REDOX-CONTROLLING PROCESSES FOR MULTIVALENT METALS AND ACTINIDES IN THE WIPP

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Abstract

The subsurface chemistry of multivalent actinide contaminants is highly dependent on their oxidation state distribution and associated redox conditions. These redox conditions are established by coupled direct and indirect subsurface processes such as microbial activity, geochemical reactions with the host rock, and the chemical effects of other co-contaminants present. The ability to predict actinide migration, especially over the very long times that are typically of concern, is directly linked to the ability to establish the nature, stability, and mobility of dissolved species formed within the bounds of the prevailing redox conditions. The measurement of system-specific redox conditions (E_h) can be problematic under the most ideal groundwater conditions but is especially problematic in high ionic strength systems such as brines with I > 5 M.

The redox chemistry and key assumptions pertaining to the key multivalent metals and actinides present in the WIPP underground, which is expected to be a strongly reducing high ionic-strength brine system, is presented. Long-term actinide solubility studies and redox kinetics of lower-valent iron show varied degrees of correlation between Pu(III)/Pu(IV) and Fe(II)/Fe(III) concentration ratios with E_h measurements. Linkages between the observed microbial activity and redox chemistry of neptunium were also observed. Overall, these system-specific results are discussed and interpreted in the context of their broader application to understanding the redox chemistry and migration behavior of multivalent metals and actinides in high ionic-strength brine systems and salt-based repositories.

1.0   Introduction

The fate and potential mobility of multivalent transuranic actinides in the subsurface is receiving increased attention as the DOE considers remedial alternatives for many of their legacy nuclear waste sites and associated groundwater contamination. The oxidation state distribution of multivalent elements is frequently linked to the redox conditions in groundwater (see Table 1). Plutonium is often the subsurface contaminant of concern in groundwater at contaminated DOE sites and remains a key contributor to potential actinide release from permanent geologic repositories. Americium and neptunium may also be key contributors for some repository conditions. The experience in the field is that the biogeochemistry of these transuranics is favorable towards their subsurface immobilization under a wide range of conditions.

The migration potential for transuranics in groundwater is highly dependent on its oxidation-state distribution and associated extent of aggregation. Under anoxic conditions in nutrient-rich groundwater where organic co-contaminants may coexist, the oxidation state distribution is primarily defined by the combined effects of reduced iron, organic chelating agents, and

microbial activity. Understanding these processes, and their synergisms, is critical to establishing the subsurface fate of transuranics, including plutonium, and explaining their apparent immobility.

Table 1. Prevalent Oxidation States of Multivalent Actinides in Groundwater				
Redox Environment	U	Np	Pu	Am
Oxic	VI	V, VI?	V, VI? IV	III, V?
Suboxic	VI IV	IV	IV III	III
Anoxic	IV	IV	IV III	III

The issue of redox, and in particular the measurement of a meaningful E_h in groundwaters has been controversial for a number of years [Lindberg and Runnels, 1984; Kehew et.al, 2000]. Redox disequilibria, rather than equilibrium is the norm and the meaning of E_h measurements to predicting the oxidation state of multivalent actinides, which are often present in much lower concentrations than other redox active metals (e.g., Fe(II/III) and Mn(II/IV), is even less clear. The interpretation of E_h measurements from high ionic strength media such as brines is even more problematic since high ionic strength can significantly affect the response of the electrode [Capdevila and Vitorge, 1990; Wiesner et.al, 2006; Degueldre et.al, 1999; Christensen et.al, 2000]. A better approach may be to link the behavior of known redox couples with the actinide oxidation state distribution, as was done in low ionic-strength systems [Masue-Slowey et.al, 2011; Holm and Curtiss, 1989; Christensen et.al, 2000], to more reliably predict the actinide redox chemistry.

Herein we report on recent progress towards understanding the key factors that influence the oxidation state distribution, fate, and potential transport of actinides in high ionic-strength brine systems present in the Waste Isolation Pilot Plant (WIPP) transuranic repository. This research, although not directly performed as part of the Recosy project, reflects many of the scientific interests on redox controlling systems that influence all subsurface actinide chemistry. Our research [Reed et.al, 2006, Reed et.al, 2007, Reed et.al. 2011; Lucchini et.al, 2007; Borkowski et.al, 2009] is centered on the speciation of key actinides under WIPP-specific conditions. The goals of this research are to improve the robustness and quantify conservatisms in the geochemical conceptual models for the WIPP site. As a component of this research, the key linkages that help predict oxidation state distributions in high ionic strength systems are being investigated. This is an important consideration for the ongoing recertification of the WIPP, which is the only United States transuranic nuclear waste repository, as well as other nuclear repository options being considered in a salt geology.

2.0   Redox Environment and Actinide Oxidation-State Distribution in the WIPP

The WIPP transuranic repository remains a cornerstone of the U.S. Department of Energy's (DOE) nuclear waste management effort. Waste disposal operations began at the WIPP on March 26, 1999 however the WIPP is required to be recertified every five years for its disposal operations. The WIPP received its second recertification in November 2010 and the geochemical conceptual model for the site provides a starting point for redox discussions that were tested in a peer and regulatory review process.

The expected redox environment in the WIPP, based on the current conceptual model, is that strongly reducing conditions will prevail early in repository history leading to a lower-valent actinide oxidation state distribution [Reed et al., 2011]. Early after repository closure (within a few hundred years) self-sealing of the salt will occur that will geologically isolate the repository. Very shortly thereafter the excess iron and microbial activity is predicted to consume all the oxygen initially present leading to an anoxic environment. The expected scenario is that the repository will remain anoxic and "dry" throughout repository history unless low probability human intrusions lead to brine inundation. At the point of brine inundation, should this occur, the reactivity of the remaining zero-valent iron and activity of facultative and anaerobic halotolerant and halophilic micro-organisms will maintain a strongly reducing environment that promotes and stabilizes lower-valent actinides in solution. Although some localized oxidizing conditions may exist, e.g. due to radiolysis, these are quickly overwhelmed by the excess of reduced iron present and do not significantly contribute to the overall chemistry of the repository. The predominantly lower-valent actinides have low solubility and a high tendency towards sorption which leads to a low probability of migration and subsequent release from the WIPP.

For the low-probability inundated brine scenarios, some release through migration of dissolved actinides is possible. The potential dose-to-man contribution of the actinides, where both activity and solubility are considered, leads to the following overall ranking of the actinides with respect to release from the WIPP:

$$Pu \sim Am > U \gg Th \text{ and } Np$$

Uranium, based on current assumptions, has the highest potential for release by mass. The relative importance of oxidation states, also from a dose-to-man perspective, is:

$$An(III) > An(IV) \gg An(VI)$$
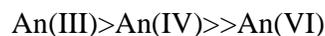
Both plutonium and americium speciate as An(III) species, with plutonium as the main contributor to An(IV) release. The An(V) oxidation state is largely ignored since Np, which is the only actinide that speciates significantly as in the An(V) oxidation state, has a very low inventory in the WIPP and does not contribute significantly to the predicted release of actinides.

The oxidation state distribution that is used in WIPP performance assessment (PA) is shown in table 2. These distributions are designed to be conservative with respect to potential for actinide release and are based on expert judgment that reflects the expected redox conditions in the WIPP. In this context, they are not calculated values nor are they based directly on measurements made in the laboratory. In the calculated releases, an oxidized (50% of the PA vectors) and reduced (50% of the PA vectors) bounding condition, are used. In the reduced bounding condition, the multivalent actinides are in their lower oxidation state. This is U(IV), Pu(III), and Np(IV). In the oxidizing bounding state, the multivalent actinides are in their higher oxidation state. This is U(VI), Pu(IV) and Np(V). In all cases, thorium is only present as Th(IV); americium and curium are only present as Am(III) and Cm(III).

The calculated oxidation-state-specific actinide solubility, for the past certification and recertification of the WIPP are tabulated in Table 3. These base solubilities are coupled with assumptions about colloid enhancement to generate an oxidation-state-specific dissolved concentration that is used in the assessment of actinide release from the WIPP.

Table 2. Actinide Oxidation State Distribution Assumed in the WIPP Performance Assessment Model (Reed et al, 2011)					
Actinide	**Oxidation State**				**Speciation Data used in Model Predictions**
	III	**IV**	**V**	**VI**	
Thorium		100%			Thorium
Uranium		50%		50%	Thorium for U(IV), 1 mM fixed value for U(VI)
Neptunium		50%	50%		Thorium for Np(IV), neptunium for Np(V)
Plutonium	50%	50%			Americium/neodymium for Pu(III) and thorium for Pu(IV)
Americium	100%				Americium/neodymium
Curium	100%				Americium/neodymium

Table 3. Calculated Oxidation-state-specific solubility (M) of actinides in Salado (high magnesium) and Castile (high sodium chloride) brines (Reed et. al, 2011)				
Actinide Oxidation State	**Brine**	**[a]PAVT 1999**	**[b]PABC 2004**	**[c]PABC 2009**
An(III)	Salado	1.2×10^{-7}	3.9×10^{-7}	1.7×10^{-6}
An(III)	Castile	1.3×10^{-8}	2.9×10^{-7}	1.5×10^{-6}
An(IV)	Salado	1.3×10^{-8}	5.6×10^{-8}	5.6×10^{-8}
An(IV)	Castile	4.1×10^{-9}	6.8×10^{-8}	6.8×10^{-8}
[a] Performance Assessment Verification Test - initial WIPP license application				
[b] Performance Assessment Baseline Calculation - 1st recertification in 2004				
[c] Performance Assessment Baseline Calculation - 2cnd recertification in 2009				

3.0   Investigations of High Ionic-Strength Redox Linkages

Research to understand the detailed mechanisms by which redox conditions are established and their impact on actinide speciation is ongoing within the WIPP project [Reed et.al, 2011]. The two most important processes that will impact oxidation-state distribution are the effects of redox-active multivalent metals, such as iron or manganese, and the direct and indirect effects of microbial processes. The goal of this research effort is to quantify the degree of conservatism present in the current assumptions and move towards a more realistic but still conservative conceptual model for the WIPP site.

3.1 E_h Measurement in Brine Systems

The measurement of E_h, for reasons mentioned previously, is problematic in high ionic strength brine systems. In this context, these types of measurements, at best, provide qualitative but rarely quantitative data on the redox conditions in the brine experiment.

To investigate these qualitative relationships, E_h measurements were made on a series of plutonium solubility and redox speciation studies that contained excess reduced iron. All measurements were made in the nitrogen glovebox where the experiments were conducted ($P_{O2} < 0.1$ ppm). These experiments were not sampled frequently and were doubly sealed/isolated to minimize the effects of occasional elevated oxygen levels in the glovebox due to routine experiments and operations. An Orion epoxy sure-flow combination redox/ORP electrode (model 9678-BNWP) was used with the high ionic strength internal Ag/Cl reference solution provided by the manufacturer. This electrode was pre-conditioned in the glovebox for several hours. The manufacturer-supplied ORP standard was used to calibrate the electrode and frequent checks of the electrode response were made throughout the E_h measurement operations.

The results of the E_h measurements made are given in Table 4. Typical electrode equilibration times were 20-30 minutes. In the absence of iron and plutonium, the brines used (high magnesium GWB, and sodium chloride ERDA-6 – see Lucchini et.al 2007 for brine compositions), had a measured E_h of $+464 \pm 5$ mV in the presence and absence of air.

Table 4. Qualitative Redox Indicators for Iron Interactions with Plutonium under Anoxic Conditions				
Experiment	**Description**	**[a] Oxidation State of Pu Solid**	**[b] $[Fe]_{total}$ in mM (%Fe^{2+} in solution)**	**[c] E_h Measured (± 3 mV)**
PuFe23OX	ERDA-6 brine at pH ~9 with excess magnetite	~87% Pu(III), rest Pu(IV)	0.12 (25%)	-122 mV
PuFeCE8	ERDA-6 brine at pH ~8 with Fe coupon	~100 % Pu(III)	ND	ND
PuFeCE10	ERDA-6 brine at pH ~ 9.6 with Fe coupon	~100% Pu(III)	0.27 (100%)	ND
PuFeP	ERDA-6 brine at pH~9 with excess Fe powder	~100% Pu(III)	0.18 (100%)	-175 mV
PuFeC	ERDA-6 brine at pH ~ 9 with Fe coupon	~90% Pu(III), rest Pu(IV)	0.18 (58%)	-110 mV
PuFeG7	GWB brine at pH ~6.7 with Fe coupon	~ 100% Pu(III)	12.62 (97%)	-210 mV
a. Pu(III) content established by XANES analysis of solids b. Fe(II) content established by analysis using FerroZene® c. E_h measurement made using an Orion combination ORP electrode ND – not determined				

In the presence of soluble/measureable amounts of dissolved iron species the E_h became negative, as expected, with a range of -100 mV to -220 mV. This seemed to qualitatively correlate with the measured concentration of Fe^{2+} in solution. Equilibration times under these conditions were ~ 20 minutes, slightly shorter than in the absence of Fe. Fe^{2+} and Fe^{3+} concentrations were measured using a modified method based on the FerroZene®

complexation of Fe^{2+} [Pepper et al., 2008].   Under the conditions of our experiments, approximately 1 mM carbonate was present in the brine (except experiment PuFeG7), so some solubilisation of Fe(III), as Fe^{3+}, was possible and observed.   These results were reproducible over the course of the five hours that samples were analyzed in the glovebox environment.

Our overall results in the presence of iron are consistent with what has been shown for low ionic strength systems [Christensen et.al., 2000; Holm and Curtiss, 1989] where somewhat good correlations and fast electrode response was seen when the Fe^{2+}/Fe^{3+} couple set the redox potential and defined the electrode response. We are continuing to further quantify this response and explore lower concentration limits for the applicability of this technique.

3.2   Effect of Reduced Iron on Redox and Actinide Oxidation States

Long-term (~ 5.5 year) experiments to establish the oxidation state distribution of actinides in brine systems under a wide range of subsurface conditions are ongoing. In our investigations ^{242}Pu, initially as PuO_2^{2+}, was used to minimize radiolytic effects. In these brine systems, Pu(VI) is stable for years when no reducing agent is present [Reed et.al, 2007].

Two WIPP-relevant brines [Lucchini et.al., 2007], GWB as a high magnesium brine typical of MgO-reacted brine and ERDA-6 as a high sodium chloride brine typical of brine found in the far field, were used in these studies.   The initial oxidation state was established using absorption spectrometry (Varian CARY 5000) and solids are prepared from these brines using established methods. Liquid scintillation counting (Beckman-Coulter LS 6500) and ICP-MS (Agilent) were used to determine total concentration. Aqueous iron chemistry was established using a combination of a FerroZene® colorimetric method and ICP-MS. XANES analysis, combined with anoxic dissolution and UV-VIS-NIR spectroscopy (Varian CARY 5000) were used to establish the oxidation state of the precipitated plutonium.

Iron reduction experiments were performed by adding iron and iron oxides to stable anoxic Pu(VI) solutions with different pH values. The reactivity of Fe^{2+} and Fe^{3+} towards various plutonium oxidation states was also established. At the end of the kinetic studies, samples of plutonium precipitates were recovered and analyzed by XANES. After equilibration for an additional 5.5 years, the solutions were analyzed to establish the iron speciation, plutonium speciation and E_h. Selected data for these experiments were shown in Table 4. Plutonium concentration trends are shown in Figure 1.

Initially, only Pu(IV) was evident in the XANES analysis (see Figure 2). This correlated with a plutonium concentration that was in the range of 2×10^{-9} M to as high as 1.5×10^{-7} M at the lower end of the pH range (pH = 7).   These data agreed with the results obtained in a prior study after approximately two years when Pu-239 was the plutonium isotope. After ~5.8 years, these same solid samples were re-analyzed and found to be mostly Pu(III) with some Pu(IV). These results are summarized in Table 4. The observation of Pu(III) in the solid phase correlated with an increase in the plutonium solution concentrations from 1×10^{-8} M to 3×10^{-7} M. This is a slight elevation in concentration, by a factor of ~ 2 to 5, when compared to the earlier Pu(IV)-relevant data. This increased solubility is also consistent with the phase transformation to Pu(III) since the solubility of Pu(III) is expected to be somewhat higher than Pu(IV) – see Table 3.
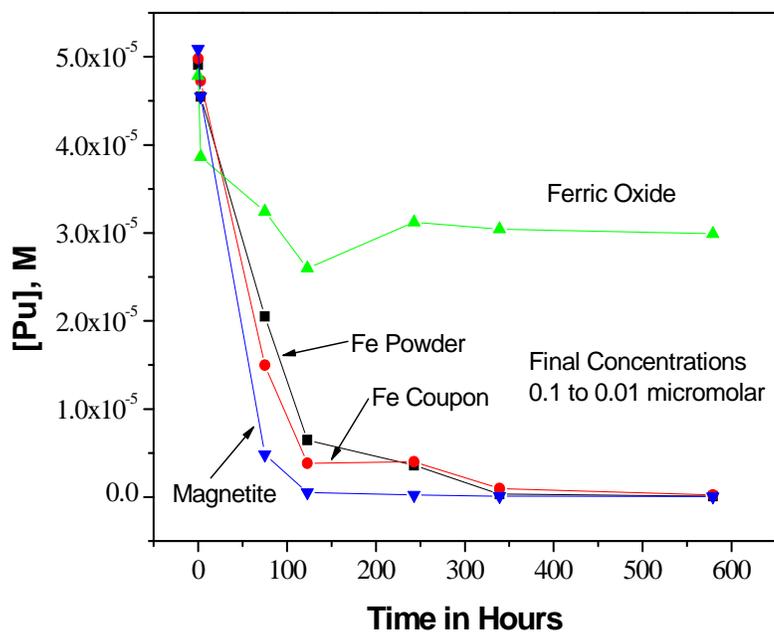
Figure 1.   Concentration of Plutonium as a Function of Time after
                    Contact with Iron and Iron Oxide Phases in ERDA-6
                    Brine. Fe powder is experiment PuFeP, Fe coupon
                    is experiment PuFeC, magnetite is experiment
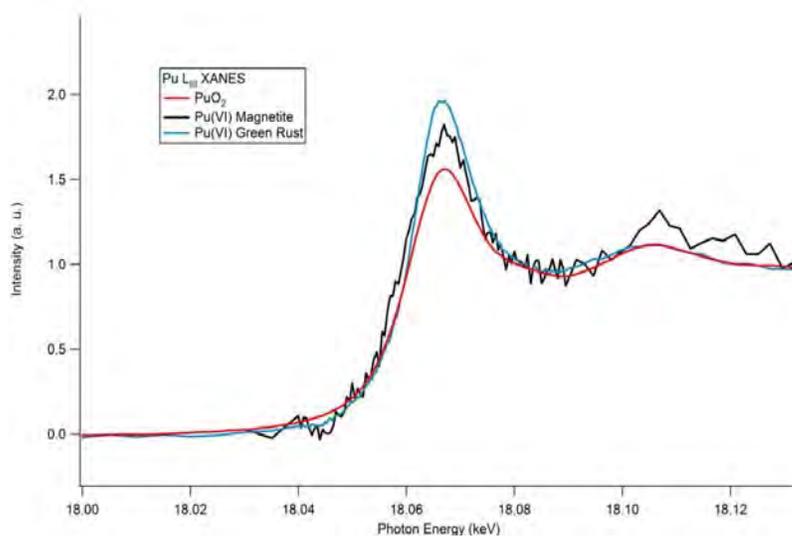   PuFe23OX, and ferric oxide is experiment PuFe3OX.

Figure 2.   XANES Analysis of Plutonium Precipitates in the Magnetite
                    and Iron Reduction Experiments at 3 months. Pu(IV) phases
                    were predominantly noted.

The plutonium (III/IV) solids data show a qualitative correlation with the Fe(II)/Fe(III) ratio and measured E_h. Experiments with less negative E_h also had a greater amount of Fe(III) and Pu(IV) species present in the system. This adds to the linkages seen by others between the iron and plutonium chemistry in subsurface conditions. Although these specific experiments were performed in brine, they are consistent with the correlation between iron chemistry and other metals observed in low ionic strength groundwater [Masue-Slowey et.al, 2011; Holm and Curtiss, 1989; Christensen et.al, 2000]. Although not discussed in this paper we have also demonstrated that U(VI) and Np(V) are reduced by zero-valent iron and Fe(II) aqueous/solid species and this also confirms the lower oxidation states expected in the WIPP for these actinides.

3.3   Influence of Halotolerant and Halophilic Microorganisms on Redox and Actinide Oxidation State

Microorganisms affect the redox behavior of multivalent actinides in two important ways: (1) indirectly, by helping impose reducing conditions in subsurface environments via the reduction of oxygen and by generating reducing agents, such as dissolved organic species and Fe^{2+}, and (2) directly, by enzymatic reduction, and in less common cases oxidation of multivalent actinides such as plutonium. This redox effect has been well demonstrated for bacteria typically found in low ionic-strength groundwater, soils, sediments, and porewaters [Rittmann et.al, 2002; Banaszak et.al, 1999; Reed et.al, 2007; Lovely, 1993; Caccavo et.al, 1992; Gorby and Lovley, 1992; Boukhalfa et.al, 2007; Francis and Gillow, 2008].

This potentially important microbial process has, however, not been extended to the halotolerant and halophilic *Bacteria* and *Archaea* that are typically present in high ionic-strength brine systems. In fact, little is known about the effects of these organisms on metal redox reactions, with the exception of marine sediments. It may be that iron and other metals are only present as minor constituents in these systems and the concentration of sulfate too high for metals to be feasible terminal electron acceptors. We are addressing the lack of data concerning metal reduction in high ionic strength matrices and expect to show that some of the same processes that are known to occur at lower ionic strengths will also occur in brine systems. For the specific example of the WIPP, the nutrients present in the TRU waste (nitrates, organics, phosphates and sulfates) are expected to promote significant microbial growth and the potential effects of microbial growth are already factored into aspects of PA.

Our current emphasis is to investigate the impact of halotolerant and halophilic microorganisms on plutonium over a range of ionic strengths. The growth of many of these organisms during early repository history when oxygen is available will help create a reducing environment. Many of the extremely halophilic Archaea (ionic strengths greater than 2.5 M) are also efficient nitrate reducers; while, at lower ionic strengths (up to 2.5 M), many halotolerant and halophilic Bacteria may be capable of metal or sulfate reduction.

We have measured iron reduction in incubations of a mixed culture of halophilic Bacteria and Archaea (Figure 3). This incubation selected for specific organisms (Figure 3), and we are in the process of elucidating the mechanism for iron reduction. Thus far, separate incubations of the bacterial species alone have also yielded Fe^{2+}, albeit incomplete. The formation of Fe^{2+} in solution will actively reduce Pu(V/VI) down to Pu(III). The demonstration of Fe(III) reduction also links, at least qualitatively, to what we have observed for soil bacteria.
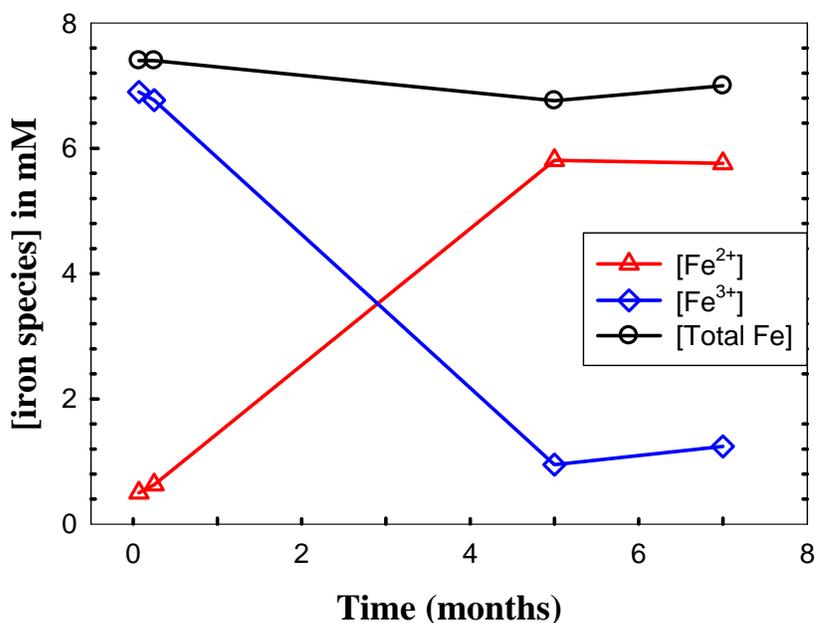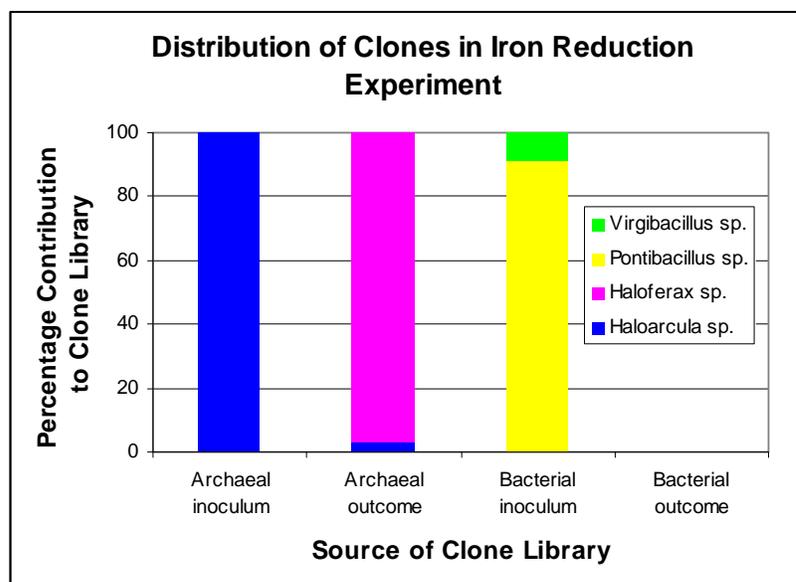
Figure 3. Top: Graph depicting the distribution of clones with two distinct libraries, Bacterial and Archaeal. Shows almost complete disappearance of *Haloarcula* sp. and complete disappearance of Bacterial species during the course of incubation, with selection for *Haloferax* sp.. Bottom: Results for iron analysis in incubation tube C of PZ-13 iron-reduction experiment. Levels of iron(III) decrease with a concomitant increase in iron(II). Total iron remains constant throughout the incubation period.

We have also noted the enhanced reduction of Np(V) when added to Fe(III) incubations with halophilic microorganisms (see Figure 4). It is not however clear if this is result is due to a direct enzymatic or co-metabolic mechanism due to the generation of reducing agents. The microbial effects on the oxidation state distribution of the multivalent actinides, particularly U, Pu and Np, continues to be the focus of ongoing studies.
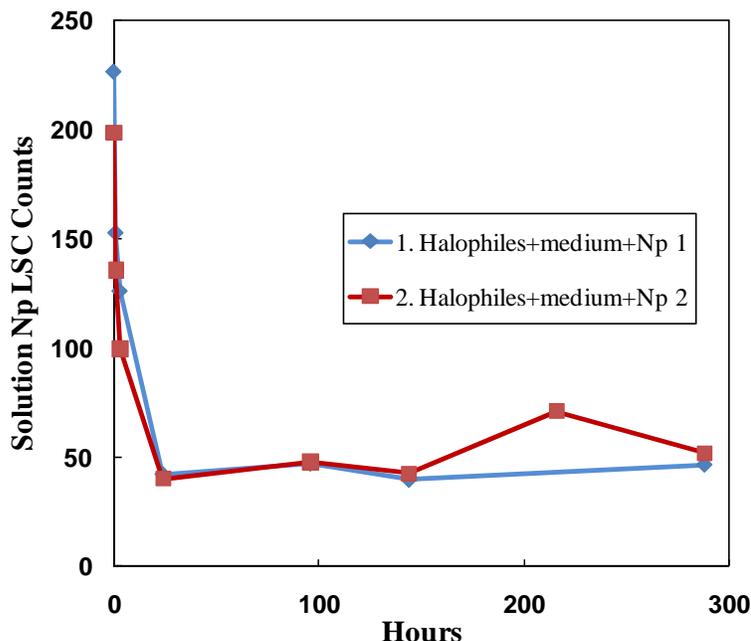

Figure 4. Bio-enhanced Np(V) Reduction Using Fe(III) High Ionic Strength Medium

4.0   Summary and Conclusions

The factors that will define E_h in a brine system were discussed. WIPP assumptions, based on expert opinion, are being supported by ongoing site-relevant research even though little site relevant data existed at the time they were established.

E_h brine measurements, when performed with excess reduced iron in solution, qualitatively correlated with the Fe^{2+} content in the brine systems. Equilibration times were relatively rapid and effort to quantify this effect more rigorously is underway. This reduced iron is very reactive in brine across a wide pH range and is very effective in reducing multivalent actinides to their lowest possible oxidation state: U(IV), Pu(III) and Np(IV). These experimental results support the overall WIPP PA assumptions and establish them to be conservative with respect to overall solution concentration of mobile actinide species. The one important and key area that is not fully resolved is the long-term stability of the Pu(III) phases being observed and in particular the effects of radiolysis, the more repository-relevant condition, will have on the distribution of plutonium between Pu(III) and Pu(IV). It was already demonstrated that reduced iron is very effective in reducing Pu(V/VI) in radiolysis-

affected systems [Reed et.al., 2007]. This lower oxidation-state equilibration remains the focus of our ongoing research.

Lastly, progress is reported on establishing the effects of microbial growth, for the halotolerant and halophilic *Bacteria* and *Archaea*, typically found in high ionic strength brine systems. Oxygen consumption and Fe^{3+} reduction were observed. Bio-enhanced reduction of Np(V) was likely observed and there is an expectation that the Fe^{2+} formed will certainly lead to the reduction of high-valent plutonium. This work is expected to show that many microbial controls and effects that are well demonstrated for soil bacteria will also function for the microorganisms typically found at high ionic strength.

5.0 Future Directions of the Research

Research to understand the key subsurface processes that control and determine actinide redox reactions in the WIPP repository will continue. Near-term emphasis is on work to establish the key mechanisms of the reduced-iron plutonium interactions. Experiments to establish the long-term stability of reduced plutonium phases (both Pu(III) and Pu(IV)) are planned. The characterization of WIPP-indigenous microorganisms is ongoing with continued emphasis on halotolerant and halophilic microorganisms that biodegrade organic chelating agents and are important in the bioreduction of higher-valent actinides.

Acknowledgement

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