Subsurface pH and Oleate Manipulation for the Immobilization of Uranium

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ABSTRACT

The groundwater at the Oak Ridge IFC Area-3 site is characterized by a low pH (~3.5) but extremely high contents of U (~60 mg/L), Al (~500 mg/L), nitrate (~10,000 mg/L), and other toxic metals and ions. Few treatment options currently exist to effectively remove or immobilize U(VI) and other toxic metals in situ. This work was performed to evaluate (1) the subsurface pH manipulation for immobilizing U(VI) through co-precipitation with Al and other metal ions and (2) biological reduction and precipitation of U(IV) through amendments of oleate at a less contaminated site (IFC Area 2) at circumneutral pH conditions. Initial laboratory investigations indicate that a controlled addition of KOH provided a rapid yet effective means of sequestering U(VI), Tc(VII), and other toxic metals (Ni^{2+} and Co^{2+}) in soil and groundwater at Area 3 site. Greater than 90% of soluble U(VI) and Tc(VII) could be precipitated or immobilized at pH >4.5 through the precipitation or adsorption onto Al-oxyhydroxides and minerals. The sparingly soluble Ca-oleate is hypothesized to provide a long term source of electrons for biological U(VI) reduction. The results of initial microcosm tests appeared promising: Amended sediments showed nearly complete removal of soluble U(VI). The reduction of U(VI) to U(IV) was verified by XANES analysis. *Deltaproteobacteria* populations increased significantly compared to unamended controls as revealed through 16s rDNA analysis. A clone type showing ~98% similarity to *Desulforegula* conservatrix constituted ~30% of recovered clones in libraries originating from the oleate-amended sediment. This *d-proteobacter* oxidizes long chain fatty acids, produces acetate and propionate and reduces sulfate to sulfide. However, this organism is not known to reduce Fe(III) or U(VI). Iron reducers such as *Geobacter spp.* were also present in enrichments, but in much lower abundances (~5%).

U and Tc Immobilization by pH Manipulation

Batch titrations of contaminated groundwater and sediments from the IFC site indicate rapid and efficient co-precipitation of U, Tc, and other toxic metals (Fig. 1). The co-precipitation of uranyl with Al-oxyhydroxide was validated by EXAFS analysis (Fig. 3) and the leaching tests of uranyl sorbed onto precipitated Al-hydroxides or co-precipitated along with Al-hydroxides (Fig. 4). The presence of clays and other ions such as Si and sulfate influenced co-precipitation of uranyl and Al.

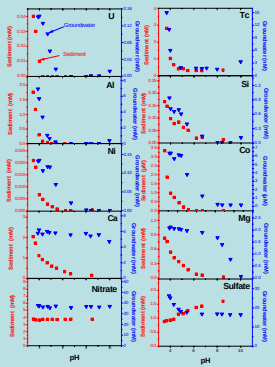

Figure 1. Aqueous U, Tc, Al, Si, Ni, Co, Ca, Mg, nitrate and sulfate concentration change during batch titration with 20 mL groundwater and sediment (5 g sediment in 20 ml 0.03 M KCl)

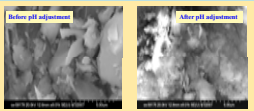

Figure 2. SEM images showing coatings of precipitated Al hydroxides with sorbed or coprecipitated U and other metals.

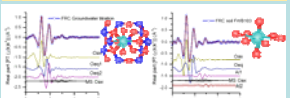

Figure 3. EXAFS analysis of sorbed or co-precipitated U. Uranyl appeared to bound to aluminate in sediments but was sorbed or co-precipitated as hydrated uranyl in groundwater after titration.

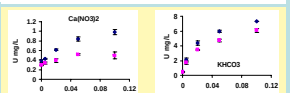

Figure 4. Leaching of sorbed or co-precipitated uranyl by $Ca(NO_3)_2$ or $KHCO_3$. Sorbed uranyl (added after Al precipitation) was more readily desorbed or dissolved than those co-precipitated uranyl.

pH Manipulation in Column Flow Systems

Small to intermediate-scale column flow-through experiments were performed to determine the effectiveness of controlled base addition on U(VI) immobilization in a contaminated IFC sediment and potential impact of pH manipulation on hydrogeochemical properties and microbial activity. Results indicate that more than 92% of U(VI), Tc(VII) and toxic metals such as Co(II), and Ni(II) could be retained through the adsorption and/or co-precipitation in sediments. However, excessive addition of base (at pH above 5.5) may cause remobilization of U(VI) due to the formation of carbonate complexes. No significant changes in hydraulic properties and no sign of denitrification were observed to date.

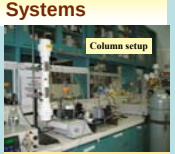

Figure 5. Contaminated FW106 groundwater was circulated through the column in a closed system with a continuous addition of KOH.

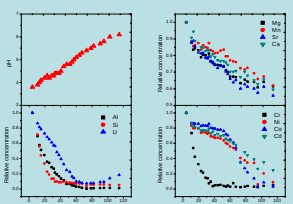

Figure 6. pH and effluent concentrations of U and other metal ions during pH manipulation in a column packed with IFC sediment and groundwater.

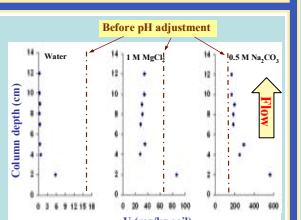

Figure 7. U distribution and selective leaching by water, 1 M $MgCl_2$ or 0.5 M Na_2CO_3 in the column before and after pH manipulation.

U(VI) Bioreduction and Immobilization by Oleate – Microcosm Studies

Oleate acts as a slow release electron donor source for anaerobic dechlorination of TCE *in situ*. Oleic acid is a long-chain unsaturated fatty acid ($C_{18}H_{34}O_2$, MW 282.26) with low water solubility and a density of 0.895-0.947 g/cm^3. In the presence of Ca^{2+} ions, oleate forms calcium-oleate precipitates:

$$2\ C_{18}H_{33}O_2^- + Ca^{2+} \rightarrow Ca(C_{18}H_{33}O_2)_2 \downarrow$$

When oleate is delivered to the subsurface where it reacts with Ca^{2+} in groundwater, it may serve as a long-term energy source for microbial growth and biological reduction processes. Under anaerobic conditions, oleate is degraded via β-oxidation with hydrogen as an intermediate:

$$C_{18}H_{33}O_2^- + 16\ H_2O \rightarrow 9\ C_2H_3O_2^- + 15\ H_2 + 8\ H^+$$

The degradation may be performed by syntrophic acetogens or sulfate-reducing bacteria (SRB) with sulfate or bicarbonate as electron acceptors. Hydrogen and acetate are also used as electron donors, and Fe(III) and U(VI) are thus bioreduced during the process.

Molecular structure of oleic acid

Figure 8. Formation of Ca-oleate precipitates in groundwater from well FW231-2 at IFC Area 2. Groundwater contained 2.8 mM Ca.

Microcosm Setup - Microcosm tests were performed in 160-mL serum bottles under ambient temperature conditions (21-23 ºC) with sediments groundwater from Area 2 and Area 3.

Table Microcosm test conditions (volume 130 mL in 160 mL serum bottle)

Sediments	FB107	FW102-2	FW102-3
Location at FRC site	Area 2	Area 3	Area 3
U content (mg/kg)	617	325	1725
Reducing condition	Oxidized	Oxidized	Partially reduced
pH	7.2	7.2	6.9
Alkalinity (mM)	14	8	6
Oleat added (mM)	0.88	0.77	0.77
Ca^{2+} (mM)	3.5	1.85	1.2
U (mg/L)	4.4	2	7.3

U content and valent change after biostimulation (50 days)

Microcosm		FB107	FW102-2	FW102-3
U content (mg/kg)		617	310	1725
U(VI) %	before	100	90	90
	after	90	10	30
U(IV) %	before	0	10	90
	after	10	90	70
U (mg/L)	before	4.4	2	7.3
	after	0.57	0.05	0.03

The color of sediments turned black after incubation (Fig. 10), indicating the stimulation of oleate-degrading microorganisms in IFC sediments (Fig. 11). Acetate was produced, and sulfate reduced during the biostimulation. Aqueous phase U(VI) concentration decreased over time, and U reduction confirmed by XANES analysis (Fig. 12 & table above).

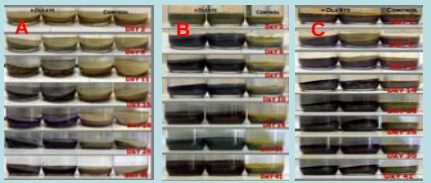

Figure 10. Microcosm studies of oleate amendments on biological reduction of U(VI). IFC sediments used were: (A) FB107, Area 2; (B) FW102-2, Area 3; and (C) FW102-3, Area 3. Note that color changes due to reducing conditions.

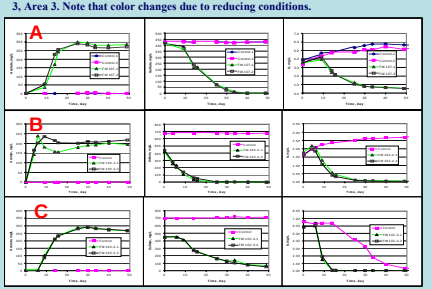

Figure 112. Concentration profiles of acetate, sulfate and U(VI) in microcosms amended with oleate. Acetate was accumulated as a byproduct. Sulfate was reduced along with U(VI).

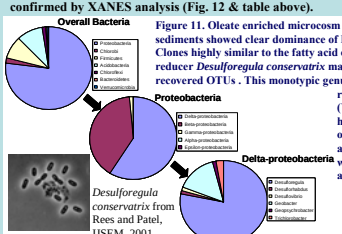

Figure 11. Oleate enriched microcosm libraries from area 2 sediments showed clear dominance of Delta-Proteobacteria. Clones highly similar to the fatty acid oxidizing sulfate reducer *Desulforegula conservatrix* made up over 30% of recovered OTUs . This monotypic genus is not known to reduce Fe (III) or U (VI) so it is hypothesized that these organisms may be acting syntrophically with iron reducers such as *Geobacter*.

SUMMARY

- **Controlled pH manipulation offers an effective means of precipitating or immobilizing >92% of uranium, technetium, and other heavy metals at the Oak Ridge IFC Area 3 site.**
- **Co-precipitated uranyl appears to bound to aluminate in sediments and is less exchangeable or extractable than those sorbed uranyl.**
- **Oleate forms Ca-oleate precipitates in IFC groundwater and may serve as a slow-releasing electron donor source for *in situ* U(VI) reduction and immobilization.**
- ***Desulforegula* and *Geobacter* spp. may be syntrophically responsible for oleate degradation and U(VI) reduction.**

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