The Function of Sn(II)-Apatite as a Tc Immobilizing Agent

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ABSTRACT At the U.S. Department of Energy Hanford Site, Tc-99 is a component of low-activity waste (LAW) fractions of the nuclear tank waste and removal of Tc from LAW streams would greatly benefit the site remediation process. In this study, we investigated the removal of Tc(VII), as pertechnetate, from deionized water (DIW) and a LAW simulant through batch sorption testing and solid phase characterization using tin (II) apatite (Sn-A) and SnCl₂. Sn-A showed higher levels of Tc removal from both DIW and LAW simulant. Scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/XEDS) and X-ray absorption spectroscopy (XAS) of reacted Sn-A in DIW showed that TcO₄⁻ is reduced to Tc(IV) on the Sn-A surface. The performance of Sn-A in the LAW simulant was lowered due to a combined effect of the high alkalinity, which lead to an increased dissolution of Sn from the Sn-A, and a preference for the reduction of Cr(VI).

1. INTRODUCTION Technetium-99 (Tc , $t_{1/2} = 213\,000\text{ a}$) is a radioactive contaminant of high concern at many global nuclear waste storage sites, [1-4] as evidenced by the Tc remediation and cleanup efforts at the U.S. Department of Energy (DOE) Hanford Site.[5] Current plans call for the low activity waste (LAW) stored in tanks at the Hanford site, which contain Tc, to be solidified through vitrification at the Hanford Tank Waste Treatment and Immobilization Plant (WTP). However, there are limitations for the incorporation of Tc in mid- to high-temperature immobilization processes due to the volatility of Tc compounds.[6] Additionally, Tc has high environmental mobility in aerobic environments when it exists in the anionic Tc (VII) form, pertechnetate (TcO_4^-).[7] Thus, providing a suitable disposal matrix with a high chemical durability for wastes that contain and stabilize Tc is imperative.

Treatment of waste streams to selectively remove Tc and other redox active species is a potential process that can aid in Tc management. Two removal pathways for TcO_4^- from aqueous environments are prevalent: (1) ion exchange, and (2) reduction of Tc(VII), as TcO_4^- , to a highly insoluble Tc(IV) species, such as $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ ($K_{\text{sp}} = 10^{-32}$).[8, 9] The separated Tc can then be immobilized in a waste form where it can be safely disposed. Several candidate materials for the uptake and immobilization of TcO_4^- from aqueous solutions have been previously studied, including minerals, organic compounds, inorganic compounds and redox active materials, with varying levels of success.[10-13] However, many of these studies were performed in deionized water (DIW), or in solutions with simple compositions. A successful candidate material for Tc immobilization through a redox process needs to have two ideal characteristics: high removal capacity/selectivity for TcO_4^- and sufficient reductive potential to convert it to Tc(IV). Materials with these traits would also need to demonstrate low rates of Tc desorption, compatibility with a final waste form, low cost and long term stability.[11]

One material that has shown potential for Tc removal in simulated groundwater is tin (II) apatite (Sn-A), ideally $\text{Sn}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$. [14, 15] The reductive capability of Sn-A arises from the presence of Sn(II), which has a favourable reduction potential for Sn(IV)/Sn(II) of 0.384 V [16] and can reduce Tc(VII) to Tc(IV). The Tc(VII)/Tc(IV) standard reduction potential is 0.738 V. [15] The reduction of TcO_4^- by Sn(II) has been used in chemical syntheses in pharmaceutical development. [17] The second component, apatite (calcium phosphate), has also been reported to have an affinity for the sorption of Tc species in artificial groundwater, [18] and also in studies of bone, as the supporting anions in the apatite could be supplanted by TcO_4^- . [19, 20] In addition, anionic selenium species (SeO_4^{2-}) similar to pertechnetate have previously been reported to adsorb to apatite structures in a substitution mechanism with phosphate. [21] However, these processes have not been tested in high alkaline environments such as LAW. Though it is understood that both the Sn(II) and supporting apatite structure may play a role in the removal of Tc by Sn-A, the contribution of each component has yet to be reported in detail.

In this study we investigate whether Sn-A exhibits high and selective affinity for Tc and can function as a material for removal of aqueous TcO_4^- from a LAW simulant and DIW. Novel work to elucidate the mechanism of removal of Tc by Sn-A will also be presented based on results from solid-state characterization techniques. In addition, SnCl_2 was tested for comparison as it is fully soluble in water and supplies a source of the Sn(II) reductant in solution without a solid interface present. The testing involved batch sorption experiments using Sn-A and SnCl_2 for Tc sequestration from solutions with high ionic strength that contain competing redox sensitive constituents found in LAW. This work represents a novel venture to investigate the nature of the Sn-A before, during, and after contact with Tc-bearing solutions. The results of this study are relevant to treatment of liquid nuclear wastes and long-term immobilization of Tc, both

necessary advancements required for the sustained use of atomic energy and safe disposal of nuclear wastes.

2. MATERIALS AND METHODS Two materials were utilized in this work: tin (II) Apatite (Sn-A), $(\text{Sn}_5(\text{PO}_4)_3(\text{X}))$ where X is a supporting anion (Cl, F, OH) and SnCl_2 (Sigma Aldrich). The Sn-A was prepared by an outside laboratory following a previously reported method.[22, 23] Sn-A prepared with this synthetic method has been reported to be comprised of an apatite $(\text{Ca}_x(\text{PO}_4)_y(\text{X}))$ structure with partial substitution of Ca(II) by Sn(II) in the lattice.[23] The exact chemical content of the supplied materials was determined using microwave digestion (per U.S. EPA Method 3051A, Revision 1 2007) and the moisture content was determined gravimetrically (per ASTM D2216). Further details can be found in the supplemental information. The Sn-A had a moisture content of 66.78 wt% and the SnCl_2 had a moisture content of 0.51 wt%. From microwave digestion and subsequent analysis with inductively coupled plasma optical emission spectroscopy (ICP-OES), the Sn-A was found to contain 25.0 wt% Ca, 14.4 wt% P and 23.5 wt% Sn, with the remainder comprised of O (29.8 wt% O if all assumed to be with P as PO_4) and supporting anions. Sn-A has previously been reported to be an amorphous pattern with only a weak crystalline hydroxyapatite peak appearing, see Appendix B of Qafoku et al. [22, 24] Without supporting anion identification, the exact formula of Sn-A cannot be determined. The likely formula for the Sn-A is $\text{Ca}_{x-y}\text{Sn}_y(\text{PO}_4)_x(\text{X})$, where X is the supporting anion. SnCl_2 was selected as a source of Sn(II) reductant in solution without a solid interface present. The reduction capacity of Sn-A was measured using the Ce(IV) method, details of which can be found in a recent work by Um et al.[25]

The performance of the materials was investigated in DIW Millipore® water (18.2 MΩ-cm) and a LAW simulant (7.8 M Na Average LAW simulant,[26] referred to as LAW simulant

from here on). The composition of the LAW simulant solution was based on the Hanford Tank Waste Operations Simulator (HTWOS) model[27] and is presented in Table 1. The LAW simulant was prepared by adding half of the target volume of DIW (500 mL for a 1L final batch) to an empty beaker or flask and then adding a stir bar. The compounds were then added in the order listed in Table 1. Each compound was fully dissolved with stirring before the addition of the next compound. If dissolution did not immediately occur, the solution was heated to 70 °C. Following the addition of the final compound, DIW was added to meet the targeted total volume. It must be noted that undissolved solids remained following completion of the LAW simulant preparation. These solids lead to some variance in the composition of the simulant, hence the nomenclature of a 7.8 M Na average simulant.

Two additional solutions based on the LAW simulant were used in this work. For experiments conducted in the absence of Cr, the LAW simulant was prepared as listed in Table 1, omitting the $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2 \text{H}_2\text{O}$. This solution is named “LAW simulant No Cr”. A simplified form of the LAW simulant was also used to investigate the effects of the minor constituents of the LAW simulant in the batch tests. This solution contained only two of the major components of the LAW simulant: NaNO_3 (1.04 mol/L) and NaOH (4.34 mol/L). The NaNO_3 and NaOH were added to DIW in the amounts listed in Table 1 and this solution is named “LAW $\text{NaNO}_3/\text{NaOH}$ ”.

The effectiveness of the Sn-A and SnCl_2 was investigated with duplicate batch sorption experiments. The data presented is the average of the duplicate measurements and error bars are the standard deviation of the mean. The experiments were contained within 250 mL polytetrafluoroethylene bottles at room temperature, ~ 22 °C, in an anaerobic chamber containing a mixed H_2/N_2 atmosphere with O_2 levels below 5 ppm. One gram of material was

added to 100 mL solution for the batch experiments. Additional tests varied the solid : solution ratio. Following addition of the DIW or LAW simulant to the bottle, the solutions were equilibrated in the anaerobic chamber overnight, then spiked with a concentrated stock solution of NH_4TcO_4 in water ($> 10\,000$ ppm) to achieve Tc concentrations of 1 $\times$, 5 $\times$ and 10 $\times$ the level predicted by HTWOS for a 7.8 M Na average LAW (5.6 ppm). Initial blank Tc concentrations were measured from identical solutions without any Sn-A or SnCl_2 added. In experiments designed to observe the release of elements (Ca, P, Sn) from the Sn-A, the solutions were not spiked with Tc. Periodic sampling was performed by acquisition of a 2 mL aliquot of solution from the test vessels, which was immediately filtered (0.2 μm). The samples were then acidified with 20 μL of 70 % HNO_3 for Tc analysis by inductively coupled plasma mass spectroscopy (ICP-MS). ICP-MS samples from DIW experiments were diluted 20 $\times$ for analyses and in samples from the LAW simulant a 5000 $\times$ dilution was used. The matrix determined detection limit for Tc resulting from these dilutions was 0.082 ppb for the 20 $\times$ and 20.5 ppb for the 5000 $\times$.

Following contact experiments, any remaining solid phase in the reaction bottle was removed and imaged by scanning electron microscopy (SEM) using a FEI Helios 600 NanoLab focused ion beam (FIB)/SEM. Images were collected at an accelerating voltage of 20 keV and elemental levels determined with energy dispersive x-ray spectroscopy (XEDS) at an accelerating voltage of 10 keV. Further characterization was performed using X-ray absorption spectroscopy (XAS). Details on the XAS measurements are included in the supplemental information.

3. RESULTS

3.1 Tc Removal Performance in DIW

Figure 1(a) displays the % Tc removal values for the Sn-A and SnCl₂ measured in DIW at three levels of initial Tc concentration (5 ppm, 28 ppm, 56 ppm). It is clear from the plot that the Sn-A outperformed the SnCl₂ in terms of Tc removal in DIW. The SnCl₂, which completely dissolved in solution, removed between 87 % of the Tc in the 5 ppm solution and 93 % of the Tc in the 56 ppm solution. The % Tc removed held near constant after 6 d of contact. The pH of the solutions containing the SnCl₂ was measured to be 1.56 ± 0.04 . This acidic environment produced by the SnCl₂ may hinder Tc(VII) reduction as the standard potential for Tc(VII) reduction increases with decreasing pH, based on the E vs pH diagram. [28] However, the Sn(II) is likely stable in its reduced Sn(II) state in the acidic environment, which in turn could assist in Tc reduction.[29] In general, the Sn-A had a slower removal of Tc over the first 2 d compared to the SnCl₂, removing between 87 %-90 % of the Tc at 2 d contact. At 4 d contact, the Sn-A had removed > 99.99 % of the Tc in all three solutions. The pH of the Sn-A containing solutions was 7.87 ± 0.08 . The DIW spiked with Tc and no Sn-A or SnCl₂ had a pH of 8.70 ± 0.03 .

The Sn(II) present in solution is likely responsible for the removal of Tc observed. Figure 1(b) displays a measure of Tc removal effectiveness comparing the Sn-A and SnCl₂ in terms of mol Tc removed per g of Sn in the DIW experiments. In the 5 ppm solutions the SnCl₂ removed 0.007 mol Tc/g Sn while the Sn-A removed 0.048 mol Tc/g Sn; in the 28 ppm Tc solutions the SnCl₂ removed 0.040 mol Tc/g Sn and the Sn-A removed 0.260 mol Tc/g Sn; in the 56 ppm Tc solution the SnCl₂ removed 0.080 mol Tc/g Sn while the Sn-A removed 0.528 mol Tc/g Sn. This comparison highlights the improved performance of the Sn-A towards Tc removal compared with SnCl₂, despite the SnCl₂ containing a higher amount of Sn(II). The solid surface present in the Sn-A likely contributed to this improved Tc removal behaviour, possibly through facilitating electron transfer or aiding in bringing the Tc in close proximity to

the reductant through a sorption process. Similar observations have been made for Fe(II) facilitated reduction of Tc, where changing the substrate bearing the Fe(II) led to improved Tc removal,[30] and sorption of Fe(II) to a solid surface increased Tc removal.[31]

The mechanism of removal via SnCl₂ is likely an aqueous phase reduction:

Whereas on Sn-A, a two step process is more likely involving sorption of Tc on the apatite surface:

Followed by a subsequent reduction of Tc:

SnCl₂ showed little additional removal of Tc after the initial contact time in all three concentrations of Tc in DIW. Two situations accounting for this behaviour are plausible:

1) following the initial removal of Tc, the lower amount of Tc in solution decreases the likelihood of a collision between Sn²⁺_(aq) and TcO₄⁻ that is required to facilitate the electron transfer for the redox process,[32] or 2) Sn²⁺_(aq) slowly oxidizes (due to residual O₂ in the anaerobic chamber) in the aqueous solution, thus limiting the amount of reductant in solution. [29] A similar trend to situation 1 has been reported for the reduction of Tc(VII) using Fe(II), in which the solution phase reduction was kinetically hindered compared with the reduction occurring on a solid surface.[9] In Sn-A experiments, the fastest relative rates of removal occurred following a two day incubation period after which the Sn-A became more effective. As evidenced in Figure 1 by the higher level of Tc removal by the Sn-A compared with the SnCl₂, an influence of the Sn-A solid surface on the removal of Tc was present, likely caused by sorption of the TcO₄⁻ to the apatite, where it could then be reduced by the Sn(II). If a sorption step is occurring, it is possible

that the nature of the supporting anions in the Sn-A structure may influence the rate of sorption, however this cannot be determined from the work here within. This behaviour is further evidenced by Sn-A exhibiting higher Tc removal despite having a lower Sn content.

3.2 Characterization of Sn-A Following DIW Exposure

The reacted Sn-A was removed from the 56 ppm Tc DIW solution following the batch experiment and used for solid state characterization. The 56 ppm Tc DIW experiment solid material was chosen to ensure sufficient presence of Tc on the Sn-A for analysis. At the time of collecting the Sn-A, the Tc concentration in solution was 1.4 ppb, as almost all the Tc was then present on the 1 g of Sn-A. Due to its solubility, no solids could be recovered from the SnCl_2 batch experiments. Figure 2 (a) shows an SEM micrograph of the Sn-A following the batch experiment in DIW with 56 ppm Tc. XEDS spot analysis was used on points on the Sn-A structure, labelled (I) and (II) with arrows, and the resulting spectra are shown in Figure 2(b) and 2(c). A homogeneous distribution of Tc on the surface of the Sn-A is confirmed in both XEDS spectra, along with strong signals for Sn, Ca, and P from the Sn-A structure. Due to the excitation volume of the electron beam, the XEDS cannot distinguish if the Tc is present solely on the surface of the Sn-A or incorporated into the Sn-A structure.

The x-ray absorption near edge structure (XANES) spectrum collected from the Sn-A sample is shown in Figure 3(a). Three standard spectra were used to model the possible local environments for Tc: 1) TcO_4^- , 2) Tc (IV) EDTA was used to model a Tc (IV) atom coordinated by oxygen atoms in a distorted octahedral environment, such as that expected for Tc(IV) sorbed to a mineral surface, and 3) Tc_2S_7 was used to represent Tc(IV) coordinated by sulfide and disulfide ligands. The XANES spectrum obtained for Sn-A has a good fit with the exception at the top of the edge (~ 21070 eV). However, this did not affect the ability to determine sample

composition from a linear combination fit. The fitting results, listed in Figure 3(c), show only one Tc species, Tc(IV) coordinated by oxygen atoms in a distorted octahedral manner. The slight mismatch at the top edge corresponds to a somewhat different local environment of Tc in this arrangement. While the contribution from TcO_4^- is approximately 5 %, the high p value of 0.123 means that the TcO_4^- signal is not meaningful.

Above the X-ray absorption edge, seen in Figure 3 (a), features were present that were utilized to probe the extended X-ray absorption fine structure (EXAFS) for the Sn-A sample. The resulting EXAFS spectrum is shown in Figure 3(b) and the corresponding fitting parameters in Figure 3(d). Further information on the fitting method can be found elsewhere.[33] Strong contribution to the spectrum from both O and Tc neighbours were confirmed by the low corresponding p values (< 0.001), and no improvement was observed upon shortening the Tc-O distance (as found in TcO_4^-). Although the spectrum is not identical to that of $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$, the Tc-O and Tc-Tc distances are similar to those of $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$, which is consistent with a surface precipitate similar in structure to $\text{TcO}_2 \cdot x\text{H}_2\text{O}$. There was no evidence of Tc-Sn interactions or Tc-Ca interactions. The combination of the SEM showing a Tc deposit on the Sn-A and XAS showing no incorporation into the apatite structure of the Sn-A strongly suggests that Sn-A functions through a surface mediated reduction (i.e., adsorption followed by reduction) of Tc(VII) to Tc(IV), which deposits evenly on the material surface as a surface precipitate. The mechanism prior to the reduction step is still to be determined; however, as discussed previously, an initial sorption to the apatite is likely based on results obtained from solution analysis in the batch experiments.

3.3 Tc Removal Performance in LAW Simulant

The averaged behaviour of the Sn-A and SnCl₂ in the LAW simulant is shown in Figure 4(a). The performance of both materials is lower in the LAW simulant. Both the Sn-A and SnCl₂ experienced a large decrease to < 20 % Tc removal by the Sn-A after 14 d contact and < 15% Tc removal by the SnCl₂ at a 1 g to 100 mL ratio. This decreased performance towards Tc removal may be a result of interference by other species in the LAW simulant on the redox processes of Sn-A and SnCl₂. The two materials rely on the reducing capacity of Sn(II), and if other oxidants are present, such as in the LAW simulant, they may be reduced in place of the Tc(VII). As was in the DIW experiments, the solid surface of the Sn-A provided an improvement over SnCl₂ in the LAW simulant when the mol Tc removed per g of Sn is compared, Figure 4(b). The Sn-A removed a maximum of 0.130 mol Tc/g Sn and the SnCl₂ removed 0.019 mol Tc/g Sn.

Following the batch experiments in the LAW simulant, the Sn-A was removed for further analysis to identify the possible interfering species. The surface of the Sn-A can be seen in the SEM micrograph, Figure 5(a). The Sn-A surface appears to be covered in a smoother desposit than the Sn-A surface following exposure to DIW, Figure 2(a). XEDS analysis of two spots, labeled I and II, show high levels of Na from the solution, along with signals for Al and Cr in both spots, Figure 5(b) and 5(c). The Al likely is present from incomplete washing following the experiment. Cr(VI) is a stronger oxidant than Tc(VII), was present in a much higher amount in the LAW simulant (1800 ppm Cr to 56 ppm Tc) and may be interfering with the performance of the Sn-A (it may get reduced to Cr(III) and precipate in Cr(III)-bearing solid phases). This makes Cr likely to interfere with the Tc reducing ability of the Sn-A, and led to its deposition on the Sn-A surface.

3.4 Competition Between Cr and Tc

The marked decrease in Tc removal by the Sn-A in the LAW simulant can be further understood through batch testing using the altered simulant compositions from Table 1, “LAW simulant No Cr” and “LAW NaNO₃/NaOH”. Figure 6 (a) compares % Tc or %Cr removed from batch experiments performed with the LAW solutions using Sn-A at a 1 g : 100 mL ratio. As discussed in the previous section, the lowest performance by Sn-A was in the removal of Tc in the LAW simulant, with < 20 % Tc removed. However, upon exposure of Sn-A to the “LAW simulant No Cr” containing 56 ppm Tc, a 59 % removal of Tc was observed at 3 d and increased to 78 % Tc removed at 14 d. While lower than the Tc removal levels observed in DIW, it is confirmation that Cr(VI) interferes with the removal of Tc from the LAW simulant. In measurements of Tc removal from the “LAW NaNO₃/NaOH” spiked with 56 ppm Tc, 79 % Tc removal was observed after 3 d and increased slightly to 82 % Tc removal at 14 d contact. The absence of Cr(VI) from the LAW simulant, and the absence of other species in the LAW simulant, facilitated an increase in Tc removal, yet not to the levels observed in DIW. The similar Tc removal by Sn-A observed in the “LAW simulant No Cr” and “LAW NaNO₃/NaOH” solutions suggests that the high alkalinity of the LAW simulant also affects removal of Tc by Sn-A. These results also suggest that the other metallic species (Al, Ni, Cd) and other ions (SO₄²⁻, NO₂⁻ etc.) in the LAW simulant solution have little effect on the removal of Tc. For comparison, the removal of Cr(VI) from the “LAW NaNO₃/NaOH” solution spiked with 23 ppm Cr(VI), equivalent on a molar basis to 56 ppm Tc, was studied and the results are also presented in Figure 6 (a). The Sn-A was able to remove > 98% of the Cr from the “LAW NaNO₃/NaOH”. This result shows Sn-A to be effective in the removal of Cr in the highly alkaline simulant environment, yet slightly hindered towards Tc removal. No changes in the

levels of Cr can be quantified in the LAW simulant from Figure 4(a) due to the high initial Cr concentration (1800 ppm).

Based on the findings of Figure 6(a), potential affinity for Cr(VI) removal over Tc(VII) by Sn-A was investigated through batch experiments with Tc and Cr added in equimolar amount to solution. The solution used was the “LAW simulant No Cr” with initial concentrations of 53 ppm Tc(VII) and 28 ppm Cr(VI) spiked in the solution (equivalent to 0.5 mM concentrations of each) containing Sn-A at a 1 g : 100 mL ratio. The initial stages of removal were of interest so sampling intervals were much shorter. The resulting behaviour is shown in Figure 6(b). In the initial stages of contact (< 6 h) there was little difference in the removal of Cr and Tc. After 6 h, Cr was removed to a much higher degree than Tc. At 48 h, the Cr concentration had dropped to 0.06 mmol/L while the Tc had only lowered to 0.28 mmol/L; at 288 h the concentration of Cr was 0.01 mmol/L and 0.15 mmol/L Tc. This result confirms what was seen in the “LAW NaNO₃/NaOH” environment (Figure 6(a)) with Cr being removed with a higher efficiency than Tc. This preference for Cr(VI) reduction may result from the more positive reduction potential for Cr(VI)₂O₇²⁻ of 1.33 V compared with 0.78 V for Tc(VII)O₄⁻. [34]

The high alkalinity of the LAW simulant also interferes with the Sn-A removal of Tc as increasing pH can alter how the Sn-A structure is solubilized. To investigate this potential interference, 1.0 g of Sn-A was placed in 100 mL of solutions of pH 7, pH 10 and pH 13 (DIW adjusted with NaOH) and LAW simulant with and without Cr. Figure 7(a) shows the measured release of three species (Sn, Ca and P) based on the ICP-MS analysis. Results show there is little time dependence on elemental release as only slight changes were observed after 24 h of contact. The impact of pH on the dissolution of Sn-A is most evident in Figure 7 (b), which displays the average concentration of Sn, Ca and P at 48 h – 72 h at the different pH values. The pH of the

LAW simulant was measured at 13.5. Sn was released in high amounts from the Sn-A as the pH is increased with a high dissolution of Sn in the LAW, Ca showed a lower release with increasing pH, and P concentration in solution remained relatively constant. It should be noted that differences in Ca and P concentrations could not be successfully measured in the LAW simulant solution due to the initial high concentrations in solution. As pH increased, more Sn is lost from the Sn-A solid, which could account for the decrease in performance toward Tc removal at increasing pH. [22]

The initial batch experiments performed in LAW simulant were conducted at a ratio of 1 g : 100 mL. However, identification of Cr(VI) as an interfering species that is preferably reduced over Tc(VII) by Sn-A suggests that the redox active Sn(II) in the Sn-A may not have been present in sufficient amount to reduce the Tc. Two additional batch experiments were performed using increased solid : solution ratios for the Sn-A in LAW simulant. The Sn-A had a reduction capacity ranging from 1210 $\mu\text{eq/g}$ to 3460 $\mu\text{eq/g}$ using the Ce(IV) method. The reduction capacity measures the number of mols of available electrons available for redox (eq) per gram of material. The variance in the reduction capacity between batches of Sn-A resulted from the age of the material and its exposure to open atmosphere, both factors decreasing the reduction capacity.

Figure 8 displays the % Tc removed by the Sn-A in LAW simulant at increased solid : solution ratios. In LAW simulant batch experiments in Figure 4, the Sn-A was added at 7 $\times$ the Tc content (at 56 ppm) based on the 1200 $\mu\text{eq/g}$ reduction capacity of the Sn-A batch used, which lead to a maximum 18.0 % Tc removal after 14 d. Sn-A was next tested by adding a sufficient amount to reduce all of the Cr(VI) and Tc(VII) in the LAW simulant based on the reduction capacity of 1200 $\mu\text{eq/g}$ for the batch used, and an averaged maxima of 27.5 % of the

Tc was removed after 24 h. This result reaffirms that the high alkalinity of LAW interferes with Sn-A and not solely the presence of Cr(VI). Increasing the Sn-A amount to remove 3× the Cr(VI) content and 10× the Tc content, based on the 3460 µeq/g reduction capacity of the batch used, resulted in a 65 % removal of Tc after 24 h. The higher Sn-A loading amount batch experiments were performed in aerobic conditions. This does not influence Sn-A removal of Tc based on DIW Tc removal; see supplemental information Figure S1. By increasing the amount of Sn-A in the LAW simulant, significant amounts of Tc can be removed, although the relationship between Tc removal and Sn-A mass is not linear.

4. DISCUSSION

⁹⁹Tc is a component of concern in nuclear wastes owing to its long half life, high environmental mobility due to its anionic speciation as pertechnetate in aerobic environments, and challenges to its incorporation in mid- to high-temperature waste forms. Sequestering Tc from aqueous nuclear wastes can be achieved by materials that are capable of sorbing or reducing Tc. Sn-A was found to have high Tc removal capability, with > 99.99 % removal achieved in < 96 h in neutral pH conditions. This level of removal is on par with or better, than other successful Tc removal technologies in weak ionic strength, near neutral solutions when compared with the reported Tc distribution coefficients, K_d (in mL/g). K_d is calculated commonly as follows:

$$K_d = \frac{c_{i,blank} - c_i}{c_i} \times \frac{V_s}{m_g} \quad \text{Eq. 4}$$

Where $c_{i,blank}$ is the initial concentration of the species or of the blank solution, c_i is the concentration of the species at a specific interval, V_s is the volume of solution in mL, and m_g is the mass of the material added to solution in g. It should be noted that K_d calculated for Tc in such a sense is representative of the amount of Tc present in solution relative to the amount

removed from solution. Traditional calculation of K_d gives the ratio of a species present in aqueous vs. solid state.

A Sb-SnO₂ material was reported in near neutral ionic strength systems to give Tc distribution coefficients, K_d (in mL/g), of 1×10^6 mL/g;[35] nanoiron on commercially available silicone in a DIW system gave a Tc K_d of 8100 mL/g;[36] Purolite A5320E resin in a near neutral groundwater brine measured a Tc K_d of 1.2×10^3 mL/g;[14] nanoporous Sn-phosphorous measured a Tc K_d of 9×10^4 mL/g;[37] activated carbon 824 BC in artificial groundwater gave a Tc K_d of 120 mL/g;[18] calcium apatite in artificial groundwater measured a Tc K_d of 223 mL/g;[18] granular activated carbon in different groundwater gave a Tc K_d of 2.4×10^4 mL/g;[38] a macroporous poly(GMA-co-EGDMA) polymer in near neutral solutions measured a Tc K_d of 2.3×10^3 mL/g.[39] In comparison, the Sn-A in DIW in this study measured a Tc K_d of 3.7×10^7 mL/g confirming its strong performance as a Tc removal material from near neutral, low ionic strength environments. The Sn-A can function to remove Tc(VII) in both anaerobic and oxic environments based on the results shown in Figure S1 and Figure 8. This is an added benefit for any eventual field applications.

In a LAW solution, simulating the tank waste present at the Hanford site, the Tc removal capacity of Sn-A was decreased, as was similarly observed for supported zerovalent iron when moving from neutral pH solutions to a LAW environment.[36] This decrease by the Sn-A was the result of two factors: 1) the high alkalinity of the LAW solution leading to increased release of Sn from the Sn-A, and 2) competition with Cr(VI), which is kinetically favoured, for the reduction of Tc. This issue can be overcome through increasing the amount of Sn-A in the LAW.

A possible application of the Tc removal ability of Sn-A is in the fabrication of low temperature cementitious waste forms (such as Cast Stone at the Hanford Site and Saltstone at Savannah River site). [40, 41] Cast Stone and Saltstone are comprised of blast furnace slag, fly ash and ordinary Portland cement. The current end of life destination for Hanford Site immobilized low-activity waste (ILAW) and solidified secondary wastes is disposal at the Integrated Disposal Facility (IDF) on the Hanford Site. Previous performance and risk assessments to evaluate any potential impact resulting from the disposal of various solidified LAW waste forms have shown that release rates from non-glass waste forms may not be sufficiently low over long durations to meet drinking water standards. Preliminary leaching experiments (up to 91 d duration) on Cast Stone monoliths containing different LAW and secondary waste simulants have provided promising Tc release rates,[26, 42] although the short term measurements do not account for any potential long term release of Tc due to exposure to the dissolved oxygen in vadose zone pore water and susceptibility of Tc(IV) species to reoxidation.[43] Therefore an opportunity exists for improved retention of Tc within cementitious waste forms. One possibility for improving the long term retention of radionuclides in cementitious waste forms is through the incorporation of “getters”, such as Sn-A, into the waste form formulation. A getter would reduce Tc(VII) in the waste stream to Tc(IV), as shown in this work, prior to inclusion in the waste form, and then provide a stable matrix that would limit re-oxidation and release of Tc. Presence of Sn-A in such a waste form may also lower Tc leaching rates as the apatite of the Sn-A has an affinity for Tc, and can sorb any prematurely released Tc (as Tc(VII)O_4^-), and facilitate its reduction to an immobile Tc(IV) form. While a higher amount of Sn-A was required for significant Tc removal from the LAW simulant, such an increase would not significantly impact the composition of a cementitious waste form. If Sn-A

were to be added at a 10 g : 100 mL ratio to the LAW, this would only account for ~3 wt% of the total mass of the waste form, based on the 0.55 free water to dry mix recipe commonly used for Cast Stone.[26] Future work will expand on what is presented here, and include incorporation of Sn-A as a Tc-getter within Cast Stone in lab scale leach testing to further test its capability as a getter for Tc in terms of Tc desorption, long term stability and compatibility with Cast Stone.

5. CONCLUSIONS

Sn(II)-apatite (Sn-A) was investigated for the removal of Tc(VII) from aqueous environments. In DI water, high levels of Tc removal (> 99.99 %) were observed after 4 d contact with the Sn-A. Compared with SnCl₂ this higher removal is attributed to the presence of a solid interface on the Sn-A facilitating the reduction of Tc(VII) to Tc(VI). In LAW simulant, the Tc removal ability of the Sn-A was decreased due to the alkalinity of the LAW simulant and a preference for the reduction of Cr(VI) over Tc(VII) by the Sn-A. However, increasing the amount of Sn-A added to the LAW simulant led to appreciable amounts of Tc removal. Sn-A can thus be considered as a candidate Tc-getter to be included in cementitious waste form testing.

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TOC/Abstract Art

Captions

Table 1 – Composition of the three variants of the LAW simulant solution used in this study

Figure 1 – a) % Tc removed as a function of time by Sn-A and SnCl₂ in DIW at Tc $\approx$ 5ppm, 28 ppm and 56 ppm, b) comparison of Tc removal, in mol, based on the Sn content of the Sn-A and SnCl₂, in g, over time. The two materials were added at a 1 g: 100 mL solution ratio.

Figure 2 – a) SEM micrograph of the Sn-A following exposure at 56 ppm Tc in DIW and the corresponding XEDS spectra from the spots labelled b) I and c) II

Figure 3 – a) XANES spectrum collected from the Sn-A following exposure in 56 ppm Tc DIW with fit from c) and b) EXAFS spectrum collected from the Sn-A following exposure in DIW, and the resulting fit from data in d). The numbers in parentheses represent the standard deviations of the contribution of that component for the ending digit, p is the probability that improvement of the fit, when this standard is included, is due to random error. $S_o^2 = 0.9$ *fixed), $\Delta E = 4(1)$ eV for the fit

Figure 4 – a) % Tc removed as a function of time by Sn-A and SnCl₂ in LAW simulant at Tc $\approx$ 5ppm, 28 ppm and 56 ppm. b) comparison of Tc removal, in mol, based on the Sn content of the Sn-A and SnCl₂, in g, over time. The two materials were added at a 1 g: 100 mL solution ratio.

Figure 5 – a) SEM micrograph of the Sn-A getter following exposure at 56 ppm Tc in LAW simulant and the corresponding XEDS spectra from the spots labelled b) I and c) II.

Figure 6 – a) % removal values for Tc removal with Sn-A in LAW simulant with 53 ppm Tc and 1800 ppm Cr (black), LAW simulant No Cr with 53 ppm Tc and 0 ppm Cr (red), LAW NaNO₃/NaOH with 53 ppm Tc (green) and Cr removal from the LAW NaNO₃/NaOH with 28 ppm Cr (blue). b) Change in concentration for Tc and Cr following contact with Sn-A in “LAW simulant No Cr” spiked with Tc= 53 ppm and Cr = 28 ppm (equivalent to 0.5 mM each).

Figure 7 - Following placing 1 g of Sn-A in 100 mL of DIW at various pH (adjusted with NaOH) and LAW simulant a) change in concentration of Sn and P over exposure time and b) comparison of the release of Sn, P and Ca as a function of pH

Figure 8 – removal of Tc by Sn-A in LAW simulant in varying amounts of Sn-A added based on the reduction capacity of the Sn-A. The 7X Tc(VII) content and 1X Cr(VI) + 10X Tc(VII) content batch experiments used Sn-A with a reduction capacity of 1200 μ eq/g and the 3X Cr(VI) + 10X Tc(VII) experiment used Sn-A with a 3460 μ eq/g reduction capacity.

Compound	Amount (g/L)		
	LAW Simulant	LAW Simulant No Cr	LAW NaNO ₃ /NaOH
KNO ₃	5.17	5.17	0
NaCl	3.85	3.85	0
NaF	2.07	2.07	0
Na ₂ SO ₄	18.95	18.95	0
NaOH (50% sol'n)	347.81	347.81	347.81
Al(NO ₃) ₃ · 9 H ₂ O	179.54	179.54	0
Na ₃ PO ₄ · 12 H ₂ O	29.18	29.18	0
NaC ₂ H ₃ O ₂	4.91	4.91	0
Na ₂ CO ₃	45.33	45.33	0
NaCr ₂ O ₇ · 2 H ₂ O	4.96	0	0
NaNO ₂	60.80	60.80	0
NaNO ₃	88.70	88.70	88.70
Pb(NO ₃) ₂	0.13	0.13	0
Ni(NO ₃) ₂ · 6 H ₂ O	1.49	1.49	0
Cd(NO ₃) ₂ · 4 H ₂ O	0.08	0.08	0

Table 1

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8