Technetium stabilization in low solubility sulfide phases: A review

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Abstract

Technetium (Tc) contamination remains a major environmental problem at nuclear reprocessing sites, e.g., the Hanford Site, Washington State, USA. At these site, Tc is present in liquid waste destined for immobilization in a waste form or has been released into the subsurface environment. The high environmental risk associated with Tc is due to its long half-life (213,000 years) and the mobility of the oxidized anionic species $Tc(VII)O_4^-$. Under reducing conditions, TcO_4^- is readily reduced to Tc(IV), which commonly exists as a relatively insoluble and therefore immobile, hydrous Tc oxide ($TcO_2 \cdot nH_2O$). The stability of Tc(IV) sequestered as solid phases depends on the solubility of the solid and susceptibility to re-oxidation to TcO_4^-, which in turn depend on the (bio-geo)chemical conditions of the environment and/or nuclear waste streams. Unfortunately, the solubility of crystalline TcO_2 or amorphous $TcO_2 \cdot H_2O$ is still above the maximum contaminant level (MCL) established by the US EPA (900 pCi/L), and the kinetics of TcO_2 oxidative dissolution can be on the order of days to years. In addition to oxygen, sulfur can form complexes that significantly affect the adsorption, solubility and re-oxidation potential of Tc, especially Tc(IV). The principal technetium sulfides are TcS_2 and Tc_2S_7 but much less is known about the mechanisms of formation, stabilization and re-oxidation of Tc sulfides. A common assumption is that sulfides are less soluble that their oxyhydrous counterparts. Determination of the molecular structure of Tc_2S_7 in particular has been hampered by the propensity of this phase to precipitate as an amorphous substance. Recent work indicates that the oxidation state of Tc in Tc_2S_7 is Tc(IV), in apparent contradiction to its nominal stoichiometry. Technetium is relatively immobile in reduced sediments and soils, but in many cases the exact sink for Tc has not been identified. Experiments and modeling have demonstrated that both abiotic and biologic mechanisms can exert strong controls on Tc mobility and that Tc binding or uptake into sulfide phases can occur. These and similar investigations also show that extended exposure to oxidizing conditions results in transformation of sulfide-stabilized Tc(IV) to a $Tc(IV)O_2$-like phase without formation of measurable dissolved TcO_4^-, suggesting a solid-state transformation in which Tc(IV)-associated sulfide is preferentially oxidized before the Tc(IV) cation. This transformation of Tc(IV) sulfides to Tc(IV) oxides may be the main process that limits remobilization of Tc as $Tc(VII)O_4^-$. The efficacy of the final waste form to retain Tc also strongly depends on the ability of oxidizing species to enter the waste and convert Tc(IV) to Tc(VII). Many waste form designs are reducing (e.g., cementitious waste forms such as salt stone), therefore, attempt to restrict access of oxidizing species such that diffusion is the rate-limiting step in remobilization of Tc.

Keywords: technetium sulfide; radioactive waste; redox reactivity; x-ray absorption spectroscopy; environmental mobility; cementitious waste forms

1. Introduction

The discovery of technetium near the middle of the last century (Pierre and Segre, 1937) was hailed as a major breakthrough in chemistry, but interest in this enigmatic and elusive element could have been fated to fade over time into the domain of exotic element enthusiasts. Buried inauspiciously in the middle of the Periodic Table (element 43), it may have garnered scant attention as a rare element (like, for example, indium) because, at the time of its discovery, no useful purpose for this element could be surmised. In addition, the abundance of natural technetium is vanishingly low, given that it is the lightest element with no stable isotopes, has scant probability of generation through natural fission, and because its longest-lived isotope has a half-life that is too short for the preservation of primordial technetium. Yet, interest in technetium has exploded since its discovery for two principal reasons: (1) its utility in nuclear medicine as a radioimaging agent, and (2) its disproportionate production during nuclear fission. In the first case, it was discovered that the meta-stable ^{99m}Tc undergoes an isomeric transition to ^{99}Tc (with a concomitant decrease in radioactivity of a factor of $\sim 1 \times 10^9$) that yields a "hard" gamma decay (141.5 KeV), which is easily detected by medical instrumentation. When bonded with ligands containing functional groups that adhere to specific organs or tissue, an extremely effective imaging tool is realized. Many of these substances are designed as Tc-sulfides (e.g., Blum, 1967; Boak and Agwunobi, 1978), Tc-Re-sulfide (Mochiki et al. 2006; Watanabe et al., 2001) or Tc-Sb-sulfide colloids (Wanebo et al., 1985). In the case of nuclear fission, the fission yield of ^{99}Tc, the only important isotope from the standpoint of half-life longevity, is 6%, rivaling that of other environmentally significant fission products, ^{137}Cs, ^{90}Sr and ^{129}I. Because ^{99}Tc is long-lived ($t_{1/2} = 2.12 \times 10^5$ years), extremely mobile in the environment and moderately radiotoxic, ^{99}Tc is an important radioisotope in the field of environmental chemistry.

This intriguing paradox, in which Tc is both a health aid and a threat, has led to a proliferation of peer-reviewed literature. Since 2005, the last year that a compilation of the thermodynamic properties of Tc was published (Rard 2005), there have been $\sim$15,000 papers published on Tc chemistry, most of these in the medical literature. The fast pace of Tc scholarship merits an occasional abstraction, and reviews of the Tc literature are published from time-to-time. Among the recent reviews of the behavior of Tc in the natural environment are Icenhower et al. (2010), and Meena and Arai (2017).

In the present review, we seek to elucidate a relatively neglected aspect of Tc geochemistry: The Tc sulfides. Although generally overlooked, Tc sulfides are extremely important to understanding the transport and fate of Tc in the environment. Indeed, isolation and discovery of Tc was accomplished by the precipitation of Tc sulfides by Perrier and Segre (1937; their "black precipitate"). Tc sulfides also provided the matrix by which the properties of technetium were first documented (e.g., Boyd et al., 1960). Because of the nearly universal presence of sulfide in reducing environments, especially through the agency of sulfate reducing bacteria, it is likely that interactions between Tc and sulfide will strongly affect the mobility of Tc in the subsurface. In addition, because of its propensity to form nanoparticles and colloids, Tc sulfide chemistry touches on other aspects that are of fundamental interest to the geochemical and mineralogical communities. Finally, the ability of Tc to bond with sulfide in unusual and unexpected ways

makes this a topic of interest to inorganic chemists. In short, investigations into the properties and behavior of Tc sulfides provide a confluence of interests for nuclear waste management agencies, biologists, geochemists, mineralogists and surface, inorganic and physical chemists.

2. Overview of Technetium Behavior in the Natural Environment

Meena and Arai (2017) and Icenhower et al. (2010) have recently reviewed the salient aspects of technetium biogeochemistry. Here, we briefly summarize Tc behavior. Because of the relatively short half-lives of Tc isotopes, there is no primordial Tc left over from formation of the solar system. A vanishingly small amount of Tc is produced through spontaneous fission of U (Kenna and Kuroda, 1961), so the clear majority of Tc present on Earth is anthropogenic. Tc can be found as a relic of atmospheric nuclear weapons testing, in low activity water discharges from nuclear reprocessing plants, in accidental airborne releases from nuclear facilities and in spent nuclear fuel in the form of metallic "epsilon particles" (c.f., Icenhower et al. 2010). In addition, Tc is present in numerous types of materials related to nuclear power or weapons production including sludges, salts, solutions, slurries, and raffinates.

The redox chemistry of Tc is the key to understanding its mobility. Tc speciation is complex, with valence states ranging from VII to –I, the most stable valence states in the environment are +VII and +IV under oxidizing and reducing conditions, respectively (Figure 1). Dissolved Tc is present in oxic systems (E_h >200 mV) at neutral and basic pH, as the aqueous Tc(VII) oxyanion species pertechnetate (TcO_4^-) TcO_4^- is highly mobile in the environment because of its high solubility (~11.3 molal; Boyd, 1978) and because it exhibits negligible
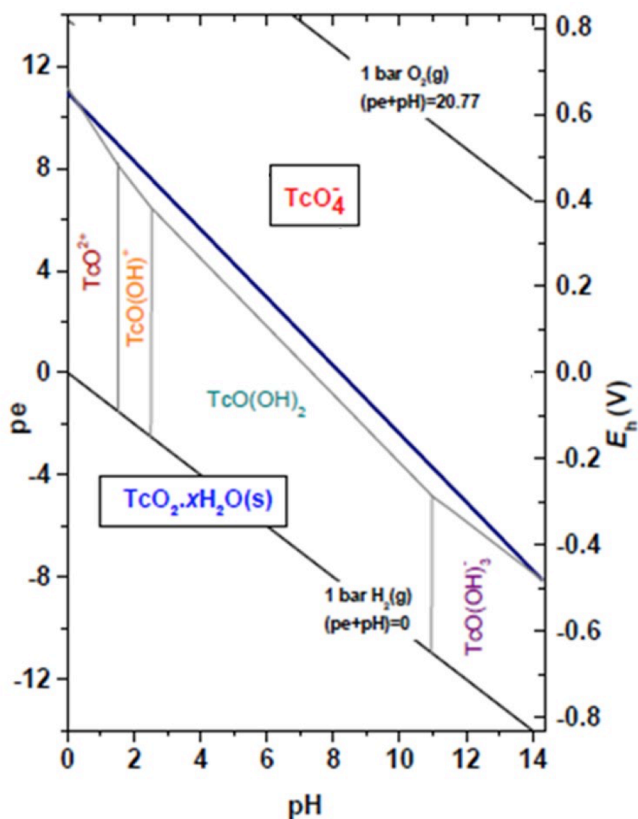

Figure 1. Tc Pourbaix diagram calculated with thermodynamic da[...] from Nuclear Energy Agency Thermochemical Database (Rard et [...] al., 1999). Tc(VII)/Tc(IV) equilibrium in equation 1 (blue line). 50:50 distribution between aqueous Tc species (grey lines). Black lines indicate upper and lower decomposition lines of water (pe + pH = 13.8). [Tc] = 10^{-5} M. (produced with permission from

sorption to typical rock-forming minerals in oxic environments (e.g., Palmer and Meyer, 1981).

Meena and Arai (2017) and Icenhower et al. (2010) both discuss the radiotoxicity and the pathways by which ^{99}Tc could affect human health.

For a variety of conditions and natural settings, there are mechanisms, both abiotic and biotic, that can reduce Tc to its +IV form, as expressed in equation (1).

$$Tc(VII)O_4^- + 4H^+ + 3e^- = Tc(IV)O_2 \cdot 2H_2O \text{ (s)} \tag{1}$$
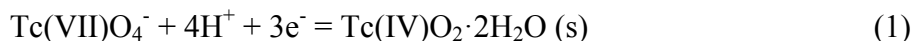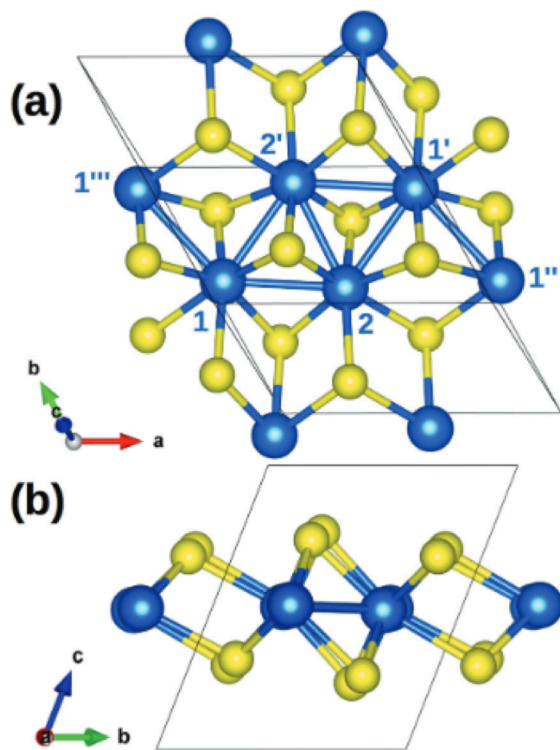
Abiotic reduction may occur, for example, when ferrous iron [Fe(II)] is added to pertechnetate solutions. However, the kinetics of reduction are typically slow (Cui and Eriksen, 1996). Faster reduction kinetics are realized when Tc sorbs onto iron-bearing phases in the presence of sorbed Fe(II) (Cui and Eriksen, 1996; Zachara et al., 2007; Peretyazhko et al., 2008). It is also the case that reduction can occur, directly or indirectly, through the agency of reducing bacteria. When reduced to the +IV state [typically as $Tc(IV)O_2 \cdot 2H_2O$], technetium is far less soluble (Tc = 3.08×10^{-9} M or ~5200 pCi/L; ~190 Bq/L; Meyer et al., 1991), but this concentration is still higher than the drinking water standard of 5.3×10^{-10} M (900 pCi/L, ~33 Bq/L) (U.S. EPA, 1977). Yet the solubility of Tc is further diminished through formation of sulfides, principally TcS_2 and Tc_2S_7. Although the solubility products of the sulfide phases have not yet been quantified, some investigators have suggested that the solubility of technetium is reduced by a factor of 10× below that of the hydrated oxide (e.g., Bruggeman et al., 2007). The lack of quantification is due, in part, because solids like Tc_2S_7 display a propensity to precipitate in amorphous or partly crystalline forms. As discussed below, the lack of long-range periodicity in Tc_2S_7 also frustrates efforts to characterize the structure of this solid.

In the following sections, we discuss the complex and fascinating mineralogy of the Tc-sulfide compounds, chiefly TcS_2 and Tc_2S_7. Following this, we turn our attention to the behavior of technetium in natural sediments and soils, with an emphasis on understanding the role that sulfide minerals play in retention and immobilization of technetium. Both abiotic and biologic mechanisms are discussed, as well as the potential for oxidation and remobilization of technetium in these settings. We then proceed to the topic of Tc behavior in a variety of waste streams and waste forms containing sulfides. Again, we assess the potential for oxidation and remobilization. Then, we address the potential for exploiting Tc-sulfides in waste forms. Finally, we review the formation and stability of technetium sulfide nanoparticles.

3. Technetium Sulfides

Perrier and Segre (1937) first described the formation of a "black precipitate" upon addition of hydrogen sulfide to <5 M HCl solutions containing 'element 43'. To quantify preliminary physical properties of Tc, Boyd et al. (1960) were able isolate sufficient concentrations of Tc from Mo metal irradiated in a graphite moderated neutron reactor. Therefore, the association between Tc and sulfide has always been an important component of Tc mineralogy.

A detailed description of the mineralogy of the principal technetium sulfides, TcS_2 and Tc_2S_7, were slow to develop, in part because of the difficulty of obtaining sufficient Tc and because Tc_2S_7 typically precipitates as an amorphous or semi-crystalline substance. Wildervanck and Jellinek (1971) were the first to determine the structure of TcS_2, $TcTe_2$ and $TcSe_2$ (as well as related compounds ReS_2, $ReSe_2$ and $ReTe_2$) through X-ray diffraction analyses of single crystals and polycrystalline material. The reported structure of TcS_2 is triclinic (pseudo-monoclinic) that can be described as a distorted $Cd(OH)_2$ unit cell with hexagonal closest packing (HCP). The structure of the ReS_2 compound, in contrast, is a distorted $CdCl_2$ lattice with cubic closest packing (CCP). A representation of the crystal structure of TcS_2 is given in Figure 2. The TcS_2 structure was confirmed by a more detailed study by Lamfers et al. (1996), and the structure of ReS_2 was refined by doubling the c-axis length.
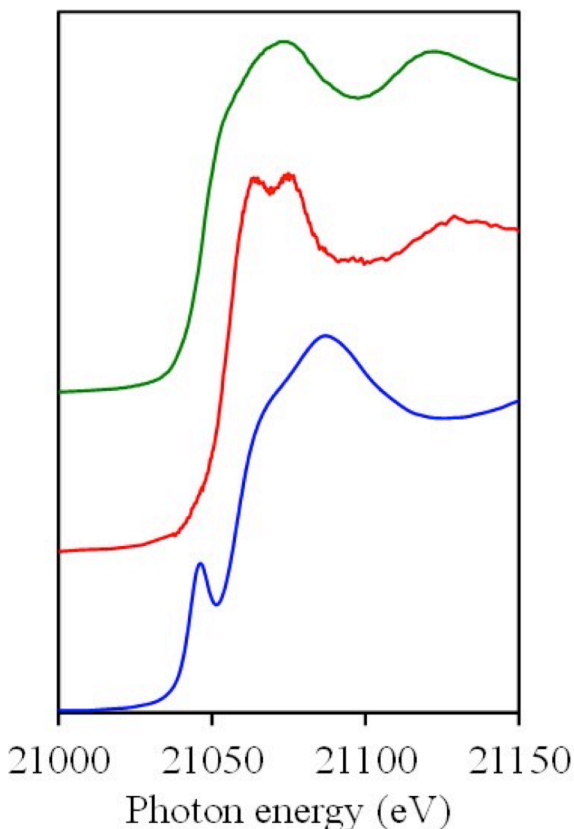

Figure 2: Ball-and-stick representation of the TcS_2 crystal unit cell. (a) Top view along the normal to the (a, b) plane and (b) side view along the a-axis of the TcS_2 layered structure. Color legend: Tc, blue; S, yellow (Weck et al., 2013).

More recently, interest in the Tc sulfides, especially TcS_2, has been stimulated by the recognition of the interesting electronic properties displayed by the transition metal dichalcogenides (TMS). These materials consist of two dimensional sheets that form layers held together by van der Waals bonds (e.g., Wildervanck and Jellinek, 1971). Stacking of dissimilar materials and tuning the distances between layers has led to a plethora of new functionalities in the TMS's. Systematic variations using elements with similar properties (e.g., Re, Mo, W) allows investigators to predict the properties of these materials to identify those with desirable functionalities (e.g., Wolverson and Hart, 2016; Weck et al. 2013). As pointed out by Wolverson and Hart, 2,500 publications on MoS_2, the archetypical structure, were written in 2015 alone. Study of the TcS_2 has always been hampered by the small quantities of materials yielded by traditional synthesis routes. Three new synthesis routes for TcS_2 were also recently reported (Ferrier et al., 2013). These new synthesis routes allow one to obtain larger yields of technetium sulfides at lower temperatures. More routine synthesis of larger batches of TcS_2 will lead to

better experiments exploring the efficacy of using TcS_2 as a waste form (see below). TcS_2 may also be prepared by heating Tc_2S_7 to 1000 °C in the presence of excess sulfur (Boyd, 1959).

The other principal technetium sulfide compound, Tc_2S_7, is far less understood than TcS_2. Synthesis experiments appeared to show that Tc_2S_7 appeared first and attempts to characterize this solid were limited in their success, mainly because this material is typically poorly crystalline. Early attempts to characterize this solid include Lee and Bondietti (1983), who reported a stoichiometry of $Tc_2S_{6.5}$ on an amorphous sample. In comparison to Tc_2O_7, and from our training as chemists, one would expect that the oxidation state of Tc in Tc_2S_7 would be heptavalent [i.e., Tc(VII)]. This led to several investigators to mistakenly identify "oxidized" technetium in environmental samples. However, heptavalent Tc should be unstable with respect to reduction in the presence of S^{2-}, [the standard reduction potential of sulfate to sulphide is -0.22 V vs. the standard hydrogen electrode (SHE), pH 7] (Drake et al. 2006). Because of these, and other ambiguities in the data, some investigators began to question the existence of Tc_2S_7.

Figure 3: Tc K-Edge XANES spectra for Tc(VII)O_4^- (blue line), Tc(IV)O_2 (red line) and 'Tc(IV)$_2S_7$' (green line). Data were collected at SSRL BL 11-2. Tc_2S_7 is a Tc(IV) compound but its XANES spectrum is distinct from TcO_2.

With the advent of materials characterization by X-ray absorption spectroscopy (XAS), including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) methods, a new and exciting picture of bonding in transition metal compounds emerged (Figure 3) (Lukens et at. 2005). The advantage offered by XAS is that the sample does not have to be crystalline for a detailed model of its structure to be obtained. Cramer et al. (1984) re-evaluated the structure of amorphous molybdenum and tungsten trisulfides and triselenides, compounds that share many characteristics to Tc sulfides, and argued for the existence of clusters of Mo or W with both S_2^{2-} and S^{2-} ligands. Weber et al. (1995) used X-ray photoemission (XPS) and vibrational spectroscopy to further characterize amorphous MoS_3. They showed that the structure of this compound is based on {Mo(IV)$_3$—S_9} moieties, thereby demonstrating that the valence of metals cannot necessarily be inferred from its apparent stoichiometry. These moieties are also

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designated as $Mo_3(\mu^3\text{-}S)(S_2)_3$. Lukens et al. (2005) examined the EXAFS spectra of Tc sulphides produced by addition of excess sodium sulphide (pH ~12) to a solution of TcO_4^- just prior to incorporation into grout. The resulting EXAFS spectra are almost identical to earlier spectra that were referred to as TcS_2 by Allen, at al. (Allen, et al., 1997). The EXAFS results on Tc_2S_7 are similar to those of the Mo sulphides, which suggests the presence of similar moieties based on Tc(IV). In this "TcS_x" structure the first two coordination shells for Tc consist of seven S neighbors at 2.37 Å and two Tc neighbors at 2.77 Å (Figure 4). In fact, this similarity suggests that the TcS_x structure also contains the same triangular core $Tc_3[\mu^3\text{-}S(S_2)_3S_6]$, with the Tc-Tc distance typical of triangular complexes composed of seven-coordinated metal centers (Figure 4). The outer coordination shells confirm that the Tc centers are linked together through a combination of disulfide and sulfide bridges. In this proposed structure, the Tc is in a Tc(IV) oxidation state with a Tc K-edge absorption energy 12 eV below that of $Tc(VII)O_4^-$ (Figure 3). The stoichiometry of $Tc_3S_2(S_2)_4$, or Tc_3S_{10}, is the same as $TcS_{3.2}$ determined for "Tc_2S_7", confirming that they are the same compound with Tc present in the lower valence state of Tc(IV) (Lukens et al., 2005). Based on these results, a Tc(IV) sulfide with the stoichiometry Tc_2S_7 is consistent with $Tc_2(S_2)_3S$; that is, Tc_2S_7 is primarily a disulfide complex.

$Mo_3(\mu^3\text{-}S)(S_2)_6{}^{2-}$ $Tc_3(\mu^3\text{-}S)(S_2)_3S_6$ core $Tc_3S_2(S_2)_4$ ("TcS$_x$")
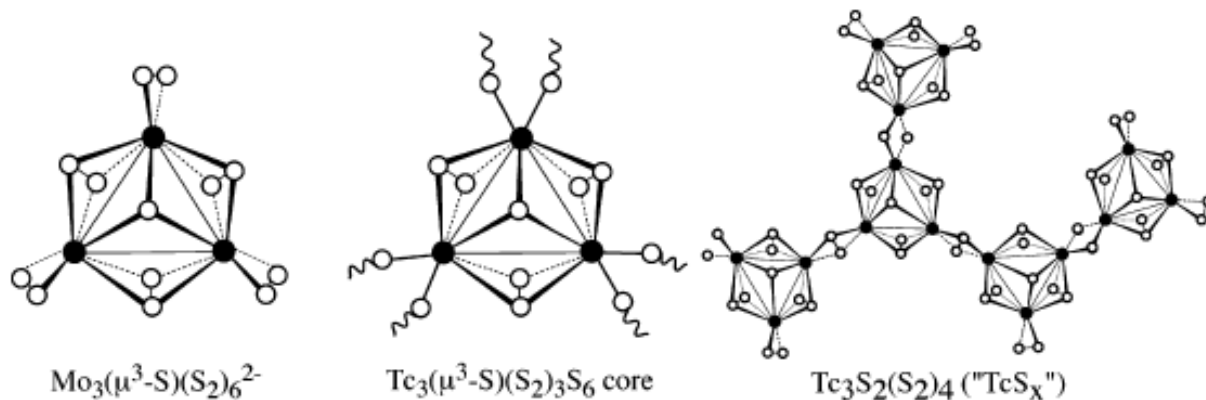
Amorphous Tc_2S_7 can be synthesized by transformation of $Tc(VII)O_4{}^-$ with H_2S in aqueous solution under aerobic and anaerobic conditions (Liu et al., 2007). Under acidic conditions (pH $\leq$ 4), $TcO_4{}^-$ reacts with H_2S according to Equation (2):

$$2TcO_4{}^- + 7H_2S + 2H^+ \leftrightarrow Tc_2S_7 + 8H_2O \qquad (2)$$
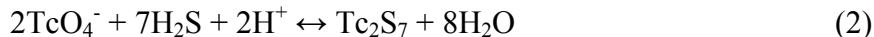
The reaction is first order with respect to both $[H_2S]$ and $[TcO_4{}^-]$, under aerobic and anaerobic conditions, and reaction rates and yields increased with the concentration of acid. Under anaerobic alkaline conditions, the speciation of sulfide changes with pH, so $Tc(IV)_2S_7$ might precipitate according to either Equation (3):

$$2TcO_4{}^- + 7HS^- * + H_2O \leftrightarrow Tc_2S_7 + 9OH^- \qquad (3)$$
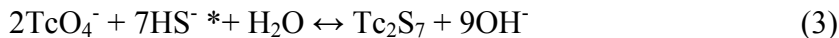
The yield of Tc(IV) sulfide was highest in the pH range 9-11, where HS^- is the dominant S(-II) species (equation 2), and then decreased at pH 13, possibly due to a competing hydrolysis reaction. The reaction rate is first order with respect to both $[H_2S]$ and $[TcO_4{}^-]$ under anaerobic

Figure 4: Structures of $Mo_3(\mu^3\text{-}S)(S_2)_6{}^{2-}$, the $Tc_3(\mu^3\text{-}S)(S_2)_3S_6$ core that forms the building block of TcS_x, and a portion of the proposed structure of TcS_x (Lukens et al., 2005). Solid circles = metal atoms, open circles = sulfur atoms.

conditions, but no reaction was observed under aerobic alkaline conditions, possibly because oxygen suppressed this reaction. The precipitation of $Tc(IV)_2S_7$ from solution in these experiments was confirmed by XANES. Figure 5 shows that XANES analysis can be used to distinguish between $Tc(VII)O_4{}^-$, $Tc(IV)O_2$ and '$Tc(IV)_2S_7$'. The $Tc(IV)_2S_7$ precipitated these experiments was readily hydrolyzed to yield $TcO_4{}^-$ under both acidic and especially alkaline conditions in the presence of oxygen (Liu et al., 2007). Of note with respect to amorphous Tc_2S_7 is its propensity to form nanoparticles rather than depositing as surface coatings.

4. Technetium Behavior in Sediments and Soils

As discussed above, when technetium is released into oxidizing surface waters, its most stable form is $TcO_4{}^-$, which is transported in the water column relatively unaffected by the presence of suspended particles. There is, therefore, an expectation that Tc should have a long

residence time in natural waters and behave as a conservative tracer. This expectation is belied, in part, by the observation of measurable Tc profiles in natural sediments, ranging in depositional environments from marine, to terrestrial through transitional. This observation has stimulated numerous studies that investigate the mobility and fate of technetium in sediments (e.g., Aarkrog et al., 1997; Peretrukhin et al., 1996; Morris et al., 2000; Keith-Roach et al., 2003; Keith-Roach and Roos, 2004; Burke et al., 2006; Jenkinson et al., 2014; German et al., 2003; Standring et al., 2002). These studies show that once pertechnetate is transported below a critical redox boundary in water, reduction occurs and the resulting Tc(IV) is readily bound to suspended particles. Typical K_D (concentration of Tc on the mineral surface divided by its concentration in solution) values for Tc(IV) between suspended particles and seawater are 10^{-2} to 10^{-3} (McCubbin et al., 2006). However, even in cases where pertechnetate is not reduced and the affinity for sorption is low, a large amount of technetium can become bound to particles when a high density of suspended particles is present (Morris et al., 2000). Tc-bearing particles then become incorporated into sediments accumulating on water body floors. The mechanism(s) responsible for retaining Tc in sediments is not always clear-cut, as discussed below.

Interaction between Tc and the minerals that make up soils is complex. Under oxic conditions in a variety of soils TcO_4^- exhibits low sorption (e.g., Kaplan 2003; Hu et al., 2008), as quantified by the parameter K_D. The reason for low sorption is that the constituent minerals in soils possess pH-dependent surface charge; under relatively acidic conditions, the surface charge is positive, and under relatively basic conditions, the surface charge is negative. The pH at which neutral surface charge occurs is the so-called point of zero charge or PZC. Most soil-forming minerals exhibit PZC values that are less than the pH of typical ground or pore waters, so the surface charge is negative. Negative surface charge will repel anions like TcO_4^-. In some sediments, the negative charge on the pertechnetate anion is such that it can exhibit *negative K_D* values (Kaplan and Serne, 1998). In capillary fringe sediments proximal to groundwater, redox conditions can fluctuate, as the water table rises or falls. In addition, the presence of iron, nitrate and sulfate reducing bacteria, coupled with organic matter, can produce localized pockets or broad horizons of reducing environments in the subsurface. In these reducing regions technetium may undergo reduction.

Close examination of Tc-contaminated sediments and soils does not readily reveal the sink into which Tc is sequestered. Several hypotheses have been advanced for the strong retention of Tc in sediments. For example, German et al. (2003) and Peretrukhin et al. (1996) attribute the strong association of Tc in lacustrian sediments to the presence of organics and the agency of bacteria. Lovely (1993) demonstrated that many indigenous microorganisms can couple oxidation of organic matter with reduction in metals, setting the stage for a robust field of biogeochemistry research. Reduction of metals may take place either through direct enzymatic processes or through indirect means, including production of metallic biominerals that act as substrates for reduction. Other investigators have suggested sorption, in some cases irreversible sorption, of Tc onto the surfaces of Fe-bearing phases. Keith-Roach et al. (2003) used sequential

extraction to infer the sink for Tc and found that it resides in the most chemically labile fraction. The labile fraction includes phases such as carbonates and amorphous iron sulfides, so a precise sink could not be identified. Henrot (1989) was one of the first to suggest that technetium in soils is immobilized in the form of TcS_2 or Tc_2S_7 due to biological activity. Still other investigators (e.g., Wharton et al., 2000;) propose co-precipitation of Tc with iron sulfide phases, which may result in sequestration of Tc in the mineral structure by a similar mechanism to that observed with Fe oxides (Skomurski et al., 2010; Kobayashi et al., 2013; Marshall et al., 2014; Lukens et al., 2016; Smith et al., 2016; Smith et al., 2015; Saslow et al., 2017).

The problem with identifying the ultimate sink or sinks for Tc in sediments is that concentrations of Tc are very low, making it difficult to pinpoint the association of Tc with a particular phase. In addition, many sediments have been perturbed by post-accumulation processes, including bioturbation (Morris et al., 2000). Therefore, investigators resort to experimentation to demonstrate or disprove how retention of Tc may occur in nature. These experiments, include those testing either abiotic or biologically mediated mechanisms, or both, are reviewed next.

4.1 Tc Reduction in Sediments through Abiotic Processes

4.1.1 Iron sulfide mineral interactions with technetium

The investigation of Strickert at al. (1980) was an early study that set the stage for additional work on pertechnetate sorption onto iron sulfide minerals. They reported that, in contrast to its typically low sorption affinity, $Tc(VII)O_4^-$ was strongly sorbed from aqueous solutions (pH not given) by several natural Fe- and sulfide-bearing minerals including mackinawite (FeS) and tetrahedrite [$(Cu, Fe)_{12}Sb_4S_{13}$]. Their reported K_D values of 100-2,000 ml/g for the iron sulfides stand in contrast to the relatively minor degree of pertechnetate sorption onto oxide minerals [(K_D = 1 ml/g) including quartz (SiO_2), calcite ($CaCO_3$), chlorite (($Mg,Fe,Li)_6AlSi_3O_{10}(OH)$), witherite ($BaCO_3$), feldspar ($KAlSi_3O_8$) and clay minerals]. To explain this enhanced sorption affinity, Strickert et al. (1980) proposed two sorption mechanisms other than ion exchange that could potentially retard the pertechnetate anion: (i) chemical reduction to an immobilized form; and (ii) incorporation into a crystal lattice to form an insoluble matrix. Results from batch sorption experiments using crushed minerals suggested that reduction of $Tc(VII)O_4^-$ to $Tc(IV)O_2$ was involved in the sorption process for minerals containing Cu(I) and Fe(II) ions. This was evidenced by the fact that sulfide compounds containing metal ions in the highest oxidation state absorbed little $Tc(VII)O_4^-$. Potential mechanisms for incorporation of reduced $Tc(IV)O_2$ into the crystal lattice of the mineral phases were not explored in that study.

Exploration of the effects of redox potential (E_h) on TcO_4^- removal by Fe sulfide minerals in natural waters was carried out by Lieser and Bauscher (1987, 1988). In these studies, sorption and reduction experiments were conducted with the ferrous sulfides pyrrhotite ($Fe_{1-x}S$, the non-stoichiometric variant of troilite (FeS)) and pyrite (FeS_2), in the presence of 10^{-6} mol/L TcO_4^-.

They found that: (i) at pH 7, the Tc sorption coefficient drops by three orders of magnitude at ~170 mV (vs. SHE) due to the transition from the Tc(IV) stability field to that for Tc(VII) (Figure 1); (ii) at high pH, TcO_4^- is relatively stable and the transition of Tc(VII) to Tc(IV) is shifted to lower redox potential; and (iii) at low pH, the transition of Tc(VII) to Tc(IV) occurs at higher redox potential resulting in higher sorption ratios. Under the aerobic conditions of the experiment, pyrrhotite undergoes hydrolysis and Fe(II) is oxidized to insoluble iron hydroxide $Fe(OH)_3$ per Equation (4):

$$2FeS + 5H_2O + 0.5O_2 \rightarrow 2Fe(OH)_3 + 2H_2S \qquad (4)$$

A decrease in pH (pH 5.4 to 3.6) occurred, possibly due to the formation of H_2S, and it was hypothesized that the H_2S reacted with TcO_4^- to form insoluble $Tc(IV)_2S_7$, which drastically increased Tc sorption/precipitation. The hydrolysis reaction between pyrite and water to form $Fe(OH)_3$ and sulfuric acid (H_2SO_4) was slower, resulting in a smaller pH change (pH 5.9 to 4.8) and lower Tc sorption. The mode of Tc-uptake by pyrite for a range of Tc concentrations (10^{-12} to 10^{-6} mol/L) under aerobic conditions at pH 7 was suggested to be oxidation of FeS_2 to form $S_2O_3^{2-}$ or SO_3^{2-}, with concurrent reduction of Tc(VII) to Tc(IV) close to the FeS_2 particle surface (Winkler et al., 1988).

Differences in K_D for TcO_4^- (concentration range: 10^{-12} and 10^{-6} mol/L) and $Fe_{1-x}S$ and FeS_2 under aerobic conditions (~50,000 ml/g and 70-100 ml/g respectively) was also shown by Bock et al. (1989). Sorption experiments were initially buffered to pH 7 with bicarbonate (CO_3^{2-}), but oxidation and hydrolysis processes led to large pH and E_h drifts over longer contact times. FeS_2 showed a drastic pH decrease, producing positively charged mineral surfaces for total TcO_4^- adsorption. Under anaerobic conditions, an increase in aqueous Fe^{2+} concentration occurred in the presence of pyrite, resulting in a decrease in the redox potential, and making sorption/precipitation of Tc onto pyrite more favorable (Lieser and Bauscher, 1988). However, under aerobic conditions, TcO_4^- reduction in solution is unlikely due to the positive E_h of the system, and it has been proposed that Fe^{2+} is only present in localized reducing microenvironments on mineral surfaces where the reduction of Tc(VII) to form TcO_2 is promoted (Bock et al., 1989).

The reduced iron-sulfide mineral mackinawite (FeS) can also reduce TcO_4^- to Tc(IV) to form co-precipitates (Wharton et al., 2000; Yalcintas., 2016). Tc(IV) could potentially be incorporated into the poorly ordered structure of the FeS solid, but EXAFS results suggest that it is precipitated as a TcS_2-like phase (Wharton et al. 2000) or a Tc_2S_7-like phase (Yalcintas et al., 2016). Livens et al. (2004) also investigated the interaction of TcO_4^- and Tc(IV) (10^{-5} mol/L) with microcrystalline mackinawite (FeS) under anoxic conditions. TcO_4^- was reduced to Tc(IV) with three S atoms at 2.36 Å and three at 2.41 Å around the Tc center as in a TcS_2-like species (Lamfers et al., 1996). The product of the reaction between mackinawite and Tc(IV) was similar but had a short Tc-S distance (1.99 Å), suggesting that the Tc(IV) is present in square-based pyramidal geometry in the interstices.

Bruggeman et al. (2007) also explored the sorption of Tc(IV) onto pyrite (FeS$_2$). In this study, the investigators did not seek to examine the reduction efficacy of Tc(VII) to Tc(IV) but, rather, to quantify the sorption behavior of a reduced technetium species. They reported that sorption dynamics could be modeled as a Langmuir isotherm and proposed that the adsorbing species is TcO(OH)$_2$. Unlike other studies, they did not postulate precipitation of TcS$_2$ or co-precipitation of TcO$_2$·2H$_2$O, but rather an immobilization mechanism based on sorption alone. Also note that the solid material consisted of a mixture of clay, humic substances and powdered pyrite. They were careful to design their experiments to distinguish between the diverse sinks for Tc. They found that the combination of these sinks typically lowered the concentration of Tc in solution ($<2\times10^{-9}$ to 1.77×10^{-7} M) to concentrations below that expected if TcO$_2$·2H$_2$O were the solubility-limiting phase (3.08×10^{-9} M; Meyer et al., 1991).

Other investigations that explored the relationship between Tc reduction and iron sulfides include Shen et al. (2002). They conducted pertechnetate sorption and desorption experiments with "pyrrhotine" (= pyrrhotite). Under both aerobic and anaerobic conditions, the concentrations of pertechnetate decreased, suggesting sorption or precipitation. The rate of the disappearance of pertechnetate from solution was faster under anaerobic conditions. At low pH values, obtained by addition of sulfuric acid, technetium desorbed from the pyrrhotite surface. Geraedts et al. (2002) and Palmer and Meyer (1981) also carried out experiments in which interactions between pertechnetate and iron sulfide minerals were quantified. In general, they found that sorption of technetium onto iron sulfides was minimal, in both oxic and reducing conditions. Geraedts et al. (2002) argued that Tc was present as colloids associated with humic substances, thereby minimizing the role of iron sulfides in the reduction of pertechnetate.

4.1.2 Other sulfide mineral interactions with technetium

In addition to ferrous sulfides, other sulfide minerals that contain potential reducing or coprecipitating components can interact with Tc(VII)O$_4^-$. Chalcocite (Cu$_2$S) and bournonite (CuPbSbS$_3$) strongly sorbed or precipitated Tc(VII)O$_4^-$ from aqueous solutions (K_D = 200-2,000 ml/g) (pH not given), with cuprous and/or plumbous ions potentially involved in the redox reaction (although they are stable in solution) (Strickert at al., 1980). Stibnite (Sb$_2$S$_3$) could irreversibly sorb/precipitate 99% of 10^{-8} mol/L TcO$_4^-$ in batch experiments under aerobic conditions (pH 3.84-6.22) (Zhuang et al.,1988). Further column experiments demonstrated that particle size did not affect sorption of TcO$_4^-$ by Sb$_2$S$_3$, and that sorption/precipitation kinetics were slow, possibly due to the insolubility of Sb$_2$S$_3$ limiting the concentration of sulfide in solution. In addition, flow rate had a significant effect on TcO$_4^-$ retardation, suggesting that sorption was strongly affected by kinetics and it was concluded that the retardation mechanism was due to the chemical reduction of Tc(VII)O$_4^-$ to Tc(IV) (Zhuang et al., 1995). TcO$_4^-$ (10^{-7} M) sorbed completely onto powdered Sb$_2$S$_3$ (10 g/L) under both aerobic and anaerobic conditions (Peretroukhine et al., 2006), with increased sorption rates at higher temperatures (60 °C). TcO$_4^-$ sorption in the absence of oxygen was due to: (i) the oxidation of sulfide ions in aerobic conditions; and (ii) the role of Fe(II) impurities in reduction of Tc(VII) with subsequent sorption

of Tc(IV) onto the stibnite. The sorption products were found to be Tc_2S_7, $TcO_2 \cdot nH_2O$ and TcS_2 under anaerobic conditions, and Tc_2S_7 under aerobic conditions, suggesting that the Fe(II) impurity may have been responsible for Tc reduction under anaerobic conditions, affecting Tc speciation. Hydrolysis of the surface of Sb_2S_3 at pH 9-12 inhibited Tc immobilization and resulted in the formation of nanoparticles with Tc present as Tc_2S_7 (Peretroukhine et al., 2006).

The sorption/precipitation properties of a range of natural metal sulfides including Sb_2S_3, galena (PbS), Cu_2S and sphalerite (ZnS), under aerobic conditions, with respect to TcO_4^- (10^{-12} and 10^{-6} mol/L) were studied by Bock et al. (1989). As in previous work, the antimony- and lead-containing minerals Sb_2S_3 and PbS had very high affinity (~50,000 ml/g and 50–1000 ml/g respectively) for TcO_4^-. The reduction of Tc(VII) was promoted by a combination of low valent metal cations (although Pb^{2+} is stable in solution) and sulfur species (S^{2-} or SO_3^{2-}), to form $Tc(IV)_2S_7$ as a black precipitate. During subsequent desorption experiments, the strong fixation of TcO_4^- by metal sulfides suggested that the Tc-sulfides formed were less soluble than secondary oxidation products such as oxides or hydroxides (Bock et al., 1989). The sorption behavior of TcO_4^- on cadmium sulfide (CdS) under aerobic conditions and over a pH range of 1.3-12.5 was investigated by El-Wear et al. (1992). CdS showed increasing sorption ratios with decreasing pH and this was attributed to the partial dissolution of CdS producing S^{2-} ions in solution. This observation suggests that the sulfur species, rather than the metal cations, are responsible for the reaction with TcO_4^- to form Tc_2S_7.

Very little molecular modelling has been performed to aid understanding of adsorption in the Tc-S system. However, Anderson et al. (2007) performed quantum mechanical calculations to understand the adsorption behavior of TcO_4^- onto PbS, including geometry, adsorption energies and electronic structure. In vacuum, TcO_4^- was calculated to have a formation (i.e., self-binding) energy of -388.7 eV, and a Tc-O bond length of 1.73 Å. It was also calculated to have a hydration energy of -2.4 eV. The adsorption energy of TcO_4^- onto a PbS terrace, including the effect of partial dehydration, according to Equation (5) is -0.087 eV.

$$Pb_{16}S_{16} + TcO_4^- \rightarrow Pb_{16}S_{16} - TcO_4^- \tag{5}$$
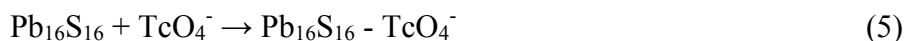
In the most stable configuration, two O atoms sit above two Pb atoms (Figure 5a). After adsorption, the Tc atom becomes slightly more positive. The two O atoms closest to the cluster have bond lengths of 1.75 Å to the central atom (0.04 Å longer than the bond lengths of the upper oxygens) and are more negative according to Mulliken charges. The shift in electron density and atomic position show the effects of polarization as the molecule approaches the positively charged Pb atoms in the cluster, however, the TcO_4^- retains its original total charge, indicating that the interaction is ionic. TcO_4^- was found to adsorb more strongly to step edges below the ledge (E_{ads} = -0.21 eV), and particularly when the anion sits above the ledge on a highly-distorted step (E_{ads} = -1.15 eV) (Figure 5b). The Mulliken charges in the latter case show a reduction of the anion from total charge of -1 to -2, indicating transfer of one electron from the

PbS cluster to TcO$_4^-$ and the initial pertechnetate reduction facilitated by sulfide in the PbS lattice (Anderson et al., 2007).
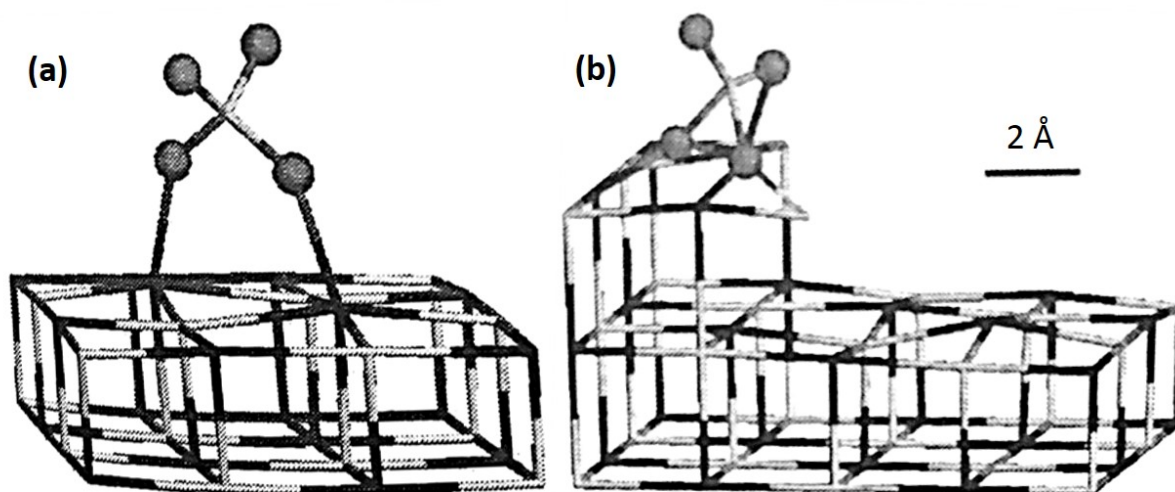
Figure 5: The most stable geometry for TcO$_4^-$ adsorption onto a galena cluster (a). Final position for TcO$_4^-$ on a cluster representing a galena step. Light atoms in the slab are S, darker atoms in the slab are Pb, the central atom is Tc, and the four outer atoms in the adsorbate are O (Anderson et al., 2007).

4.2 Interactions between sulfate-reducing bacteria and technetium

As discussed above, dissimilatory metal reduction can occur with a wide variety of indigenous bacteria (Lovley, 1993) and these processes can also influence the behavior of Tc in the environment. Investigations indicate that during nitrate reduction technetium is not reduced, but iron and sulfate reduction results in Tc immobilization (e.g., Abdelouas et al., 2002; 2005; Burke, 2005; Lloyd et al. 1998; 2000; 2001). The expectation is that sediments and soils containing sulfur should yield technetium sulfide phases after sulfate reduction. However, despite the sulfidic conditions present in several sites studied, there was no evidence that TcS$_2$ had precipitated suggesting that sulfides are not a common binding phase for Tc in the environment. TcO$_4^-$ in anoxic estuarine sediments was removed from solution by reduction to Tc(IV) under Fe(III)-reducing conditions and with a heterogeneous microbial community of nitrate-, metal-, and sulfate-reducing bacteria (Burke et al. 2005). Again, analysis by XAS showed that the reduced Tc was precipitated as Tc(IV)O$_2$.nH$_2$O, rather than Tc sulfide, even when exposed to sulfate-reducing sediments.

In contrast, significant Tc sorption was observed on natural lake sediments, with the inferred mechanism of microbial reduction and sequestration by sulfides (German et al., 2003). In this study, batch experiments were performed using low concentrations of pertechnetate (10^{-4} to 10^{-6} M). Uptake of Tc was strong in unmodified sediments, but sterilized samples exhibited far less

uptake, thus implying the activity of microorganisms. Reoxidation of the sediments did not result in the release of Tc unless a strong oxidant, such as peroxide, was used. The authors attributed this recalcitrance to release as the effects of Tc sulfides. (Peretrukhin et al., 1996) carried out similar experiments on lake bed sediments exposed to Tc. They reported that sulfidogenic pure cultures of the sulfate-reducing bacterium *Desulfovibrio desulfuricans* ATCC 29577 supplied with sulfate and lactate as an electron acceptor and donor, respectively, could reduce TcO_4^- under anaerobic conditions. Sulfur was the major element detected in precipitates from these cultures at ~5-fold stoichiometric excess to Tc, indicating that the Tc was precipitated as an insoluble sulfide, e.g. Tc_2S_7 contaminated with elemental sulfur. The high concentrations of the S-containing extracellular precipitate suggested that the Tc precipitated outside the cell after reaction with microbial-derived H_2S. This also indicates that Tc(VII) did not compete effectively with sulfate as an electron acceptor for *D. desulfuricans*, despite the lower reduction potential of SO_4^-/HS^- ($E'^\circ = -0.217$ V) compared to that of TcO_4^-/TcO_2 ($E'^\circ = +0.748$ V) (Lloyd et al., 1998). Abdelouas et al. (2002) also investigated the reduction of TcO_4^- (10^{-7} M) by subsurface sulfate-reducing bacteria using soil and groundwater amended with lactate as an electron donor, and either nitrate or sulfate as electron acceptors. TcO_4^- was not reduced under denitrifying conditions, but stimulation of sulfate-reducing bacteria in the soil resulted in near complete removal of TcO_4^- from solution. This removal was attributed to Tc(VII) reduction in the presence of sulfide, however, addition of sulfide abiotically did not result in complete Tc(VII) removal from solution. Analysis of the products by electron microscopy showed Tc in the presence of Fe and S, therefore it was hypothesized that co-precipitation of TcO_2 and/or TcS_2 occurred with biogenically formed iron sulfide (presumably mackinawite, FeS) (Abdelouas et al., 2002).

Because Tc–S species are present in some sulfidic sediments but not in others, Lee et al. (2014) sought specific evidence for their presence or absence as reduction products generated by microbial activity. Complete bioreduction of TcO_4^- (10^{-5} M) occurred in hyporheic zone sediments, with or without sulfate, stimulated by addition of organic carbon. No reduction of Tc(VII) was observed in non-stimulated sediments, despite the presence of lithogenic Fe(II). EXAFS spectroscopy revealed the presence of three types of reaction products: Tc(IV) surface cluster complexes with Fe(III), Tc(IV)O_2-like phases and a significant fraction of a TcS_x-like phase in sediments that had experienced SO_4^{2-} reduction and acid volatile sulfide (AVS) formation (Lee et al., 2014). Results suggest that the relative amounts of these reaction products depend very much on the local environmental conditions.

The influence of reactions mediated by sulfate-reducing bacteria on the behavior of Tc in the environment has been extended to promote bioremediation of TcO_4^-. A magnetic iron sulfide material produced by sulfate-reducing bacteria and characterized as a mixture of mackinawite (FeS) and greigite (Fe_3S_4) was used in a bioreactor for the remediation of TcO_4^- (Watson and Ellwood, 2003; Watson et al., 2001). In batch tests, TcO_4^- (10^{-6} M) was completely removed from solution with the addition of 4.81 g/L of the Fe-S sorbent. EXAFS confirmed that TcO_4^-

was chemically reduced by the Fe-S sorbent and that Tc remained chemisorbed at the surface by a Tc-S bond, with a significant Tc-Fe interaction at longer bond lengths (Watson et al., 2001).

4.3 Technetium sulfide reoxidation mechanisms

Many of the investigations that examined Tc binding in sediments and soils also addressed the issue of reoxidation and the potential for remobilization of technetium in the event of changes to environmental conditions (e.g., Burke et al., 2005; 2006; Fan et al., 2013; German et al., 2003; Keith-Roach et al., 2003; Keith-Roach and Roos, 2004; Morris et al., 2000; Strandring et al., 2002; Wharton et al., 2000). In general, the findings of these studies indicate that the identity of the phase that harbors or acts as a sorption substrate and the presence of organic matter have a strong bearing on the extent of Tc remobilized.

As discussed above, Wharton et al. (2000) conducted experiments in which mackinawite was co-precipitated with a TcS_2-like phase. Upon oxidation of the mackinawite in air to form goethite, Tc remained reduced but in a $Tc(IV)O_2$-like environment with six O atoms at ~2 Å, rather than a TcS_2 environment, suggesting that oxidation of the FeS is not immediately accompanied by oxidation of the Tc(IV) to Tc(VII). Because the goethite structure is based in octahedral $Fe(O,OH)_6$ units, and Tc is octahedrally-coordinated in TcO_2, it is hypothesized that Tc(IV) can be incorporated in the goethite lattice and thus stabilized in a reduced, insoluble form (Livens et al., 2004). Experiments demonstrate that uptake of Tc(IV) into the goethite structure and that retention of Tc during reoxidation events is strong (Um et al., 2011; 2012). First principles calculations agree with the experimental evidence (Smith et al., 2015; and Skomurski et al., 2010), showing that Tc(IV) can occupy Fe(III) coordination environments in goethite and hematite with charge compensating Fe(II).

More extensive remobilization of Tc occurred in contaminated sediments in which the presence of Tc sulfides could not be substantiated (Burke et al., 2006). As shown by experiment, re-oxidation of Fe(II) and sulfide occurred when exposed to air, accompanied by 50% remobilization of Tc to solution as TcO_4^-. Similar remobilization behavior of Tc during air oxidation of both sulfate- and Fe(II)-reducing sediments, along with no direct correlation between sulfide oxidation and Tc remobilization, indicated that reduced Tc sulfides were not important Tc sinks in reduced sediments (Burke et al., 2005) and Tc retention could not be explained by sulfide stabilizing sediment–bound Tc(IV) (Burke at al., 2006).

In field studies, the remobilization of Tc in contaminated sediments was also investigated. In most cases the conclusions drawn from these studies contrast with those from experimental studies. Keith-Roach et al. (2003) and Keith-Roach and Roos (2004) suggested that even in sulfidic systems, Tc sulfides may not be prominent. They contended that Tc reduction and immobilization occurred after Fe reduction, but before sulfate reduction. They further argued that mobilization of Tc was governed by the presence of organic matter. A similar conclusion was reached by Standring et al. (2002) who found that the most likely sink for ^{99}Tc was organic

material, not sulfides. To summarize these studies, Tc sulfides and Tc adsorbed or co-precipitated onto the surface of an iron sulfide is likely to remain relatively immobile. In the case of Tc adsorbed onto the surface of an iron sulfide, Tc will remain immobile even after the iron and sulfide oxidized. On the other hand, the existence of sulfate reducing bacteria, or the establishment of sulfidic conditions, does not guarantee the existence of technetium sulfides.

To assess the stabilization of Tc in low solubility sulfide phases, potential pathways for re-oxidation and remobilization of Tc must be considered. The redox potential for the oxidation of TcO_2 to TcO_4^- is +0.738 V; therefore, for Tc sulfides to offer enhanced resistance to remobilization from a thermodynamic perspective, their stability field must extend such that more oxidizing conditions are required for the transformation from Tc^{4+} to Tc^{7+}. Oxidation of TcO_2 to TcO_4^- involves a decrease in the number of coordinating oxygen ligands and a change in coordination geometry from octahedral to tetrahedral. By comparison, oxidation of TcS_x requires the additional step of replacing the sulfur ligands with oxygen. Thus, conceptually, oxidation of Tc(IV)-sulfides should at least be kinetically slower than oxidation of TcO_2. Exploring the mechanism of Tc sulfide oxidation in detail is essential for providing information on how environmental conditions can be manipulated to limit release of TcO_4^-. Much can be gleaned from studies on the oxidation of transition metal sulfides generally, particularly the wealth of information on environmentally-relevant Fe sulfides as discussed below. Also informative are oxidation mechanisms for Mo- and Re-sulfides, given their propensity to form stable triangular metal frameworks, with a capping sulfur, three edge-bridging S_2, and six linking sulfur ligands ($M_3(\mu^3\text{-}S)(S_2)_3S_6$) similar to that for TcS_x (Lukens et al., 2005). In addition, the role of different oxidants must be considered, with Fe^{3+}, O_2 and H_2O being the most important in the environmental systems considered here. Other factors that will make major contributions to the rates of relevant TcS_x redox reactions are temperature, pH, microbial activity and aqueous HS^- concentration.

When considering the intermediate steps in the oxidation of Tc sulfides, it is helpful to first revisit their formation mechanisms. Gaseous hydrogen sulfide (H_2S), leads to Tc sulfide precipitation when bubbled through a TcO_4^- solution, but the specific products formed are determined, in part, by pH (as described in Section 3). In alkaline solutions, a stepwise substitution reaction is thought to occur by reaction with S_2^- via the formation of TcO_3S^-, $TcO_2S_2^-$, $TcOS_3^-$ or TcS_4^-, or direct formation of Tc_2S_7 by reaction with S^{2-} or HS^-. In the reaction between TcO_4^- and bis(trimethylsilyl) sulfide [$(Me_3Si)_2S$] in acetonitrile, a Tc(V) trioxo-sulfide TcO_3S^- species is formed in solution as a precursor to the formation of a solid containing Tc(IV), S and O (Ferrier et al., 2012). Only amorphous Tc_2S_7 is obtained from the reaction of TcO_4^- with $H_2S(g)$ in acidic solutions of HCl or H_2SO_4 (Boyd et al, 1960). Ferrier et al (2014) studied the speciation of Tc present in the aqueous supernatant from Tc-sulfur precipitates by the reaction between TcO_4^- and $H_2S(g)$ in H_2SO_4, in order to elucidate Tc sulfide dissolution mechanisms. A black solid and a brown supernatant were the products of the reaction, with ~80% of the original Tc remaining in solution. Based on the UV/Visible and EXAFS spectroscopic data, TcO_4^- was

not stable in 12 M H_2SO_4, and is converted to polymeric Tc-O-Tc surrounded by sulfate, water and/or hydroxide ligands. The mechanism of formation was described as a successive reduction of $Tc^{VII}O_3(H_2O)_2(OH)$ (Figure 6b) to green $Tc^VO(HSO_4)_3(OH)^-$ (Figure 6c) and to Tc(IV) complexes (i.e., $Tc(HSO_4)_2(H_2O)(OH)_2$ (Figure 6d) and $Tc_2O(HSO_4)_4(H_2O)_2(OH)_2$) (Figure 66).
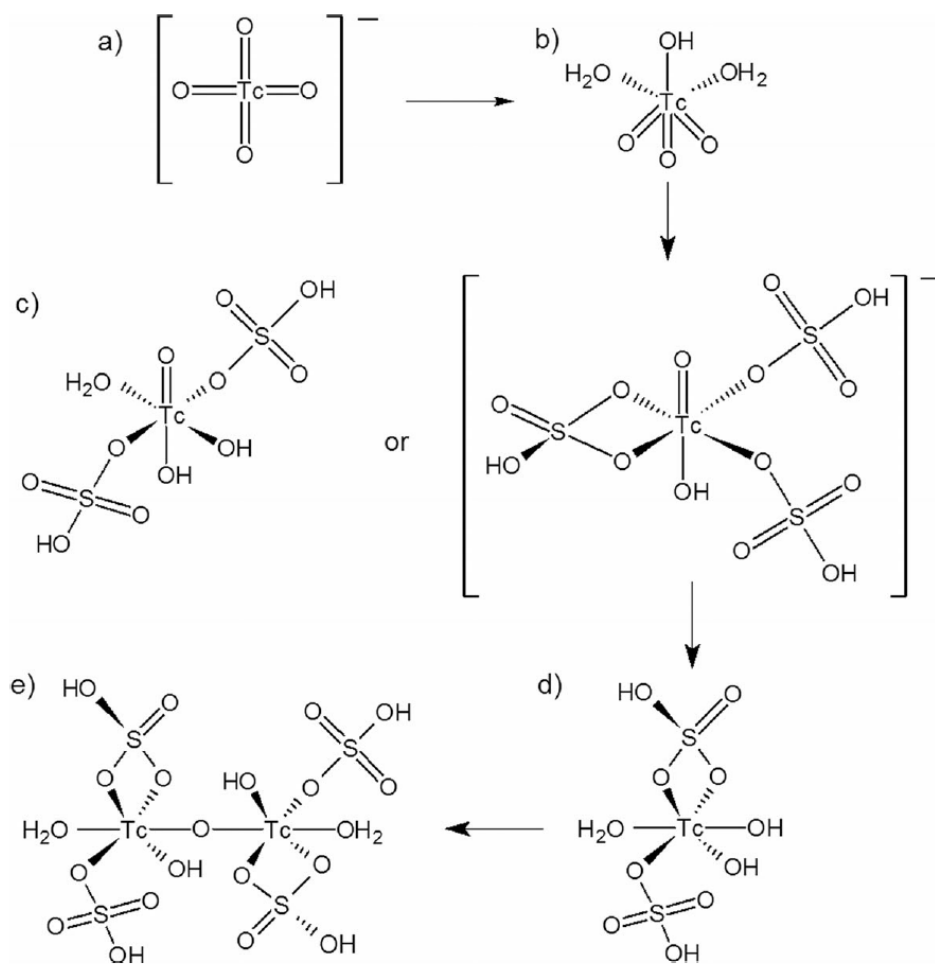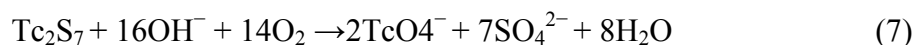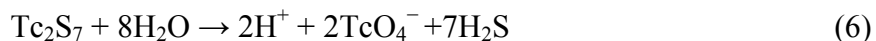

Figure 6: Proposed mechanism for the formation of the Tc(IV) species in 12 m H_2SO_4/H_2S solution (Ferrier et al, 2014).

These oxosulfide and sulfate complexes tend to polymerize because of the high proton affinity of oxygen compared to sulfur. Also, both Tc and S may undergo redox reactions, typically involving induced internal electron transfer, which are an important part of their reactivity. The bound sulfide (S^{2-}) ligands can transfer electrons to the metal center, with the counter intuitive consequence that Tc can be reduced upon exposure to oxidizing conditions. Thus, in neutral to acidic aqueous solutions, condensation of oxothiometalates takes place, involving intramolecular redox processes [$2S^{2-} \rightarrow (S_2)^{2-}$ and Tc(VII) $\rightarrow$ Tc(IV)], with the

condensation reaction influenced by the ratio of sulfur to metal, reaction time and temperature (Muller et al., 1981). The product of this polymerization reaction is colloidal Tc_2S_7.

Because of this polymerization pathway, it can be anticipated that oxidative dissolution of Tc_2S_7 to form TcO_4^- could be the reverse of the mechanism shown in Figure 6. Liu et al (2007) investigated the effect of O_2 on the stability of Tc_2S_7 in aqueous solution and demonstrated dissolution to form TcO_4^-, possibly due to hydrolysis (Equation 6) or sulfide oxidation (Equation 7), although no direct evidence for the mechanism of oxidation was presented.

$$Tc_2S_7 + 8H_2O \rightarrow 2H^+ + 2TcO_4^- + 7H_2S \tag{6}$$

$$Tc_2S_7 + 16OH^- + 14O_2 \rightarrow 2TcO4^- + 7SO_4^{2-} + 8H_2O \tag{7}$$

In environments with lower water activity, for example when in Tc_2S_7 is present in a grout waste form (see Section 5), there is evidence from Tc K-edge XANES to suggest that $Tc(IV)_2S_7$ is stable with respect to $Tc(IV)O_2$ under leaching conditions and the mechanism of Tc dissolution is via oxidation of the $Tc(IV)O_2$ to $Tc(VII)O_4^-$, with the amount of $Tc(IV)_2S_7$ present remaining constant (Asmussen et al.2018). This additional oxidation step from $Tc(IV)_2S_7$ to $Tc(IV)O_2$ can also be inferred from the evolution of the fraction of Tc present as TcO_4^- as a function of O_2 diffusion into grout waste forms in a study by Lukens et al., (2005).

Although the discussion of Tc sulfide re-oxidation above has focused on Tc_2S_7, TcS_2 is the more thermodynamically stable sulfide compound for Tc (Rard et al., 1999). Ferrier et al (2013) examined these two binary Tc sulfides using Tc and S K-edge XAS and found that they have different sulfur contents, and Tc_2S_7 contains a mixture of S(-I)/S(-II), whereas TcS_2 contains only S(-II). Thus, the oxidation pathways for these Tc sulfide structures will be different. Although neither Tc_2S_7 nor TcS_2 are stable in the presence of O_2, both have the potential to offer additional energy barriers to re-oxidation in comparison to $Tc(IV)O_2$. Work by Weber et al. (1995) on Mo sulfides, which have a very similar structure to Tc sulfides, suggests that formation of TcS_2 would provide yet another additional energy barrier to re-oxidation. In the oxidation reaction, $Tc(IV)S_2$ is converted to $Tc(IV)_2S_7$ as an intermediate, which would require subsequent oxidation to $Tc(IV)O_2$, and then to $Tc(VII)O_4^-$, prior to release of Tc(VII) into solution as follows:

$$Tc(IV)S_2(s) \rightarrow Tc(IV)_2S_7(s) \rightarrow Tc(IV)O_2(s) \rightarrow 2Tc(VII)O_4^-(aq.)$$
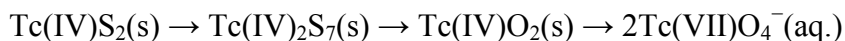
Thus, tuning the HS^- concentration and redox potential to form $Tc(IV)S_2$ represents an appealing option in terms of stabilizing Tc in the solid phase.

The presence of Fe in the system further complicates understanding of Tc re-oxidation potential, due to the mixture of products formed; $Tc(IV)O_2$ is the product of TcO_4^- reduction by Fe(II)-bearing oxides, whereas Fe sulfides, such as FeS and FeS_2, offer a direct path to the formation of TcS_2 rather than Tc_2S_7 (Fan et al., 2014; Wharton et al. 2000; Livens et al. 2004). In

the surface oxidation of Fe sulfides such as pyrite (FeS_2) in air, the most reactive surface sulfide component is S^{2-} (present as a surface defect), followed by the surface atom of the first disulfide layer (S_2^{2-}), with sulfur atoms of disulfide groups beneath the surface layer (bulk coordinated sulfurs) being least reactive (Rosso and Vaughan, 2006).
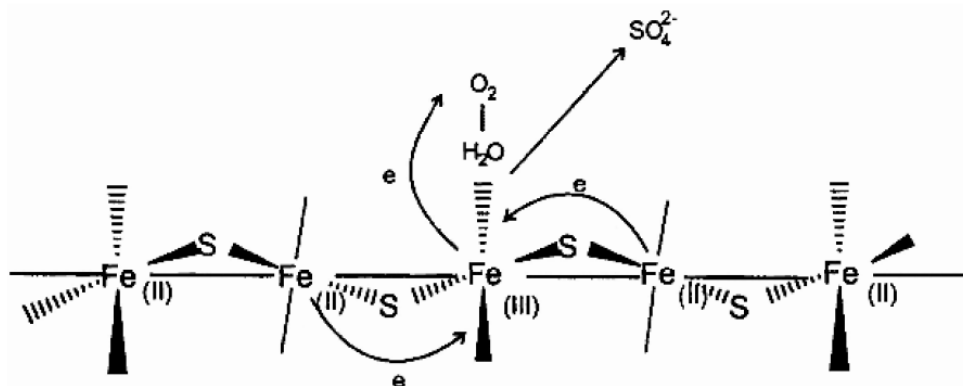
Figure 7: Proposed reaction mechanism of pyrite oxidation in air. Molecular oxygen mounts an electrophilic attack on Fe(II), reducing charge density on adjacent sulfur that undergoes nucleophilic attack by adsorbed water, producing sulfate bearing oxygen dominantly from water (Rosso and Vaughan, 2006)

The reaction mechanism first involves the formation of Fe^{3+} states (Eggleston et al. 1996; Rosso et al. 1999a; 1999b). This occurs naturally after partial breaking of the S-S bonds to form defect S^-, which oxidizes Fe^{2+} and then rapidly reacts to form sulfate, or by direct oxidation of Fe^{2+} by dissociative chemisorption of O_2 which concomitantly oxidized adjacent S_2^{2-} that then also reacts with water to form sulfate. Product sulfate is displaced from its site bonded to Fe^{3+} by competitive adsorption of, for example, O_2. As shown in Figure 7, O_2 can adsorb as an outer sphere complex. The transfer of an electron from an adjacent Fe^{2+} to the Fe^{3+} formed by defect S^-, followed by electron transfer to O_2 producing unstable O_2^- and the formation of a second Fe^{3+}-O bond, initiates the formation of an Fe_2O_3 overlayer. Likewise, competitive adsorption of O_2 can displace water bound to Fe^{2+} allowing its direct oxidation, form unstable O_2^- and incipient Fe^{3+}-oxides. Conduction band electrons in the nascent Fe_2O_3 patches are a stronger O_2 reductant than Fe^{2+} in FeS_2, thus electron migration from pyrite through surface Fe_2O_3 to O_2 in combination with facile Fe^{2+}/Fe^{3+} cycling results in the build-up of Fe^{3+} oxide coatings across the FeS_2 surface.

Formation of these surface Fe^{3+}-oxides may play a role in the stabilization of Tc in its reduced form. Livens et al. (2004) demonstrated that, upon oxidation of FeS/TcS_2, Tc remained as Tc(IV), while the coordination environment changed to that of TcO_2-like environment. Similar to the pyrite case, oxidation of FeS forms poorly crystalline goethite, with a structure is based on octahedral $Fe(O,OH)_6$ units, and Tc is in octahedral coordination in TcO_2, it is possible that Tc(IV) is stabilized by incorporation in the goethite lattice.

5. Technetium sulfide in radioactive waste forms and use of sulfides for remediation

5.1 Technetium sulfide in waste forms

Much can be learned from studying the synthetic chemistry of Tc sulfides and their biogeochemical reactions; however, applying this information to the management of Tc-containing nuclear waste streams remains a challenge due to the extreme nature and complexity of the environments. Many factors can negatively influence the ability of targeted materials to sequester Tc from nuclear waste streams, including high ionic strength, extreme pH range, radiation fields and presence of competing redox active components (e.g. chromate, $Cr(VI)_2O_7^{2-}$, and nitrate/nitrite, NO_3^-/NO_2^-). Examples of this include the decrease in Tc removal capability observed for many compounds such as Sn(II)-treated apatite, zerovalent Fe and others in simulated low activity waste (LAW) or low level waste (LLW) (Darab et al. 2007; Qafoku et al. 2014; Asmussen et al. 2016). Despite this, Fe-sulfides have been suggested as possible treatments for Tc containing nuclear wastes (Watson and Ellwood 2003) and recent work has shown that sulfide based materials are adept at sequestering Tc from LAW.

Research is underway to design Tc-sequestering materials that function in a broad range of chemical environments relevant to aqueous nuclear waste. A potassium metal sulfide (KMS-2), initially developed to remove hazardous cationic species such as U, Cs, Ag from aqueous environments through ion exchange, was observed to remove $Tc(VII)O_4^-$ from a high ionic strength, high pH Hanford LAW simulants with high efficiency (Neeway et al. 2016; Manos and Kanatzidis 2012; Mertz et al. 2013; Hassanzadeh et al. 2015). KMS-2 is comprised of sheets of edge-sharing $[(M_2^{2+})S_6]^{2-}$ octahedra (M = Sn, Mg) with intercalated K^+ ions and its ability to remove Tc(VII) arises from its high reductive capacity (~ 20,000 micro-equivalents of electrons/g of material) resulting from the sulfide linkages. As stated previously, S is increasingly redox active with increasing pH, which is ideal for the highly alkaline LAW environment. With the high reductive capacity of the material, the reduction of $Tc(VII)O_4^-$ can readily occur, even in the presence of an excess of Cr(VI), as the KMS-2 can reduce both species with minimal material addition. Characterization of the KMS-2 following Tc removal from LAW showed a loss of crystallinity of the KMS-2 and formation of a $Tc(IV)_2S_7$ final product, confirming the role of S in the Tc reduction. To date, KMS-2 represents the most efficient material for Tc removal from LAW (Neeway et al., 2016).

Following removal of Tc from the aqueous phase of a waste stream by a targeted material, the Tc-bearing material will need to be placed into a final waste form, either with or without the parent waste stream. Cementitious waste forms (CWFs) present a viable method to immobilize liquid nuclear waste present at many global nuclear waste storage sites. The most widely used category of reducing CWF, slag saltstone (45 wt% BFS, 45 wt% fly ash and 10 wt % OPC) was developed by Langton et al. (1988) at the Savannah River site, South Carolina, by substituting a high content of hydraulic blast furnace slag (BFS) for Portland cement, in combination with fly ash as a functional extender to control heat of hydration and reduce permeability. Substitution of the BFS significantly reduces release of TcO_4^- and $Cr(VI)_2O_7^{2-}$ from the monolithic CWF through maintenance of reducing conditions. It was initially thought that this chemical

stabilization was brought about by the reduction of Tc(VII) and Cr(VI) by Fe(II) and Mn(II) in the slag, with subsequent precipitation of insoluble Cr(III)(OH)$_3$ and Tc(IV)O$_2$. However, a study of the chemistry of Tc in CWFs by XANES/EXAFS revealed that the sulfide component of the slag produced the most extensive reduction of TcO$_4^-$ while FeO, Fe$_3$O$_4$ and Mn$_3$O$_4$ were relatively unreactive (Allen et al, 1997). The reduced, insoluble Tc clusters present in the slag-containing CWF possessed a first shell S coordination. Thus, reducing conditions develop in the CWF as a result of the sulfur component of the BFS, primarily present as oldhamite Ca,MgS (Um et al. 2015).

A similar CWF under development for use at the Hanford Site, is Cast Stone, which is comprised of 47 wt% BFS, 45 wt% fly ash and 8 wt% of ordinary Portland cement. Cast Stone has been investigated as a possible candidate technology for the solidification of Tc-containing LAW. The leachability of Tc from Cast Stone is variable based on waste loading and mixing conditions; however, Cast Stone still shows promise as a possible candidate waste form (Westsik et al. 2013). One method of further improving Tc retention in Cast Stone, or other CWFs, would be through the incorporation of targeted materials, capable of reducing Tc to increase stability within the CWF. KMS-2 is an ideal candidate to serve as a Tc-getter, as discussed above. Tc-loaded KMS-2 from LAW simulant was subsequently solidified into Cast Stone. Leach testing using simulated Hanford vadose zone pore water (similar to the expected CWF disposal conditions) demonstrated over an order of magnitude improvement in Tc effective diffusivity for the KMS-2 containing Cast Stone compared with a KMS-2-free control (Asmussen et al. 2018). This improvement was achieved with KMS-2 addition of < 0.1 wt% of the overall mass of the waste form. It was found that the presence of KMS-2 in Cast Stone led to the development of distinct Tc "hot spots" within the Cast Stone samples, compared with a homogenous distribution of Tc in Cast Stone without KMS-2. The sequestered Tc remained associated with KMS-2 after fabrication of the CWF and, in turn, resulted in increased Tc stability. The Tc-retention mechanism is like that described by Lukens et al. (2005) for the limited re-oxidation of Tc in CWF's containing BFS. Experiments were conducted to investigate oxidation of TcO$_4^-$ in reducing CWFs containing waste simulant with and without NO$_3^-$. TcO$_4^-$ was completely reduced by Na$_2$S to form "Tc(IV)$_2$S$_7$", with the structure given in Figure 4, as determined by EXAFS. NO$_3^-$ had no significant effect on the rate of Tc oxidation and it was demonstrated that Tc stability in the CWF was improved by the reducing conditions provided by the BFS. Exposure of the samples to atmospheric O$_2$ resulted in oxidation of the lower-valent Tc sulfide species to TcO$_4^-$ (Lukens et al., 2005). In the KMS-2 containing Cast Stone system, the Tc(VII)O$_4^-$ is nearly completely converted to a stable Tc-sulfide prior to being solidified in the CWF. The re-oxidation, and subsequent mobility, of the Tc would be slowed by the initial Tc-S state and the presence of the BFS.

An analogous study using saltstone, showed that Tc release under anoxic conditions was controlled by the solubility of TcO$_2$.xH$_2$O. Although Tc is present predominantly as 'Tc(IV)$_2$S$_7$' in the KMS-2 containing Cast Stone, initial release of Tc will be controlled by the TcO$_2$.xH$_2$O

component because of its higher solubility (Cantrell and Williams, 2013). As mentioned previously, the solubility of $TcO_2.xH_2O$ is enhanced under alkaline conditions (pH >10.5), and is in the range of 10^{-9}-10^{-8} $mol \cdot dm^{-3}$ due to the formation of aqueous $TcO(OH)_3^-$ Thus, in radioactive waste disposal scenarios involving CWF, where the initially high pH values (12.5-13) decrease due to uptake of carbon dioxide (which produces carbonic acid), the solubility of $TcO_2 \cdot xH_2O$ should decrease, providing the carbonate concentration remains relatively low (Cantrell and Williams, 2013).

As well as the wasteform itself, immobilized Tc-bearing radioactive waste will have an outer container (typically steel), along with additional engineered barrier(s) to protect the container and limit radionuclide release. As the container materials ultimately corrode, it is possible that Fe phases formed during the corrosion process will inhibit Tc migration through redox and sorption reactions. Kunze et al. (1996) showed that the concentration of Tc in solution decreased in the presence of corroding steel, zircalloy and UO_2, and supplementing these systems with sulfide had an additional positive influence on the immobilization of Tc. While the presence of sulfide (from sulfate reducing bacteria) is a concern for the corrosion integrity of nuclear waste containers (Rao et al. 2000; Smith et al. 2007), its presence may also act to slow the transport of redox sensitive radionuclides. Further investigations into these Tc-sulfide-waste package interactions are required to assess the risk of corrosion versus the benefit of reductive immobilization.

5.2 Sulfides for remediation

The potential for the use of Fe- and sulfide-bearing minerals to remove TcO_4^- from solution led to new strategies for removing ^{99}Tc from raffinate waste generated during decontamination and uranium recovery operations. Raffinates are challenging because they typically possess high nitric acid concentrations, contain a variety of heavy metals, but contain low concentrations of [233]U and [99]Tc. The strategy entails dilution of the raffinate waste and pH adjustment to ~8.5 to precipitate hydrolyzable heavy metals, followed by filtration of the precipitated slurry to yield a heavy metal sludge, with the TcO_4^- remaining in the filtrate. Ferrous sulfides remove soluble ^{99}Tc, predominantly by reduction to insoluble $Tc(IV)_2S_7$, and ^{99}Tc removal efficiency correlated with solution redox potential (E_h). Greigite (Fe_3S_4) was the most effective (K_D: ~110 –6100 ml/g), and its use for ^{99}Tc removal was advantageous in terms of cost, compared with organic ion-exchange resins. In addition, its magnetic moment allows for efficient concentration and removal. However, it could only remove ^{99}Tc from the slightly alkaline heavy metal sludge filtrate and not from the raw acidic raffinate. In addition, the kinetics of the reaction were relatively slow, with the development of higher surface area materials required for use in continuous operations for large volumes of water contaminated with low concentrations of [99]Tc (del Cul et al. 1993).

Liu et al. (2007) proposed the injection of H_2S into the subsurface for remediation of TcO_4^- contaminated groundwater. They argued that $Tc(IV)_2S_7$ would form, but most of the H_2S would

be consumed by iron in the formation to produce iron sulfides. Liu et al. (2008) subsequently studied the anaerobic reaction between $FeS_{0.97}$ (0.15 mg/ml, point of zero charge = pH 7.4) and TcO_4^- (10^{-4} M) at pH 6.7-9 and a range of pH and ionic strengths (0.1-1 M NaOH), including the nature of the products generated and their stability under aerobic and anaerobic conditions. Reductive immobilization of TcO_4^- with FeS was accelerated by increasing ionic strength and at pH values below the point of zero charge. XANES and EXAFS analysis showed that $Tc(IV)O_2$ was generated as a layer on the FeS surface during the reductive immobilization reaction, with concurrent oxidation of FeS according to Equation (8).

$$10TcO_4^- + 6FeS + 11H_2O \leftrightarrow 10TcO_2 + 6Fe^{3+} + 3S_2O_3^{2-} + 22OH^- \qquad (8)$$
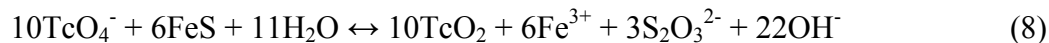
The reductive capacity of the FeS for TcO_4^- was calculated to be 867 mg TcO_4^-/g FeS. The TcO_2 product was slowly oxidized in air, but the resulting TcO_4^- in solution was subsequently sorbed onto the oxidized Fe oxyhydroxide surface of FeS (Liu et al., 2008). These results contrast with the reaction between TcO_4^- and H_2S which produced $Tc(IV)_2S_7$. The contrast is curious given that Rickard and Luther (1997) showed that FeS reduces H_2S (which is more oxidizing relative to FeS) and thus seems more likely to produce a Tc(IV)-sulfide rather than Tc(VI)-oxide relative to H_2S.

To examine the influence of environmental conditions on the reductive immobilization reaction between TcO_4^- and H_2S, the effect of competing inorganic anions (nitrate), chelating agents (ethylenediaminetetraacetic acid, EDTA), low molecular weight organic acids, and surface effects of non-reducing minerals (goethite) were subsequently investigated (Liu et al., 2009). The presence of nitrate, EDTA and goethite did not affect the immobilization reaction, and the product was identified as $Tc(IV)_2S_7$ in all cases by XANES and EXAFS. Only maleic acid and fumaric acid inhibited the immobilization process by forming anionic water-soluble complexes with TcO_4^- (Liu et al., 2009).

Szecsody et al. (2014) found that alkaline and acidic waste streams had an impact on Hanford sediments and that the waste composition significantly altered contaminant speciation and mineralogy. Alkaline pore water can cause mineral dissolution, releasing Fe^{2+} into solution and creating reducing conditions at the pore water–mineral interface that result in the reduction and precipitation of TcO_2 or Tc_2S_x. As the pH becomes neutral, subsequent aluminosilicate or phosphate precipitation can coat the Tc precipitate and prevent re-oxidation (Szecsody et al., 2014; Jansik, 2013). Szecsody et al. (2015) also explored the efficacy of using H_2S gas as a mechanism to remediate vadose zone sediments contaminated with technetium. To enhance the effect and decrease TcO_4^- mobility in the subsurface, H_2S was combined with NH_3 (Szecsody et al., 2015). The H_2S gas created reducing conditions at mineral surfaces, specifically clays, FeS_2 and Ti-magnetite ($Fe_{3-x}Ti_xO_4$) which temporarily reduced the TcO_4^- to precipitate TcS_x, while the NH_3 gas created alkaline conditions causing aluminosilicate mineral dissolution. As the pH neutralized, subsequent aluminosilicate precipitation coated TcS_x precipitates and rendered them less mobile. These systems highlight the important influence of Fe (and other) minerals on the

nature of the Tc-bearing phase that is produced by reactions in the presence of sulfide. Much future work is needed to unravel mechanistic pathways in these complex ternary Tc/Fe/S redox systems.

Recognizing that the facile re-oxidation of $Tc(IV)O_2.nH_2O$ to TcO_4^- is a major limitation in any plan to sequester Tc contamination in its reduced form, Fan et al. (2013) explored the strategy of deliberately engineering conditions that favor formation of the more stable Tc sulfides. They proposed generating sulfidic conditions by adding nano zerovalent iron (nZVI), which serves multiple purposes: (i) abiotically scavenging alterative electron acceptors; and (ii) generating H_2 through Fe^0 corrosion to act as an electron donor for microbial sulfate reduction, which (iii) may produce Tc sulfides directly or Fe sulfides such as mackinawite, that can then react with TcO_4^-. In laboratory batch experiments, the highest rate of TcO_4^- (10^{-6} M) reduction was obtained with S/Fe ratios in the range 0.056-0.224, and this high Tc removal rate was explained by the formation of reactive FeS (with electron microscopy confirming that the Tc was associated with FeS phases). Higher values of S/Fe resulted in an increase in aqueous bisulfide (HS^-) concentrations and inhibited the removal of TcO_4^- from solution, possibly due to the competition of sulfide for adsorption sites on FeS or the formation of colloidal Tc_2S_7 (process (III) in Figure 8). Although sulfidation of nZVI produced heterogeneous mineral surfaces, XAS revealed that the pathway for TcO_4^- sequestration shifted from $Tc(IV)O_2.nH_2O$ to Tc(IV) sulfide phases as S/Fe increased (pathway II in Figure 8).
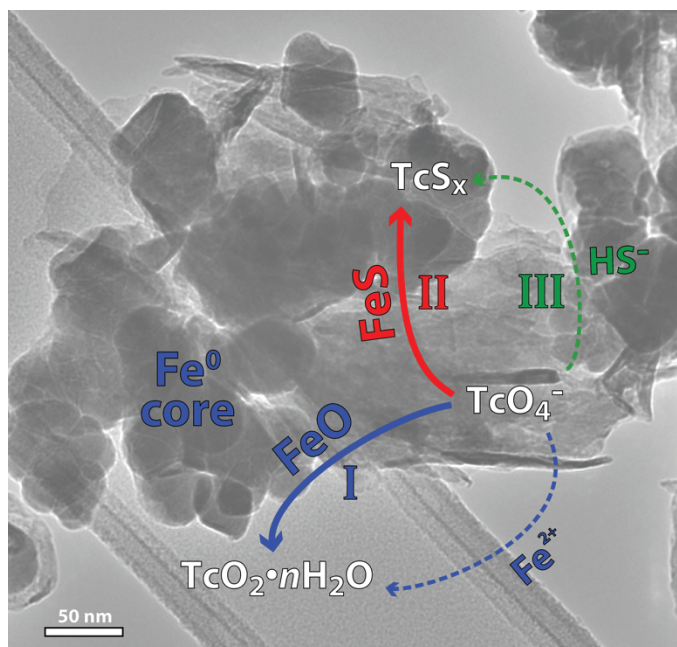
Figure 8: Conceptual model of Tc sequestration pathways under sulfidogenic conditions stimulated by nZVI. Processes (I), (II) and (III) represent pre-, initial and end stages of sulfate reduction respectively (solid arrows: mineral phase reactions, dashed arrows: solution reactions) (Fan et al., 2013, produced with permission from ACS)

However, the formation of Tc sulfides along natural redox gradients is limited due to prior Tc reduction to $TcO_2 \cdot xH_2O$ under iron reducing conditions (pathway I, Figure 8), which is why there is little evidence for Tc sulfides in naturally developed sulfate reducing sediments as demonstrated by Burke et al. (2005, 2006). To clarify the thermodynamic feasibility of the hypothetical Tc sequestration pathways presented in Figure 8, Fan et al (2013) constructed an Fe/S/Tc speciation diagram in Hanford synthetic groundwater based on thermodynamic data in Rard (1999) (Figure 9). $TcO_2 \cdot nH_2O$ was the predominant reduced Tc phase when $[HS^-]$ was low (< 0.1 nM) but above this concentration, Tc sulfides became the dominant reduced Tc phases. The sulfide concentrations investigated in the study (4 mM) represented the stability region of FeS, and both TcS_2 and Tc_2S_7 were the dominant Tc phases.
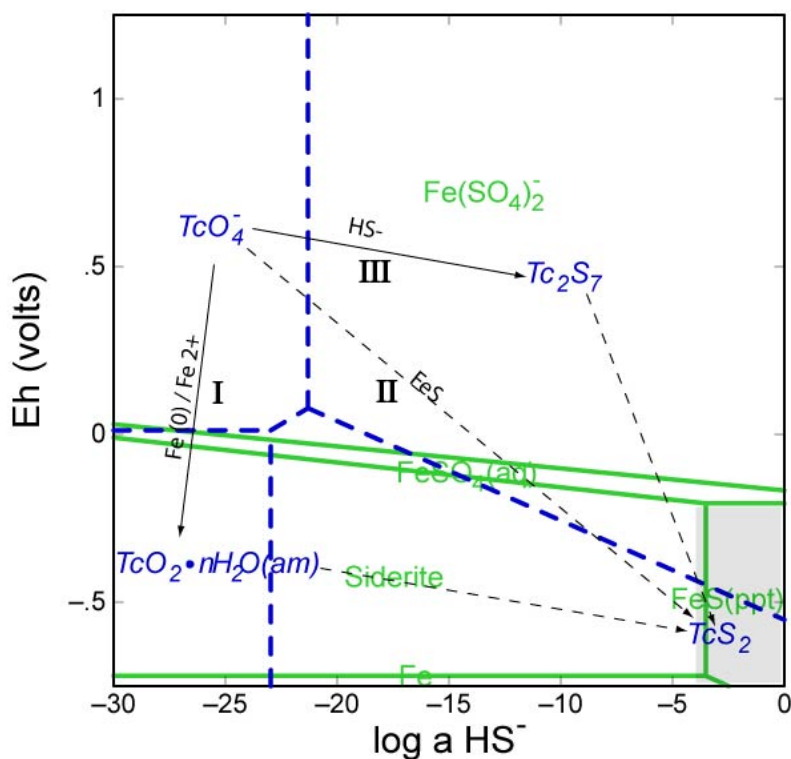
Figure 9: Fe/S/Tc speciation diagram showing Eh vs. log activity (HS^-) in Hanford synthetic groundwater ($[TcO_4^-]$ 10^{-5} M, pH 7.9, 25 °C) (Fan et al., 2013, SI, produced with permission from ACS)

Fan et al. (2014) and Szecsody et al. (2014) investigated the potential for oxidative remobilization of technetium. During TcO_4^- reduction by anaerobic vadose zone sediments, addition of sulfide did not increase the Tc(VII) reduction rate from that observed for the natural anaerobic sediment (0.01-0.03 nmol g^{-1} h^{-1}) (Szecsody et al., 2014). However, subsequent Tc oxidation was slower in the sediment systems with sulfide addition, and significant Tc remained associated with the sediment, especially at pH 12, possibly due to Tc-S surface phases oxidizing

more slowly than $Tc(IV)O_2$ precipitates produced in sediment systems containing $Fe(II)$ (Szecsody et al., 2014).

The use of sulfidated iron-based materials for water treatment and remediation was recently reviewed (Fan et al., 2017) and it was concluded that sulfidation had a positive effect on sequestration of TcO_4^-. Reduction of TcO_4^- by FeS was favored over reduction by nZVI, and the resultant TcS_2 product was less susceptible to oxidation that TcO_2.

6. Formation, stability and decomposition of technetium sulfide particles

The formation of Tc sulfide particles, and especially nanoparticles, plays an important role in the migration of Tc in the environment and understanding the conditions under which Tc_2S_7 nanoparticles nucleate and grow is essential to predict Tc migration. To test the potential for Tc to be immobilized as Tc sulfide nanoparticles in the near field conditions of a nuclear waste repository, Kunze et al. (1996) added small amounts of Na_2S to NH_4TcO_4 (10^{-5} mol/L) in water. The precipitation of Tc sulfide was not observed in water due to the alkaline conditions present because of the basic properties of S^{2-}. When the pH was adjusted to ≤ 3 using HCl black Tc sulfide did precipitate, but an appreciable concentration of Tc remained in suspension, as evidenced by a brownish colored solution. The Tc_2S_7 in suspension as nanoparticles could not be separated by filtration, which presented problems for determining the solubility equilibrium (Kunze, 1996). The nucleation and growth of these Tc_2S_7 nanoparticles, produced in a mixture of Na_2S and TcO_4^- aqueous solutions, was investigated using laser-induced photoacoustic spectroscopy (Saiki et al., 2003). The maximum particle size (10 nm) of the Tc_2S_7 nanoparticles was larger in 0.05 M Na_2S, than the particle size (7 nm) in 0.1 M Na_2S, but the number of particles in solution was smaller in the lower concentration solution. Thus, the number of Tc_2S_7 seeds that were formed initially depended on Na_2S concentration. Then, the particle size increased, but the number of nanoparticles remained constant with time, suggesting that the size increased by surface deposition of Tc_2S_7 not by nanoparticle aggregation. Tc_2S_7 nanoparticles can be formed from TcO_4^- by the reaction between sodium thiosulfate ($Na_2S_2O_3.5H_2O$) and 1 M HCl (Steigman et al., 1986). A high percentage of Tc was found in the smallest particles (<100 nm) suggesting that the Tc sulfide nuclei formed first, before the sulfur particles that were generated homogeneously from thiosulfate in hot acid solution. The excess S in solution deposited on the surface of these particles but reheating at weakly alkaline pH dissolved the deposited S by reaction with sulfite to form thiosulfate, leaving the Tc_2S_7 nanoparticles. Understanding the conditions under which Tc sulfide particles form, how this influences their structure and the effect this has on their stability is imperative knowledge for predicting their environmental behavior and expansive use in nuclear waste management

Calculation of the solubility product for both Tc_2S_7 and TcS_2 is challenging due to the hydrolysis of the sulfide ion produced by the dissolution of Tc_2S_7, in combination with the formation of nanoparticles. To address this, El-Wear et al. (1992) synthesized Tc_2S_7 according to Equation (9) to carefully calculate the exact solubility.

$$8H_2O + 7Na_2S + 2NaTcO_4 \leftrightarrow Tc_2S_7 \text{(s)} + 16NaOH \tag{9}$$
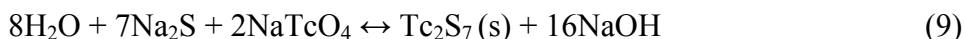
The precipitate formed was removed by centrifugation and re-suspended in distilled water for the solubility experiment. The color of the solution changed to violet within 5 hours, due to the formation of an 'intermediate Tc sulfide' species, then over a period of 3 days, the solution became colorless and the pH dropped from 7 to 2.35. The solution was centrifuged and the solubility of Tc_2S_7 in water was measured to be 6.1×10^{-4} mol/L, with dissolution proposed to occur according to Equation (10):

$$Tc_2S_7\text{(s)} + 8H_2O \leftrightarrow 2H^+ + 2TcO_4^- + 7H_2S \tag{10}$$
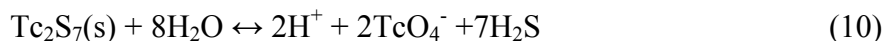
However, issues associated with partitioning of H_2S into the vapor phase and/or oxidation to sulfide/hydrosulfide anions, in addition to the possible presence of Tc in a chemical form other than TcO_4^-, preclude the extraction of thermodynamic data from this measurement (Rard et al. 1999; El-Wear et al., 1992).

Tc sulfide formation kinetics and solubility were studied by German et al. (2015) in the presence of Na_2S in phosphate buffer. The pH of the solution was maintained at 8-12 as lower pH values resulted in sulfide hydrolysis. The reduction of TcO_4^- with sulfide produced Tc(IV) sulfide and 3 elemental sulfur atoms, which reacted to form a disulfide S^- ligand as in Equation (11)

$$TcO_4^- + 5H_2S \rightarrow TcS_2 + 3S^0 \rightarrow Tc(S_2)_2^- \tag{11}$$

The product of this reaction then trimerises to form the X-ray amorphous trinuclear Tc(IV) polydisulfide $Tc_3(\mu^3\text{-}S)(S_2)_3S_6$ (Figure 10), which has a Tc:S ratio of 2:6.7. The stability of Tc_3S_{13} in solution, and thus the solubility, was found to be dependent on the Na_2S concentration, with Tc sulfide solubility found to be described by $C(Tc_3S_{13}) = -9 \times 10^{-5} \ln [Na_2S] - 2 \times 10^{-5}$ M. For $[Na_2S] > 0.05$ M, further growth of Tc polymeric sulfide particles occurred to form ($[Tc_3(\mu^3\text{-}S)(\mu^2S_2)_3(S_2)_{3/3}]$n), as shown in Figure 10. For $[Na_2S] \leq 0.04$ M, When exposed to O_2, Tc_3S_{13} is readily oxidized resulting in the re-solubilization of Tc as $Tc(VII)O_4^-$ (German et al., 2015). As this demonstrates, a significant amount of experimental work is still required to develop a thermodynamically sound understanding of Tc sulfide chemistry (Rard, et al., 1999).
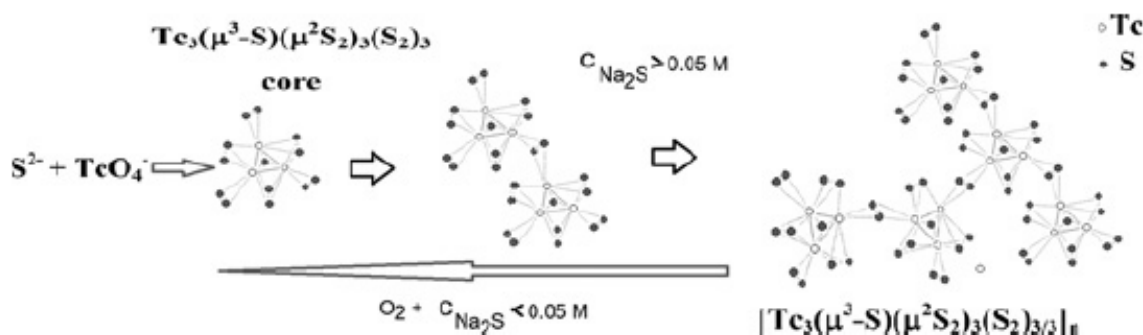
Figure 10. Reaction scheme for Tc(VII) with sulfide according to Lukens et al. (2005) and German et al. (2015).

7. Recommendations for Future Studies

Experiments and modeling have demonstrated that both abiotic and biologic mechanisms will exert strong controls on Tc mobility and that Tc binding or uptake into sulfide phases can occur. Extended periods of oxidation result in transformation of Tc speciation from Tc(IV) sulfides to Tc(IV) oxides, though no solubilization of Tc occurs suggesting that oxidation during transformation is not accompanied by Tc(IV) oxidation to Tc(VII). Thus, the change in speciation from Tc(IV) sulfides to Tc(IV) oxides provides an extra energy barrier to overcome prior to Tc re-oxidation to Tc(VII)O_4^-. In the environment, TcO_4^- removal by sulfide minerals also depends on particle size and contacting solution pH, ionic strength and E_h, with the principal mechanism of TcO_4^- attenuation being the reduction to low solubility sulfide phases. Formation pathways of Tc_2S_7 versus TcS_2 appear to be distinct, requiring more focused study to unravel these pathways in molecular detail. Predicting the long term environmental stability of sequestered Tc as a function of various chemical, physical and microbiological factors would also benefit from further mechanistic investigation that can establish the rate of oxidation and concomitant release of Tc(VII) from these Tc-sulfide phases. In addition, experiments are required to determine the rate of oxidation of Tc(IV) oxides versus Tc(IV) sulfides under a variety of conditions relevant to Tc retention in repositories for radioactive waste and for Tc mobility in the environment. These experiments must be combined with quantum mechanical modeling to understand and predict the atomic and electronic structure of Tc sulfide interfaces under environmental conditions, including examining the role of coupled iron and sulfide-induced redox processes.

References

Aarkrog, A., Chen, Q., Dahlgaard, H., Nielsen, S. P., Trapeznikov, A. and Pozolotina, V. (1997) "Evidence of 99Tc in Ural River sediments." Journal of Environmental Radioactivity **37**(2): 201-213.

Allen, P. G., Siemering, G. S., Shuh, D. K., Bucher, J. J., Edelstein, N. M., Langton, C. A., Clark, S. B., Reich, T. and Denecke, M. A. (1997) "Technetium speciation in cement waste forms determined by X-ray Absorption Fine Structure Spectroscopy." Radiochimica Acta 76(1-2): 77-86.

Anderson, B. E., Becker, U., Helean, K. B. and Ewing, R. C. (2007) "Perrhenate and pertechnetate behavior on iron and sulfur-bearing compounds." In: Scientific Basis for Nuclear Waste Management XXX (Dunn, D., Poinssot, C., and Begg, B., eds.)

Abdelouas, A. Fattahi, M., Grambow, B., Vichot, L. and Gautier, E. (2002) "Precipitation of technetium by subsurface sulfate-reducing bacteria." Radiochimica Acta **90**(9-11): 773-777.

Abdelouas A., Grambow, B., Fattahi, M., Andres, Y. and Leclerc-Cessac, E. (2005) "Microbial reduction of ^{99}Tc in organic matter-rich soils." Science of the Total Environment **336**: 255-268.

Asmussen, R. M., Pearce, C.I., Miller, B. W., Lawter, A. J., Neeway, J. J., Lukens, W. W., Bowden, M. E., Miller, M. A., Buck, E. C., Serne, R., J. and Qafoku, N. P. (2018). "Getters for improved technetium containment in cementitous waste forms" Journal of Hazardous Materials **341**: 238-247.

Asmussen, R. M., J. J. Neeway, A. R. Lawter, T. G. Levitskaia, W. W. Lukens and N. Qafoku (2016). "The Function of Sn(II)-Apatite as a Tc Immobilzing Agent." Journal Of Nuclear Materials **480**: 393-402.

Blum, A. (1967) "Technetium-99M sulfide colloid preparation." Journal of Nuclear Medicine **8**(9): 692-693.

Boak, J. L. and Agwunobi, T. C. (1978) "Study of technetium-labeled sulfide colloid uptake by regional lymph-nodes draining a tumor-bearing area." British Journal of Surgery **65**(6): 374-378.

Bock, W. -D., Brühl, H.,Trapp, C., and Winkler, A. (1989) "Sorption properties of natural sulfides with respect to technetium" Materials Research Society Symposium Proceedings (eds W. Lutze and R. C. Ewing), 127: 973-977. Materials Research Society.

Boyd, G.E. (1959) "Technetium and Promethium" Journal of Chemical Education 36: 3-14

Boyd, G. E., Larson, Q. V. and Motta, E. E. (1960) "Isolation of milligram quantities of long-lived technetium from neutron irradiated molybdenum." Journal of the American Chemical Society 82: 809-815.

Boyd, G. E. (1978) "Osmotic and activity coefficients of aqueous $NaTcO_4$ and $NaReO_4$ solutions at 25°C." Journal of Solution Chemistry **7**: 229-238.

Bruggeman, C., Maes, A. and Vancluysen, J. (2007) "The identification of FeS_2 as a sorption sink for Tc(IV)." Physics and Chemistry of the Earth **32**: 573-580.

Burke, I. T., Boothman, C., Lloyd, J. R., Livens, F. R., Mortimer, R. J. G. and Morris, K. (2005) "Effects of progressive anoxia on the solubility of technetium in sediment." Environmental Science and Technology **39**: 4109-4116.

Burke, I. T., Boothman, C., Lloyd, J. R., Livens, F. R., Charnock, J. M., McBeth, J. M., Mortimer, R. J. G. and Morris, K. (2006) "Reoxidation behavior of technetium, iron, and sulfur in estuarine sediments." Environmental Science and Technology **40**(11): 3529-3535.

Cantrell, K. J. and Williams, B. D. (2013) "Solubility control of technetium release from Saltstone by $TcO_2 \cdot xH_2O$." Journal of Nuclear Materials 437(1-3): 424-431.

Cui, D. and T. E. Eriksen (1996). "Reduction of pertechnetate by ferrous iron in solution: Influence of sorbed and precipitated Fe (II)." Environmental science & technology **30**(7): 2259-2262.

Cramer, S. P., Liang, K. S., Jacobson, A. J., Chang, C. H. and Chianelli, R. R. (1984) "EXAFS studies of amorphous molybdenum and tungsten trisulfides and triselenides." Inorganic Chemistry 23, 1215-1221.

Darab, J. G., A. B. Amonette, D. S. D. Burke, R. D. Orr, S. M. Ponder, B. Schrick, T. E. Mallouk, W. W. Lukens, D. L. Caulder and D. K. Shuh (2007). "Removal of Pertechnetate from Simulated Nuclear Waste Streams Using Supported Zerovalent Iron." Chemistry of Materials **19**(23): 5703-5713.

Del Cul, G. D., Bostick, W. D., Trotter, D. R. and Osborne, P. E. (1993) "Tc-99 removal from process solutions and contaminated groundwater." Separation Science and Technology 28(1-3): 551-564.

Drake, H. L., K. Küsel and C. Matthies (2006). Acetogenic Prokaryotes. The Prokaryotes: Volume 2: Ecophysiology and Biochemistry. M. Dworkin, S. Falkow, E. Rosenberg, K.-H. Schleifer and E. Stackebrandt. New York, NY, Springer New York**:** 354-420.

Eggleston, C. M., Ehrhardt, J. J. and Stumm, W. (1996) "Surface structural controls on pyrite oxidation kinetics: An XPS-UPS, STM, and modeling study." American Mineralogist 81(9-10): 1036-1056.

El-Wear, S., German, K. E. and Peretrukhin, V. F. (1992) "Sorption of technetium on inorganic sorbents and natural minerals." Journal of Radioanalytical and Nuclear Chemistry **157**(1): 3-14.

Fan, D., Anitori, R. P., Tebo, B. M., Tratnyek, P. G., Pacheco, J. S. L., Kukkadapu, R. K., Engelhard, M. H., Bowden, M. E., Kovarik, L. and Arey, B. W. (2013) "Reductive sequestration of pertechnetate ($^{99}TcO_4^-$) by Nano Valent Iron (nZVI) transformed by abiotic sulfide." Environmenal Science and Technology **47**: 5302-5310.

Fan, D., Anitori, R. P., Tebo, B. M., Tratnyek, P. G., Pacheco, J. S. L., Kukkadapu, R. K., Kovarik, L., Engelhard, M. H. and Bowden, M. E. (2014) "Oxidative remobilization of technetium sequestered by sulfide-transformed Nano Zerovalent Iron." Environmental Science and Technology **48**(13): 7409-7417.

Fan, D., Lan, Y., Tratnyek, P. G., Johnston, R. L., Filip, J., O'Carroll, D. M., Nunez Garcia, A., Agrawal, A. (2017) "Sulfidation of Iron-Based Materials: A Review of Processes and

Implications for Water Treatment and Remediation." <u>Environmental Science and Technology</u> **51:** 13070−13085.

Ferrier, M., Weck, P. F., Poineau, F., Kim, E., Stebbins, A., Ma, L. Z., Sattelberger, A. P. and Czerwinski, K. R. (2012) "First evidence for the formation of technetium oxosulfide complexes: Synthesis, structure and characterization." <u>Dalton Transactions</u> *41*(20): 6291-6298.

Ferrier, M., Kerlin, W. M., Poineau, F., Sattelberger, A. P. and Czerwinski, K. R. (2013) "Recent developments in the synthetic chemistry of technetium disulfide." <u>Dalton Transactions</u> **42**: 15540-15543.

Ferrier, M., Roques, J., Poineau, F., Sattelberger, A. P., Unger, J. and Czerwinski, K. R. (2014) "Speciation of technetium in sulfuric acid/hydrogen sulfide solutions." <u>European Journal of Inorganic Chemistry</u> **12**: 2046-2052.

Geraedts, K., Bruggeman, C., Maes, A., Van Loon, L. R., Rossberg, A. and Reich, T. (2002) "Evidence for the existence of Tc (IV)-humic substance species by x-ray absorption near-edge spectroscopy." Radiochimica Acta **90**: 879-884.

German, K. E., Firsova, E. V., Peretrukhin, V. F., Khizhnyak, T. V. and Simonoff, M. (2003) "Bioaccumulation of Tc, Pu, and Np on bottom sediments in two types of freshwater lakes of the Moscow Oblast." <u>Radiochemistry</u> **45**(3): 250-256.

German, K. E., Shiryaev, A. A., Safonov, A. V., Obruchnikova, Y. A., Ilin, V. A. and Tregubova, V. E. (2015) "Technetium sulfide--formation kinetics, structure and particle speciation." <u>Radiochimica Acta</u> **103**(3): 199-203.

Hassanzadeh Fard, Z., C. D. Malliakas, J. L. Mertz and M. G. Kanatzidis (2015). "Direct Extraction of Ag+ and Hg2+ from Cyanide Complexes and Mode of Binding by the Layered K2MgSn2S6 (KMS-2)." <u>Chemistry of Materials</u> **27**(6): 1925-1928.

Henrot, J. (1989) "Bioaccumulation and chemical modification of Tc by soil bacteria." <u>Health Physics</u> **57**: 239-245.

Hu, Q. H., Rose, T. P., Zavarin, M., Smith, D. K., Moran, J. E. and Zhao, P. H. (2008) "Assessing field-scale migration of radionuclides at the Nevada Test Site: 'mobile' species."<u>Journal of Environmental Quality</u> 99: 16-7-1630.

Icenhower, J. P., Qafoku, N. P., Zachara, J. M. and Martin W. J. (2010) "The biogeochemistry of technetium: A review of the behavior of an artificial element in the natural environment." <u>American Journal of Science</u> **310**, 721-752.

Jansik, D. P. (2013) "Physiochemical Mechanisms for the Transport and Retention of Technetium." Ph.D. Dissertation, Oregon State University.

Jenkinson, S. B., McCubbin, D., Kennedy, P. H. W., Dewar A., Bonfield, R. and Leonard, K. S. (2014) "An estimate of the inventory of technetium-99 in the sub-tidal sediments of the Irish Sea." Journal of Environmental Radioactivity **133**: 40-47.

Kaplan, D. I. (2003) "Influence of surface charge of an Fe-oxide and an organic matter dominated soil on iodide and pertechnetate sorption." <u>Radiochimica Acta</u> 91: 169-174.

Kaplan, D. I. and Serne, R. J. (1998) "Pertechnetate exclusion from sediments." Radiochimica Acta **81**, 117-124.

Keith-Roach, M. J., Morris, K. and Dahlgaard, H. (2003) "An investigation into technetium binding in sediments." Marine Chemistry **81**(3-4): 149-162.

Keith-Roach, M. J. and Roos, P. (2004) "Redox-dependent behaviour of technetium-99 entering a permanently stratified anoxic fjord (Framvaren fjord, Norway)." Estuarine, Coastal and Shelf Science 60: 151-161.

Kenna, H. W. and Kuroda, P. K. (1961) "Isolation of naturally occurring technetium." Journal of Inorganic Nuclear Chemistry 23: 142-144.

Kobayashi, T., Scheinost, A. C., Fellhauer, D., Gaona, X., Altmaier, M, (2013) "Redox behavior of Tc(VII)/Tc(IV) under various reducing conditions in 0.1 M NaCl solutions" Radiochimica Acta 101: 323-332

Kunze, S., Neck, V., Gompper, K. and Fanghanel, T. (1996) "Studies on the immobilization of technetium under near field geochemical conditions." Radiochimica Acta **74**: 159-163.

Langton, C. A., Oblath, S. B., Pepper, D. W. and Wilhite, E. L. (1988) "Waste salt disposal at the Savannah River Plant." Chemical Engineering Communications 66: 189-199.

Lee, Ji-Hoon, Zachara, J. M., Fredrickson, J. K., Heald, S. M., McKinley, J. P., Plymale, A. E., Resch, C. T. and Moore, D. A. (2014) "Fe(II)- and sulfide-facilitated reduction of ^{99}Tc(VII)O$_4^-$ in microbially reduced hyporheic zone sediments." Geochimica et Cosmochimica Acta **136**: 247-264.

Lee, S. Y. and Bondietti, E. A. (1983) Technetium Behavior in Sulfide and Ferrous Iron Solutions. In: Scientific Basis for Nuclear Waste Management VI, pp. 315-322.

Lieser, K. H. and Bauscher, C. (1987) "Technetium in the hydrosphere and in the geosphere. 1. Chemistry of technetium and iron in natural-waters and influence of the redox potential on the sorption of technetium." Radiochimica Acta 42(4): 205-213.

Lieser, K. H. and Bauscher, C. (1988) "Technetium in the hydrosphere and in the geosphere. 2. Influence of pH of complexing agents and of some minerals on the sorptionof technetium." Radiochimica Acta 44-45(1): 125-128.

Liu, Y., Terry, J. and Jurisson, S. (2007) "Pertechnetate immobilization in aqueous media with hydrogen sulfide under anaerobic and aerobic environments." Radiochimica Acta **95**(12): 717-725.

Liu, Y., Terry, J. and Jurisson, S. (2008) "Pertechnetate immobilization with amorphous iron sulfide." Radiochimica Acta **96**(12): 823-833.

Liu, Y., Terry, J. and Jurisson, S. (2009) "Potential interferences on the pertechnetate-sulfide reaction." Radiochimica Acta **96**(12): 823-833.

Livens, F. R., Jones, M. J., Hynes, A. J., Charnock, J. M., Mosselmans, J. F. W., Hennig, C., Steele, H., Collison, D., Vaughan, D. J., Pattrick, R. A. D., Reed, W. A., Moyes, L. N. (2004) "X-ray absorption spectroscopy studies of reactions of technetium, uranium and neptunium with mackinawite." Journal of Environmental Radioactivity **74**(1-3): 211-219.

Lloyd, J. R., Nolting, H. F., Sole, V. A. and Bosecker K. (1998) "Technetium reduction and precipitation by sulfate-reducing bacteria." <u>Geomicrobiology Journal</u> 15(1): 45-58.

Lloyd, J. R., Sole, V. A., Van Praagh, C. V. G. and Lovely, D. R. (2000) "Direct and Fe(II)-mediated reduction of technetium by Fe(III)-reducing bacteria." <u>Applied and Environmental Microbiology</u> **66**(9): 3743-3749.

Lloyd, J. R., Mabbett, A. N., Williams, D. R. and Macaskie, L. E. (2001) "Metal reduction by sulphate-reducing bacteria: physiological diversity and metal specificity." <u>Hydrometallurgy</u> **59**: 327-337.

Lovely, D. R. (1993) "Dissimilatory metal reduction." <u>Annual Reviews of Microbiology</u> 47: 263-290.

Lukens, W. W., Bucher, J. J., Shuh, D. K. and Edelstein, N. M. (2005) "Evolution of technetium speciation in reducing grout." <u>Environmental Science and Technology</u> **39**(20): 8064-8070.

Lukens, W. W., Magnani, N., Tyliszczak, T., Pearce, C. I. and Shuh, D. K. (2016) Incorporation of technetium into spinel ferrites. <u>Environmental Science and Technology</u> 50: 13160−13168

Lamfers, H.-J., Meetsma, A., Wiegers, G. A. and de Boer, J. L. (1996) "The crystal structure of some rhenium and technetium dichalcogenides." <u>Journal of Alloys and Compounds</u> **241**: 34-39.

Manos, M. J. and Kanatzidis, M. G. (2012). "Layered Metal Sulfides Capture Uranium from Seawater." <u>Journal of the American Chemical Society</u> **134**(39): 16441-16446.

Marshall, T.A., Morris, K., Law, G.T., Mosselmans, J.F.W., Bots, P., Parry, S.A. and Shaw, S. (2014). "Incorporation and retention of 99-Tc(IV) in magnetite under high pH conditions", <u>Environmental Science & Technology</u> 48: 11853-11862

McCubbin, D., Kinson, S. L., McDonald, P., Bonfield, R. and Bourst, D. (2006) "Distribution of technetium-99 in sub-tidal sediments of the Irish Sea." Continental Shelf Research 26: 458-473.

Meena, A. H. and Arai, Y. (2017) "Environmental geochemistry of technetium." <u>Enivornmental Chemistry Letters</u> 15: 241-263.

Mertz, J. L., Z. H. Fard, C. D. Malliakas, M. J. Manos and M. G. Kanatzidis (2013). "Selective Removal of Cs+, Sr2+, and Ni2+ by K2xMgxSn3–xS6 (x = 0.5–1) (KMS-2) Relevant to Nuclear Waste Remediation." <u>Chemistry of Materials</u> **25**(10): 2116-2127.

Meyer, R. E., W. D. Arnold and F. I. Case (1987). "The Solubility of Electrodeposited Tc(IV) Oxides." <u>ORNL-6374</u> Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Meyer, R. E., Arnold, W. D., Case, F. I. and O'Kelley, G. D. (1991) "Solubilities of Tc(IV) oxides." Radiochimica Acta **55**: 11-18.

Mochiki, E., Kuwano, H., Kamiyama, Y., Aihara, R., Nakabayashi, T., Katoh, H., Asao, T., Oriuchi, N. and Endo, K. (2006) "Sentinel lymph node mapping with technetium-99m colloidal rhenium sulfide in patients with gastric carcinoma." <u>American Journal of Surgery</u> **191**(4) 465-469.

Morris, K., Butterworth, J. C. and Livens F. R. (2000) "Evidence for the remobilization of Sellafield waste radionuclides in an intertidal salt marsh, West Cumbria, U.K." Estuarine, Coastal and Shelf Science **51**: 613-625.

Müller, A., Diemann, E., Jostes, R. and Bogge, H. (1981) "Transition Metal Thiometalates : Properties and Significance in Complex and Bioinorganic Chemistry." Angewandte Chemie International Edition in English **20:** 934-955.

Müller, A.; Pohl, S.; M., D.; Cohen, J. P.; Bennett, J. M.; Kirchner, R. M. (1979) "Crystal structure of $(NH_4)_2[Mo_3S(S_2)_6]$ containing the novel isolated cluster $[Mo_3S_{13}]^{2-}$." Zeitschrift Fur Naturforschung Section B-A Journal of Chemical Sciences **34**: 434-436.

Neeway, J. J., R. M. Asmussen, A. R. Lawter, M. E. Bowden, W. W. Lukens, D. Sarma, B. J. Riley, M. G. Kanatzidis and N. P. Qafoku (2016). "Removal of TcO4-from Representative Nuclear Waste Streams with Layered Potassium Metal Sulfide Materials." Chemistry of Materials **28**(11): 3976-3983.

Palmer, D. A. and Meyer, R. E. (1981) "Adsorption of technetium on selected inorganic ion-exchange materials and on a range of naturally occurring minerals under oxic conditions." Journal of Inorganic Nuclear Chemistry **43**(11): 2979-2984.

Peretrukhin, V. F., Khizhnyak, T. V., Lyalikova, N. N., German, K. E. (1996) Biosorption of technetium-99 and some actinides by bottom sediments of Lake Beloe Kosino of the Moscow region. Radiochemistry **38**(5), 440-443.

Peretroukhine, V., Sergeant C., Deves, G., Poulain, S., Vesvres, M. H., Thomas, B. and Simonoff, M. (2006) "Technetium sorption by stibnite from natural water." Radiochimica Acta **94**(9-11): 665-669.

Peretyazhko, T., Zarchara, J. M., Heald, S. M., Jeon, B.-H., Kukkadapu, R. K., Liu, C., Moore, D. A. and Resch, C. T. (2008) "Heterogeneous reductio of Tc(VII) by Fe(II) at the solid-water interface." Geochimica et Cosmochimica Acta **72**: 1521-1539.

Perrier, C. and Segre, E. (1937) "Radioactive isotopes of element 43." Nature **140**: 193-194.

Qafoku, N., J. J. Neeway, A. R. Lawter, T. G. Levitskaia, R. J. Serne, J. Westsik, J.H. and M. M. Valenta Snyder (2014). "Technetium and Iodine Getters to Improve Cast Stone Performance." PNNL-23282 **Pacific Northwest National Laboratory**(Rev. 1).

Rao, T. S., T. N. Sairam, B. Viswanathan and K. V. K. Nair (2000). "Carbon steel corrosion by iron oxidising and sulphate reducing bacteria in a freshwater cooling system." Corrosion Science **42**(8): 1417-1431.

Rard, J., M. Rand, G. Anderegg and H. Wanner (1999). Chemical Thermodynamics of Technetium. The Netherlands, Elsevier.

Rard, J. A. (2005) "Current status of the thermodynamic data for technetium and its compounds and aqueous species." Journal of Nuclear and Radiochemical Sciences **6**: 197-204.

Rickard, D. and Luther, G. W. (1997) "Kinetics of pyrite formation by the H2S oxidation of iron(II) monosulfide in aqueous solutions between 25 and 125 degrees C: The mechanism." Geochimica et Cosmochimica Acta **61**: 135-147.

Rosso, K. M. Becker, U. and Hochella, M. F. (1999) "Atomically resolved electronic structure of pyrite {100} surfaces: An experimental and theoretical investigation with implications for reactivity." <u>American Mineralogist</u> **84**(10): 1535-1548.

Rosso, K. M., Becker, U. and Hochella, M. F. (1999) "The interaction of pyrite {100} surfaces with O_2 and H_2O: Fundamental oxidation mechanisms." <u>American Mineralogist</u> 84(10): 1549-1561.

Rosso, K. M. and Vaughan, D. J. (2006) "Reactivity of sulfide mineral surfaces." In: *Sulfide Mineralogy and Geochemistry* (D. J. Vaughan, ed.), Reviews in Mineralogy and Geochemistry, vol. 61: 557-607

Saiki, Y., Fukkuzaki, M., Sekine, T., Kino, Y. and Kudo, H. (2003) "Technetium(VII) sulfide colloid growing observed by laser-induced photoacoustic spectroscopy." <u>Journal of Radioanalytical and Nuclear Chemistry</u> 255(1): 101-104.

Saslow, S. A., Um, W., Pearce, C.I., Engelhard, M. H., Bowden, M. E., Lukens, W., Leavy, I. I., Riley, B. J., Kim, D-S., Schweiger, M. J. and Kruger, A. A. (2017) "Reduction and Simultaneous Removal of ^{99}Tc and Cr by $Fe(OH)_2(s)$ Mineral Transformation" Environmental Science and Technolgoy 51: 8635-8642.

Shen, D., Fan, X. H., Su, X. G., Zeng, J. S. and Dong, Y. (2002) "Sorption of radioactive technetium on pyrrhotine." <u>Journal of Radioanalytical and Nuclear Chemistry</u> 254(1): 137-142.

Skomurski, F. N., Rosso, K. M., Krupka, K. M. and McGrail, B. P. (2010) "Technetium incorporation into hematite (α-Fe_2O_3). <u>Environmental Science and Technology</u> 44: 5855-5861.

Smith, F. N., Taylor C. D., Um, W. and Kruger, A. A. (2015) "Technetium incorporation into goethite (α-FeOOH): An atomic-scale investigation." <u>Environmental Science and Technology</u> 49: 13699-13707.

Smith, F. N., Um, W., Taylor, C. D., Kim, D.-S., Schweiger, M. J. and Kruger, A. A. (2016) Computational investigation of technetium(IV)incorporation into inverse spinels: Magnetite (Fe_3O_4) and trevorite ($NiFe_2O_4$). <u>Environmental Science and Technology</u> 10: 5216−5224.

Smith, J., Z. Qin, F. King, L. Werme and D. W. Shoesmith (2007). "Sulfide Film Formation on Copper under Electrochemical and Natural Corrosion Conditions." <u>CORROSION</u> **63**(2): 135-144.

Standring, W. J. F., Oughton, D. H. and Salbu, B. (2002) "Potential remobilization of ^{137}Cs, ^{60}Co, ^{99}Tc, and ^{90}Sr from contaminated Mayak sediments in river and estuary environments." <u>Environmental Science and Technology</u> **36**: 2330-2337.

Steigman, J., Solomon, N. A. and Hwang, L. L. Y. (1986) "Technetium sulfur colloid." <u>Applied Radiation and Isotopes</u> 37(3): 223-229.

Strickert, R., Friedman, A. M., and Fried, S. (1980) "The sorption of technetium and iodine radioisotopes by various minerals." <u>Nuclear Technology</u> 49(2): 253-266.

Szecsody, J. E., Jansik, D. P., McKinley, J. P. and Hess, N. J. (2014) "Influence of alkaline co-contaminants on technetium mobility in vadose zone sediments." <u>Journal of Environmental Radioactivity</u> **135**: 147-160.

Szecsody, J. E., Truex, M. J., Zhong, L. R., McKinley, J. P., Qafoku, N. P., Lee, B. D. and Saurey, S. D. (2015) "Remediation of technetium in vadose zone sediments using ammonia and hydrogen sulfide gases." Vadose Zone Journal **14**(7).

Um, W., Chang, H.-S., Icenhower, J. P., Lukens, W. W., Serne, R. J., Qafoku, N. P., Westik, J. H. Jr., Buck, E. C. and Smith, S. C. (2011) "Immobilization of 99-Tc (VII) by Fe(II)-goethite and limited reoxidation." Environmental Science and Technology 45: 4904-4913.

Um, W., Chang, H.-S., Icenhower, J. P., Lukens, W. W., Serne, R. J., Qafoku, N. P., Kukkadapu, R. K. and Westik, J. H. Jr. (2012) "Iron oxide waste form for stabilizing ^{99}Tc." Journal of Nuclear Materials 429: 201-209.

Um, W., J.-S. Yang, R. J. Serne and J. H. Westsik (2015). "Reductive capacity measurement of waste forms for secondary radioactive wastes." Journal of Nuclear Materials **467, Part 1**: 251-259.

United States Envrionmental Protection Agency, Office of Water Supply (1977) National Interim Primary Drinking Water Regulations, EPA-570/9-76-003, U.S. Environmental Protection Agency.

Wanebo, H. J., Harpole, D. and Teates, C. D. (1985) "Radionuclide lymphoscintigraphy with technetium 99M antimony sulfide colloid to identify lymphatic drainage of cutaneous melanoma at ambiguous sites in the head and neck and trunk." Cancer **55**(6): 1403-1413.

Watanabe, T., Kimijima, I., Ohtake, t., Tsuchiya, A., Shishido, F. and Takenoshita, s. (2001) "Sentinel node biopsy with technetium-99m colloidal rhenium sulfide in patients with breast cancer." British Journal of Surgery **88**(5): 704-707.

Watson, J. H. P., Croudace, I. W., Warwick, P. E., James, P. A. B., Charnock, J. M. and Ellwood, D. C. (2001) "Adsorption of radioactive metals by strongly magnetic iron sulfide nanoparticles produced by sulfate-reducing bacteria." Separation Science and Technology **36**(12): 2571-2607.

Watson, J. H. P. and D. C. Ellwood (2003). "The removal of the pertechnetate ion and actinides from radioactive waste streams at Hanford, Washington, USA and Sellafield, Cumbria, UK: the role of iron-sulfide-containing adsorbent materials." Nuclear Engineering and Design **226**(3): 375-385.

Weber, T., Muijsers, J. C. and Niemantsverdriet, J. W. (1995) "Structure of amorphous MoS_3." Journal of Physical Chemistry 99, 9194-9200.

Weck, P. F., Kim, E. and Czerwinski, K. R. (2013) "Semiconducting layered technetium dichalcogenides: Insights from first principles." Dalton Transactions **42**: 15288-15295.

Westsik, J. H., G. F. Piepel, M. J. Lindberg, P. G. Heasler, T. M. Mercier, R. L. Russel, A. D. Cozzi, W. E. Daniel, R. E. Eibling, E. K. Hansen, M. R. Reigal and D. J. Swanberg (2013). "Supplemental Immobilization of Hanford Low-Activity Waste: Cast Stone Screening Tests." PNNL-22747, SRNL-STI-2013-00465 Rev. 0, Pacific Northwest National Laboratory, Richland, Washington and Savannah River National Laboratory, Aiken, South Carolina.

Wharton, M. J., Atkins, B., Charnock, J. M., Livens, F. R., Pattrick, R. A. D. and Collison, D. (2000) "An X-ray absorption spectroscopy study of the coprecipitation of Tc and Re with mackinawite (FeS)." Applied Geochemistry **15**, 347-354.

Wildervanck, J. C. and Jellinek, F. (1971) "Dichalcogenides of technetium and rhenium. Journal of the Less-Common Metals." **24**: 73-81.

Winkler, A., Bruhl, H. Trapp, C. and Bock, W. D. (1988) "Mobility of technetium in various rocks and defined combinations of natural minerals." Radiochimica Acta **44-45**: 183-186.

Wolverson, D. and Hart, L. S. (2016) "Lattice dynamics of the rhenium and technetium dichalcogenides." Nanoscience Research Letters **11**:250.

Yalcintas, E. (2015) "Redox, solubility and sorption chemistry of technetium in dilute to concentrated saline systems." Ph.D. Dissertation, Karlsruhe Institute of Technology

Yalcintas, E., Scheinost, A. C., Gaona, X. and Altmaier, M. (2016) "Systematic XAS study on the reduction and uptake of Tc by magnetite and mackinawite." Dalton Transactions **45**(44) 17874-17885.

Zachara, J. M., Heald, S. M., Jeon, B.-H., Kukkadapu, R. K., Liu, C. X., McKinley, J. P., Dohnalkova, A. C. and Moore, D. A. (2007) "Reduction of pertechnetate [Tc(VII)] by aqueous Fe(II) and the nature of solid phase redox products." Geochimica et Cosmochimica Acta 71: 2137-2157.

Zhuang, H., Zeng, J. S. and Zhu, L. Y. (1988) "Sorption of radionuclides technetium and iodine on minerals." Radiochimica Acta **44-45**: 143-145.

Zhuang, H. E., Zheng, J. S., Xia, D. Y. and Zhu, Z. G. (1995) "Retardation of technetium and iodine by antimony-containing and mercury-containing minerals." Radiochimica Acta **68**: 245-249.