Title: Plutonium Speciation and Mobility In Groundwater

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PLUTONIUM SPECIATION AND MOBIITY IN GROUNDWATER

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The fate and potential mobility of plutonium in the subsurface is receiving increased attention as the DOE looks to cleanup the many legacy nuclear waste sites and associated groundwater contamination. Plutonium is often the subsurface contaminant of concern and remains a key contributor to potential actinide release in a permanent geologic repository. The experience in the field is that the biogeochemistry of plutonium is favorable towards its subsurface immobilization under a wide range of conditions. Its potential for migration 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 plutonium and explain its apparent immobility. Herein we report on recent progress towards the understanding of key subsurface processes that impact the subsurface migration of plutonium as a function of ionic strength and redox conditions.

Oxidation State Distribution of Plutonium in the Subsurface

Experiments to establish the oxidation state distribution under a wide range of subsurface conditions are ongoing[1-3]. 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. In our investigations plutonium-242, as Pu^{3+} and PuO_2^{2+}, were used in the experiments performed to minimize radiolytic effects. A range of simulated or simplified groundwaters[1-3] was also used. The initial oxidation state was established using absorption spectrometry (CARY 5000) and solids are prepared from these using established methods. Liquid scintillation counting and ICP-MS were used to determine total concentration. Aqueous iron chemistry was established using a combination of a modified FerroZine® colorimetric method[4] and ICP-MS. XANES, XRD, and electron microscopy were used to establish the oxidation state of the precipitated or bio-associated plutonium.

Iron reduction experiments were carried out by adding iron and iron oxides to stable anoxic Pu(VI) solutions as a function of pH. The reactivity of Fe^{2+} and Fe^{3+} towards various plutonium oxidation states was also established. After equilibration for over four years, the solutions were analyzed to establish the iron speciation, plutonium speciation and E_h. Selected data for these experiments are shown in Table 1. These data show a qualitative correlation between the Fe(II/III), Pu(III/IV) and measured E_h in that 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 what is observed in low ionic strength groundwater.

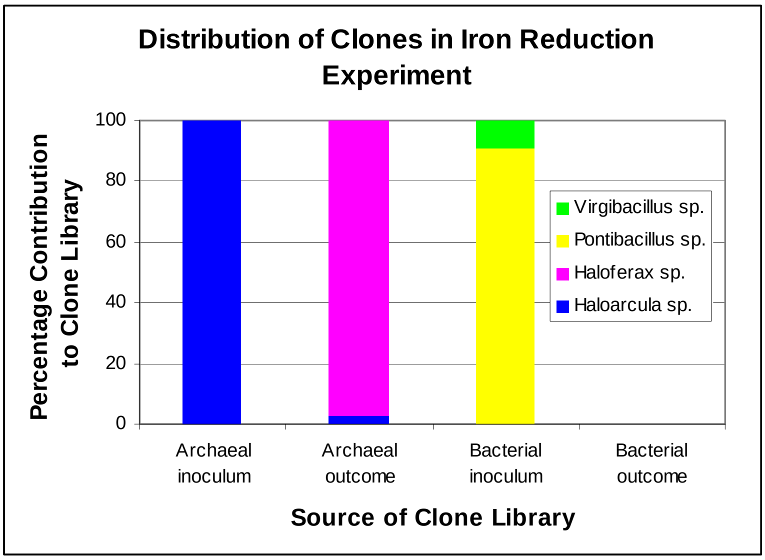
Table 1. Qualitative Redox Indicators for Iron Interactions with Plutonium under Anoxic Conditions

Experiment	Description	Oxidation State of Solid	%Fe^{2+} in dissolved iron	E_h Measured
PuFe23OX	ERDA-6 brine at pH ~9 with excess magnetite	~87% Pu(III), rest Pu(IV)	25	-122 mV
PuFeCE8	ERDA-6 brine at pH ~8 with Fe coupon	~100 % Pu(III)	ND	ND
PuFeCE10	ERDA-6 brine at pH ~ 10 with Fe coupon	~100% Pu(III)	100	ND
PuFeP	ERDA-6 brine at pH~9 with excess Fe powder	~100% Pu(III)	100	-175 mV
PuFeC	ERDA-6 brine at pH ~ 9 with Fe coupon	~90% Pu(III), rest Pu(IV)	58	-110 mV
PuFeG7	GWB brine at pH ~7 with Fe coupon	~ 100% Pu(III)	97	-210 mV

Pu(III) content established by XANES analysis of solids
Fe(II) content established by analysis using Ferrozine [4]
E_h measurement made using an orion combination ORP electrode

Effects of Microorganisms on Plutonium Oxidation State Distribution

Microorganisms affect the redox behavior of plutonium indirectly by helping impose reducing conditions in sub-oxic subsurfaces and generate reducing agents (e.g. Fe^{2+}) as well as directly reduce, and in some cases, oxidize multivalent actinides such as plutonium. In prior work, the direct and likely enzymatic reduction of plutonium was demonstrated for metal-reducing soil bacteria[3]. Our current emphasis is to extend what has been shown for soil bacteria to halo-tolerant and halophilic microorganisms to demonstrate microbial impacts on plutonium over a range of ionic strengths. Numerous facultative microorganisms were observed that were efficient at removing oxygen from the brine systems. Iron(III) reduction has been demonstrated (see Figure) which leads to the formation of mM concentrations of Fe^{2+} in solution. Enhanced bioreduction of Np(V) was also observed in the Fe(III) incubations but it is not year clear if this is directly enzymatic or co-metabolic due to the reducing agents being generated. Similar results are expected for higher-valent plutonium in these high ionic-strength microorganisms that appears to be functioning much in the same way as soil bacteria.



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.

Colloidal fraction of Plutonium

The extent of aggretation of putonium under environemtnally-relevant conditions and its contribution to plutonium migration is the focus of continued discussion. Plutonium nanocolloids have been observed in the laboratory and colloids in general are often observed[5]. This contrasts with our field experience where, although colloids are formed, they do not migrate very far and in some cases appear to help immobilize the plutonium. The colloidal fraction of actinides and analogs was establsihed by a combination of sequential filtration (down to ~ 7 nm) and by ultrafugation (up to 130,000 rpm, Beckman ultracentrifuge). The results obtained in our long-term thorium solubility studies indicate that the formation of colloids is not prevalent in long-term experiments at high ionic strength. These investigations are being extended to plutonium in iron-rich systems and these results will be reported.

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