

DOE-FIU Cooperative Agreement Annual Research Review – FIU Year 4

Remediation Research on Combination of Reduction and Sequestration Treatment

Melissa Dieguez





Overall Needs:

- Research evaluates the re-oxidation behavior of Tc and U in the presence of nitrate (NO₃-)
 after application of strong reductants coupled with ammonia gas injections for potential
 vadose zone remediation.
- A limitation of strong reductants technology is these reduced forms of U(IV) and Tc(IV) may re-oxidize over time, dissolving back into the aqueous phase after reductive capacity is consumed and conditions return to natural conditions.
 - To achieve more permanent immobilization, additional strategies are being explored that involve incorporating Tc and U into other low solubility phases or coating them.
- This is the first attempt to couple strong reductants with ammonia gas treatment to prolong the effectiveness of contaminant immobilization.

Objectives:

Quantify the immobilization of Tc(VII) using a combined treatment such as ZVI/SMI in the presence of co-contaminants, U(VI) and nitrate, followed by ammonia gas injection and investigate potential immobilization of reduced Tc(IV), U(IV) and other targeted contaminants throughout the process.





FIU Year 4 Highlights & Accomplishments:

- Test matrix:
 - Prepared synthetic solutions of PW
 - Purged with N₂; pH adjusted; spiked with ⁹⁹Tc, U(VI) & NO₃⁻
 - \circ PW (pH 8.2): 100 μg/L Tc + 150 mg/L U + 204 mg/L NO₃⁻¹ (from NaNO₃ in PW simulant solution).
 - 10 g sediment + 100 mL solution + 100 mg of ZVI or SMI (1.0 wt.% of sediment)
 - 1.0 wt% ZVI and 1.0 wt% SMI
 - 15 samples total Ringold Formation sediment <2 mm in triplicate samples
- Monitored for change in pH, ORP, DO, Tc, U, NO₃⁻, SO₄²⁻ concentrations at each sampling point
- Studied re-oxidation behavior of ⁹⁹Tc, U(VI), and NO₃⁻ after treatment with strong reductants







FIU Year 4 Highlights & Accomplishments:

- Two phases of experiments for reduction of ⁹⁹Tc, U(VI), and NO₃⁻:
 - Phase 1: In presence of 1.0 % wt of ZVI and SMI under anaerobic conditions for up to 37 days
 - Phase 2: In aerobic conditions after the addition of ammonia hydroxide for up to 49 days.
 - Total testing = 86 days.

Results:

- Phase 1:
 - DO: ~0.03-0.05 mg/L
 - ORP: -300 mV -350 mV indicative of reducing conditions
- Phase 2: DO and ORP increased:
 - o DO: 5-6 mg/L
 - ORP: +150 to +400 mV consistent with oxidative conditions.

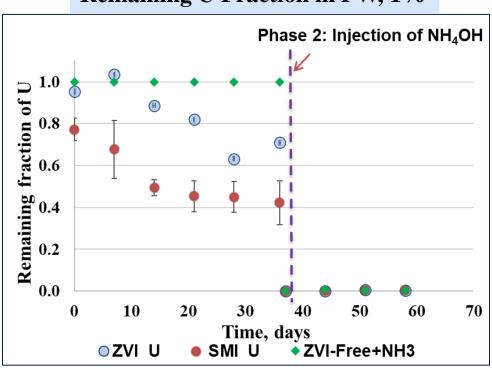




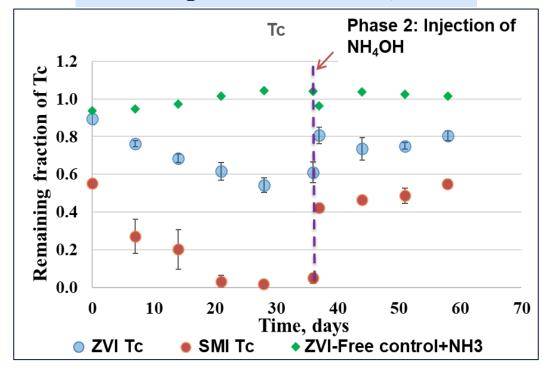


FIU Year 4 Highlights & Accomplishments: Results for U and Tc

Remaining U Fraction in PW, 1%



Remaining Tc Fraction in PW, 1%



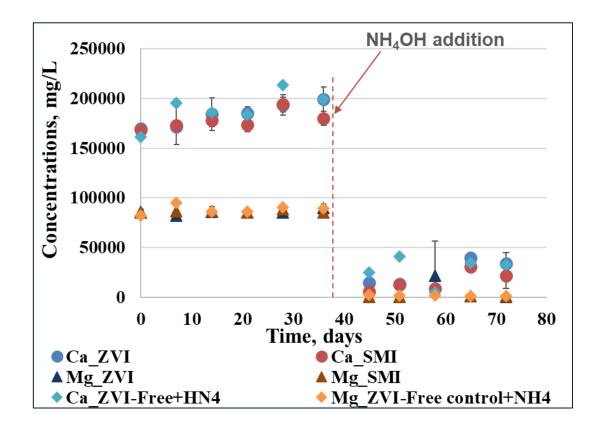
- SMI more efficient to reduce U in anaerobic conditions.
- U concentration dropped after addition of NH₄OH in aerobic conditions, probably due to formation of U hydroxide at pH ~11.

- SMI more efficient to reduce Tc in anaerobic conditions.
- Concentration of Tc rebounded after addition of NH₄OH under aerobic conditions.
- o In reductant-free control, Tc has not changed.





FIU Year 4 Highlights & Accomplishments: Changes in Ca, Mg, & Si

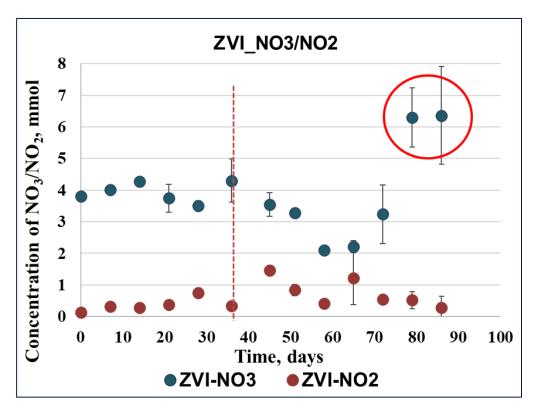


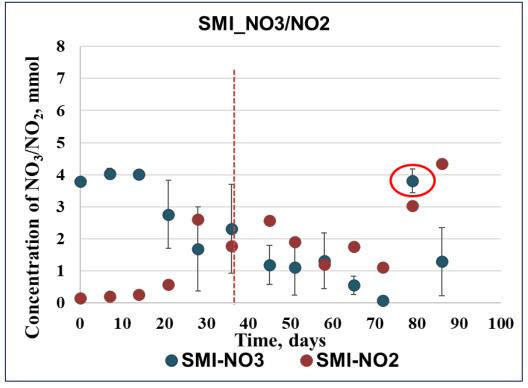


- In Phase 2, after NH₄OH addition, system traps CO₂, which precipitates as CaCO₃ and MgCO₃. Consequently, aqueous concentrations of Ca and Mg become much lower.
- Behavior of ZVI-Free control + NH₄ samples identical to samples amended with ZVI/SMI.



FIU Year 4 Research Highlights & Accomplishments: Changes in NO₃/ NO₂





NO₂ concentration higher in presence of ZVI

SMI more effective in NO₃ removal



Submitted abstract to WM 2025 on project results.



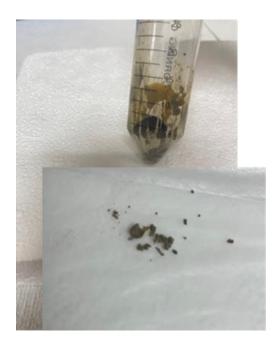
FIU Year 4 Research Highlights & Accomplishments: Solid Characterization



- Prepared samples for solids characterization
 - Separated precipitate from liquid sample
 - Centrifuged and dried sediment



Top layer



Bottom layer





Summer Internship

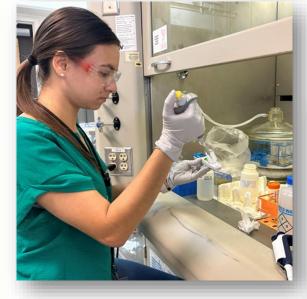
- Cyanide mobilization task
 - Analyzing behavior of cyanide in relation to various remediation technologies currently being studied
 - Abiotic and biological
 - Mentor: Dr. Alex Kugler
 - Worked with:
 Andrew Plymale &
 Hilary Emerson



















Future work

- Run last samples via ICP-OES
- Finalize Solids Characterization







- Transitioning to new position at PNNL:
 - Undergraduate Technical Intern level IV



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