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 (~40 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 site. 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(VI) through amendments of oleate at a less contaminated site (IFC Area 2) under circumneutral pH conditions. Initial laboratory investigations indicated that a controlled addition of KOH provided a rapid yet effective means of sequestering U(VI), Tc(VI), and other toxic metals (NO3− and Ca2+) in soil and groundwater at Area 3 site. Greater than 90% of soluble U(VI) and Tc(VI) could be precipitated or immobilized at pH ~4.5 through the precipitation or adsorption onto Al-sulphoxides 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(VII) was verified by XANES analysis. Desulforegula populations increased significantly compared to unamended controls as revealed through 16s rDNA analysis. A clone type showing >80% similarity to Desulforegula conservatrix constituted ~30% of recovered clones in libraries originating from the oleate-amended sediments. This Desulforegula 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 indicated rapid and efficient co-precipitation of U, Tc, and other toxic metals (Fig. 1). The co-precipitation of uranium with Al-sulphoxides was validated by EXAFS analysis (Fig. 3) and the leaching tests of uranium on precipitated Al-hydroxides or co-precipitated along with Al-hydroxides (Fig. 4). The presence of clays and other ions such as Na and sulfate influenced co-precipitation of around 85%.

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

Oleate acts as a slow release electron donor source for anaerobic dechlorination of TCE in site. Oleate acid is a long chain unsaturated fatty acid (C18H32O2, MW 282.62) with very low water solubility and a density of 0.885-0.847 g/cm3. In the presence of Ca2+ ions, oleate forms calcium-oleate precipitates: 2 Ca(OH)2 + Ca2+ + C18H32O2 → Ca2[(CH2)17COO]2 + 2 Ca(OH)2 + 16 H2O → 2 CaH2O2 + 16 H2 + 8 H2O

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

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