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Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

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Online publication date: 18 January 2011

To cite this Article Koivula, Risto and Harjula, Risto(2011) 'Selective Sorption of Technetium on Antimony-Doped Tin Dioxide', Separation Science and Technology, 46: 2, 315 – 320

To link to this Article: DOI: 10.1080/01496395.2010.506902

URL: <http://dx.doi.org/10.1080/01496395.2010.506902>

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Selective Sorption of Technetium on Antimony-Doped Tin Dioxide

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Glassy, nanocrystalline antimony-doped hydrous tin dioxide was alkali precipitated from acidic metal chloride solution. The material has good thermal stability and granular physical form that enables its use in a conventional column. The material shows excellent, almost quantitative, uptake properties for ^{99}Tc radionuclide. Its distribution coefficients (K_d values) for ^{99}Tc were typically over 1 000 000 (ml/g) in solutions of one molar ionic competition (at neutral pH) and the uptake remained high over a broad pH range (2–11). By comparison, conventional cation/anion resins yielded K_d values of less than 200. The Tc uptake mechanism of antimony-doped tin dioxide is most likely a sorption process that cannot be categorized as typical cation or anion exchange. Redox reactions between Tc and Sb were speculated as being the phenomenon. Thermal treatment increased the materials crystal size from amorphous to $\sim 15\text{ nm}$ and changes in the oxidation state of antimony from +3 to +5 occurred at temperatures above 400°C . Also, the material's Tc uptake properties were increased by the thermal treatment.

Keywords selective sorption; technetium; tin dioxide

INTRODUCTION

The use of inorganic materials for selective separations has become evermore abundant in the nuclear industry. The potential for savings in money and in radiation doses received by workers has been the major driving forces in their utilization, particularly in the nuclear industry. High selectivity combined with good radiation and thermal stabilities of inorganic sorption materials are key factors in nuclear separation processes. At the moment, several key radionuclides, such as ^{60}Co , ^{90}Sr , and ^{137}Cs -, are selectively separated from process and waste solution streams using inorganic materials at various nuclear power plants (1,2). The tendency of selective separation in the nuclear industry has been that after removing one important radionuclide the next most important radionuclide emerges that also has to be removed. After removing the previously

mentioned cationic key radionuclides, strong interest in removing other radioactive contaminants with positive, neutral, or even negative charges, such as ^{59}Fe , $^{110\text{m}}\text{Ag}$, $^{124,125}\text{Sb}$, and ^{99}Tc , has arisen in the nuclear industry. Currently, the commercially available inorganic sorption materials including zeolites, titanates, silicotitanates, and hexacyanoferrates are cation exchangers or adsorbents, which can efficiently remove cationic radioactive species. However, inorganic materials that are highly selective for anionic radionuclides have not been commercialized yet. Recently, particular interest in the removal of oxy-anionic species of antimony and technetium has grown substantially.

The isotope ^{99}Tc , and particularly in its heptavalent pertechnetate form (TcO_4^-), is one of the major substances in the management and disposal of nuclear waste. This is mainly due to its long half-life and high geochemical mobility. Solvent extraction and ion exchange are conventionally used for the separation of pertechnetate. However, the selectivity of those methods and the physical stability of the used materials are limited and thus alternative materials are sought. Large numbers of inorganic materials have been tested for their sorption properties for technetium but with little success (3,4). This is mainly due to the anionic form of the element (TcO_4^-) being found in non-reducing aqueous solutions and because inorganic anion exchange materials are quite rare and do not possess high selectivities. Nevertheless, some metal oxides have shown promising anion uptake properties including anionic technetium (5–8). Hydrous tin dioxide is one such sorption material and its basic ion exchange properties have been characterized (5,7,9–12). The transparency and semi-conductive properties of nano-crystalline antimony-substituted tin dioxide have attracted a great deal of interest as an electrochromic material. Due to this the structure of tin dioxide with varying percentages of antimony substitution has been examined extensively under different analytical methods and calculations (13–16). The somewhat ambiguous results of those studies show that even at 40 percent antimony substitution (metal percentage) the tin dioxide retains its original tetragonal, rutile (space group $\text{P4}_2/\text{mmn}$) structure

Received 1 March 2010; accepted 5 July 2010.

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and that antimony occupies the structure sites of tin in the crystal structure (16–18). Higher antimony substitution percentages are expected to precipitate a separate antimony oxide phase, resulting in a mixture of metal oxides. Moreover, the formation of antimony oxide monolayer on the surface of tin dioxide has been proposed when the doping percentage exceeds 5 percent (19).

We show in this study that antimony-doped tin dioxide has excellent selectivity for technetium, and due to its physical properties is suitable for separation processes.

MATERIALS AND METHODS

The antimony-doped tin dioxide was synthesized by alkali precipitation from an acidic metal chloride solution. A 350 g quantity of $\text{SnCl}_4 \times 5 \text{H}_2\text{O}$ was dissolved in 500 ml of 6 M HCl solution and mixed using a magnetic stirrer. Then a 3 g quantity of SbCl_3 was added and the solution was mixed for 30 minutes. The precipitation step was done by adding 25% NH_3 solution in a dropwise manner and in so doing the pH was raised to 2. Mixing was continued for 30 minutes after metal oxide precipitation. The precipitate was left to settle for 1 hour and then the clear supernatant was discharged. The precipitate was washed/mixed with de-ionized water and left to settle. This washing cycle was repeated until the settling of the precipitate became retarded and the supernatant maintained slightly turbid. The supernatant was discharged and the precipitate was dried at 70°C for 20 hours then ground to small particles (<149 μm). Sub samples of the material were heat treated at one of the following temperatures: 150, 200, 300, 400, 500, 600, or 700°C for 20 hours. The oven dried products (at 70°C) were characterized by X-ray methods. Powder X-ray diffraction (XRD) patterns were collected by a Phillips PW 1710 powder diffractometer (operating on 40 kV and 50 mA) with Cu K_α (1.54 Å) radiation. The crystalline size of the heat treated material was calculated using the Scherrer equation of the Phillips software.

Elemental analyses of the metals were carried out using an X-ray fluorescence (XRF) method and a Amptek 7 mm² Si(Li) XR-100CR detector and 500 mCi ²⁴¹Am excitation source. Solid samples were used for XRF-measurement in order to avoid possible errors from dissolving metal oxides of low solubility. A Hitachi S-4800 field emission scanning electron microscope with Oxford INCA 350 was used for energy dispersive X-ray (EDX) analysis. Thermogravimetric (TG) analysis of the materials was done with a Mettler Toledo TA8000 system equipped with a TGA 850 thermobalance.

Static batch experiments were used to evaluate the technetium uptake properties of the material. In the batch experiments, 20 mg of solid ion exchange material was equilibrated in 10 ml of test solution in a constant rotary mixer (50 rpm) for 24 hours at room temperature. The solid phase was then separated by centrifuging the vials at 3000 G for

10 minutes. Then 2 ml aliquots of the supernatant were pipetted and filtered through a 0.2 μm filter (I.C. Arcodisc, Gellman Sciences) for concentration measurements of technetium (β counting). The equilibrium pH of the remaining solution was measured.

The results from batch experiments are presented as distribution coefficients (K_d) that reveal how the element of interest is distributed between the initial sample solution and the solid material.

$$k_d = \frac{(A_i - A_{eq})}{(A_{eq})} * \frac{V}{m} \quad (1)$$

where A_i = the initial activity of technetium in the solution, A_{eq} = the activity of technetium in the solution at equilibrium, V = the volume of the solution, m = the mass of the solid material.

Radioactive ⁹⁹Tc (NH_4TcO_4 , Amersham) was used in distribution studies and the technetium's radioactivity was used for K_d calculations.

The isotope ⁹⁹Tc is a pure beta-emitting radionuclide with a β -energy of 293.7 keV, a liquid scintillation counter (Wallac 1217 BackBeta) was used to measure its activity.

The equilibrium Eh values were measured from an identical set of batch experiments that were carried out in a nitrogen atmosphere in which the oxygen content was lower than 2 ppm (Mbraun 150B-G-II glove box).

For reference, the ⁹⁹Tc sorption onto typical organic resins was studied in similar conditions. The macroporous organic ion exchangers were manufactured by Purolite International Ltd. Weak, carboxylic acid resin (C106) and strong, sulphonic acid resin (C145) were used in their sodium converted forms. Weak base, tertiary amine, resin (A105) and strong base, type 1 quaternary ammonium, resin (A500) were used in their chloride converted forms.

All reagents were of analytical grade. The radioactive ⁹⁹Tc was added to the test solutions at trace concentrations (1.6×10^{-8} M).

RESULTS AND DISCUSSIONS

Material Characterization

After a 20 h drying period at 70°C, the synthesized material had formed hard and glassy, yellow-brownish colored particles that changed color from yellow-brownish to green-blue and finally to deep blue between 400 and 500°C. The color change has been associated with changes in antimony oxidation states (16). The heat treatment increased the crystallinity of the material from amorphous to nanocrystalline (14.3 nm, calculated using Scherrer equation from peak (110)) and revealed a tetragonal ($\text{P4}_2/\text{mnm}$) structure, the same as that found in cassiterite mineral (SnO_2) (Fig. 1, Table 1).

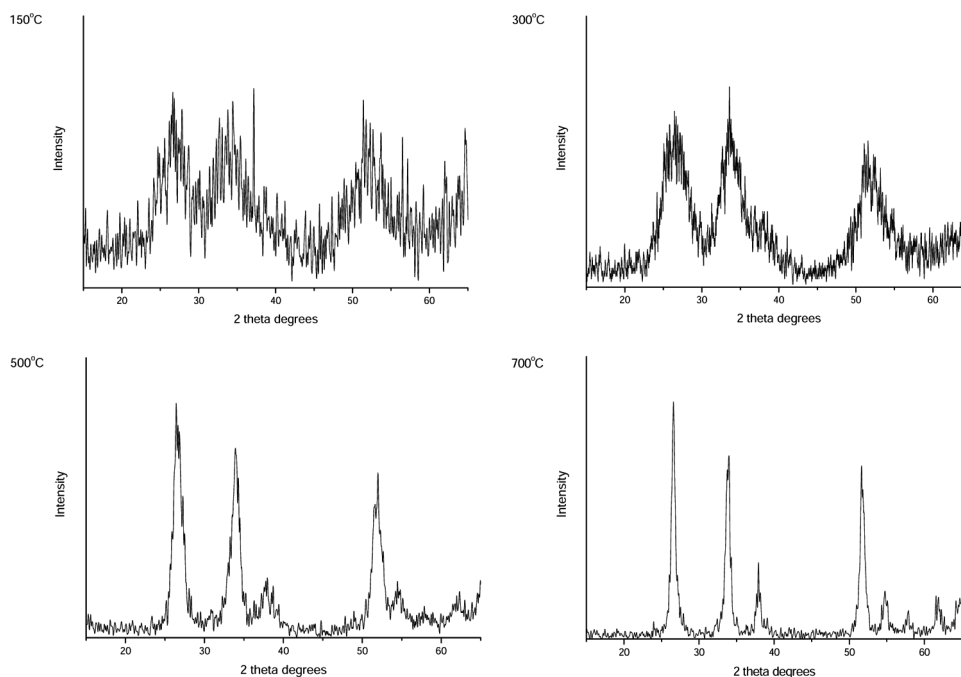


FIG. 1. XRD diffractograms of Sb-doped tin dioxide after temperature treatment in 150, 300, 500, and 700 °C.

Thermogravimetric analysis of the material showed a continual water release that is typical of hydrous tin dioxides (Fig. 2) (10,20). The XRF and EDX measurements of the synthesized material showed even distribution of the precursor metals with composition 97% and 3% of tin and antimony, respectively. The heat treatment did not affect the metallic composition of the material.

Technetium Uptake

The antimony-doped tin dioxide had excellent selectivity for ^{99}Tc both in nitrate- and chloride-containing solutions (Fig. 3). The K_d values from both of the competing salt solutions were high, and almost quantitative separation was achieved over a pH range of between 3 to 7.

For standard ion exchange processes the obtained Tc uptake curves as a function of pH (Fig. 3) could be taken as an indication of two different uptake mechanisms. First, the increase in K_d values from pH 2 to 4 resembles typical cation exchange of weakly acidic metal oxides. Second,

the slow decrease in K_d values over the 4 to 11 pH range resembles typical anion exchange of weakly basic metal oxides. Small changes occurred in ^{99}Tc uptake curves between the two different solutions, but the uptake trend itself is almost identical for both solutions. It is well known that tin dioxide, as a weakly acidic metal oxide, is an amphoteric material that typically has good cation exchange properties, but the materials anion exchange properties are rather limited (6,9,12). Considering the calculated speciation of Tc (Fig. 3), it might be argued that the uptake from the most acidic solutions was cationic in nature, but most likely the Tc was present as pertechnetate (TcO_4^-) in all the test solutions (21). However, the isoelectric point of tin dioxide is rather low in the area of 3.5 to 4, thus limiting the use of the material for anion exchange purposes in more acidic conditions (5,9). The equilibrium Eh of the test solutions containing tin dioxide varied between 500 and 700 mV.

The non-linear trend of K_d values plotted as a function of competing ion concentration reveals that Tc uptake is

TABLE 1

The effect of temperature on crystal size ($\bar{\phi}$, nm, calculated from (110) peak) and Tc-99 uptake; distribution coefficient (K_d , ml/g) from 1 M NaCl and equilibrium pH_{eq}

Temperature (°C)	70	150	300	500	700
($\bar{\phi}$, nm)	'amorphous'	<2	3.1	8.7	14.3
(log K_d , ml/g)	5.37 ± 3.52	6.11 ± 4.48	6.42 ± 4.68	6.47 ± 4.72	6.78 ± 5.0
pH_{eq}	2.0	2.3	2.4	3.4	3.8

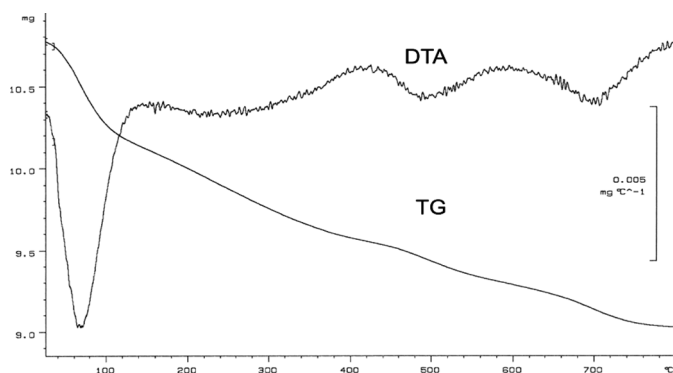


FIG. 2. Thermal analysis (TG = thermogravimetry, DTA – differential thermal analysis) of Sb-doped tin dioxide.

probably not pure ion exchange. It could be argued that by excluding the data from the most dilute solutions, a fairly linear fitting of the K_d data plot (Fig. 4) could be done. In that case, then the slope is close to 0.5 which would indicate an exchange of negative-divalent Tc into the tin dioxide—a highly unlikely scenario. The uptake trend and level of Tc from both anion solutions was similar and of the same magnitude. A finding that indicates the similarity of uptake processes even though the oxidizing characteristics of the two solutions are somewhat different.

The contradiction between the obtained results and known ion exchange properties of tin dioxide and Tc speciation suggests a Tc uptake mechanism other than that of ion exchange. The possibility of sorption of Tc as a neutral or even as a metallic species on surfaces must be considered due to the complex character of tin dioxide surface (22,23). Here the role of Sb and its different oxidation states and possible redox reactions at the material surface has to be considered as a probable reason for Tc uptake. Segregation of Sb^{3+} on the surface and diffusion of Sb^{5+}

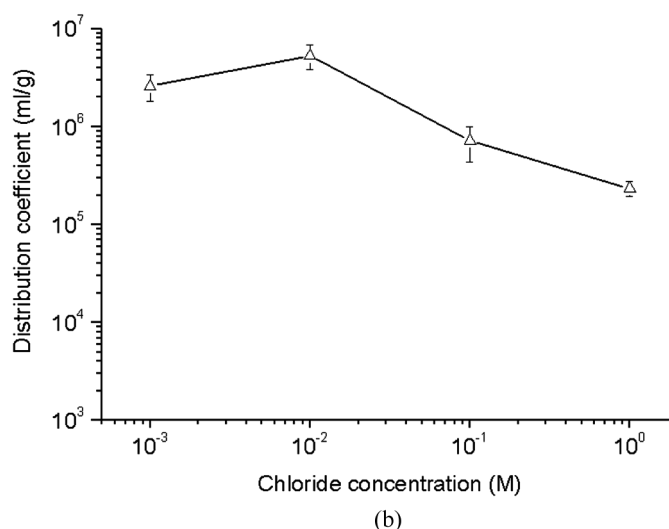
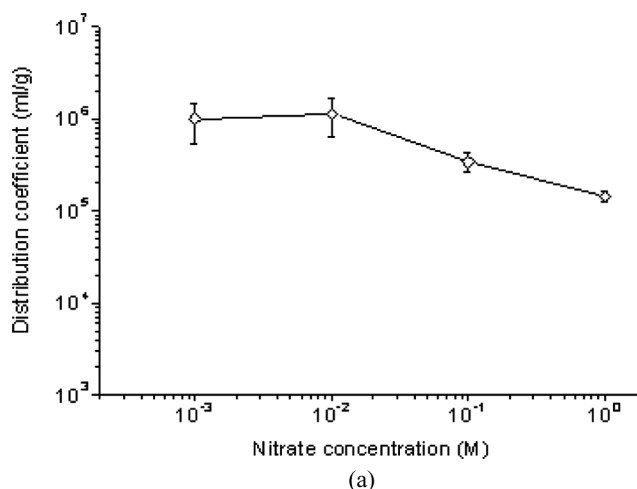


FIG. 4. Distribution coefficients (ml/g) for ^{99}Tc as a function of anion concentration from (a) nitrate solutions, and from (b) chloride solutions at equilibrium pH ~ 2 .

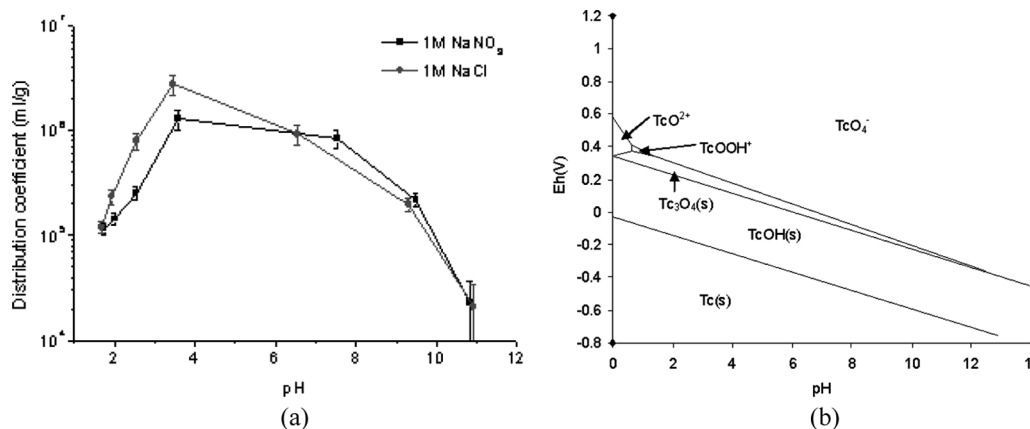


FIG. 3. (a) Technetium uptake on modified tin dioxide; distribution coefficients (ml/g) as function of pH from 1 M sodium nitrate (\square) and chloride (\circ) solutions, and (b) typical Eh-pH speciation diagram of technetium calculated using Lawrence Livermore National Laboratory's database (21).

TABLE 2

Distribution coefficients of Tc-99 for organic ion exchange resins from a solution mixture of 1M NaNO₃ and 0.001M HNO₃. The equilibrium pH of the solid/solution systems were 2.8

Cation exchangers		Anion exchangers	
Exchanger type	K _d (ml/g)	Exchanger type	K _d (ml/g)
Weak, carboxylic acid resin (Purolite, C106)	0	Weak base, tertiary amine, resin (Purolite, A105)	100 ± 3
Strong, sulphonic acid resin (Purolite, C145)	0	Strong base, type 1 quaternary ammonium, resin (Purolite A500)	190 ± 5

deeper into the lattice due to heat treatment are well known features of antimony doped tin dioxide material (19,24). The segregation of Sb³⁺ to the surface results into oxygen vacancies and reduction of Sn⁴⁺ to Sn²⁺ at the material surface (24,25). At these surface defect sites Sn²⁺ can act as particularly strong Lewis acids and so influence the Tc sorption (26). The other possibility is that SbO₂⁻ species (as remnant from the synthesis) are bound to the anion exchange site of the material (possible at pH below the materials isoelectric point). This scenario enables a spontaneous electrochemical reaction:



where Tc will precipitate to the materials surface. Considering the possible uptake processes of Tc one has to bear in mind that Tc is present at trace concentrations and so even atomic scale defects or properties may have strong influence on the uptake of Tc.

Heat Treatment

After precipitation and drying the material at 70°C, sub samples were heat treated at one of the following temperatures: 150, 200, 300, 400, 500, 600, or 700°C for 20 hours. The heat treatment increased the crystal size of the material from amorphous to ~15 nm, but it had only a little effect on the material's Tc uptake properties (Table 1). The high temperatures (>500°C) are sufficient to destroy any possible organic and precursor originated contaminants left from the material synthesis that might have been considered to have increased Tc uptake properties of the materials (27). Furthermore, it is known that the high temperatures will destroy most of the OH-groups of the material that represents the material's ion exchange sites (9). Surprisingly, the distribution values for Tc were constantly high, or perhaps even slightly higher with the higher heat treatment temperatures (Table 1). However, since the changes in Tc uptake were not so significant the observed increase in K_d values was associated with higher equilibrium pHs (Fig. 3) resulting from higher heat treatment temperatures (Table 1).

Organic Reference Material

Four macroporous organic ion exchangers (two cation and two anion exchanger) were tested along with the antimony-doped tin dioxide for comparison. The obtained K_d values from 1 M NaNO₃ at pH 2.8 were negligible for both of the cation exchangers. In contrast, the K_d values were 100 and 190 for the weak and strong base anion exchangers, respectively (Table 2). The negligible results for the cation exchangers can be explained by the anionic form of pertechnetate (TcO₄⁻, Fig. 3b). For the anion exchangers the K_d data arise from the low selectivities of normal ion exchange resins and high concentrations of competing anions (1.001 M NO₃⁻). The difference between the two anion exchangers originated most likely from the lower capacity of weak base resin. These findings underline the extreme effectiveness of the Sb-doped SnO₂ material but also verify that the Tc was in an anionic form in the test solutions.

CONCLUSIONS

Simple alkali precipitation of acidic tin and antimony chloride solutions produced uniform antimony-doped tin dioxide that has suitable physical and chemical properties for radioactive waste solution treatment. The material's granular physical form is seen as highly advantageous considering its use in conventional column separations. The material has high thermal stability and the heat treatment (up to 700°C) did not have an adverse effect on the material's technetium uptake properties. In addition, the element composition was not affected by the heat treatment. However, changes in the oxidation state of the antimony dopant may have occurred from +3 to +5, which was observed as a color change above 400°C.

An almost quantitative removal of Tc from solutions of high concentration of competing ions was observed. Based on the findings in this study, the uptake of technetium on the antimony-doped tin dioxide is most likely a sorption process that cannot be considered as typical cation or anion exchange process. The exact technetium uptake process of the material is not fully understood. This is due to the somewhat perplexing technetium uptake

occurring as a function of pH and as a function of competing anion concentration. The Tc uptake curve as a function of pH supports the ion exchange mechanism, even though the uptake level was considerably higher than expected based on reported values in the literature. However, at pH above 3.5, the material surface should have been negative (anionic) thus would exclude ion exchange uptake of TcO_4^- . At lower pHs some of the Tc will be cationic and so exchangeable at the cation exchange sites. The most important finding against the ion exchange uptake mechanism was that Tc uptake still occurred after heat treatment at which time the loss of OH groups should have actually diminished Tc uptake. However, such a reduction was not observed, on the contrary the Tc uptake slightly increased as a result of higher temperatures.

Although the extremely high distribution coefficients obtained in this study predict successful technetium separation, a broad range of general ion exchange and more detailed sorption studies on materials are required before this approach can be considered for practical application. In particular the role of antimony and its possible different oxidation states and its effects on the material surface has to be studied in detail. Here synchrotron based spectroscopy, such as X-ray absorption fine structure (EXAFS), that would give appropriate information on the oxidation states of Tc and also Sn and Sb. Moreover, the chemical stability and leaching mobility of antimony should be investigated particularly, if redox processes take place during Tc uptake.

Consequently, more selectivity experiments, simulants, and real waste solutions, should be performed in order to demonstrate the readiness of antimony-doped tin dioxide for commercial application. The possibility to reuse the material in an "ion exchange cycle" or to use it as matrix material for final disposal of technetium should then be considered and properly tested.

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