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Effect of Aging on the Reversibility of Pu(IV) Sorption to Goethite

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MOTIVATION

Plutonium exists in legacy waste from nuclear weapons production at DOE sites (Hanford Site, Nevada Test Site, Savannah River Site), and is produced in commercial nuclear power plants. In order to develop safe disposal and remediation strategies, a predictive transport model for plutonium must be developed and incorporated into risk assessments.

Sorption to mineral surfaces controls the subsurface mobility of plutonium. The effect of sorption depends on pH, natural organic matter, and soil type. Sorption of Pu(IV) to iron oxides has been observed to be strong and rapid. However, many studies were unable to completely desorb Pu(IV), and characterized Pu(IV) sorption as irreversible or hysteretic[1]. These observations may be explained by **aging**, a surface chemical process happening after initial sorption which causes a change in contaminant surface speciation over time[2]. The longer Pu(IV) ages on a surface, the less reversible the sorption reaction becomes.

METHODS

Experimental

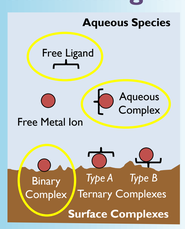
Batch experiments were run in goethite suspensions (0.1 g/L) in 10 mM NaCl which spanned the pH range 4 to 7.

1. Adsorption: Pu(IV) was reacted with goethite in ligand-free batch samples for various lengths of time (1, 6, 15, 34 and 116 days).
2. Treatment: supernatant was quantitatively replaced with 1.7 µM desferrioxamine B (DFOB) solution and…
3. After 34 more days, aqueous solutions were analyzed for Pu by liquid scintillation counting.

Experimental Parameters

pH	4 – 7
Suspended Solids	0.1 g/L
Mineral	Goethite (a common iron oxide)
Total Initial Pu(IV)	8×10^{-11} M
DFOB Solution	1.7 µM
Ionic Strength	10 mM (NaCl)

Controlling Oxidation State using DFOB



Measurements of Pu(IV) sorption are often complicated by oxidative leaching of Pu(IV) as Pu(V). DFOB minimizes oxidative leaching by forming strong Pu(IV)-DFOB complexes, thereby stabilizing Pu(IV) as the dominant aqueous oxidation state.

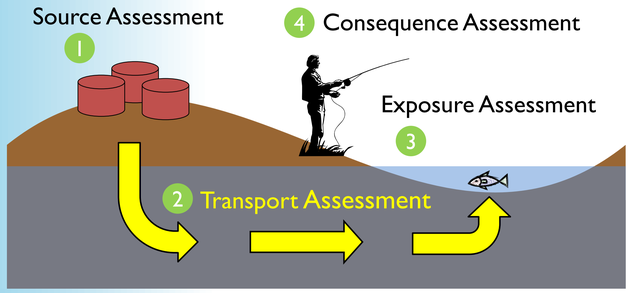
Equilibrium Speciation Modeling

In order to compare the stability of surface complexes of different ages, a single double-layer surface complexation reaction was chosen to model the sorption curves in FITEQL.

$$\equiv FeOH + Pu^{4+} + 3\ H_2O \leftrightarrow \equiv FeOPu(OH)_3 + 4\ H^+$$

RISK ASSESSMENT

The Four Components of Risk Assessment



A better understanding of plutonium geochemistry allows for improved **transport assessment** for plutonium.

RESULTS

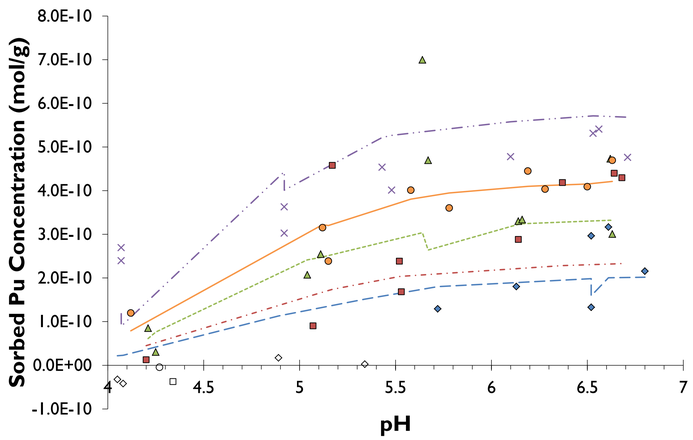
Measurements of unremoved Pu are plotted against pH for each adsorption time.

- Sorbed Pu increases with pH.
- More Pu remained sorbed with greater aging.
- Sorbed Pu continued to increase between 34 and 116 days of aging.

Model sorption curves are overlaid on the plot.

- Good fits were achieved for aging >15 days.
- For samples aged 1 and 6 days, surface complexes may not have reached equilibrium.
- Excluded data: Open symbols represent data points which were not included for modeling.

Stability constants produced by the model had logK values which increased from 0.078 to 0.953 over the course of 116 days aging.



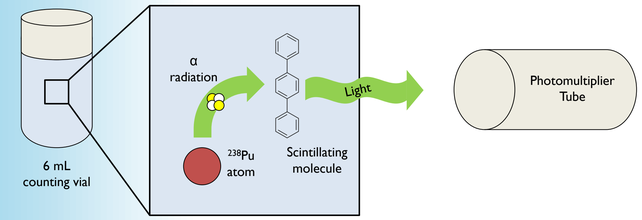
Legend & Stability Constants

Data: Modeled	Data: Excluded	Model	Aging (days)	Desorption (days)	Stability Const. logK
◆	◇	– – –	1	34	0.078 ± 0.017
■	□	–·–·–	6	34	0.164 ± 0.015
▲		·····	15	34	0.408 ± 0.016
●	○	———	34	34	0.595 ± 0.019
×		–··–··–	116	34	0.953 ± 0.026

RADIATION DETECTION

The plutonium isotope ^{238}Pu emits **alpha radiation** which can be blocked by a few centimeters of air. Therefore, to detect alpha radiation, there must be little or no material between the sample and the detector medium.

In **liquid scintillation counting**, a liquid sample is mixed with organic scintillating fluid. When radiation interacts with scintillating fluid, its energy is converted to light which is detected by photomultiplier tubes. This technique can detect alpha radiation with 100% efficiency and the minimum detectable concentration (MDC) is 2×10^{-13} mol/L of ^{238}Pu.



CONCLUSIONS

- Aging can play an important role in the reversibility of Pu(IV) sorption to goethite on a time scale of months (and possibly longer) based on the increase in sorbed Pu and logK values.
- The failure of the model to provide a good fit for 1 and 6 day aging can be attributed surface complexes having not reached equilibrium.
- The effect of aging must be considered in desorption studies. Experiments may over-predict the reversibility of Pu sorption compared to aged natural systems.
- The surface speciation of Pu on goethite is more complex than can be accounted for by a single surface complexation reaction.
- Aging may decrease Pu mobility by stabilizing Pu to sediment grains or increase Pu mobility by stabilizing Pu on colloid surfaces.
- Accurate predictive transport models for Pu should accommodate a distribution ratio for Pu which increases with aging.

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