

Selective Sorption of Technetium-99 on Modified Tin Dioxide

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ABSTRACT

A novel tin dioxide shows excellent, almost quantitative, uptake properties for technetium-99. Its distribution coefficients (K_d values) for technetium are typically over 1 000 000 in solutions near neutral pH in one molar ionic competition, and uptake remains high over a broad pH region: pH 2–11. By comparison, normal organic resins yield K_d values less than 200. The variation in technetium uptake as a function of pH indicates two types of uptake mechanisms: acidic solutions (pH 2–4) show an uptake trend typical for weakly acidic cation exchange, and near neutral to basic solutions (pH 4–11) show an uptake trend typical for weakly basic anion exchange. Here, the possible uptake mechanisms by ion exchange process are discussed, and proposals are made for elucidating the exact sorption process.

INTRODUCTION

Technetium-99, and particularly its heptavalent pertechnetate form (TcO_4^-), is one of the major problems in the management and disposal of nuclear waste in view of its long half-life and high geochemical mobility. Solvent extraction and ion exchange are normally used for the separation of pertechnetate, but usually the selectivity of those methods and the physical stability of the materials are limited and new materials for technetium separation are sought after. High selectivity and good radiation and thermal stabilities are usually associated with inorganic sorption materials. Such materials are increasingly used for the removal of key radionuclides such as Co-60, Sr-90 and Cs-137 from nuclear waste effluents [1,2]. The materials that are commercially available (e.g. zeolites, titanates, silicotitanates, hexacyanoferrates) are cation exchangers or adsorbents, which can remove efficiently cationic and neutral radioactive species. Large numbers of inorganic materials have been tested for their sorption properties for technetium with little success [3-4]. This is mainly due to the anionic form of the element (TcO_4^-) in non-reducing aqueous solutions and because inorganic anion exchange materials are quite rare and do not possess high selectivity. However, some metal oxides have shown promising anion uptake properties including anionic technetium [4-8]. We show here that slightly modified tin dioxide can have excellent selectivity towards technetium, and due to its suitable physical properties for separation processes we also present sorption studies on the material.

MATERIALS AND METHODS

The tin dioxide was synthesized by alkali precipitation from acidic tin tetrachloride solution with propriety additives. The precipitate was washed free from synthesis solution and dried at 70°C for 12 hours. X-ray diffraction patterns were collected with a Philips PW 1710 powder diffractometer (operating at 30 kV and 50 mA, Cu $K\alpha$, 1.54 Å radiation) and the material was

characterized as nanocrystalline tin dioxide. A sub sample of the material was annealed at 700°C for 20 hours that increased the crystallinity of the material from ~5 to ~200 nm and more detailed characterization of the material could be done. The crystal size of the material was calculated using the Scherrer equation of the Phillips software.

Static batch experiments were used to evaluate the metal uptake properties of the material. In 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 during which time the solid/solution system reached equilibrium. The solid phase was then separated by centrifuging the vials for 10 minutes at 3000 G, and 2 ml aliquots of the supernatant were pipetted and filtered through a 0.2 µm filter (I.C. Arcodisc, Gellman Sciences) for measurements of technetium concentration by liquid scintillation counting (Wallac 1217 RackBeta). The equilibrium pH was measured from the remaining solution. 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 after 1 day equilibration time. It was calculated as follows:

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

The selectivity of the material toward technetium was tested against the most common anions: chloride and nitrate. The effect of concentration of competing anions and pH was investigated with sodium nitrate and chloride solutions that were spiked with Tc-99.

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

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. Radioactive tracer Tc-99 (β^- , 293.7 keV) was added to the test solutions at trace concentrations.

RESULTS AND DISCUSSIONS

The uptake of Tc-99 on modified tin dioxide was superb from slightly acidic to neutral pH solutions: the supernatant beta activities were typically close to the detection limits of the scintillation counter thus indicating extremely high distribution coefficients (K_d values, ml/g), values exceeding 10^6 .

Four macroporous organic ion exchangers were tested along with the modified tin dioxide for comparison (Table 1). Two cation exchangers, weak acid resin (C106) and strong acid resin (C145), and two anion exchangers, weak base resin (A105) and strong base resin (A500), were tested for their Tc-99 uptake properties in a solution of 1M NaNO₃ and 0.001M HNO₃. The obtained K_d values for 1M NaNO₃ at pH 2.8 were negligible for both of the cation exchangers and 100 and 190 for the weak and strong base anion exchangers, respectively. These results for the cation exchangers can be explained by anionic form of pertechnetate (TcO₄⁻), and for the

anion exchangers by low selectivities of normal ion exchange resins. The difference between the two anion exchangers originated most likely from the lower capacity of weak base resin.

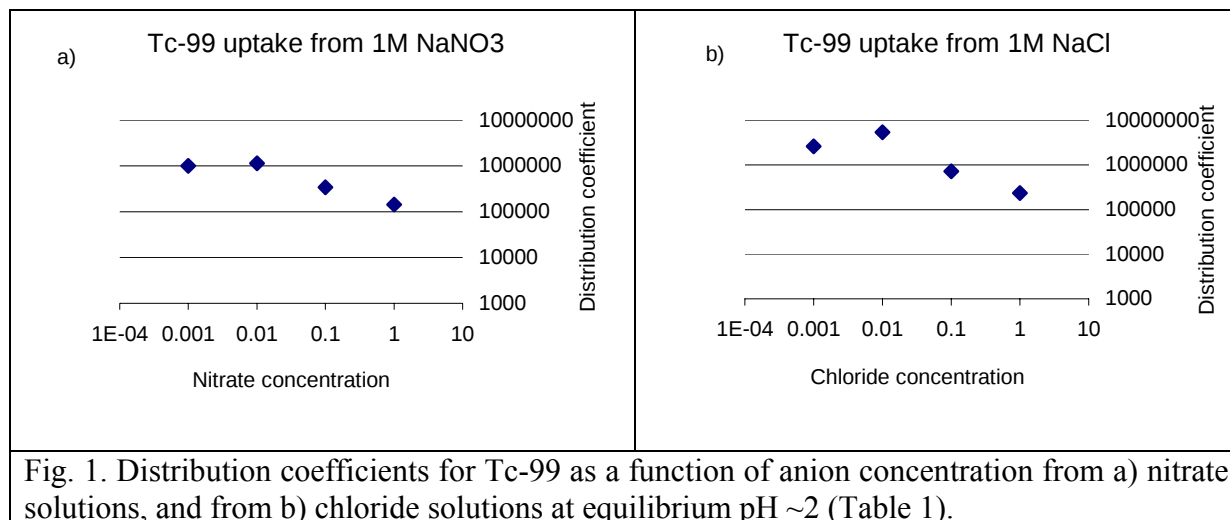
Table 1. K_d values of organic ion exchange resins for Tc-99 from a solution of 1M NaNO_3 and 0.001M HNO_3 . The equilibrium pH of the solid/solution systems were 2.8.

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

As stated above, the modified tin dioxide showed excellent selectivity for Tc-99 both in nitrate- and chloride-bearing solutions (Table 2). The K_d values from the both competing anion solutions were high, and almost quantitative separation was achieved from more dilute solutions. Comparing these values to those of organic ion exchangers that are presently used to separate Tc, the extreme selectivity and the possibilities of inorganic materials become evident. The non-linear trend of K_d experimental values plotted as a function anion concentration reveal that Tc uptake is probably not pure ion exchange (Fig. 1). The slope of a linear fitting to the data would have indicated what kind of ion exchange process has taken place, for example in the case of uni-uni ion exchange the slope is 1. It could be argued that by excluding the data from the most dilute solutions, a fairly linear fitting of the K_d experiment points (Fig. 1) could be done. In that case the slope is close to 0.5 indicating exchange of negative-divalent technetium into the tin dioxide — a highly unlikely scenario.

Table 2. Distribution coefficients of modified tin dioxide for Tc-99 from sodium nitrate and from sodium chloride solutions. The equilibrium pH of the batch experiments was approximately 2.

NaNO_3	K_d (^{99}Tc , ml/g)	NaCl	K_d (^{99}Tc , ml/g)
0.001 M	1 003 750 $\pm$ 47 650	0.001 M	2 606 500 $\pm$ 147 950
0.01 M	1 140 550 $\pm$ 54 950	0.01 M	5 303 650 $\pm$ 330 550
0.1 M	340 480 $\pm$ 8 100	0.1 M	716 700 $\pm$ 28 350
1M	144 150 $\pm$ 1 800	1M	234 050 $\pm$ 4 100



The separation level for Tc from both anion solutions was of the same magnitude that indicates the same sort of uptake processes even though the oxidizing characters of the two solutions are somewhat different.

The Tc uptake curves as a function of pH (Fig. 2) indicate 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 from pH 4 to 11 is typical for anion exchange of weakly basic metal oxides. Small changes can be seen in Tc-99 uptake curves between the two different competing anions, chloride and nitrate, but the uptake trend itself is almost identical in both solutions. It is well known that tin dioxide, as a weakly acidic metal oxide, can have some cation exchange properties, but its anion exchange properties are rather limited. Considering the calculated speciation of Tc (Fig. 2) [9], uptake from the most acidic solutions might be argued as cation uptake, but generally the Tc was present as pertechnetate (TcO_4^-) in all test solutions. Typically, the equilibrium Eh of the test solutions containing tin dioxide varied between 500 and 700 mV. Also the results from organic resins indicate that the form of Tc was completely anionic at pH 2.8 since no uptake by cation exchangers was observed. However, the point of zero charge (i.e. the pH above which the OH groups of the metal oxide are deprotonated and anion exchange cannot occur on a negatively charged surface) of tin dioxide is rather high, in the area of pH 3.5 to 4, thus limiting the use of the material for anion exchange purposes in more alkaline conditions. The contradiction between the obtained results and known ion exchange properties of metal oxides suggests a Tc uptake mechanism other than ion exchange. The possibility of sorption of Tc as a neutral or even as a metallic species on the surfaces must be considered due to its complex character of the surface of tin dioxide [10-11].

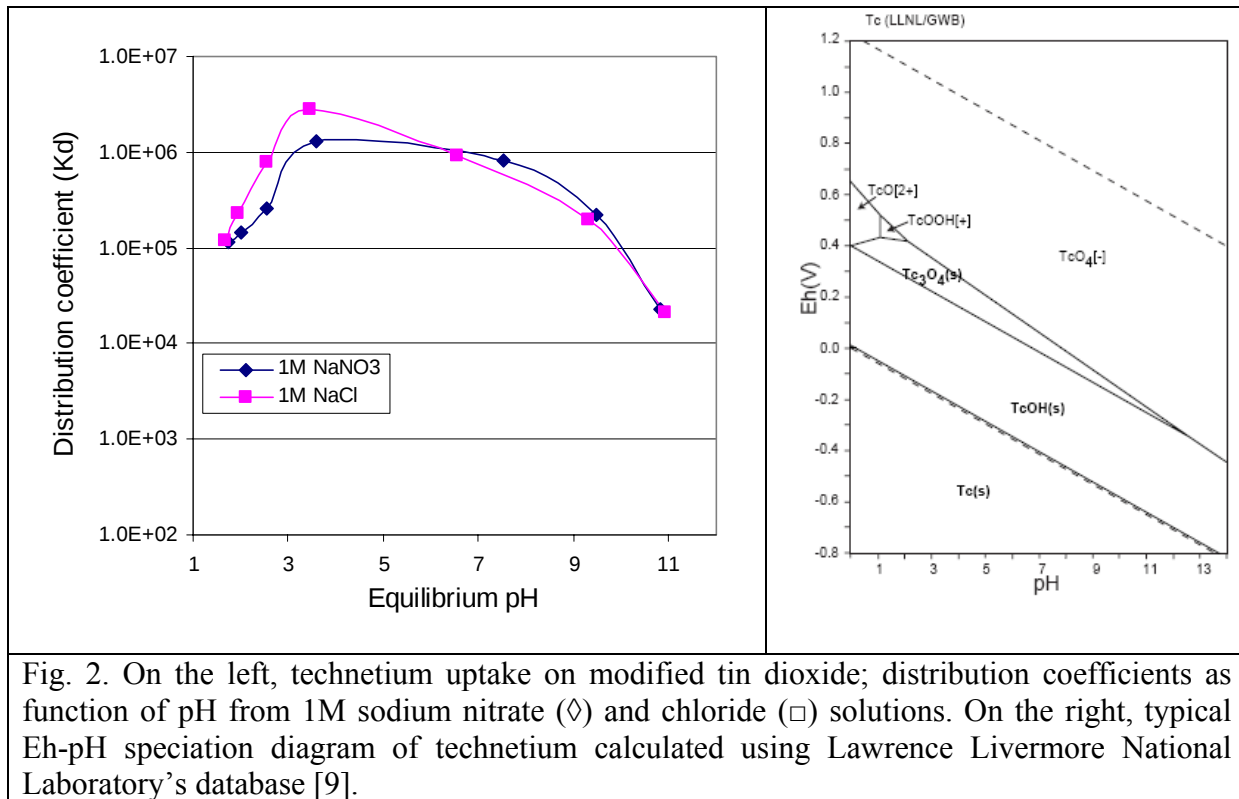


Fig. 2. On the left, technetium uptake on modified tin dioxide; distribution coefficients as function of pH from 1M sodium nitrate ($\diamond$) and chloride ($\square$) solutions. On the right, typical Eh-pH speciation diagram of technetium calculated using Lawrence Livermore National Laboratory's database [9].

Annealing the material at 700°C increased the crystal size of the material from ~5 to ~200 nm but had only a little effect on Tc uptake properties (Fig. 3). The XRD pattern of the annealed sample is consistent with the tetragonal structure (space group $P4_2/mnm$) of cassiterite (SnO_2). The high temperature (700°C) is sufficient to destroy most of the possible organic and precursor originated contaminants left from the material synthesis that might have increased Tc uptake properties. Log K_d values increased only slightly from 6.44 ($\text{pH}_{\text{eq}} 3.5$) to 6.57 ($\text{pH}_{\text{eq}} 3.8$) from 1M NaCl due to annealing of the material. This increase can also be result of higher equilibrium pH of the annealed material (Fig.2).

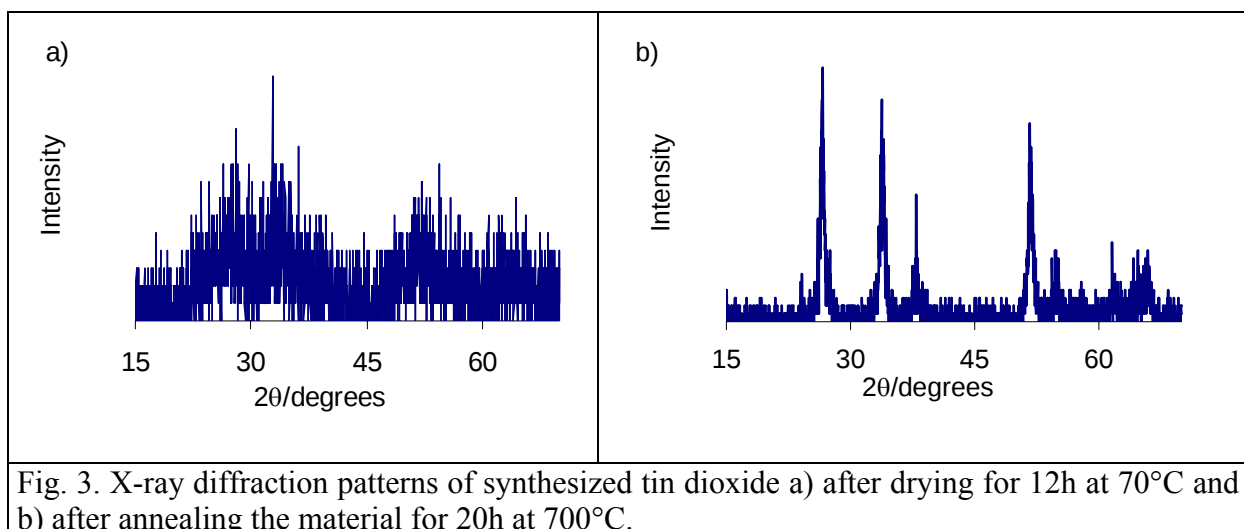


Fig. 3. X-ray diffraction patterns of synthesized tin dioxide a) after drying for 12h at 70°C and b) after annealing the material for 20h at 700°C.

CONCLUSIONS

On the basis of good preliminary technetium uptake tests, the modified tin dioxide is considered a potential material for selective technetium separation applications. The material has good physical properties for radioactive waste treatment and it can be made as granulates for traditional column use. Although the obtained extremely high distribution coefficients predict successful technetium separation, a broad range of general ion exchange and more detailed sorption studies on materials have to be done. Due to the perplexing technetium uptake curve as a function of pH and competing anion concentration the exact technetium uptake process of modified tin dioxide is not fully understood. Based on the findings in this study, the uptake of technetium on the modified tin dioxide is a sorption process that cannot be identified as typical cation or anion exchange. In this case the identification of exact sorption process goes beyond normal ion exchange experiments and more powerful structure characterization techniques such as extended X-ray absorption fine structure (EXAFS) could be useful.

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

REFERENCES

1. Harjula, R. and Lehto, J., *Radiochim. Acta*, 86, 1999, 65. (Selective Separation of Radionuclides from Nuclear Waste Solutions with Inorganic Ion Exchangers)
2. Harjula, R., Paajanen, A., Lehto, J., Tusa, E., Smith, R. and Standring, P., *Proceedings of Waste Management 2004 Conference*, February 29- March 4, 2004, Tucson, AZ., (Additional Testing Of CoTreat Inorganic Ion Exchange Media For The Removal Of Co-60 From Thorp Pond Water)
3. Dyer, A. and Jamil, M., in: M. Streat (Ed.), *Ion Exchange for Industry*, Ellis Horwood, 1988, 494.
4. Dyer, A., and Jamil, M., in: M.J. Slater (Ed.), *Ion Exchange Advances*, Elsevier Applied Science, London and New York, 1992, 350.
5. Jaffrezic-Renault, N., *J. inorg. nucl. Chem.*, 40, 1978, 539. (Ion-Exchange Properties of Weakly Hydrated, Crystalline Tin Dioxide)
6. El-Naggar, I. M., Shabana, R.I and El-Dessouky, M.I., *Talanta*, 39, 1992, 653. (Ion Exchange Behaviour of Hydrated Tin Oxide: Kinetics of Anion Exchange)
7. Harjula, R., Myllymaa, H. and Koivula, R., *Proceeding of Waste Managements 2005 Conference*, February 27- March 3, 2005, Tucson, AZ, (Removal of antimony-125 from simulated liquid radwaste by novel adsorbents)
8. Harjula, R., Koivula, R. and Paajanen, A., *Proceeding of Waste Managements 2006 Conference*, February 26- March 2, 2005, Tucson, AZ, (Removal of Sb-125 and Tc-99 from Liquid Radwaste By Novel Adsorbents)
9. Atlas of Eh-pH diagrams, Intercomparison of thermodynamic databases, Geological Survey of Japan Open File Report No. 419, <http://www.gsj.jp/GDB/openfile/files/no0419/openfile419e.pdf>
10. Pulkkinen, U., Rantala, T.T., Rantala, T.S. and Lantto, V., *Journal of Molecular Catalysis A: Chemical*, 166, 2001, 15. (Kinetic Monte Carlo simulation of oxygen exchange of SnO₂ surface)

11. Kilc, C. and Zunger, A., Physical review letters, 88(9), 2002, 095501-1 (Origins of Coexistence of Conductivity and Transparency in SnO_2)