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The Function of Sn(II)-Apatite as a [99]Tc Immobilizing Agent

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ABSTRACT. Technetium-99 is a radioactive contaminant of high concern at many global nuclear waste storage sites. At the Hanford Site, ^{99}Tc is a component of low-activity waste (LAW), which is highly caustic, has high ionic strength and high concentrations of chromate. Removal and immobilization of ^{99}Tc from LAW streams would greatly benefit the site remediation process. In the present study, we investigated the removal of ^{99}Tc from deionized water (DIW) and a LAW simulant by Tin(II) Apatite (Sn-A) and $SnCl_2$ through batch sorption testing and solid phase characterization. Sn-A showed higher levels of removal of Tc in both DI and LAW simulant compared with the $SnCl_2$. SEM/XEDS and X-ray adsorption spectroscopy (XAS) of Sn-A following batch experiments in DIW showed that TcO-4 is reduced to Tc(IV), on the Sn-A surface and with no incorporation into the lattice structure of Sn-A. The performance of Sn-A in the LAW simulant was lowered due to a combined effect of increased pH, which led to an increased dissolution of Sn from the Sn-A, and a preference for the reduction of Cr(VI) over Tc(VII).

INTRODUCTION Technetium-99 (^{99}Tc, $t_{1/2}$ = 213 000 a) is a radioactive contaminant of high concern at many global nuclear waste storage sites, [1-4] as evidenced by the ^{99}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 Hanford, which contains ^{99}Tc, to be solidified through vitrification at the Hanford Tank Waste Treatment and Immobilization Plant (WTP). However, there are limitations for the incorporation of ^{99}Tc in mid- to high-temperature immobilization processes due to the volatility of technetium compounds.[6] Additionally, ^{99}Tc has high environmental mobility in oxidizing subsurface environments when it exists in the anionic Tc(VII) form[7], pertechnetate (TcO_4^-). Thus, providing a suitable disposal matrix with a high chemical durability for wastes that contain and stabilize ^{99}Tc is imperative.

Pretreatment of waste streams to remove Tc is a potential initial process that can aid in managing the mobile radionuclide. Two removal pathways for ^{99}Tc from aqueous environments are prevalent: (1) ion exchange and (2) reduction of Tc(VII), as TcO_4^-, to a highly insoluble Tc(IV) species, mainly $TcO_2 \cdot xH_2O$ ($K_{sp} = 10^{-32}$)[8, 9]. The separated Tc can then be immobilized in a waste form where it can be safely disposed. Several candidate materials for the removal of ^{99}Tc from the aqueous phase, termed "getters", have been previously studied. The materials include minerals, organic compounds, inorganic compounds and redox active materials with varying levels of success in aqueous environments.[10-13] However, many of these studies were performed in deionized water (DIW), or in solutions with simple chemistry. A successful candidate getter for Tc immobilization needs to have two ideal characteristics: high sorption capacity and high selectivity for Tc. To effectively retain Tc, the getter needs low rates of Tc desorption, compatiblity with a final waste form, low cost, and long term stability.[11]

One technetium getter that has shown success in simulated groundwater, is Tin(II) Apatite (Sn-A), ideally $Sn_5(PO_4)_3(F,Cl,OH)$. [14, 15] The reductive capability of Sn-A arises from the presence of Sn^{2+} in the getter, which has a favorable reduction potential for Sn^{4+}/Sn^{2+} of 0.384 V[16] and can reduce Tc(VII) to Tc(IV) since the Tc(VII)/Tc(IV) standard reduction potential is 0.738 V.[15] Reduction of TcO_4^- by Sn(II) is used in pharmaceutical synthetic chemistry to reduce pertechnetate.[17] The second component, apatite (calcium phosphates), commonly existing with alkaline earth cations or in the hydroxyapatite form, has also been reported to have an affinity for the sorption of Tc-bearing species in studies of bone as the supporting anions in the apatite could be supplanted by TcO_4^-.[18, 19] 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.[20] Though it is understood that both the Sn^{2+} 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 getter for removal of aqueous TcO_4^- from a simulated LAW solution 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 (electron microscopy and X-ray adsorption spectroscopy). In addition, a second material, $SnCl_2$, is tested for comparison as its high solubility in water supplies a source of the Sn^{2+} reductant in solution in the absence of solids in the system, as is the case with Sn-A. The testing involved batch sorption experiments using Sn-A and $SnCl_2$ for Tc sequestration from solutions with high ionic strength containing competing redox sensitive elements as found in LAW. This work represents a novel venture to investigate the nature of the Sn-containing getters, Sn-A and $SnCl_2$, 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 ^{99}Tc, both necessary advancements required for the sustained use of atomic energy and safe disposal of nuclear wastes.

MATERIALS AND METHODS

Experimental Materials Two getter materials were utilized in this work: $SnCl_2$ (Sigma Aldrich) and Tin (II) Apatite (Sn-A)[$Sn_5(PO_4)_3(X)$,where X is a supporting anion (Cl, F, OH)]. The Sn-A was prepared by an outside laboratory following a previously reported method.[14, 21] Sn-A prepared with this synthetic method has been reported to be comprised of an apatite [$Ca_x(PO_4)_y(X)$] structure with substitution of Ca^{2+} by Sn^{2+} in the lattice.[22] The exact chemical content of the supplied getters was determined using microwave digestion and the moisture content was determined gravimetrically. The specific surface areas of the getters were determined using the N_2 adsorption/desorption Brunauer-Emmett-Teller (BET) method.[23] Further information on these methods is presented 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% and the specific surface areas of Sn-A and $SnCl_2$ were 104.8 m^2/g and 0.06 m^2/g respectively. From microwave digestion, 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 and supporting anions.

The performance of the getters was investigated in DIW Millipore ® water (18.2 MΩ-cm) and a LAW simulant (7.8 M Na Ave LAW simulant,[24] referred to as LAW simulant from here on) . The LAW simulant solution was based on the Hanford Tank Waste Operations Simulator (HTWOS) model.[25] Additional variants of this simulant were made to examine the effects of various solution components on Tc removal. The composition of the LAW simulant

solution is presented in Table 1 (note: there are mistakes in Table 1. The compound and waste constituent columns do not agree). It must be noted that undissolved solids remained following completion of solution preparation. For experiments conducted in the absence of Cr, $Na_2Cr_2O_7 \cdot 2 H_2O$ was not added. A simplified LAW simulant was also used in the batch tests; it contained only $NaNO_3$ and $NaOH$ in the amounts listed in Table 1.

Batch Testing The effectiveness of the getters was investigated with duplicate batch sorption experiments, with the baseline concentrations of Tc and other species measured from identical solutions without any getter added. The experiments were contained within 250 mL polytetrafluoroethylene bottles at room temperature, ~ 22 °C, in an anaerobic chamber with O_2 levels below 5 ppm. 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 $NaTcO_4$ (> 10 000 ppm) to achieve Tc concentrations of 1×, 5× and 10× the level predicted by HTWOS (5 ppm). 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 analysis by inductively coupled plasma mass spectroscopy (ICP-MS). A summary of batch experiments performed can be found in Table 2.

Getter Characterization Following contact experiments any remaining solid phase in solution 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 5 keV, and elemental levels determined with energy dispersive x-ray spectroscopy (XEDS). Further characterization was performed using X-ray absorption spectroscopy (XAS) obtained at the Stanford Synchrotron Radiation Lightsource. Details on the XAS measurements are included in the supplemental information.

RESULTS AND DISCUSSION The performance of the getters in DIW and LAW simulant

during the batch experiments was quantified using distribution coefficients, K_d (mL/g),

calculated with the following equation:

$$K_d = \frac{c_{i,blank} - c_i}{c_i} \times \frac{V_s}{m_g}$$ Eq. 1

Where $c_{i,blank}$ is the concentration of the species, i, in the blank solution with no getter present in

µg/L, c_i is the concentration of the species at a specific interval in µg/L, V_s is the volume of

solution in mL, which is corrected to account for the removal of 2 mL aliquots collected at each

sampling interval, and m_g is the mass of the getter added to solution in g adjusted for moisture

content.

Getter Performance in DIW

Figure 1 displays the averaged log K_d values for the Sn-A and SnCl$_2$ 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 SnCl$_2$ in terms of Tc removal in DIW despite the fact that Sn-A contains

significantly less Sn than does SnCl$_2$. The SnCl$_2$, which completely dissolved in solution, was

observed to have log K_d values near 3 mL/g with little change after two days of exposure. In

general, the Sn-A had a slow increase in log K_d over the first six days before leveling off at ~ 6.5

for 5 ppm$_{init}$ [15], 6.9 for 28 ppm$_{init}$ [15] and 7.5 for 56 ppm$_{init}$.[15] This is a 3 – 4 orders of magnitude

improvement over SnCl$_2$, which showed log K_d values near 3.5 for all three initial concentrations

of Tc. After 35 days of exposure, all of the Sn-A systems attained a log K_d of 7.0. This behaviour

suggests that the solid surface provided by the Sn-A participated in the removal of Tc. This can

be through faciliting electron transfer or helping bring the Tc in close proximity to the reductant

through a sorption process. This is also higher performance than other getter materials
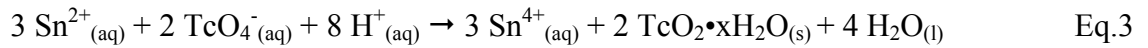
previously tested.[26]

A marginal difference in the performance of the getters was observed when adjusted for surface area (Figure S1). A more likely influence is the amount of reductant, Sn^{2+}, present in the getter as reduction of Tc is the most effective route of getter immobilization. Figure 3 presents a comparison between the two materials (i.e., Sn-A and $SnCl_2$) corrected for Sn content, using the natural amount of 62.8 wt% in $SnCl_2$ and 23.5 wt% for Sn-A. The original distribution coefficients were presented in terms of the total mass of getter, i.e. 1.0 g. Correction of the distribution coefficients for Sn content, K_{d-Sn} replaced the mass of the getter with the mass of Sn, m_{Sn}, added in the following equation:

$$K_{d-Sn} = \frac{(C_{blank} - C_{sol'n})}{C_{sol'n}} \times \frac{V_{mL}}{m_{Sn}} \qquad \text{Eq. 2}$$

Figure 2 shows the Sn-A performed much better for Tc removal than $SnCl_2$, despite its relative lower Sn content. Initially, up to one day, the two getters had similar log K_d of ~ 3 mL/g. As time progressed, the Sn-A continued to remove Tc reaching log K_d values of 6.8 in 5 ppm Tc and 8.2 in 56 ppm Tc.
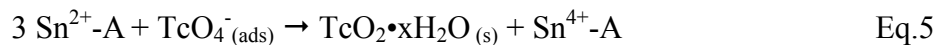
The mechanism of removal via $SnCl_2$ is likely an aqeous phase reduction:

$$3\ Sn^{2+}_{(aq)} + 2\ TcO_4^-{}_{(aq)} + 8\ H^+_{(aq)} \rightarrow 3\ Sn^{4+}_{(aq)} + 2\ TcO_2{\cdot}xH_2O_{(s)} + 4\ H_2O_{(l)} \qquad \text{Eq.3}$$

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

$$TcO_4^-{}_{(aq)} + Sn\text{-}A_{(s)} \rightarrow TcO_4^-{}_{(ads)} + Sn\text{-}A \qquad \text{Eq.4}$$
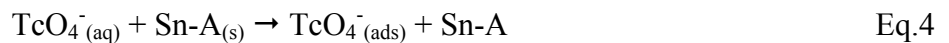
Followed by a subsequent reduction of Tc:

$$3\ Sn^{2+}\text{-}A + TcO_4^-{}_{(ads)} \rightarrow TcO_2{\cdot}xH_2O_{(s)} + Sn^{4+}\text{-}A \qquad \text{Eq.5}$$

The K_d values in Figures 1 and 2 are relative to the initial amount of Tc in solution. In order to investigate the kinetics for the removal mechanism, changes in rate of removal by the two getters is required. Treating each sampling interval as an individual experiment can provide

an approximation of the removal rate of Tc. In this case, the c_{blank} in Eq. 1 is replaced with the

concentration of Tc at the end of the previous interval. Figure 3 presents these individual

distribution coefficients, corrected for the duration of each interval, in mL/g/day. Figure 3 (a)

shows the behaviour of Sn-A at the three Tc concentrations. In the first day there was a small

decrease in K_d after which the removal rate increased in all three solutions reaching maximum

values at four days for 5 ppm Tc and 6 days for 28 ppm Tc and 56 ppm Tc. The rate of removal

then dropped becoming near zero for the remainder of the exposure. This is in contrast to the

$SnCl_2$ trend. Figure 3 (b) demonstrates this trend where initial high rates of removal were

observed followed by a sharp decrease occurring after one day. In the $SnCl_2$ system, all of the

Sn^{2+} in the getter was available for reduction of Tc, creating the rapid initial rate. However, as

time progressed little change was seen in the Tc removal rates and the getter activity had ceased.

Two reasons for this beahviour are plausible: 1) following the intial removal of Tc, the

lower amount of Tc in solution decreases the likelihood of a collision between Sn^{2+} and TcO_4^-

that is required to facilitate the electron transfer for the redox process,[27] or 2) Sn^{2+} slowly

oxidizes in the aqueous solution, thus limiting the amount of reductant in solution. [28] In Sn-A,

the fastest relative rates of removal occurred following a two day incubation period after which

the getter became more effective. As evidenced in Figure 1 an influence of the Sn-A solid

surface on the removal of Tc was present. This was likely caused by sorption of the TcO_4^- to the

apatite structure, where it could then be effectively reduced by the Sn^{2+}. Due to this trait, Sn-A

may be an effective long term getter as the apatite will be present in the waste form to sorb any

prematurely released Tc and facilitate its reduction in the presence of a reductant. (While this

may be effective if the Sn-A is in the grout, Sn-A will not be an effective long-term getter if used

as backfill. Atmospheric oxygen will oxidize the Sn(II) to Sn(IV). All reductive getters have the same problem – Wayne)

Characterization of Sn-A Following DIW Exposure

The solid Sn-A was removed from the 56 ppm Tc solution following the batch sorption experiment and used for solid state characterization. The 56 ppm Tc solution was chosen to ensure sufficient presence of Tc on the solid for analysis. Due to its solubility, no solids could be recovered from the $SnCl_2$ batch experiments. Figure 4 (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 4 (b) and 4 (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.

The XANES spectrum collected from the Sn-A sample is shown in Figure 5 (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 corrodinated 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 representative of a 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 Table 3, 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 envrionment of Tc in this arrangement. While the contribution from TcO_4^- is approximately 5% the high p value, 0.123, means that the TcO_4^- signal is not meaningful.

Above the x-ray adsorption edge, seen in Figure 5(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 5(b) and the corresponding fitting parameters in Table 4 Further information on the fitting method can be found elsewhere.[29] 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 $TcO_2 \cdot 2H_2O$, the Tc-O and Tc-Tc distances are similar to those of $TcO_2 \cdot 2H_2O$, which is consistent with a surface precipitate similar in strcuture to $TcO_2 \cdot xH_2O$. There was no evidence of Tc-Sn interactions or Tc-Ca interactions.,. The SEM and XAS analyses strongly suggest 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 getter 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 assay in the batch experiments.

Getter Performance in LAW Simulant

The averaged behaviour of the Sn-containing getters in the LAW simulant is shown in Figure 6. The performance of the two getters is lower in the LAW simulant. The Sn-A experienced a nearly six order of magnitude decrease in log K_d to < 1.5 mL/g compared with DIW, Figure 1. The $SnCl_2$ also had decreased performance in the LAW simulant with a log K_d less than 1. This decreased performance may be a result of interference with the getter by secondary ions in the LAW simulant. The two getters rely on the reducing capacity of Sn, and if other oxidants are present such as in the LAW simulant, they may be reduced in place of the

Tc(VII). As in the DI experiments, the solid surface of the Sn-A provided an improvement over SnCl$_2$ in the LAW simulant.

Following the batch experiments in the LAW simulant, the Sn-A was removed for further analysis to identify possible interferent species. The surface of the Sn-A can be seen in the SEM micrograph, Figure 7(a). The Sn-A surface appears to be covered in a smoother desposit than the Sn-A surface following exposure to DIW, Figure 4 (a). XEDS analysis of two spots, labeled (b) and (c), show high levels of Na from the solution, along with signals for Al and Cr from both spots. The Al likely is present from incomplete washing following the experiment, whereas the Cr 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). Cr(VI) is a stronger oxidant than Tc(VII) and was present in a much higher amount in the LAW simulant (1800 ppm Cr to 56 ppm Tc). This makes Cr likely to interfere with the ^{99}Tc reducing ability of the Sn-A, and leads to its deposition on the Sn-A surface.

Competition Between Cr and Tc

The hinderance of Tc reduction on Sn-A in the LAW simulant limits the effectiveness of the Tc getter and must be completely understood. Figure 8 compares log K$_d$ values from batch experiments with several altered compositons of the LAW simulant. Including a LAW simulant without Cr and a solution consisting solely of NaOH and NaNO$_3$,in the amounts listed in Table 1 containing either Tc or Cr (NaOH/NaNO$_3$+Tc and NaOH/NaNO$_3$+Cr). As discussed in the previous section, the lowest performance by Sn-A was in the removal of Tc in the LAW simulant, log K$_d$ ~1.2 mL/g (it says 1.5 ml/g above).. However, upon exposure of Sn-A to the LAW simulant without Cr, an order of magnitude increase in Tc removal was observed up to log

K_d 2.5, Figure 8. While smaller than the Tc removal seen in DIW, it is confirmation that CrO_4^{2-} interferes with the removal of Tc from the LAW simulant. In measurements of Tc removal from the NaOH/NaNO$_3$+Tc, log K_d values were similar to those in the LAW simulant without Cr. The similar Tc removal in the NaNO$_3$/NaOH +Tc solution and in the LAW simulant without Cr, suggestst that the high pH of the LAW simulant affects absorption of Tc by Sn-A. This results also suggests that the other metallic species (Al, Ni, Cd) and secondary ions in the LAW simulant solution have little effect on the removal of Tc.. For comparison, the removal of Cr from the NaNO$_3$/NaOH+Cr solution with an intial concentration of 23 ppm, equivalent on a molar basis to 56 ppm Tc, was also studied, and the results presented in Figure 8. The log K_d values for Cr removal by Sn-A were close to 4.0, which correspond to the detection limit for Cr by ICP-MS used in the study, showing a near complete removal of Cr. This result shows Sn-A to be effective in the removal of Cr at high pH, yet slightly hindered towards Tc removal. No changes in the levels of Cr can be measured in the LAW simulant due to the high intial Cr concentration (1800 ppm).

To investigate any potential affinity for Cr removal over Tc by Sn-A, an equimolar solution of Tc and Cr was prepared in DIW. The intial stages of removal were of interest, so sampling intervals were much shorter and the total experimental duration was three days. Initial concentrations of 53 ppm Tc and 28 ppm Cr were spiked in DIW (equivalent to 0.5 mM concentrations of each) containing Sn-A, and the resulting behaviour are shown in Figure 9. In the intial stages of contact (< 6 h) there was little difference in the removal of Cr and Tc from the DIW. 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. This

result confirms what was seen in the NaNO$_3$/NaOH environment with Cr being removed with a higher efficiency than Tc.

The high pH of the LAW simulant may also interfere with the Sn-A removal of Tc as increasing pH can alter the solubility of of the Sn-A structure. To investigate this potenital interference, 1.0 g of Sn-A was placed in 100 mL of solutions of pH 7, pH 10 and pH 13 and LAW simulant with and without Cr. Figure 10 (a) shows the measured release of three species (Sn, Ca and P) from ICP-MS. Results show there is litte 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 10 (b), which displays the average concentration of Sn, Ca and P at 48 h – 72 h at the different pH values. Sn was released in high amounts from the Sn-A as the pH is increased, 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 concentations could not be successfully measured in the LAW simulant 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 and its decrease in performance toward Tc removal at increasing pH.[21]

These findings give excellent insight into the capability of Sn-containing materials as potential getters for Tc sequestration through testing of a solid phase getter, Sn-A, and a getter which dissolved in solution, SnCl$_2$. After 72 h in DIW, SnCl$_2$ removed 89.3%, 92.5% and 93.7% of technetium from solutions with initial concentrations of of 5ppm, 28 ppm amd 53 ppm Tc, respectively. By providing a solid interface for the Tc to be reduced by Sn, Sn-A Tc removal was observed with 99.9 %, 99.5% and 99.5 % Tc removed at 72 h in the same solutions. An intial sorption step of the TcO$_4^-$ prior to the reduction is postulated as the cause of the improved

performance by the Sn-A, as at Tc(IV) surface precipitate was identified on the Sn-A surface following the experiment. This suggests that solid phase getters may hold an advantage over aqueous active species in neutral pH and weak ionic strength waste streams.

In the highly caustic, high ionic strength LAW simulant, both getters saw a decrease in performance, with Tc removal between 2.3 % and 11 % for the Sn-A and <5 % removal for the $SnCl_2$ at 72 h. In this shorter time frame (<72 h), relevant to processing in a treatment facility, some Tc was removed, although not as high as in DIW. Cr was found on the surface of the Sn-A following the experiment, and Sn-A was found to have increased dissolution of Sn in the LAW solution. Further investigations found that Tc could be removed by Sn-A more effectively in the absence of interfering species such as Cr (59.0% Tc removal at 48 h) and in simplified caustic simulants containing only NO_3^- and OH^- (78.5% at Tc removal at72 h). Interference by both Cr and high pH work against removal Tc by Sn-A in LAW environments. However, this should not eliminate Sn-A as a possible getter for Tc in such environments as some Tc can still be removed in the presence of Cr and at higher pH. A preferential removal of Cr does occur and this would need to be accounted for in preparation of the waste stream prior to solidification in the desired waste form. Higher amounts of getter (i.e., > 1 g : 100 mL solution ratio) would be required to reach higher Tc removal in LAW environments.

ENVIRONMENTAL IMPLICATIONS

[99]Tc is a component of concern in nuclear wastes due to its long half life, high mobility in subsurface environments, and challenges to its incropation in mid- to high temperature waste forms. Sequesternig ^{99}Tc from aqueous nuclear waste environments can be achieved by getters, which are solids that are capable of sorbing or reducing [99]Tc. Sn-A was found to have high sorption capacity, an ideal getter characteristic, for ^{99}Tc in neutral pH conditions. In a LAW

solution, simulating the tank waste present at the Hanford site, the sorption capacity of Sn-A was reduced. This decrease is hte result of the high alkalinity of the solution and competition with Cr^{6+} for the reduction of Tc, demonstrating limited efficiency of Sn-A for Tc. This issue can be overcome through increasing the getter mass to solution volume ratio in the application of Sn-A as a getter.

A possible application of Sn-A as a getter is in the fabrication of low temperature cementitious waste forms, (such as Cast Stone at the Hanford site and Saltstone at Savannah River site) [30, 31] The current end of life destination for immobilized low-activity waste (ILAW) and solidified secondary wastes is disposal at the Integrated Disposal Facility (IDF) at 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 Preliminary leaching experiments (up to 91 day duration) on Cast Stone monoliths containing different LAW and secondary waste simulants have provided promising ^{99}Tc release rates,[24, 32] although the short term measurements do not account for any potential long term release of ^{99}Tc due to exposure to the dissolved oxygen in vadose zone pore water and susceptibility of Tc(IV) species to reoxidation.[33] Therefore an opportunity exists for improved retention of ^{99}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. The getter would be able to reduce Tc(VII) in the waste stream to Tc(IV), as shown in this work, prior to inclusion in the waste form, then provide a stable matrix that would limit re-oxidation and release of Tc. 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.

Acknowledgement.

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