

⁶³Ni AND ⁵⁷Co UPTAKE FROM SIMULATED FLOOR DRAIN WATERS AND ACIDIC DECONTAMINATION SOLUTIONS ON TIN ANTIMONATES

R. Koivula, A. Paajanen, R. Harjula
Laboratory of Radiochemistry, Department of Chemistry
University of Helsinki
P.O.Box 55, FI-00014 Helsinki, Finland

ABSTRACT

High decontamination levels (DF over 1 000) were measured when tin antimonate of high Sn/Sb metal substitution was tested for nickel and cobalt uptake in dynamic column experiments. In these experiments large volumes, up to 18 000 bed volumes, of crude floor drain water simulate were decontaminated with respect to radioactive nickel (⁶³Ni) and cobalt (⁵⁷Co). The DF-level of nickel was observed to be higher when compared to cobalt, which is in contrast to earlier batch experiments. Considerable peptisation of one tin antimonate, pyrochlore-structured, was observed that will probably prevent their column use at decontamination processes. It was also demonstrated that tin antimonates can be used for actinide uptake: high distribution coefficients for plutonium and americium were measured, over 100,000 ml/g and 4,000,000 ml/g from acidic solutions, respectively.

INTRODUCTION

Decontamination of waste solutions from activated corrosion heavy metal elements such as ⁶⁰Co and ⁶³Ni is challenging with existent inorganic ion exchangers. These contaminants are becoming more relevant now that many nuclear reactors are approaching their licensed operation time and decommissioning will occur in the near future. Decommissioning produces large volumes of acidic waste solution that has to be dealt in accordance with increasingly strict waste effluent regulations. Suitable separation materials should have high tolerances for acidity and also against interfering ions, especially for calcium, since the above mentioned radionuclides are often present in floor drain waters after spills and maintenance work.

In this study we sought a material useful for the separation of activated corrosion products from the above-mentioned waste solutions, and in particular a material selective for nickel uptake. Although a considerable number of articles on the ion exchange properties of tin antimonates have been published, some important elements have gone almost unnoticed. The separation of activation/corrosion elements, e.g. Co, Ni and Fe, originating from nuclear power plants has attracted only minor attention in ion exchange research. Although some papers dealing with cobalt uptake on tin antimonates have appeared, studies on nickel uptake are almost non-existent. Only a few distribution coefficients have been reported for nickel, and merely as supplementary results of larger studies (1,2). Yet ⁶³Ni, with its reasonably long half-life (100 a), will be the major source of radioactivity from activation/corrosion products at about 20 years after shut down of nuclear reactors.

Tin-substituted antimony oxides and antimony-substituted tin oxides, commonly called tin antimonates, were chosen as separation material candidates in view of their good chemical and physical characteristics in ion exchange processes. Earlier, the ion exchange properties of tin antimonates have been mainly investigated as ion exchangers for fission nuclides, such as ^{137}Cs and ^{90}Sr and some actinides. In these experiments, tin antimonates showed good ion exchange properties, i.e. high selectivities for certain elements and relatively high ion exchange capacities (2 meq/g for Na^+). (2-5) In our earlier study an extensive series of tin antimonates with from 0 to 100% Sn/Sb substitution were tested for their ^{63}Ni and ^{57}Co uptake properties. The tin antimonates were be divided into three groups on the basis of structure: materials with pyrochlore structure (structure of antimony pentoxide), materials with rutile structure (structure of tin dioxide) and mixed metal oxides including both pyrochlore and rutile structures (Fig. 1.).(6) The progressive Sn for Sb substitution of the pyrochlore phase, based on the structure of crystalline antimony pentoxide, resulted in a slight distortion and opening of the tunnel structure of the material. This opening enables easier access inside the material where majority of the ion exchange sites of the material are located and higher metal uptake (7). In turn, the Sb for Sn substitution of the rutile phase, based on the structure of tin dioxide, acidified the material and lowered the point of zero charge of the material. The Sn/Sb substitution improved the metal uptake properties of tin antimonates, and high distribution coefficients for cobalt were measured: 600,000 and 650,000 ml/g in 0.1 M HNO_3 and 0.1 M $\text{Ca}(\text{NO}_3)_2$ solutions, respectively.

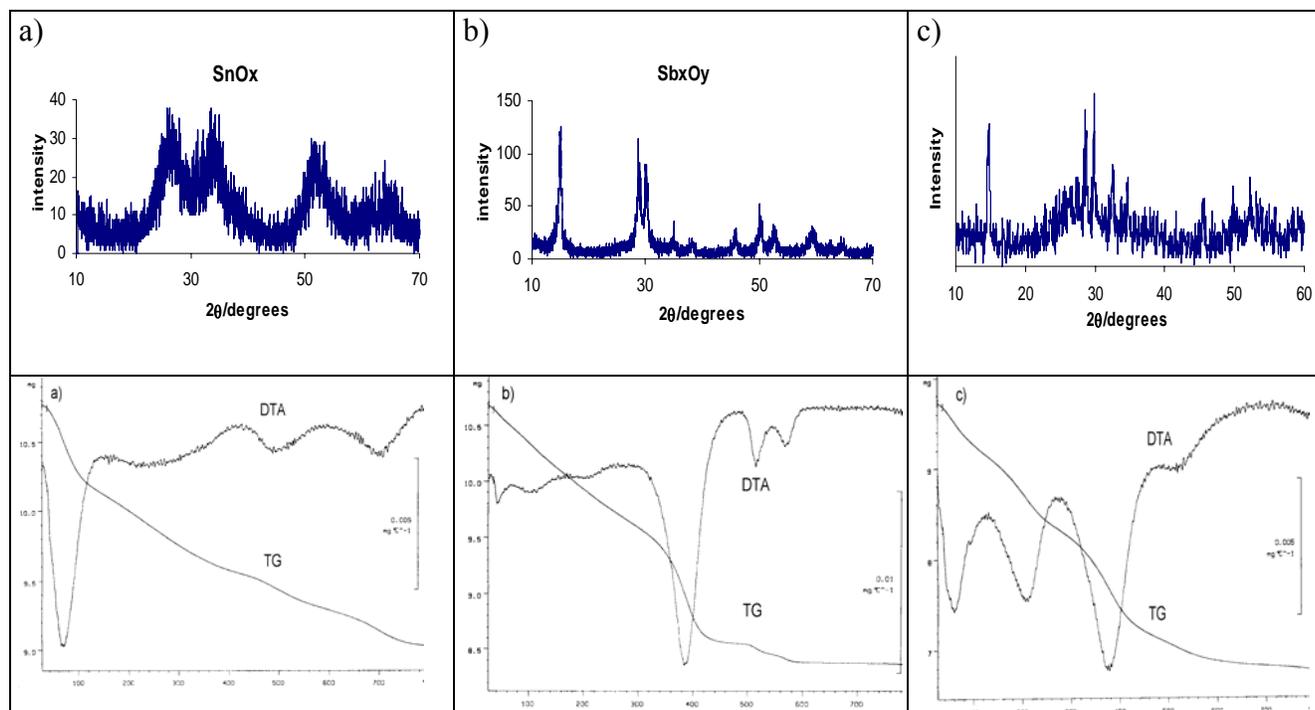


Fig. 1. Selection of typical XRD patterns of tin antimonates: a) pure tin dioxide, b) pure antimony pentoxide, c) tin antimonate with 38% Sn and 62% Sb (metal percentages) and their thermogravimetric curves, respectively. The TG curve represents the weight loss of the material and the DTA curve the endothermicity (downward) of the weight loss (temperature on the x-axis and mass of the material on the y-axis).

The focus of this study was on tin antimonates and their performance in ion exchange columns used for the decontamination of radioactive waste solutions. Unlike several other inorganic ion exchange materials tin antimonates can be prepared as granular material that permits their use in columns. Decontamination factors and ion exchange capacities for radioactive nickel and cobalt were of interest. Also the possibility to separate these two metals from each other was studied. Often the peptisation of inorganic ion exchange material in dilute solutions (well known for antimony pentoxides) diminishes the decontamination performance of the material, particularly in their column use, and was thus of special interest. Out of curiosity, the potential of the tin antimonates to take up trans uranium elements, such as plutonium and americium, was tested using simple batch experiments from acidic solutions.

MATERIALS AND METHODS

X-ray diffraction patterns were collected with a Philips PW 1710 powder diffractometer (Cu K α , 1.54 Å) and thermogravimetric (TG) analysis were performed using Mettler Toledo TA800, TGA 850 Thermobalance (10°C/min).

Both static batch experiments and dynamic column experiments were used to evaluate the metal uptake properties of the materials. 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 5 ml subsamples were pipetted and filtered through a 0.2 µm filter (I.C. Arcodisc, Gellman Sciences) for measurements of cobalt concentration (Wallac, 1480 Wizard 3" NaI gamma counter). Subsamples of 2 ml were taken for measurements of nickel concentration (Wallac 1217 BackBeta liquid scintillation counter). The equilibrium pH was measured from the remaining solution. 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 1d equilibration time. It was calculated as follows:

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

Column experiments were done in mini-columns (BioRad, Bio-Scale MT2 with radius of 3.5 mm and 28 µm bed support) where pumping the rate was set to approximately 30 bed volumes (BV) per hour.

Test solutions were crude simulants of real radioactive waste solutions. Nitric acid (0.1M HNO₃) was used to mimic acidic decontamination solution and calcium nitrate (0.01M Ca(NO₃)₂) was used to simulate a neutral bond water. Also a crude floor drain water (FDW1) simulant solution, containing 100, 0.7 and 1.5 ppm of Na⁺, Mg²⁺ and Ca²⁺, respectively, was used.

All reagents were of analytical grade. Radioactive tracers ⁶³Ni (β⁻, 67keV) and ⁵⁷Co (γ, 122 keV) were added to the test solutions at trace concentrations. For actinide experiments tracers ²³⁶Pu and ²⁴¹Am were used.

For peptisation experiments 1 kD ultrafilters (Filtron MicrosepTM, centrifugal concentrators) and 10 kD ultrafilters (Sartorius 10 kD polysulfone) were used and the radioactivities (metal concentrations) of the samples were measured before and after ultrafiltration.

RESULTS AND DISCUSSIONS

The synthesised tin antimonates had showed good uptake properties for activated corrosion products, and the Sb/Sn substitution of the materials had improved their metal uptake properties. K_d -values up to 7,000 and 600,000 ml/g for ^{63}Ni and ^{57}Co , respectively, in 0.1 M HNO_3 solution, and 3,000 and 650,000 ml/g in 0.1 M $\text{Ca}(\text{NO}_3)_2$ solution were measured in previous batch experiments (6,8).

Peptisation Experiments

The possible peptisation of pentoxide-structured tin antimonates was of concern before column experiments due to its diminishing effect on the decontamination performance of ion exchange columns and its effect on column clogging. The tendency for peptisation of pyrochlore-structured tin antimonates in dilute solutions (severe for pure antimony pentoxides) was investigated by ultrafiltration. Three tin antimonates with different structures, i.e. different Sn/Sb metal percentages, were tested against peptisation in dilute (0.001 M HCl) solution using 10 kD ultrafilters (Table I. (a)). It was evident that tin antimonate of pyrochlore structure (21% of Sn and 79% of Sb \rightarrow $(\text{SnSb}(\text{P}_2))$) suffered the most from peptisation whereas nickel uptake of other tin antimonates (mixed metal oxide structured, 46% Sn and 54% Sb \rightarrow $(\text{SnSb}(\text{A}_3))$) and rutile structured, Sn 93% and 7% Sb \rightarrow $(\text{SnSb}(\text{R}_3))$) was not affected by peptisation. Due to the surprisingly low nickel uptake of $\text{SnSb}(\text{P}_2)$ compared to other tin antimonates, the peptisation of $\text{SnSb}(\text{P}_2)$ was tested in hydrochloric acid series of different concentrations and also in pure water. Furthermore, the ultrafilters were changed to 1 k Dalton; The pore size of 1 kD filters was small enough to filter the peptisized tin antimonite. Relatively high K_d -values were observed (Table I. (b)), and the increase of K_d -values with increasing pH was almost linear (typical for ion exchange processes) indicating sufficient removal of peptisized material.

Table I. Peptisation experiments of tin antimonates; a) Distribution coefficients (K_d -values) of three different tin antimonates for ^{63}Ni in 0.001M HCl solution before and after 10 kD ultrafiltration, b) K_d -values of pyrochlore-structured tin antimonate ($\text{SnSb}(\text{P}_2)$) for ^{63}Ni in HCl solutions of different concentrations and pure water (18 M Ω) before and after 1 kD ultrafiltration.

Table I. (a) Solution 0.001 M HCl

SnSb(P ₂), K _d (ml/g)		SnSb(A ₃), K _d (ml/g)		SnSb(R ₃), K _d (ml/g)	
	10 kD		10 kD		10 kD
170±4	537±13	11 300±269	12 235±291	6 630±158	6 600±157

Table I. (b) Material SnSb(P₂)

1 M HCl		0.1 M HCl		0.01 M HCl		0.001 M HCl		water (18 M Ω)	
	1 kD		1 kD		1 kD		1 kD		1 kD
32±1	44±1	698±17	2 333±56	172±4	4 399±105	152±4	8 490±202	165±4	13 230±315

Column Experiments

On the basis of earlier batch and peptisation experiments, a tin antimonate with high Sn for Sb substitution and low crystallinity ($\text{SnSb}(\text{A}_3)$) was chosen for column experiments (6,8). Due to the open tunnel structure of this material it had high cobalt uptake properties in batch experiments but since those tunnels were also distorted (7) the uptake of cobalt in dynamic column experiments was not equally great. By contrast, the uptake of nickel was perplexingly high.

In calcium-bearing FDW1 solution the uptake of nickel was very high and good decontamination factors (DF) were observed (Fig. 2a). The column maintained high decontamination performance for approximately 10,000 bed volumes (BV) in which time the DF-level was maintained at close to 1,000. The decontamination performance of tin antimonate for cobalt was not as good and a DF-level of about 200 was observed. The different ion exchange sites of pyrochlore-structured materials may explain the high nickel uptake. There are two types of ion exchange sites in pyrochlore materials: on the external surfaces and in the internal tunnels and cavities. The latter are responsible for most of the ion exchange capacity of the materials (9,10). The high uptake of cobalt in batch experiments may be associated with ion exchange inside the material due to the slightly smaller hydration radius and lower hydration cell enthalpy of cobalt when compared to nickel, whereas the uptake of nickel is proposed to take place on outer surfaces of the material (7). The kinetic constraints of dynamic column experiments will favour metal uptake on the surfaces rather than inside the tunnels of the material, the surfaces being more favourable for nickel uptake than cobalt uptake. The higher breakthrough level of cobalt than of nickel in the column experiment can thus be explained by the restricted flow of ions inside the tunnels of the exchange material, resulting in a lower ion exchange rate for cobalt than for nickel. In acidic solution the uptake of nickel diminished quickly most likely due to the high proton concentration ($0.1 \text{ M } [\text{H}^+]$) and its coverage at the material surface (Fig. 2. (b)). In turn, the cobalt uptake was higher in acidic solution compared to its uptake from calcium-bearing solution. A straightforward explanation for this would be the competition of the ion exchange sites between calcium versus cobalt that is harder compared to proton versus cobalt. Also the higher mobility of protons compared to calcium ions inside the tunnels of the pyrochlore-structured material relates to preferable ion exchange sites of cobalt inside the material. It has also been reported that metal selectivity series of tin antimonates changes as a function of pH (11).

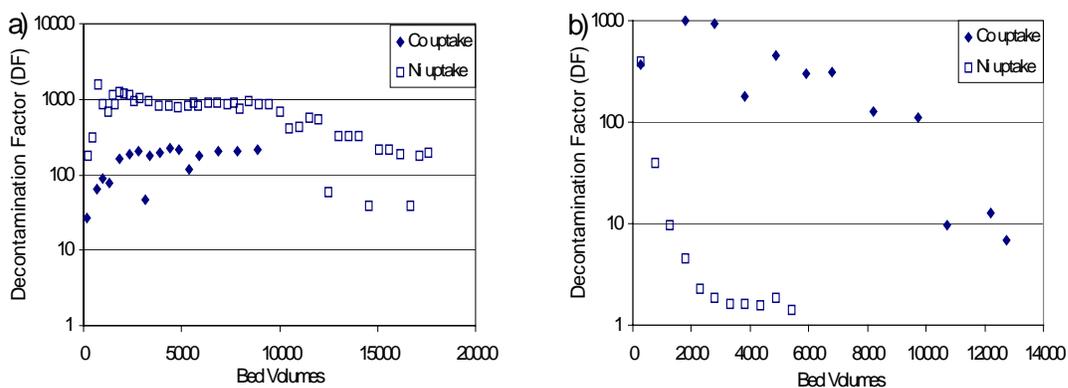


Fig. 2. Nickel and cobalt uptake of the SnSb(A3) exchanger from a) calcium-bearing FDW1 solution and b) from 0.1 M HNO₃ solution. Each curve represents a separate experiment.

The same uptake preference of nickel over cobalt was also evident in the column experiment where the two metals were in the same solution (0.01 M Ca(NO₃)₂, used to simulate neutral bond water) and the pH of the eluent was varied (Fig. 3.). This experiment also demonstrated the change in the selectivity sequence with pH. In addition, the marked differences in the DF-levels of the metals suggest that nickel and cobalt might themselves be separated through variation in acid concentration of the eluent. This finding agrees with reported enthalpies of the ion exchange reaction on crystalline antimony pentoxide: ΔH° of $M^{2+} \rightarrow H^+$ is 9.0, 79.5 and 159.1 kJ eq⁻¹ for Ca, Ni and Co, respectively (12).

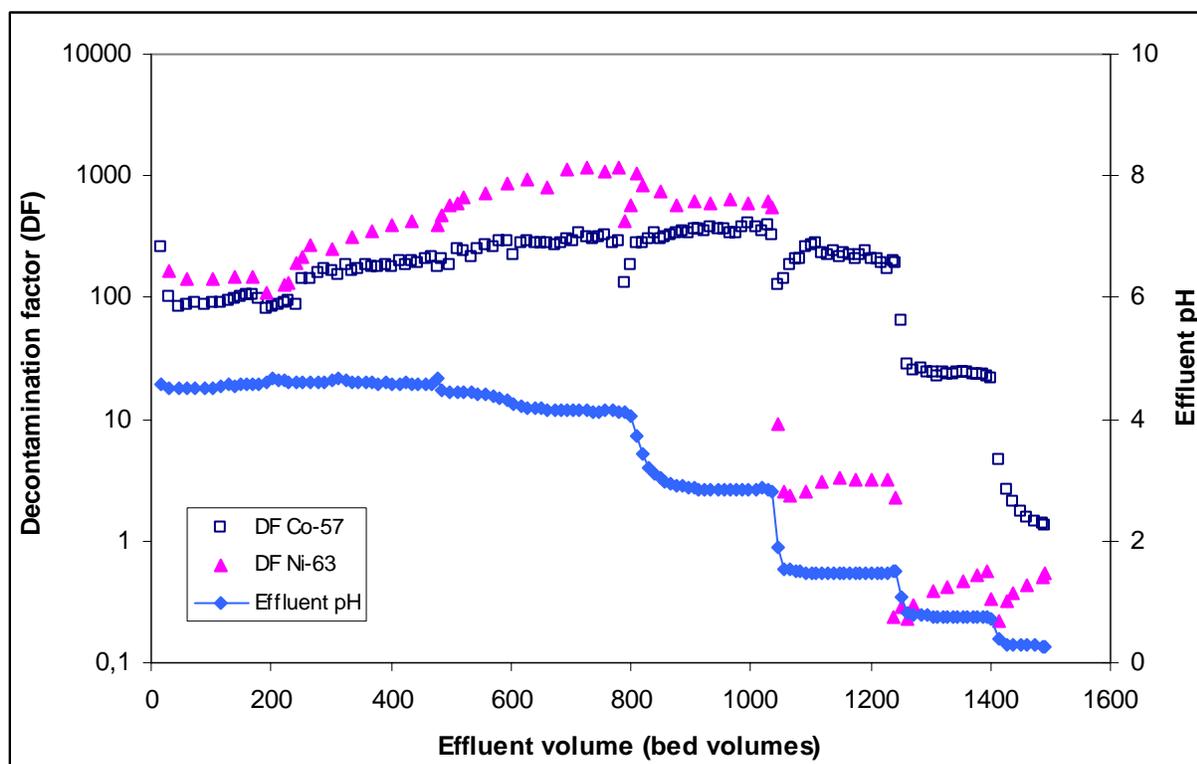


Fig. 3. Decontamination curves of ⁵⁷Co (□) and ⁶³Ni (Δ) for mixed metal oxide tin antimonate (SnSb(A3)) in 0.01 M Ca(NO₃)₂ solution.

Uptake of Actinides

The uptake of actinides was tested in batch experiments in 0.1, 0.01 and 0.001 M HNO₃ solutions. The distribution coefficients measured in these experiments were relatively high but also somewhat perplexing (Table 2). The plutonium uptake increased with the acidity of the solution, which contradicts the typical cation exchange process of the tin antimonate investigated ((SnSb(P₂), characterised as a weak cation exchanger). A study of the probable speciation of the

plutonium in the solutions showed that the plutonium uptake more or less followed the speciation curve of $\text{Pu(III)(NO}_3\text{)}^{2+}$, although the valence of plutonium should be +IV in these solutions (13,14). The nitrate species of Pu(IV) did not correlate with the uptake trend. Likewise, the uptake of americium was difficult to interpret. An extremely high K_d value was measured in 0.1 M HNO_3 and good K_d values in 1 M and 0.01 M HNO_3 solutions. The solution chemistry of actinides is highly complicated, especially with solids that may introduce redox potential to the system. Since the measured K_d values for both plutonium and americium were high, no further studies on actinide uptake were carried out, although peptisation studies could shed light on this problem.

Table II. The K_d Values of Plutonium and Americium for the SnSb(P₂) Exchanger in Nitric Acid Solutions

Solution	K_d (Pu), ml/g	K_d (Am), ml/g
0.01 M HNO_3	$6\ 170 \pm 85$	$16\ 060 \pm 84$
0.1 M HNO_3	$85\ 750 \pm 3950$	$4\ 234\ 376 \pm 1\ 839\ 000$
1 M HNO_3	$100\ 300 \pm 7250$	$4\ 432 \pm 16$

CONCLUSIONS

On the basis of the good cobalt and nickel uptake both in batch and in dynamic column experiments, the application of rutile-structured and mixed rutile- and pyrochlore-structured tin antimonates for the decontamination of NPP floor drain and neutral pond waters is considered to be promising. However, peptisation of pyrochlore-structured tin antimonates will probably prohibit their successful use in column application. Further tests with real waste solutions would be needed to confirm the profitable use of these materials in decontamination of waste solutions from activation products.

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WM'05 Conference, February 27-March 3, 2005, Tucson, AZ

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