



## Influence of alkaline co-contaminants on technetium mobility in vadose zone sediments



Jim E. Szecsody<sup>a,\*</sup>, Danielle P. Jansik<sup>b</sup>, James P. McKinley<sup>a</sup>, Nancy J. Hess<sup>a</sup>

<sup>a</sup> Pacific Northwest National Laboratory, P.O. Box 999, MSIN K3-61, Richland, WA 99354, USA

<sup>b</sup> Washington State Department of Ecology, Yakima, WA, USA

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### ABSTRACT

Per technetate was slowly reduced in a natural, untreated arid sediment under anaerobic conditions ( $0.02 \text{ nmol g}^{-1} \text{ h}^{-1}$ ), which could occur in low permeability zones in the field, most of which was quickly oxidized. A small portion of the surface Tc may be incorporated into slowly dissolving surface phases, so was not readily oxidized/remobilized into pore water. In contrast, per technetate reduction in an anaerobic sediment containing adsorbed ferrous iron as the reductant was rapid ( $15\text{--}600 \text{ nmol g}^{-1} \text{ h}^{-1}$ ), and nearly all (96–98%) was rapidly oxidized/remobilized ( $2.6\text{--}6.8 \text{ nmol g}^{-1} \text{ h}^{-1}$ ) within hours. Tc reduction in an anaerobic sediment containing 0.5–10 mM sulfide showed a relatively slow reduction rate ( $0.01\text{--}0.03 \text{ nmol g}^{-1} \text{ h}^{-1}$ ) that was similar to observations in the natural sediment. Per technetate infiltration into sediment with a highly alkaline water resulted in rapid reduction ( $0.07\text{--}0.2 \text{ nmol g}^{-1} \text{ h}^{-1}$ ) from ferrous iron released during biotite or magnetite dissolution. Oxidation of NaOH-treated sediments resulted in slow Tc oxidation ( $\sim 0.05 \text{ nmol g}^{-1} \text{ h}^{-1}$ ) of a small fraction of the surface Tc (13–23%). The Tc remaining on the surface was  $\text{Tc}^{\text{IV}}$  (by XANES), and autoradiography and elemental maps of Tc (by electron microprobe) showed Tc was present associated with specific minerals, rather than being evenly distributed on the surface. Dissolution of quartz, montmorillonite, muscovite, and kaolinite also occurred in the alkaline water, resulting in significant aqueous silica and aluminum. Over time, aluminosilicates, cancrinite, zeolite and sodalite were precipitating. These precipitates may be coating surface  $\text{Tc}^{\text{IV}}$  phases, limiting reoxidation.

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### 1. Introduction

Technetium-99 ( $^{99}\text{Tc}$ ) is a byproduct of extraction of plutonium from irradiated uranium fuel rods (Chen et al., 2000) for or the isotopic enrichment of uranium and is of significant concern due to the long half-life ( $2.1 \times 10^5$  years) and weak sorption to soils (Wildung et al., 1984; Rudin et al., 1992; Kaplan and Serne, 1998; Lukens et al., 2002) and therefore, in oxic systems, will migrate nearly unretarded to groundwater. Intentional discharges at the surface or through wells or unintentional  $^{99}\text{Tc}$  (as per technetate,  $\text{Tc}^{\text{VII}}\text{O}_4^-$ ) discharges from to soils at U.S. Hanford site ( $\sim 68,800 \text{ GBq}$ ), U.S. Savannah River site, the UK Sellafield reprocessing facility (Begg et al., 2007), the Japanese Fukushima-Daiichi Plant (Ohnishi, 2012), or groundwater at the U.S. Paducah Gas Diffusion Plant, Oak Ridge site, and the Idaho National Engineering and Environmental

Laboratory (Waite, 1991; Jones et al., 1998; Beasley et al., 1998), or UK estuaries and North Sea (Burke et al., 2010; Brown et al., 1999), generally show rapid migration in oxic environments although the biogeochemistry, climate, and physical system of each of these sites varies greatly. While technetium can exist in multiple oxidation states in nature (III, IV, V, and VII), the most stable oxidation states under environmental conditions are VII and IV. As  $\text{Tc}^{\text{VII}}$ , Tc in aqueous solution exists as per technetate, whereas  $\text{Tc}^{\text{IV}}$  forms the sparingly soluble  $\text{TcO}_2 \cdot x\text{H}_2\text{O}$  amorphous solid in aqueous solution, and thus, is relatively immobile in the absence of strongly complexing ligands (Rard, 1999). Even in the presence of a variety of organic compounds (EDTA, NTA, IDA, citrate, diphenyl phosphate, dibutyl phosphate, ethanol), per technetate still exhibits nearly no sorption in an oxic sediment environment (Lukens et al., 2002), and in the presence of EDTA and NTA in a reducing sediment environment, remained immobilized (Maset et al., 2006). With no organic ligands present, a previously reduced air-oxidized estuarine sediment retained both some  $\text{TcO}_2$  and per technetate (Morris et al., 2008), and oxic, vadose zone sediments that have not been reduced also show Tc physical and geochemical retention (Jansik

\* Corresponding author. Tel.: +1 509 372 6080; fax: +1 509 371 7174.

E-mail addresses: [jim.szecsody@pnnl.gov](mailto:jim.szecsody@pnnl.gov) (J.E. Szecsody), [daja461@ecy.wa.gov](mailto:daja461@ecy.wa.gov) (D.P. Jansik), [james.mckinley@pnnl.gov](mailto:james.mckinley@pnnl.gov) (J.P. McKinley), [nancy.hess@pnnl.gov](mailto:nancy.hess@pnnl.gov) (N.J. Hess).

et al., 2013a; Szecsody et al., 2010). Oxidation of iron- and sulfate-reduced sediments (and Tc remobilization) occurred to a greater extent for when air and not nitrate was the oxidant (Burke et al., 2006). An understanding of the mechanism(s) retaining Tc in the sediments is needed in order to predict future migration and develop long-term remediation strategies.

Subsurface mechanisms that decrease pertechnetate mobility include reduction/precipitation, complexation, and sorption under specific geochemical or microbial conditions (Viani, 1999). Pertechnetate homogenous reduction (and precipitation/immobilization) by aqueous ferrous iron is thermodynamically feasible, but the kinetics of the reaction may prevent it from occurring in some cases (Cui and Eriksen, 1996a,b). Pertechnetate heterogenous reduction by Fe(II)-containing mineral solids (magnetite, chlorite, and Fe(OH)<sub>2</sub>) is reported (Vandergraaf et al. 1984), by sulfur-reducing bacteria (Renshaw et al., 2004), iron-reducing bacteria (Marshall et al., 2009; Plymale et al., 2011), and at field scale under bio-reducing conditions (Istok et al., 2004; Ishii et al., 2004; Tagami and Uchida, 1996; Michalsen et al., 2006). In a recent study, slow initial pertechnetate reduction by aqueous ferrous iron (pH 7–8) was followed by rapid reduction by Fe(II) adsorbed to the Fe-Tc(IV) precipitate (Zachara et al., 2007). This mixed precipitate phase oxidizes about an order of magnitude slower than TcO<sub>2</sub>·xH<sub>2</sub>O likely as a result of intraparticle diffusion. Tc(IV) incorporates into other surface phases, including goethite and sodalite (Livens et al. 2004; Wharton et al., 2000), iron sulfides (Fan et al., 2013), phyllosilicates (Pierce et al., 2010), and possibly siderite (Icenhower et al., 2010). Tc(IV) precipitates may also oxidize more slowly due to limited oxygen diffusion with a 2:1 Fe-rich clay nontronite (Jaisi et al., 2009), or association with Fe(III) within intragrain domains of a mica celadonite (Fredrickson et al., 2009). Pertechnetate is also reduced by aqueous sulfide in acidic conditions (Liu et al., 2007), FeS (Wharton et al., 2000), zero valent iron (Del Cul and Bostick, 1995), sulfide/nZVI (Fan et al., 2013), ferragel (Mallouk et al., 2000), and sulfide/nZVI/sediment (Jansik et al., 2013b). Sulfide reduction is more rapid under alkaline conditions as HS<sup>-</sup> is the dominant sulfide species, and Tc<sub>2</sub>S<sub>7</sub> appears to be the dominant species formed (Liu et al., 2007). Anionic adsorption of TcO<sub>4</sub><sup>-</sup> occurs at low pH (Farrell et al. 1999; Barney, 1979), but in oxic Hanford Site sediments at relatively low ionic strength (10<sup>-3</sup> M) at pH ~8, adsorption is essentially zero ( $K_d = -0.04 \pm 0.02 \text{ mL g}^{-1}$ ; Kaplan and Serne, 1998), based on 30 different sediment samples. At high ionic strength, some adsorption occurs, possibly due to the double layer at sediment surfaces decreasing in thickness. A  $K_d$  value of  $3.94 \pm 0.99 \text{ cm}^3 \text{ g}^{-1}$  is reported in Hanford Site sediments at  $1.0 \text{ mol L}^{-1} \text{ NaClO}_4$  (Serne et al., 1993; Kaplan et al., 1996; Kaplan and Serne, 1998).

It has been demonstrated that alkaline dissolution of Hanford sediments can result in the production of sufficient ferrous iron to reduce chromate and precipitate Cr(OH)<sub>3</sub> (Qafoku et al., 2003) and U(VI)-carbonate aqueous species (Szecsody et al., 2013), possibly from the dissolution of biotite and magnetite. In addition, because alkaline dissolution results in significant aluminum and silica release to solution and subsequent aluminosilicate precipitation (as the pH is neutralized), coating of these precipitates on reduced U(IV) phases may also slow or limit reoxidation (and remobilization). Results from scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and X-ray diffraction (XRD) indicated that sodalite, Na<sub>8</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>(Cl or NO<sub>3</sub>)<sub>2</sub>, or cancrinite, Na<sub>6</sub>Ca<sub>2</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>(Cl or NO<sub>3</sub>)<sub>2</sub>, precipitates were formed depending on the Si/Al ratio in solution (Qafoku et al., 2003). The same mechanism may result in the reduction of pertechnetate and the subsequent precipitation of TcO<sub>2</sub>·xH<sub>2</sub>O(am). Field scale measurements show that additional mechanisms slow the release of Tc from sediments. Water extractions from sediments beneath the Hanford

SX 109 tank (acidic) removed only a fraction of the sorbed Tc (Myers et al., 1998), with calculated desorption  $K_d$  values of 23–332 mL g<sup>-1</sup>. At one alkaline disposal site (Hanford BC crib), where the pH at some depths is as high as 9.65 (Um et al., 2009) decades after disposal, as much as 70% of Tc is associated with surface phases in the oxic, dry sediment and is not mobilized by water (Szecsody et al., 2010). At another alkaline (pH 8–11) disposal site (Hanford B Plant), with high concentrations of sodium nitrate, as much as 50% of Tc was associated with surface phases in oxic, dry sediment (Jansik et al., 2013a), based on sequential liquid extractions. There was some association of surface Tc with Fe and Mn, although the Tc surface phase was not identified due to the low Tc concentration.

The purpose of this study is to quantify the geochemical processes that control <sup>99</sup>Tc migration in sediments when co-disposed with alkaline solutions. We hypothesize that low solubility Al precipitates coat the Tc<sup>IV</sup> precipitates when pertechnetate is co-disposed with alkaline solutions, thus preventing oxidation of some of the precipitated Tc. These coupled dissolution, reduction, and precipitation reactions depend on the differing rates of several reactions. Therefore, Tc immobilization will be greatest in zones of Al precipitation, and as a result, there will be some dependence on flow rates through sediments. Batch sediment–water experiments were conducted to quantify the pertechnetate reduction rate in natural anaerobic sediments, highly alkaline solutions, and in sediments with two model reductants (adsorbed ferrous iron, sulfide). Reduction rates were then quantified in 1-D sediment columns, which limits pertechnetate-surface phase contact, as would occur during field scale infiltration. The rate of silica, aluminum, and iron leaching in alkaline solutions was also quantified in flow experiments with differing contact times (i.e., flow rates). Pertechnetate oxidation (and remobilization) was then evaluated in the four different sediment–water systems and rates were compared. Sequential liquid extractions and autoradiographs were used to quantify spatial location of Tc surface phases that remained after system oxidation. Scanning electron microscopy (SEM) was used to determine the spatial distribution of Tc in the sediments and to identify possible mineralogic associations. The oxidation state of Tc and elemental associations was determined using spatially resolved micro X-ray absorption spectroscopy.

## 2. Materials and methods

### 2.1. Sediments and characterization

The sediment used in this study consists of a mixture of two subsurface sediments from opposite ends of the Hanford Site (WA) 200 east high-level waste tank farms (119°31'16"W longitude, 46°33'22"N latitude). One sediment is a fine sandy silt collected at a 40' depth north of the Hanford 200E area (submarine pit), and the second sediment is a fine sand collected at a 20' depth south of the Hanford 200E area (ERDF pit). Mineralogical characterization of these sediments (Zachara et al., 2004) shows quartz was the dominant mineral, with lesser amounts of plagioclase, potassium feldspars, micas, magnetite, chlorite, vermiculite, and smectite. The clay content was 2.7%. X-ray diffraction analysis of the micas indicated a mixture of muscovite, biotite, and vermiculitized biotite.

Because of the potential for reactivity with pertechnetate, iron extractions were conducted on Hanford sediments and specific minerals (biotite, magnetite) that were untreated, or pretreated with  $4 \text{ mol L}^{-1} \text{ NaOH}$  (200 or 400 h) or sodium dithionite/potassium carbonate solution (200 h, Table 1). The sodium dithionite/potassium carbonate treatment dissolves and reduces some (20–30%) ferric oxides and produces primarily adsorbed ferrous iron (Szecsody et al., 2004). Iron extractions conducted in parallel were used to quantify changes in the available ferrous and ferric iron. The

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