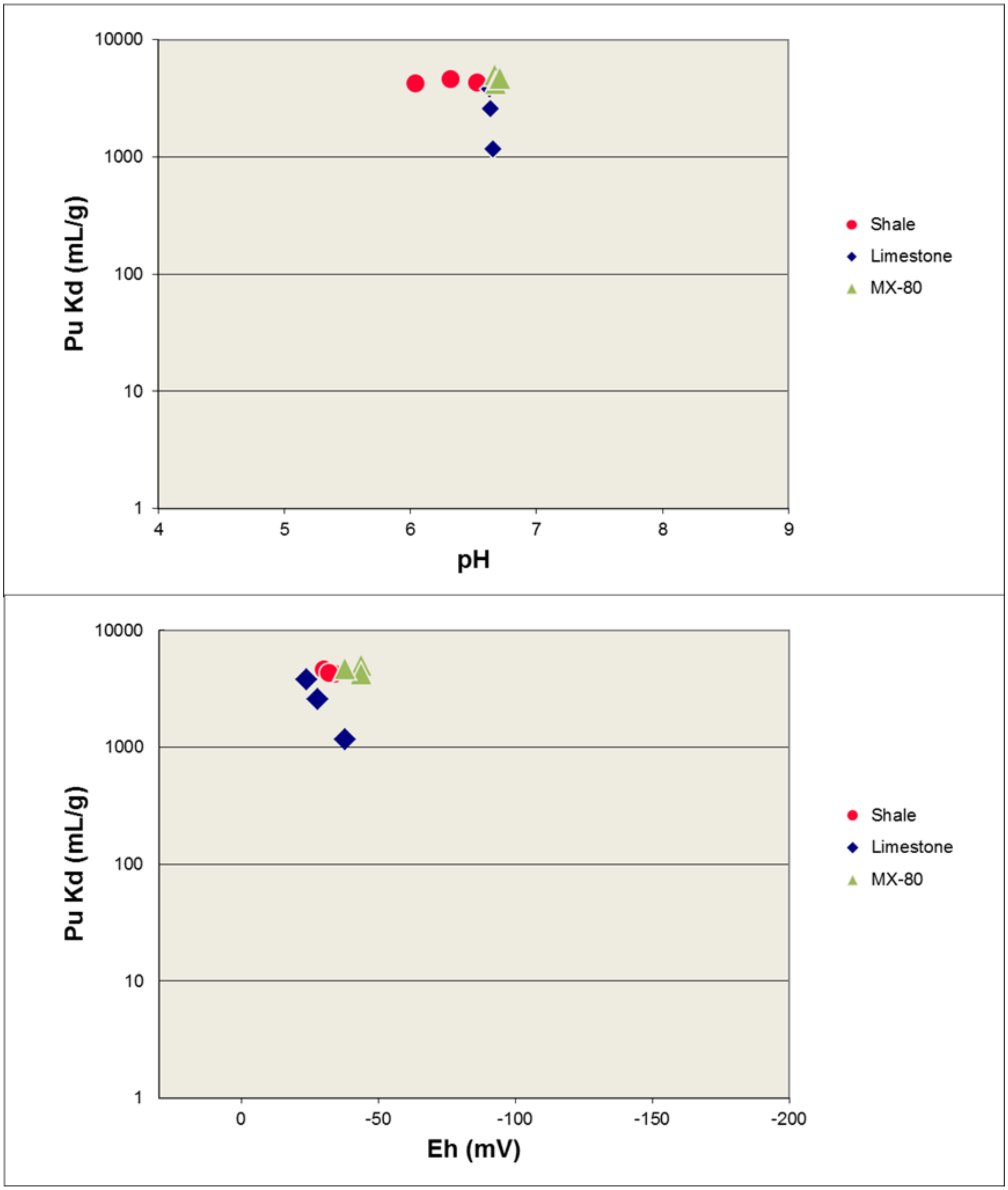

Figure 52: Results of Sorption of Pu with Respect to pH (Top) and Eh (Bottom) onto Shale, Limestone, and MX-80 in Brine Solutions

As demonstrated in the second U batch sorption test, hydrazine-bearing Pu spike solution significantly impacted pH and Eh values. Measured pH values for the brine and dilute experiments were 8.2 and 8.7, respectively. Measured Eh values at the time of sampling were approximately −230 mV for the brines and −380 mV for the dilute solutions. If the chemical reduction of the Pu by hydrazine successfully produced a Pu(III) solution as indicated by Karraker (1981), the results for the Pu(III) sorption in brines were not significantly different, but were lower than the previous batch sorption test, which did not have hydrazine added and ended at an Eh near −50 mV.

A summary of Pu batch and kinetic sorption experiments for the project is provided in Figure 55. Like the summary plot for Np and U, the Pu data from this study are presented as averaged or representative Pu K_d values for each substrate. Also shown in Figure 55 are Pu(IV) and Pu(III) K_d values taken from literature sources (Berry et al., 2007; Andra, 2005b; Vilks, 2011). Berry et al. (2007) measured Pu sorption onto bentonite (DI-B), crushed tuff (DI-T), and crushed granodiorite (DI-G) in dilute solutions under strongly reducing conditions (Eh of −400 to −600 mV SHE). As seen in Figure 55, the magnitude and range of Pu K_d values measured by Berry et al. (2007) are equivalent to the Pu K_ds determined for dilute solutions in this study [the lower values from Berry et al. (2007) may be associated with particulates]. The Andra (2005b) recommended range of Pu(III) K_d values for the COx argillite is similar to the measured range of K_d values in the Pu-brine tests. Recommended values (geometric means and maximum and minimum reported values) for sorption of Pu(IV) and Pu(III) on bentonite are also shown in Figure 55. Note that the mean Vilks (2011) recommended value for Pu(III) is similar to the measured Pu K_ds for the hydrazine-reduced sorption tests, while the mean value for Pu(IV) sorption is similar to the Pu K_ds measured in the first set of Pu batch experiments. While comparison of recommended ranges and values from literature compilations does not explicitly demonstrate the valance state of Pu in our experiments, it does provide a basis for confidence in the results.

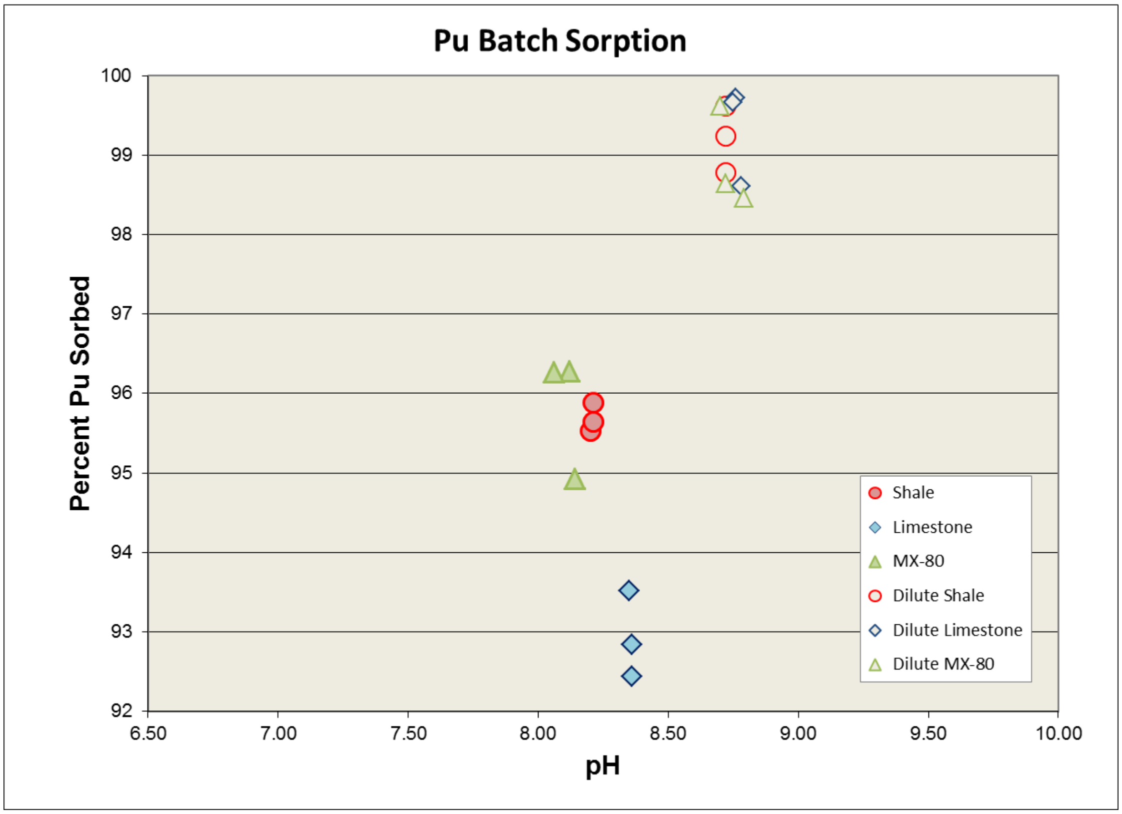

Figure 53: Sorption of Pu onto Shale, Limestone, and MX-80 in Brine and Dilute Solutions (Hydrazine Used to Reduce Pu). Individual Results for Replicate Solutions are Shown (3 Brine and 3 Dilute)

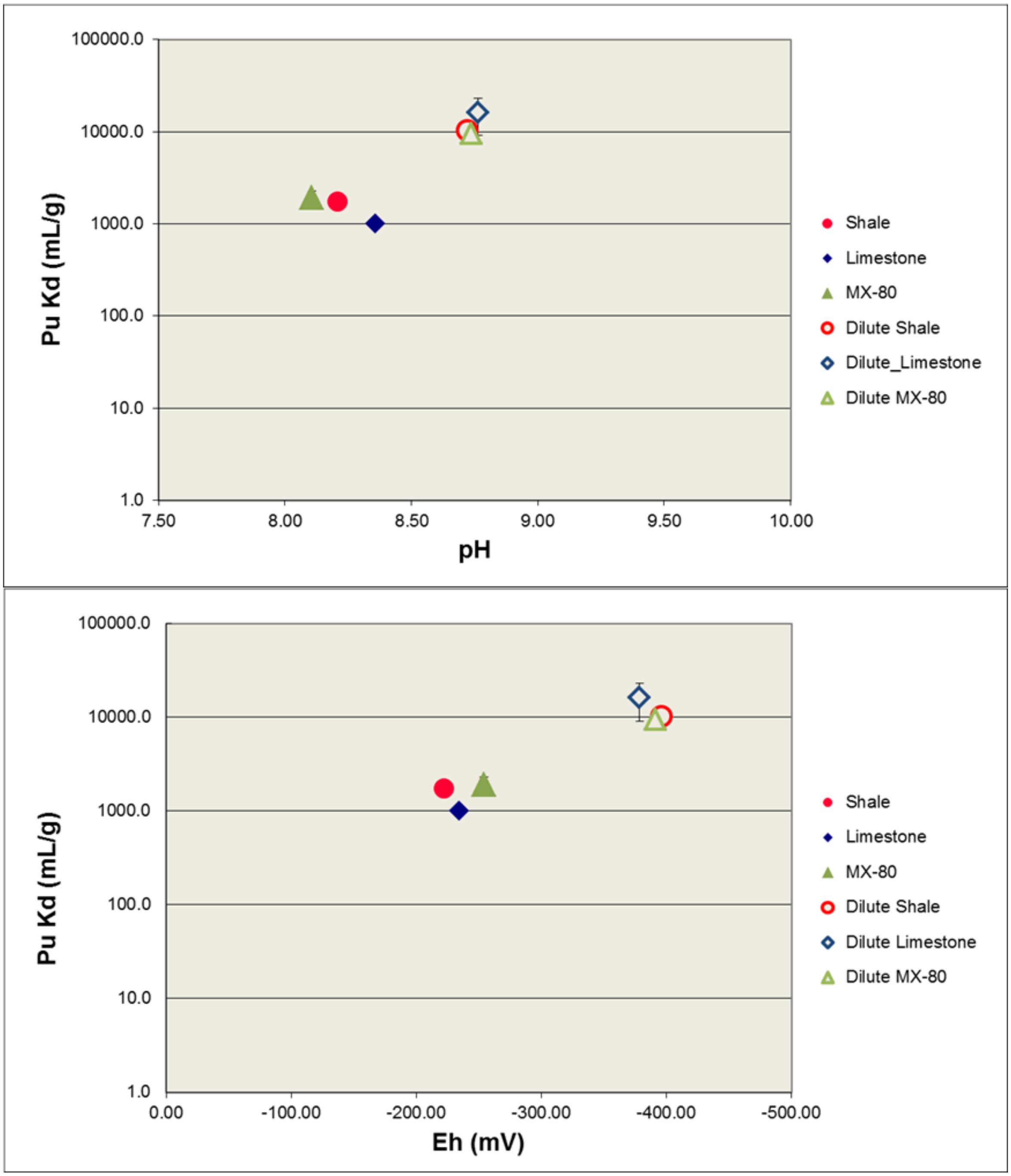

Figure 54: Results of Sorption of Pu with Respect to pH (Top) and Eh (Bottom) onto Shale, Limestone, and MX-80 in Brine and Dilute Solutions. The Results Reflect Effects of Processing the Pu Using Hydrazine to Reduce the Pu Prior to the Experiment

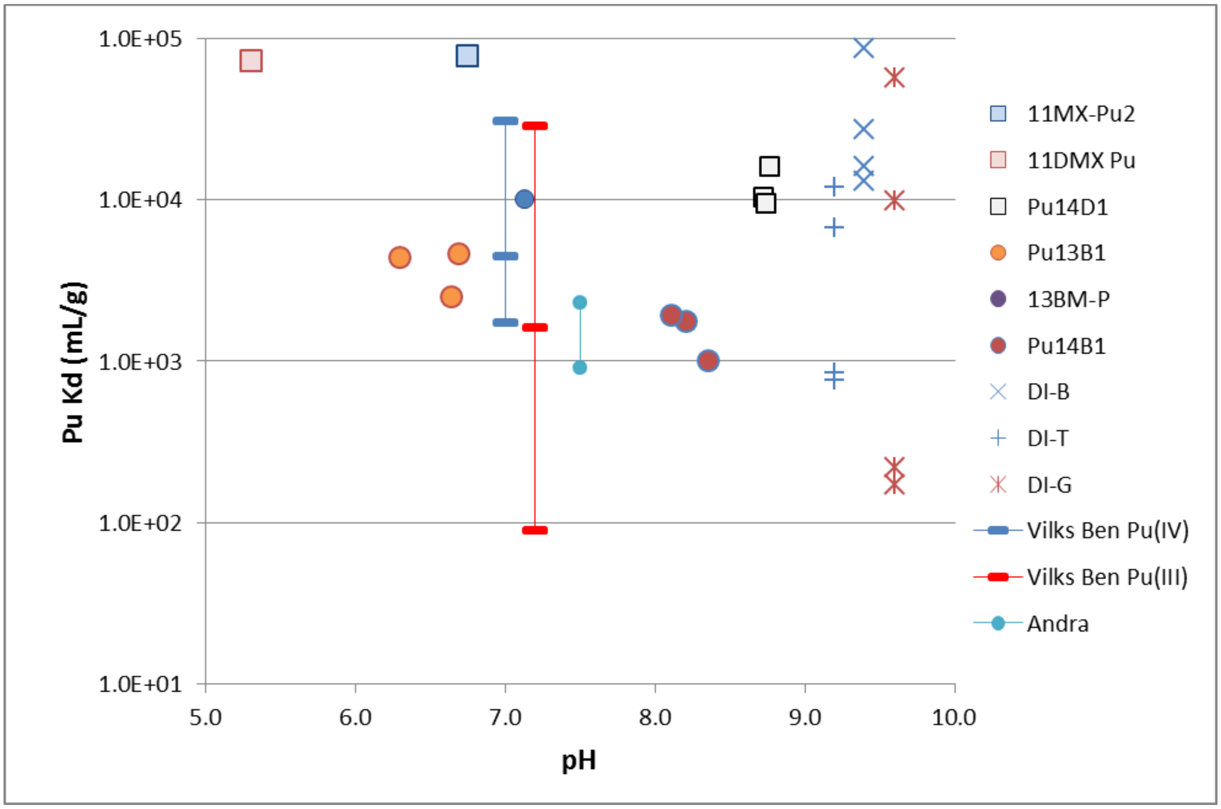

Figure 55: Summary of Results for all Pu Sorption Experiments. Representative Values of K_d are Shown for Each Substrate in Each Experiment (Legend Codes are the Same as Used in Table 10). Also Included are Results from Berry et al. (2007) for Pu(IV) Sorption on Bentonite (DI-B), Tuff (DI-T), and Granodiorite (DI-G) in Dilute Solutions. Recommended Pu(III) Sorption Values from Andra (2005b) (Argillite) and Vilks (2011) [Pu(III) and Pu(IV) on Bentonite] are also Shown

3.2.5 Arsenic Batch Sorption

The As batch sorption tests were the only set of experiments conducted without a radioactive tracer. Instead, $AsCl_3$ was diluted in ddH_2O and used to make an As(III)-bearing stock solution. The As was quantified by ICP-MS analyses. One group of batch sorption experiments was conducted using As. This group of tests included brine and dilute solutions (Solution 14 and 14D) and shale, limestone, and MX-80. The experiments investigating As were conducted over a 43-day period following the addition of the As spike. Kinetics experiments for As sorption were not conducted, but previous studies have used equilibration times on the order of a few days (e.g., Chien et al., 2012; Manning and Goldberg, 1997). Six replicate solutions were used in the brine experiments and three replicate solutions were used in the dilute tests.

Results of the As batch sorption studies are provided in Figures 56 and 57. Figure 56 presents results in terms of percent As lost from solution, and Figure 57 shows averaged measured As K_d, pH, and Eh values for each group of replicates, along with error bars (if larger than the symbol) showing the $\pm 1\sigma$ uncertainty in the K_d values for each group. The As K_d values for brine (11–20 mL/g) and dilute solutions (~20 mL/g) are similar. The starting concentration of As was approximately 7.0×10^{-7} M for the brine solutions and 8.7×10^{-7} M for the dilute solutions, so solubility issues should have been avoided. The measured K_d values are consistent with previously reported As(III) K_ds in the literature (Vilks, 2011).

The final measured pH and Eh values for the As experiment varied somewhat differently than in the other experiments. The brine solutions exhibited a final pH of 6.9 and a final Eh ranging from +20 to −15 mV. With the exception of the shale experiments, the dilute solutions had higher pH values (8.6 to 8.9) and generally lower Eh values of about −140 mV, consistent with the trend of lower Eh with higher pH. However, the dilute shale experiments had measured pH of about 8.6 but had high Eh values of +60 mV. This result is driven by one solution in particular, which was measured and recorded with an Eh value of +273 mV, while the other dilute shale solutions measured −24 and −94 mV. A review of the measurement data suggests that the value for the high Eh solution is likely to be incorrect, and a more reasonable average Eh for the dilute shale should be −60 mV, which is shown in Figure 57 for comparison. All data for the As experiments were retained in calculations of average K_d. Thus, the dilute shale solutions still have an average Eh value about 100 mV greater than the dilute limestone and MX-80 solutions, but the value is not unreasonably high.

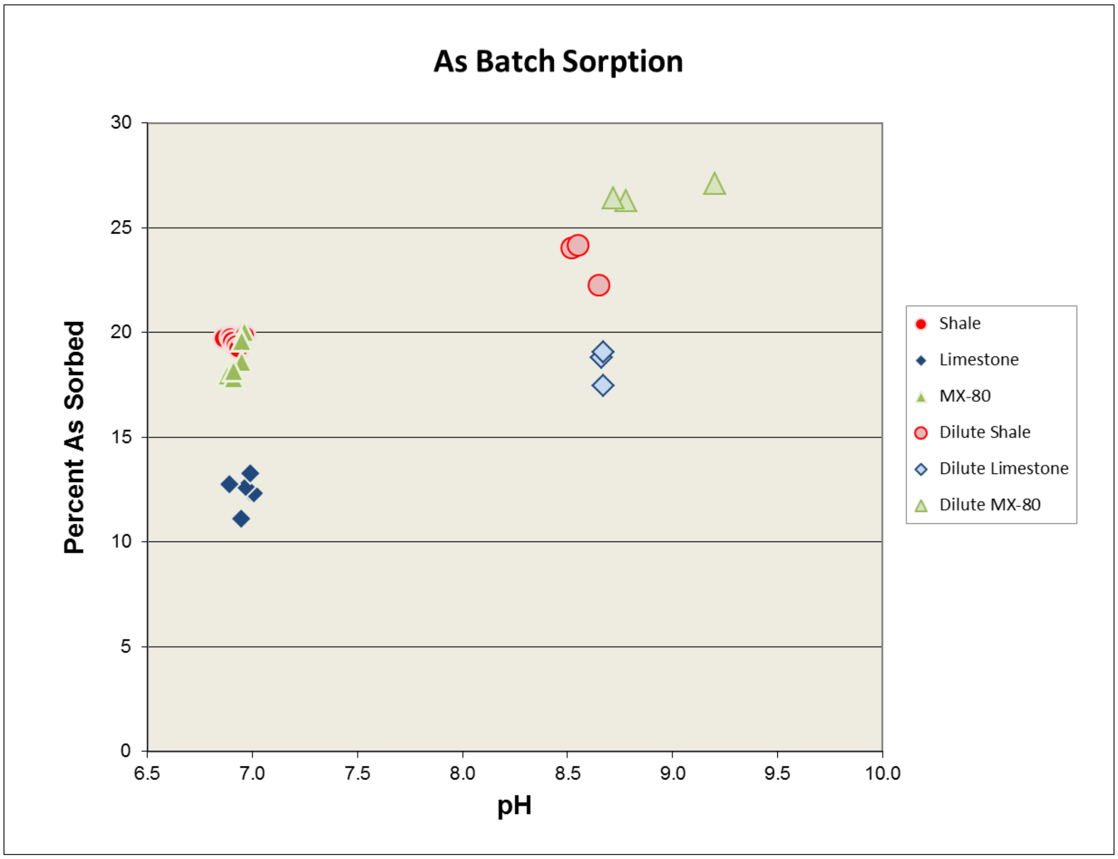

Figure 56: Sorption of As onto Shale, Limestone, and MX-80 in Brine and Dilute Solutions. Individual Results for Replicate Solutions are Shown (6 Replicates Brine, 3 Replicates Dilute)

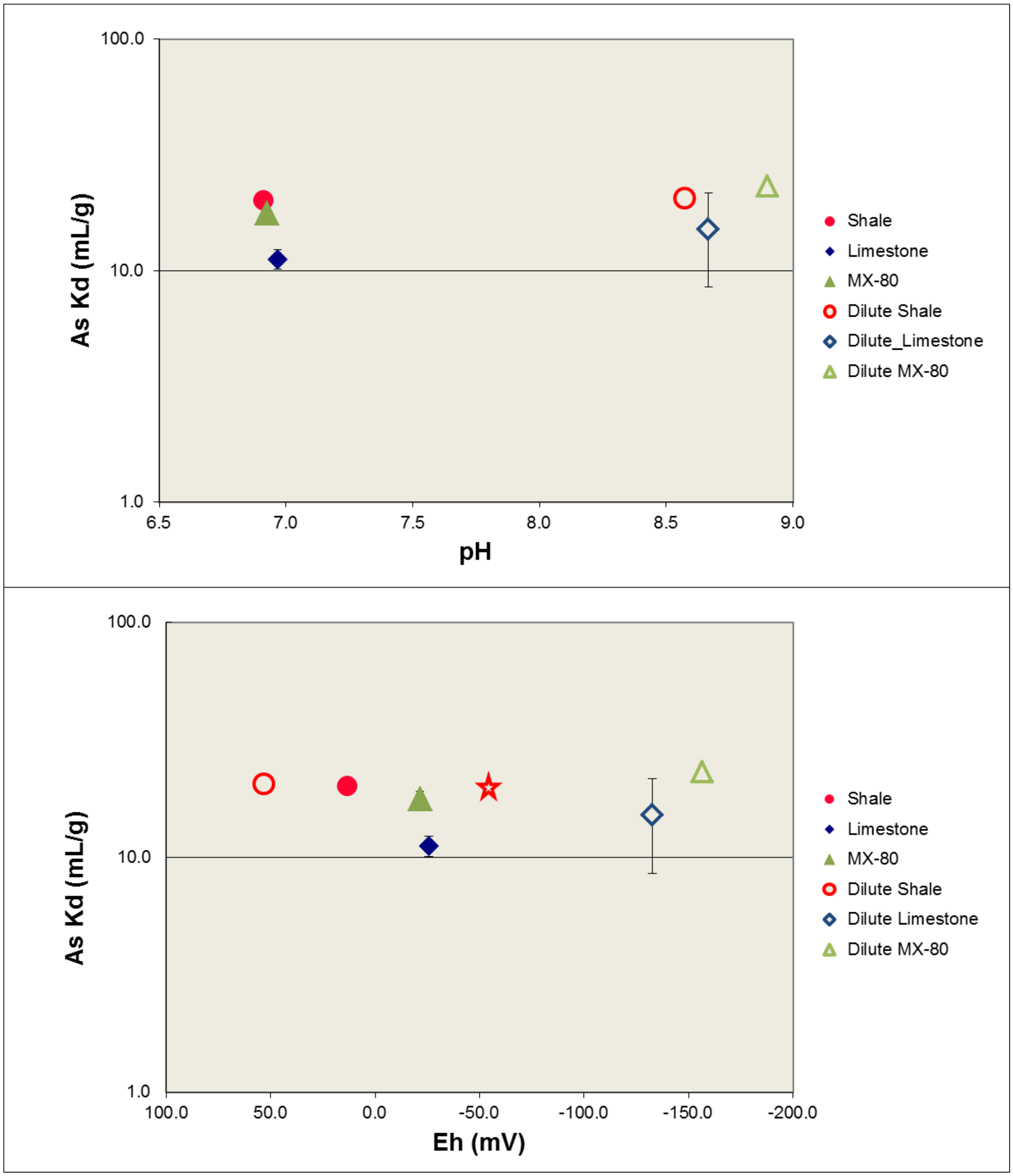

Figure 57: Results of Sorption of As with Respect to pH (Top) and Eh (Bottom) onto Shale, Limestone, and MX-80 in Brine and Dilute Solutions. Symbols Represent Averaged Values for All Replicates in a Group (6 Replicates for Each Brine and 3 Replicates for Each Dilute). The Average Eh Value for the Dilute Shale Samples (Hollow Red Circle) is Controlled by a Likely Measurement Error for One Experiment. The Red Star Indicates the Location of a Corrected Average Eh for These Dilute Shale Solutions

3.2.6 Selenium Batch Sorption

Selenium was analyzed using one set of batch sorption experiments that included both brine and dilute solutions (Solutions 14 and 14D) containing shale, limestone, and MX-80. As described previously, the Se-75 standard solution was preprocessed using hydrazine to create an Se(−II) stock solution. The stock solution was stored in the glove box, and addition of Se to the experiments was conducted in the glove boxes. The Se batch sorption tests were conducted for a period of 30 days following addition of the Se spike (Iida et al., 2011). The Se experiments utilized six replicates per solid for the brine tests and three replicates per solid for the dilute solution tests.

The results of the Se batch sorption experiments are shown in Figures 58 and 59. Figure 58 presents the Se sorption data in terms of percent Se lost from solution and depicts each replicate. Figure 59 presents average measured Se K_d, pH, and Eh values for each group of replicates, along with error bars (if larger than the symbol) showing the ±1σ uncertainty associated with the averaged K_d values for each replicate group.

With the exception of two dilute experimental samples, the sorption of Se is clustered around 56–60%, which is equivalent to Se K_d values of 80–100 mL/g. Sorption of Se in the brine experiments appears slightly greater, but not significantly so. The effects on pH and Eh from addition of the hydrazine-bearing Se spike are evident. Brine experiments have pH values ranging from 7.8 to 8.4 with Eh values from −200 to −240 mV. The dilute experiments have pH values of about 9.3 and Eh values ranging from −340 to −420 mV. The initial concentration of Se was about 1.5×10^{-7} M for both the brine and dilute systems. Iida et al. (2010) examined Se(−II) solubility at high ionic strength in reducing conditions and concluded that an amorphous solid, Se(am), was the limiting phase at pH values near 8. These results suggest that the initial concentrations of Se in the batch experiments were below solubility limits.

Also shown in Figure 59 are data for Se(−II) sorption on Na-montmorillonite under reducing conditions at solution ionic strengths of 0.05 and 0.5 M (Iida et al., 2011). Comparison of the Se(−II) K_ds in the higher ionic strength solutions by Iida et al. (2011) and brine data from our experiments indicates similar K_d values for both studies. Iida et al. (2011) also noted a reduction in measured sorption with increasing pH for dilute solutions. The Se sorption results for dilute solutions in our experiments are consistent with the trend and magnitude of Se(−II) sorption presented by Iida et al. (2011). The Iida et al. (2011) Se experiments were conducted using an initial Se concentration of 5×10^{-9} M, thus the similar measured K_ds also suggest that precipitation of Se was not an issue for our tests.

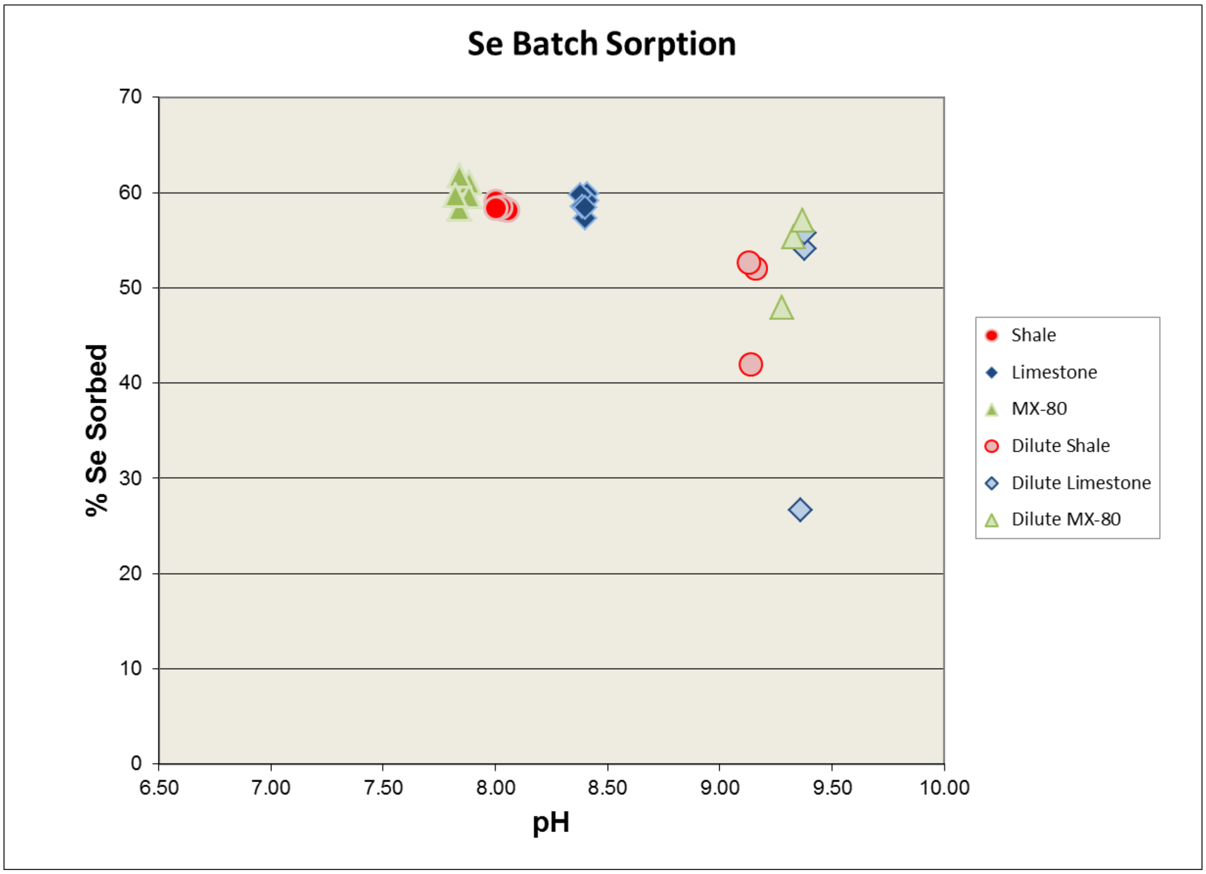

Figure 58: Sorption of Se onto Shale, Limestone, and MX-80 in Brine and Dilute Solutions. Individual Results for Each Replicate Solution are Shown (6 Brine Replicates and 3 Dilute Replicates)

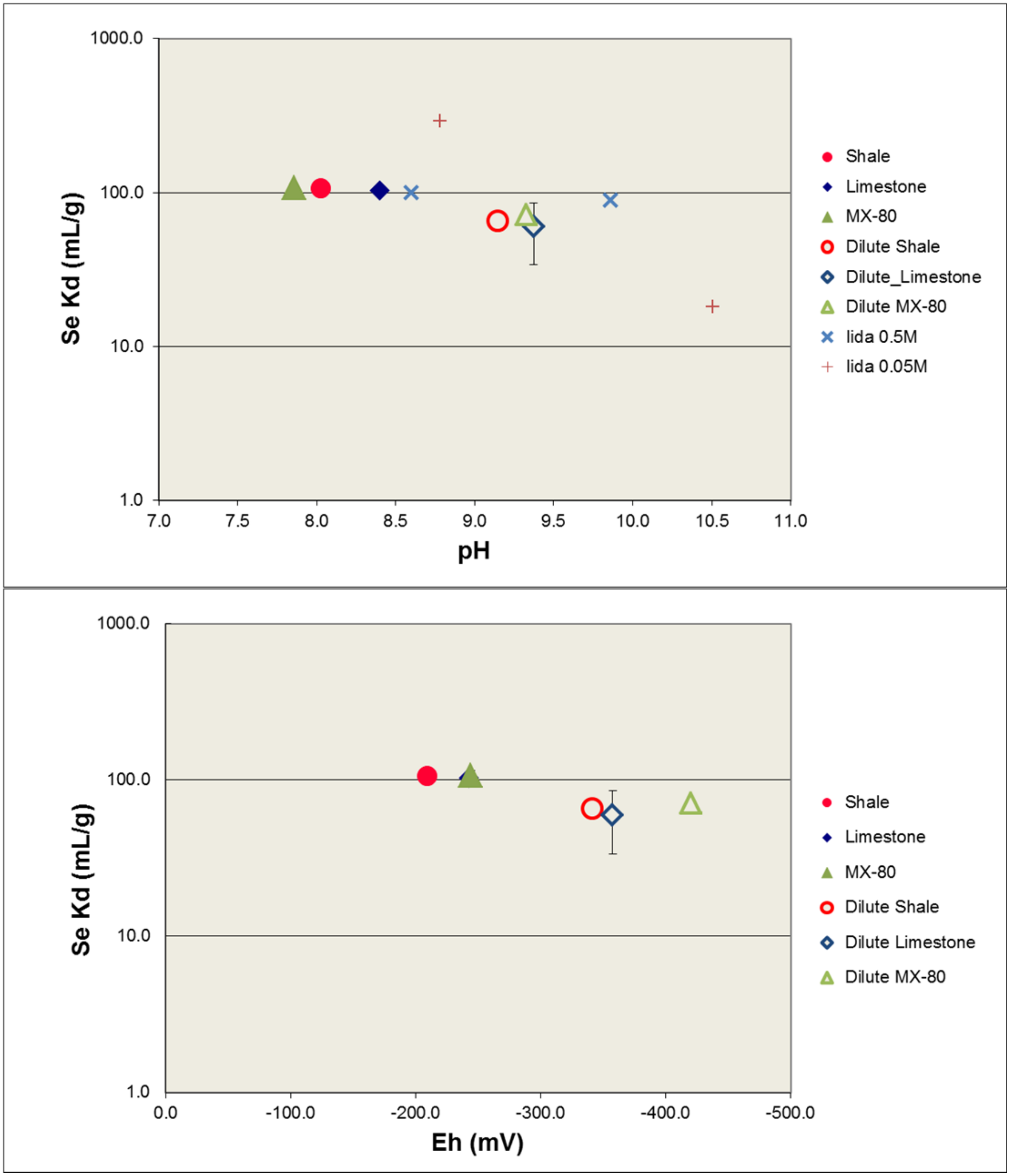

Figure 59: Results of Sorption of Se with Respect to pH (top) and Eh (bottom) onto Shale, Limestone, and MX-80 in Brine and Dilute Solutions. The Initial Concentration of Se is 1.5x10^{-7} M. Sorption on Na-Montmorillonite at Ionic Strength of 0.05 M and 0.5 M by Iida et al. (2011) Also Shown

4. SUMMARY AND DISCUSSION

A series of batch and kinetic sorption tests was conducted in brine (with TDS of 275 g/L or ionic strength of 6.0 M) and dilute (with TDS of 0.55 g/L or ionic strength of 0.01 M) solutions equilibrated with a low-O_2 environment. Solution conditions were confirmed to be significantly reducing for most of the dilute experiments and targeted Eh values were met in most cases. Initially, Eh values for the experimental solutions were targeted to the nominal -200 mV associated with the SR-270-PW composition. Generally, Eh values of the brines were higher, but were also low enough to favour the reduced oxidation states desired. Where Eh values were higher than anticipated or even drifted toward zero, the experimental results did not indicate changes in behaviour of the elements being tested.

With the exception of Np, it is likely that the experiments adequately evaluated the targeted valence state for the radioelements tested [As(III), Pu(III/IV), Se(−II), Tc(IV), and U(IV)]. Although not confirmed by direct measurement, support for these valence states includes preparation of stock solutions in the expected form (As), preparation based on previously known techniques to generate reduced valence state (Pu, Se, and U), and comparative evidence from the literature for sorption of oxidized and reduced forms (Tc, U, and Pu). Sorption of Np was variable and could be attributable to factors other than valence state, such as low CO_2(g) conditions, so its transition to Np(IV) cannot be conclusively demonstrated.

For some elements such as Np, Pu, and U, multiple experiments demonstrated consistent sorption results over various conditions. Sorption in brines was lower for Np, Pu, and U than in dilute solutions. Sorption in brine and dilute solutions was similar for As, Se, and Tc. There was typically no significant difference in measured sorption for the different substrates examined in these tests. Although the measured surface area of the substrates ranged over an order of magnitude, generally there was no discernable difference in sorption based on the substrate type. Exceptions included the low sorption of Tc onto shale in both brine and dilute solutions and relatively lower sorption of Np on the shale samples.

Results of the sorption experiments indicated that the highest K_ds in brine and dilute solutions were associated with Pu (1.5×10^3 – 1.0×10^4 mL/g in brine, and 1.2×10^4 – 7.8×10^4 mL/g in dilute solution) and U (4.2×10^2 – 2.2×10^3 mL/g in brine, and 1.5×10^3 – 2.0×10^4 mL/g in dilute solution). Sorption of Se and As was moderate in the brine and dilute solutions (100 mL/g in brine and 80-100 mL/g in dilute solution for Se; 11-20 mL/g in brine and 20 mL/g in dilute solution for As). Tc and Np showed variable sorption behaviour. In a long running batch test, Tc showed strong sorption to limestone (10^4 mL/g in brine, and 10^5 mL/g in dilute solution) and MX-80 (5×10^3 mL/g in brine, and 10^4 mL/g in dilute solution), but low sorption on shale (20 mL/g in brine, and 10 mL/g in dilute solution). Measured Np sorption was low in brine solutions but strong (equivalent to that of U) in dilute solutions (12-30 mL/g in brine, and 5.0×10^2 – 3.5×10^4 mL/g in dilute solution).

In some experiments, sorption results suggest solubility control, but calculation of starting and final solute concentrations indicate solubility limitations are unlikely (Se and As) or the results inconsistent with observations for concurrent experiments under equivalent environmental conditions (Tc).

Thus, despite numerous uncertainties, the sorption experiments conducted as part of this project appear to have developed a reasonable first estimate of sorption characteristics for As, Np, Pu, Se, Tc, and U in brine and dilute solutions at low-Eh and low-O_2(g) conditions.

4.1 LIMITATIONS AND CHALLENGES

The project required many technical adaptations to (i) consistently establish and maintain the required environmental conditions, and (ii) ensure that pH and ORP were reliably measured in the high ionic strength brine solutions. Significant effort was expended to set up and maintain an experimental environment that met the requirements for the study. Although there were many successes and reasonable results were achieved for the experiments, there remain some limitations, uncertainties associated with use of data presented in this report and technical challenges for potential future sorption studies in brine solutions at low Eh.

One major technical difficulty was associated with the establishment and maintenance of the low-O_2 atmospheric conditions needed to maintain Eh on the order of −200 mV in solutions in contact with that atmosphere. Once an adequate gas mixture was employed and solutions with added solids equilibrated at low Eh, the stability of the solution conditions was not as expected. Even with verified maintenance of low-O_2 conditions using continuous monitoring and addition of H_2, periodic checks of solutions indicate a slow increase in Eh over time. The cause of these observed changes is unknown, but it should be considered in future work. Included in the glove box apparatus was an O_2 scavenging system designed to maintain very low-O_2 conditions. For the experimental setup employed in this project, removal of $O_2(g)$ could not be achieved without loss of $CO_2(g)$. The lack of $CO_2(g)$ in the experimental systems likely adds uncertainties to the sorption results. It can be difficult to separate increases in sorption due to redox state from those caused by the lack of competing carbonate species in solution. This is especially true for actinides such as U and Np. An experimental setup utilizing a gas flow-through design would be better suited to maintenance of an atmosphere with low-O_2 but with the elevated concentrations of CO_2 and H_2 required for experimentation at the desired Eh values. Use of gas flow would require substantial volumes of special mix gas, especially given that atmosphere control for equipment and material transfers would still be required. Low volume single reaction cells could be utilized, but this would severely limit the number of experiments that could be conducted.

A second technical challenge is that quantification of the radioelements of interest depends on several factors. For the brine solutions in particular, the high TDS content requires significant dilution of the solution for analyses by standard chemical methods such as ICP and ICP-MS. While use of these analyses is possible and can be successful, it is difficult to match the anticipated detection and quantitation limits for a trace element in brine with the dilution required for use of sensitive analytical equipment. Moreover, at the potentially low initial concentration limits necessary to avoid solubility constraints, subsequent detection can be difficult to achieve. Selection of radioactive tracers is a reasonable approach to dealing with analytical and dilution requirements, and this approach was used in this project with the exception of the experiments on As. However, the selection of nuclide is critical as well. The nuclide must have a high enough specific activity to be counted at trace quantities using the methods selected. For example, liquid scintillation counting of Np-237 may have a lower quantitation limit of 10^{-10} to 10^{-11} M, but the acceptable range of initial concentrations to ensure avoidance of solubility issues is 10^{-9} to 10^{-10} M. Because of the small difference in starting concentration and the minimum concentrations for accurate detection, the ability to quantify Np sorption with less uncertainty is limited for LSA (liquid scintillation analysis). Often, there are no available nuclides that meet analysis criteria or the nuclides that might work best are difficult to acquire and store. An example of this type of limitation involves Np as well. For Np(IV) experiments, the solubility of Np may be near or below 10^{-9} M (depending on the source of data used to estimate the solubility). For Np-237, the most readily available isotope, counting limitations for use of LSA (or α-spectrometry) are present. While Np-239, which offers a much higher specific activity (and resulting concentration values several orders of magnitude lower), has been used in sorption tests, observations in this project suggest that initial activities required to overcome the potential slow kinetics behaviour of Np may be impractical. It may be that alternative analytical methods like ICP-MS (Nagasaki et al., 2016) or the use of surrogate elements will be required to fully assess Np sorption in the brines.

Adding additional reductants to the experimental systems is effective in lowering Eh, but alters the system state, especially pH (and may not be stable as the solution evolves over time, such as in the case of the Tc experiments). One consideration may be the need to limit the HNO_3 content of radionuclide stock solutions in favour of HCl, which may have less impact on the redox state of the system.

There is some conflict between the need for low concentration solutions in the experimental samples and the more concentrated solutions required for most readily available species analysis methods. Adequate confirmation of valence state was not accomplished in this work. The results reported here require additional work to establish valence states for Np and Tc in particular.

Evaporative effects were significant in the long running experiments. The low humidity of the supply gas mixture and removal of H_2O vapour by the scavenging system contributed to evaporation. Evaporation was enhanced through efforts to ensure adequate gas-exchange and equilibration of stock and experimental solutions. Experimental protocols were modified to minimize evaporation and reported results were corrected for any solution losses prior to spiking and prior to sampling. However, measurable changes in solute concentration and pH were observed and interpreted to result from evaporation.

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