



Technetium and iodine aqueous species immobilization and transformations in the presence of strong reductants and calcite-forming solutions: Remedial action implications

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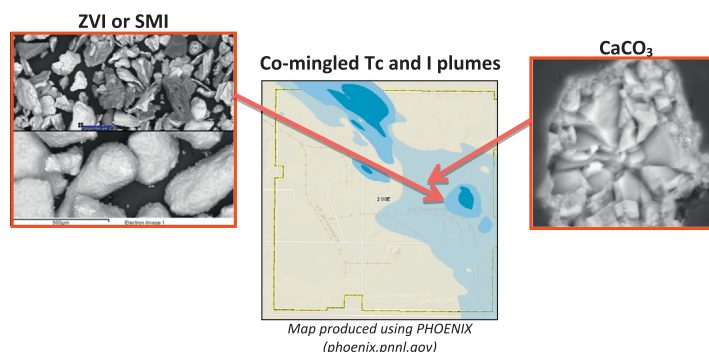
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HIGHLIGHTS

- Co-mingled contaminants can affect remediation attempts.
- ⁹⁹Tc and ¹²⁹I remediation strategies may not be compatible.
- Remediation efforts can change microbial communities with possible long term effects.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 2 February 2018
 Received in revised form 17 April 2018
 Accepted 17 April 2018
 Available online xxxx

Editor: Frederic Coulon

Keywords:

Tc removal
 Radioiodine (¹²⁹I) removal
 Groundwater remediation
 Groundwater contamination
 Nuclear waste
 Hanford site

ABSTRACT

At the Hanford Site in southeastern Washington, discharge of radionuclide laden liquid wastes resulted in vadose zone contamination, providing a continuous source of these contaminants to groundwater. The presence of multiple contaminants (i.e., ⁹⁹Tc and ¹²⁹I) increases the complexity of finding viable remediation technologies to sequester contaminants in situ and protect groundwater. Although previous studies have shown the efficiency of zero valent iron (ZVI) and sulfur modified iron (SMI) in reducing mobile Tc(VII) to immobile Tc(IV) and iodate incorporation into calcite, the coupled effects from simultaneously using these remedial technologies have not been previously studied. In this first-of-a-kind laboratory study, we used reductants (ZVI or SMI) and calcite-forming solutions to simultaneously remove aqueous Tc(VII) and iodate via reduction and incorporation, respectively. The results confirmed that Tc(VII) was rapidly removed from the aqueous phase via reduction to Tc(IV). Most of the aqueous iodate was transformed to iodide faster than incorporation into calcite occurred, and therefore the I remained in the aqueous phase. These results suggested that this remedial pathway is not efficient in immobilizing iodate when reductants are present. Other experiments suggested that iodate removal via calcite precipitation should occur prior to adding reductants for Tc(VII) removal. When microbes were included in the tests, there was no negative impact on the microbial population but changes in the makeup of the microbial community were observed. These microbial community changes may have an impact on remediation efforts in the long-term that could not be seen in a short-term study. The results underscore the importance of identifying interactions between natural attenuation pathways and remediation technologies that only target individual contaminants.

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1. Introduction

Zero valent iron (ZVI) and sulfur modified iron (SMI), often in nano form, have been tested previously as waste removal and immobilization technologies for contaminants including pertechnetate (TcO_4^-) (Livens et al., 2004; Darab et al., 2007; Liu et al., 2008; Fan et al., 2013), Cr(VI) (Astrup et al., 2000), and other agricultural and industrial contaminants (Kim et al., 2011; Allred, 2012; Xu et al., 2016). Use of these iron materials for groundwater and sediment remediation has been reviewed in Crane and Scott (2012), Gong et al. (2016), and Zhao et al. (2016), and the materials have proven effective at reductively precipitating compounds such as Tc-99. At the Hanford Site, Tc is primarily in the form of TcO_4^- (Peretyazhko et al., 2012). Pertechnetate is highly soluble in aqueous solutions, so the potential for migration is high (Serne et al., 2014). The reductive capacity of ZVI can reduce the mobile pertechnetate [Tc(VII)O_4^-] into TcO_2 , a less mobile form. Studies using SMI have shown that the sulfidated iron enables formation of Tc sulfides instead of Tc oxides, which are more stable and less likely to re-oxidize than the Tc oxides produced by ZVI alone (Fan et al., 2013; Fan et al., 2014).

At the Hanford Site, radioactive wastes were buried in tanks or released in cribs and trenches during Pu production activities beginning in the 1940's (Gephart and Lundgren, 1995). Evaluation of technologies that could be used to remediate the contaminated Hanford Site subsurface, including those found in this paper, is ongoing. Tc is commonly found with co-contaminants, such as iodine, chromium, and uranium. In-situ Tc immobilization strategies must be effective without negatively affecting the removal of co-contaminants. For example, Asmussen et al. (2016) determined that different materials should be used for immobilizing Tc and I. Whereas a potassium metal sulfide (KMS) was best for sequestering Tc, a silver-based material (e.g., silver zeolite and argentite) was better for sequestering I. Although each of these materials performed well separately (i.e., $\geq 97\%$ of the I and Tc were removed), when combined, the silver-based materials preferentially reacted with the sulfur instead of the iodine, resulting in a reduced iodine removal (i.e., only 24% of iodine was removed when Tc getters were also present). This demonstrates the need to identify unintended impacts associated with remedies when multiple contaminants (and remedies) exist.

In addition to considering the effects of co-mingled contaminants, it is important to consider the environmental impact of remediation technologies. Studies have shown that ZVI can be toxic to microbes, causing interference in energy transduction, protein damage, and oxidative stress (Xie et al., 2017); some microbial species are more resistant to ZVI (specifically, gram-positive bacteria) (Hajipour et al., 2012), but favoring one bacterial species over another in the environment could have adverse effects. In addition, some microbes have the potential to enhance performance of iron amendments; for example, sulfate-reducing bacteria has been shown to enhance the performance of sulfide-amended iron (Lloyd and Macaskie, 1996; Lloyd et al., 1998).

In this laboratory study, ZVI and SMI were tested to determine the ability of these iron materials to immobilize Tc(VII) in double de-ionized (DDI) water and in site-relevant synthetic vadose zone porewater (VZPW). Previous testing has shown that calcite-forming species (i.e., dissolved Ca^{2+} and CO_3^{2-} present in the porewater) in the Hanford Site vadose zone have the potential to immobilize chromate and/or iodate through incorporation or adsorption of these contaminants into or onto calcite (Truex et al., 2017). Therefore, the calcite-forming solutions used in previous experiments were included in several tests to determine if the two contaminant removal strategies (i.e., ZVI/SMI and/or calcite formation) interfere with performance. This is important for areas within the Hanford Site where Tc and I plumes coexist. In this study, iodate (IO_3^-) was used as the iodine co-contaminant as previous studies have shown that IO_3^- is the dominant iodine species found in the Hanford Site (Zhang et al., 2013; Truex et al., 2017). Additional experiments were conducted with the inclusion

of natural organic matter (NOM) and/or microbes to test the effects of these constituents on the performance of ZVI/SMI to determine if there are interferences or improvements in the immobilization of contaminants and to evaluate changes in the microbial community caused by the various amendments.

2. Materials and methods

The ZVI (Ferox-Target, Hepure, Delaware, USA) used in this study was -325 mesh, or $<44 \mu\text{m}$. The SMI (Hydrex 9670, Veolia, Saint-Maurice, France) was 20–80 mesh, or 177 to 841 μm . These materials are commercial grade, not lab grade, and may not contain only Fe(0). See Section 3.2 for solid characterization. Their use is described in the sections that follow.

2.1. Batch experiments

2.1.1. Abiotic experiments

Experimental methods are summarized here (see the ESI for additional method details). The test matrix for the batch experiments are shown in Table 1, and were conducted to test ZVI and SMI in DDI water and synthetic VZPW (ESI Table S1). Tests were conducted with 0.42-ppm Tc and 0.1-ppm IO_3^- . The IO_3^- concentration was chosen to represent field conditions at the Hanford Site. The Tc concentration was chosen based on preliminary testing conducted to determine how much Tc could be reduced by the ZVI and/or SMI ($>99\%$ of 44 ppm Tc was removed from solution by 1 g of ZVI/SMI; tests A1–A12; see also the ESI for additional information about these tests). The solids remaining from the preliminary tests using 44-ppm Tc and 1 g of ZVI/SMI were also used for X-ray absorption near edge structure (XANES) analysis and Mössbauer spectroscopy.

For each test, 0.01 g of ZVI or SMI was added to a 125-mL Polytetrafluoroethylene (PTFE) bottle and then 50 mL of VZPW or DDI water was added. The IO_3^- and TcO_4^- spikes were then added by pipette. Controls were prepared in the same way, with the omission of Fe solids for one control and the omission of Tc/ IO_3^- in the other control. The time of TcO_4^- addition was considered time 0, and the first samples were taken 4 h later. Subsequent sampling took place after 1, 3, 6, 9, 14, 30, and 49 days. For each sampling, 2 mL of solution was removed from the bottle and filtered through a 0.2- μm syringe Millipore syringe filter. The bottle was then capped and gently swirled. The 2-mL sample was used to measure pH and was then analyzed for Tc and I.

The final sampling took place after 49 days. Following this final sampling and pH measurement, for the experiments containing Fe solids and calcite-forming solutions, all solids were collected by first gently scraping the sides and bottom of the poly bottle, then filtering the

Table 1

Matrix for tests A13–A20 and B5–B10. “A” tests indicate abiotic experiments and “B” tests indicate biotic experiments. A matrix of the preliminary tests (A1–A12) is included in the ESI; data from preliminary tests B1–B4 are not discussed or included in this paper.

Test ID	Tc (ppm)	IO_3^- (ppm)	ZVI/SMI	Solution(s) ^a	NOM	Microbes
A13	0.42	0.1	0.01 g ZVI	VZPW	–	–
A14	0.42	0.1	0.01 g SMI	VZPW	–	–
A15	0.42	0.1	0.01 g ZVI	VZPW, CS	–	–
A16	0.42	0.1	0.01 g SMI	VZPW, CS	–	–
A17	0.42	0.1	0.01 g ZVI	DIW	–	–
A18	0.42	0.1	0.01 g SMI	DIW	–	–
A19	0.42	0.1	0.01 g ZVI	DIW, CS	–	–
A20	0.42	0.1	0.01 g SMI	DIW, CS	–	–
B5	0.42	0.1	–	M9	0.01 g	–
B6	0.42	0.1	–	M9	–	10^7 cell/mL
B7	0.42	0.1	–	M9	0.01 g	10^7 cell/mL
B8	0.42	0.1	–	M9, CS	0.01 g	10^7 cell/mL
B9	0.42	0.1	0.01 g ZVI	M9, CS	0.01 g	10^7 cell/mL
B10	0.42	0.1	0.01 g SMI	M9, CS	0.01 g	10^7 cell/mL

^a VZPW = vadose zone porewater; DIW = double de-ionized (DDI) water; M9 = M9 media; CS = calcite solutions.

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