Re-oxidation Behavior of Technetium-99 and Uranium Immobilized by Zero Valent and Sulfur Modified Iron Reductants.

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Background

Figure 1. Hanford Site, WA.

- Hanford Site is a U.S. Department of Energy site that formerly produced plutonium and has legacy vadose, perched water (PW), and groundwater (GW) contamination zones with ^{99}Tc commingled with ^{238}U and NO_3^-.
- ^{99}Tc is highly mobile under oxidizing conditions (solubility of ~11 M) in subsurface environments.
- Remediation technologies are crucial to reduce and subsequently sequester ^{99}Tc.

Objectives

- Investigate re-oxidation behavior of ^{99}Tc (commingled with ^{238}U and NO_3^-), after initial reduction using strong reductants, such as sulfur-modified iron (SMI) and zero-valent iron (ZVI), in laboratory batch experiments.
- Conduct solids characterization studies using XRD and SEM-EDS analyses with samples collected from anaerobic and aerobic phases.

Materials & Methodology

Sediment

- Uncontaminated Ringold Formation sediment from Hanford Site.
- Added 10 ± 0.01 g of < 2mm fraction of homogenous sieved sediment to 100 mL of GW & PW solution in 250 mL plastic containers.

Artificial GW & PW Preparation

- GW contaminants: 420 µg/L ^{99}Tc(VII), 124 mg/L NO_3^-.
- PW contaminants: 10 µg/L ^{99}Tc(VII), 150 mg/L ^{238}U(VI).
- 0.1 ± 0.01 g (SMI & ZVI)/100 mL of GW & PW.
- 1:10 solid to liquid ratio.

Experimental Conditions

Phase 1: Anaerobic

Collected weekly ~0.4 mL aliquot samples at various times (7, 15, 21, and 30 days) using 0.2 µm syringe filters.

Phase 2: Aerobic

Aerated twice a week for 30 sec. under consistent air flowrate.
Samples centrifuged at 12,000 rpm for 6 mins.

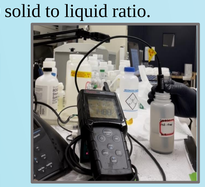

Figure 2. pH, dissolved oxygen (DO), & oxidation-reduction potential (ORP) measurements taken weekly.

Liquid analysis

Measured ^{99}Tc, U, and Fe by inductively coupled plasma mass spectrometry (ICP-MS, Thermo Fisher Scientific, iCAP RQ) after filtration and acidification in 2% HNO_3.

Figure 3. Phase 1 samples inside of anaerobic glovebox.

Anion Analysis

Analysis of NO_3^-, NO, and SO_4^{2-} via ion chromatography (IC).

Solid Characterization

Dried Phase 1 sacrificial controls and Phase 2 samples in a vacuum oven at 30°C and kept in anaerobic glovebox for analysis by X-ray diffraction (XRD) & Scanning electron microscope/ Energy-dispersive spectroscopy (SEM-EDS).

Liquid Analysis

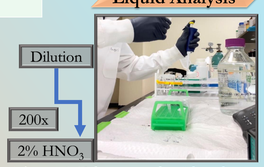

Figure 4. Dilutions or liquid analysis of U, Tc via ICP-MS.

Results

Liquid Phase Analysis

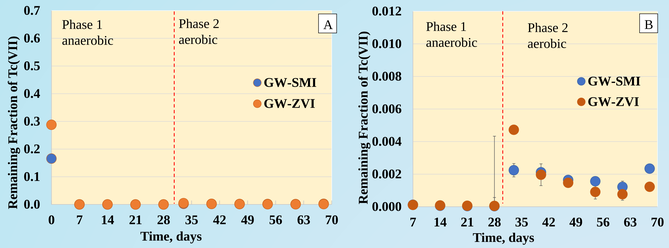

Figure 5a, b. Remaining aqueous fraction of Tc(VII) over time in triplicate GW samples amended with 1.0% of ZVI and SMI and collected in Phases 1 & 2. A) from day 0 – 68; B) from day 7 – 68.

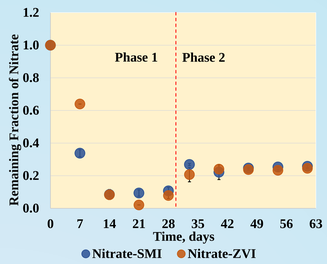

Figure 10. Remaining Aqueous Fraction of Nitrate in GW (1% ZVI &SMI) samples.

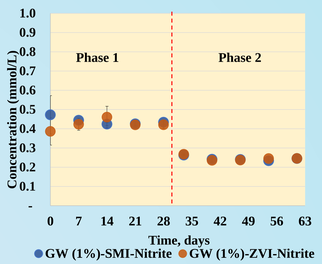

Figure 11. Concentration of nitrite vs. time in GW samples amended with 1% ZVI and SMI.

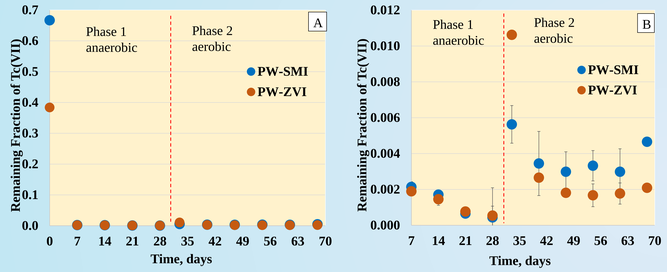

Figure 6a, b. Remaining aqueous fraction of Tc(VII) over time in triplicate PW samples amended with 1.0% of ZVI and SMI and collected in Phases 1 & 2. A) from day 0 – 68; B) from day 7 – 68.

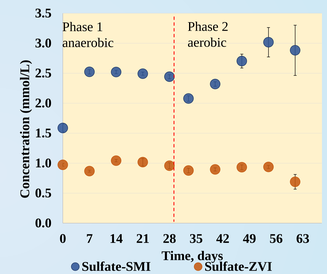

Figure 12. Concentration of Sulfate in SMI- and ZVI-treated (1.0 %) GW samples.

SEM/EDS maps

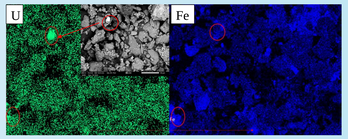

Figure 13. U and Fe EDS maps of PW sample treated with 1% SMI and sacrificed after Phase 1.

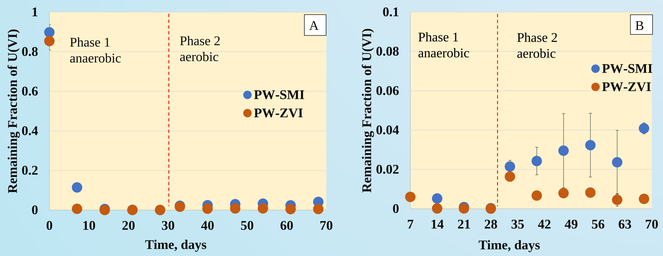

Figure 7a, b. Remaining aqueous fraction of U(VI) over time in triplicate PW samples amended with 1.0% of ZVI and SMI and collected in Phases 1 & 2. A) from day 0 – 68; B) from day 7 – 68.

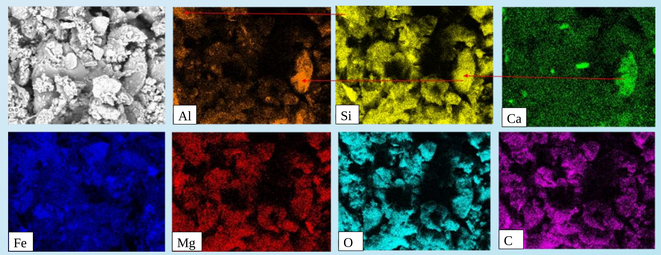

Figure 14. EDS maps of GW sample treated with 1% ZVI.

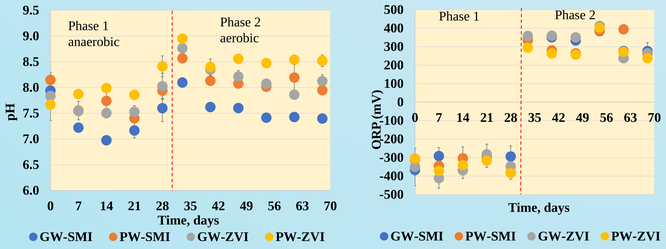

Figure 8. Changes in pH vs. time in GW and PW solutions.

Figure 9. Change in ORP vs time in GW & PW solutions.

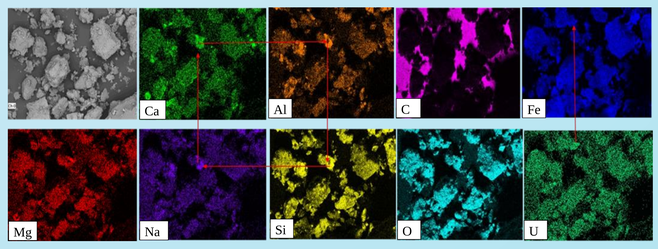

Figure 15. EDS maps of PW sample treated with 1% ZVI.

Conclusions

Analytical Results

- Both ZVI and SMI were effective reductants in anaerobic conditions.
- ZVI was marginally more effective in resisting re-oxidation in aerobic conditions.
- Both ZVI and SMI were effective in NO_3^- removal by the end of the anaerobic Phase 1.
- The increase in nitrate concentration at the end of aerobic Phase 2 might be due to the accumulation of nitrite in Phase 1, which was subsequently re-oxidized to nitrate under aerobic conditions.
- SO_4^{2-} content decreased from the initial value in the GW simulant treated with ZVI.
- SO_4^{2-} was consistently higher in SMI-amended samples throughout both phases of the experiment. This is due to the presence of sulfur in SMI, which can be oxidized to SO_4^{2-}.

SEM-EDS

- Iron content increased to 30-48% in 1.0% ZVI- and SMI-amended samples.
- SEM has not identified typical iron oxide crystals resembling octahedral for magnetite or needle-like for goethite in samples amended with ZVI and SMI.
- U and Fe maps reveal the presence of a uranium-rich particle on a fine sediment grain's surface (Figure 13).
- This uranium-rich particle is newly reduced UO_2, precipitated on the sediment surface in anaerobic conditions. It lacks alignment with any elemental maps per EDS analysis.
- No presence of Tc due to low content.

Environmental Significance

- Laboratory experiments evaluated re-oxidation behavior of ^{99}Tc initially reduced by strong reductants, 1.0 % ZVI (Hepure Technologies) or SMI (SMI-PS Inc), in batch scale experiments under sequential anaerobic conditions followed by aerobic conditions.
- ZVI and SMI reductants can be efficiently used to minimize Tc(IV) and U(IV) remobilization under conditions relevant to the Hanford Site.

Path Forward

- Study re-oxidation of PW and GW contaminants, ^{99}Tc(VII) comingled with NO_3^- and UO_2^{2+} initially reduced by 0.5 % or 5.0% calcium polysulfide (CPS).
- Reducing conditions with sulfides may immobilize ^{99}Tc as one or more Tc^{IV} precipitates- $Tc^{IV}O_2$ or TcS_x.
  - liquid phase analysis, ORP, and elemental analysis by SEM-EDS.

Acknowledgements

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