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The effect of 0–100% Sn/Sb substitution on nickel uptake of tin antimonates

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The nickel uptake properties of an extensive series of tin antimonates were studied. Distribution coefficient values (K_d) for ^{63}Ni were measured in acidic and calcium solutions and illustrated as a function of Sn/Sb substitution from 0 to 100%. High K_d values for nickel from acidic solution (0.1 M HNO_3) were obtained, and K_d values from 0.1 M $Ca(NO_3)_2$ solution followed in a similar manner but at a considerably lower level. It was suggested that the nickel uptake was governed by structural hindrance in the pyrochlore phase and by electrostatic forces in the rutile phase. The dependence of pH on nickel uptake from floor drain water simulate was investigated using three materials with different Sn/Sb ratios, and excellent K_d values, even over 175 000 ml g^{-1}, were obtained.

Introduction

The advantage of inorganic ion exchangers over organic resins is their ability to resist decomposition at elevated temperatures and in ionising radiation. This feature has made the materials of interest in nuclear waste management. Some of these materials such as zeolites, titanosilicates, sodium-titanates and hexacyanoferrates have already made their way to commercial application mainly for separation of fission nuclides ^{137}Cs and ^{90}Sr.[1–5] Nevertheless inorganic ion exchangers have some serious disadvantages. The operating pH-range is usually rather narrow due to the low acidic nature of the exchange material (typical $pK_a > 4$), thereby limiting ion exchange use. Furthermore, the chemical stability of inorganic materials can be problematic, for example, dissolution of aluminium from zeolites at pH extremes. Slow kinetics has also limited the use of some materials but modern separation technology such as precoat filter systems have opened up new possibilities.[6] The emphasis in earlier studies has been on removal of fission nuclides but removal of activation/corrosion nuclides has become an increasingly interesting topic in recent times. ^{60}Co has been perhaps the most studied activation nuclide in radioactive waste management while some other important nuclides such as ^{63}Ni, with a reasonably long half-life (100 years), have gone almost unstudied. These activation/corrosion nuclides are usually found in floor drain water after spills and maintenance work in nuclear power plants. The decontamination of floor drain waters sets special demands, such as tolerance for competing ions, for the ion exchanger, since the water often contains macro-amounts of non-radioactive ions *e.g.* Na^+, K^+, Mg^{2+} and Ca^{2+}. Despite extensive and still ongoing research, there is a demand for ion exchangers that have selectivity for fission and corrosion nuclides, and improved retention in acidic solutions and solutions containing macro-amounts of competing ions that interfere with radionuclide uptake.

Tin-substituted antimony oxides and antimony-substituted tin oxides (tin antimonates) have been studied for various applications. Sb-substituted tin oxides have interesting semiconducting properties, and since SnO_2 can be made transparent the potential use of the material in photovoltaic and optoelectronic devices has been studied in detail.[7,8] Tin-substituted antimony oxides also have a wide range of commercial applications; *e.g.* as catalytic compounds in petro-chemistry and as fire retardants.[9,10] The ion exchange properties of both metal oxides as substituted and pure hydrous oxides have also been studied. Hydrous antimony pentoxide, $Sb_2O_5{\cdot}4H_2O$ (often referred to antimonic acid), is the most extensively studied of all. A theoretical ion exchange capacity of 5.1 meq g^{-1} and a high affinity for strontium ions in acidic solution have made the material a potential '^{90}Sr exchanger'.[11–13] However, a major disadvantage of this material has been the low tolerance for competing ions, especially for calcium ions. The number of publications on the ion exchange properties of hydrous tin oxides is much lower than those for antimonic acid. Since hydrous tin dioxide shows the classical behaviour of an amphoteric ion exchanger, the point of zero charge (p.z.c.) occurs at a pH of ∼4, it possess both anionic and cationic ion exchange properties. Some basic ion exchange data on hydrous tin oxides have been reported by various authors.[14–16]

High chemical stability in acidic solutions and resistance to ionising radiation are key features of tin antimonates. In addition, the relatively high ion exchange capacity (1.5–2.0 meq g^{-1} for Na^+) and excellent selectivity for certain nuclides have made the material very attractive for radioactive waste treatment. Basic ion exchange studies with most important radionuclides, such as ^{137}Cs, ^{90}Sr and some actinides, have been made quite thoroughly.[17–21] Direct comparison of these separate investigations has been problematic and rather difficult, mainly because the materials have been categorised simply as tin antimonates. Synthesis parameters (especially the synthesis pH) have a strong influence on tin antimonates and differences in reported selectivity series and structure measurements can be explained, at least in some cases, by differences in the synthesis procedures *i.e.* by slightly different materials.

The aim of this study was to investigate the feasibility of using tin antimonates for decontaminating the floor drain water of nuclear power plants from ^{63}Ni, which is known to be a troublesome nuclide to ion exchange from such solutions. The optimal Sn/Sb ratio for high ^{63}Ni selectivity and tolerance to calcium ions was explored with an extensive Sn/Sb substitution series, ranging from pure tin dioxide to pure antimony pentoxide. The synthesis and ion exchange experiments were planned and executed in a way that direct comparison of the results between different synthesis products could be made.

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Materials and methods

Reagents

All reagents were of analytical grade (Fluka, Merck, Aldrich, J.T. Baker) and used without further purification. The radioactive ^{63}Ni tracer for these ion exchange studies was obtained from Amersham International.

Synthesis

The main objective in the material synthesis was to dissolve and retain all the precursors in the solution phase before tin–antimony precipitation, to ensure a homogeneous distribution of the elements in the product material.

Starting reagents, $SnCl_4 \cdot 5H_2O$ or $SnCl_4 \geqslant 99\%$ for tin and $SbCl_5$ 98% for antimony, were dissolved and/or diluted with 6 M HCl to a concentration of 0.1 M. The starting reagents were mixed and stirred with a magnetic stirrer and the products were precipitated by raising the pH of the synthesis solution (to pH 2) using 25% NH_3. Various metal solution proportions were used to achieve various Sn/Sb substitution levels to the products. The synthesis has been described earlier in detail.[22]

Characterisation

Products were characterised with X-ray methods. Powder X-ray diffraction (XRD) patterns were collected by a Phillips PW 1710 powder diffractometer (operating at 30 kV and 50 mA) with Cu Kα (1.54 Å) radiation. Elemental analysis of the metals were carried out with X-ray fluorescence (XRF) using an Amptek 7 mm^2 Si(Li) XR-100CR detector and a 500 mCi ^{241}Am excitation source. Solid samples were used for XRF measurement in order to avoid possible errors caused by dissolving metal oxides of low solubility. Thermogravimetric (TG) analysis of the materials was done with a Mettler Toledo TA8000 system equipped with a TGA 850 thermobalance.

Structure of the tested materials

The synthesised metal oxides were divided into three categories: materials with pyrochlore structures, materials with rutile structures and a combination of both. The rutile structure was identified as a solid solution of tin dioxide (space group $P4_2/mnm$), with antimony substitution up to ~35%. The structures of the pyrochlore materials were similar to that of antimony pentoxide (space group $Fd3m$), with tin substitution up to ~35%. The structures of the materials between 35 and 65% Sn/Sb substitutions were more or less amorphous since the materials were mixtures of the aforementioned metal oxides at various metal substitution levels. A low crystallinity was favoured because of the possible positive effects on the ion exchange properties of the materials. Therefore no additional heating or pressure was applied in the synthesis. In addition, the time before solid/liquid separation was kept short, resulting in products of poorly crytalline or nano-crystalline structure (Fig. 1). The structures of the materials used have been described earlier in more detail.[22]

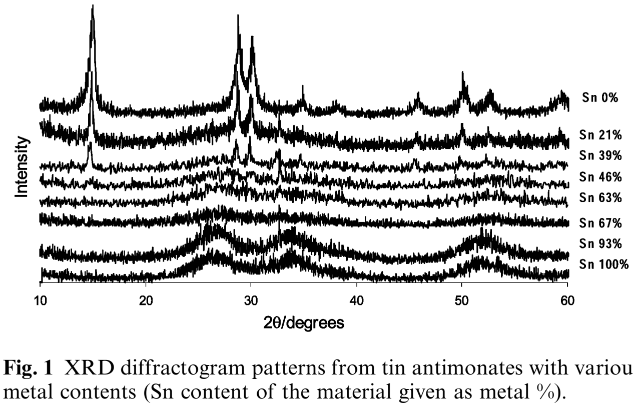

Fig. 1 XRD diffractogram patterns from tin antimonates with various metal contents (Sn content of the material given as metal %).

Ion exchange studies

The ion exchange properties of the materials synthesised could be altered in various ways. A straightforward way was applied, where changing the amounts of the starting reagents of the synthesis solution changed the Sn/Sb ratio of the synthesised material. A decrease in the p.z.c. was observed after an increase in the Sb content of the tin dioxide structure materials.[22] The possibility of lowering the p.z.c. of these materials was utilised in order to produce cation exchange properties for the materials when used in solutions of low pH. The Sn/Sb substitution may also have an effect on the framework structure of the material, and thereby change the selectivity and the diffusion rate within the tunnels or cavities of the material and in this way have an effect on the measured K_d values.

The ion exchange properties of the product materials were studied by measuring their distribution coefficients (K_d) using batch experiments. The K_d values were used to represent the selectivity of the material for nickel ions. The selectivity determines how efficiently a certain element is separated from other elements. In applications, such as radioactive waste treatment, these 'other elements' are usually present in vast concentrations and they compete for the ion exchange sites of the exchanger. Due to this, the K_d values, *i.e.* the selectivity of the exchanger for the radionuclides, have to be high for meaningful separation. In the batch experiments, 25 mg of finely ground (sieved between 74 and 149 μm), synthesised material was placed in a polyethylene vial with 10 ml of test solution. Samples were equilibrated for 3 days in a constant rotary mixer (50 rpm), during which time the solid/solution system reached equilibrium. The solid phase was then separated by centrifuge (10 min at 3000*g*) and filtered with a 0.2 μm filter (I.C. Arcodisc, Gellman Sciences). 2 ml subsamples were pipetted for concentration measurements (β-counting) and the equilibrium pH was measured from the remaining solution. The distribution coefficient illustrates the distribution, after a certain equilibration time (3 days), of the element within the initial solution and the solid material, and it was calculated as follows:

$$K_d = \frac{(A_i - A_{eq})}{A_{eq}} \times \frac{V}{m}$$

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

When using radioactive tracers, the activity of the tracer can be used instead of the element concentrations. ^{63}Ni was used as the radioactive tracer and since it is a pure beta-emitting nuclide with a β^--energy of 66.9 keV, a liquid scintillation counter (Wallac 1217 BackBeta) was used for the radioactivity measurements.

One of the applications of the synthesised materials could be in the decontamination of floor drain water at nuclear power plants, so 0.01 M $Ca(NO_3)_2$ solution was used to simulate those conditions. This solution was chosen on the basis of earlier experiments, where Ca^{2+} ions were found to be the most interfering ions for radionuclide uptake of solutions with typical ions (Na^+, K^+, Mg^{2+}, Ca^{2+}).[23,24] The K_d experiments in 0.01 M $Ca(NO_3)_2$ solution were carried out using ion exchange materials that had been changed into calcium form by sequential shaking in 0.1 M $Ca(NO_3)_2$ solution. The pH of this solution was adjusted to ~7 with 0.01 M $Ca(OH)_2$ and shaking was continued until the equilibrium pH was neutral.

Table 1 K_d values and their equilibrium pH values for ^{63}Ni in 0.1 M HNO_3 and 0.1 M $Ca(NO_3)_2$ solutions for the synthesised materials. Sn content as metal %

		0.1 M HNO_3		0.1 M $Ca(NO_3)_2$	
Sample code Sn content (%)	Structure	K_d value/ml g^{-1}	pH$_{eq}$	K_d value/ml g^{-1}	pH$_{eq}$
SnSb(**P$_1$**), Sn 0%	Pyrochlore	240 ± 6	1.1	120 ± 3	2.5
SnSb(**P$_2$**), Sn 21%	Pyrochlore	690 ± 12	1.1	250 ± 6	2.5
SnSb(**A$_1$**), Sn 34.1%	Amorphous	2780 ± 66	1.1	590 ± 14	2.8
SnSb(**P$_3$**), Sn 38.5%	Pyrochlore	6780 ± 161	1.1	1350 ± 32	2.9
SnSb(**A$_2$**), Sn 42.1%	Amorphous	4190 ± 99	1.1	1000 ± 24	2.9
SnSb(**A$_3$**), Sn 45.8%	Amorphous	5370 ± 127	1.1	1403 ± 33	2.9
SnSb(**A$_4$**), Sn 46.4%	Amorphous	4470 ± 106	1.1	1290 ± 31	3.0
SnSb(**A$_5$**), Sn 63.1%	Amorphous	7220 ± 176	1.1	3090 ± 73	3.0
SnSb(**R$_1$**), Sn 67%	Rutile	3490 ± 83	1.1	3080 ± 73	3.2
SnSb(**R$_2$**), Sn 83.1%	Rutile	40 ± 1	1.1	2190 ± 61	4.4
SnSb(**R$_3$**), Sn 93.1%	Rutile	18 ± 1	1.1	590 ± 14	2.7
SnSb(**R$_4$**), Sn 100%	Rutile	5 ± 1	1.1	85 ± 2	2.9

Results and discussions

The substitution of metals had a great influence on the ion exchange properties of the synthesised tin antimonates. The distribution coefficients (K_d) of the pure oxides, Sb_2O_5 and SnO_2, were low for ^{63}Ni but metal substitution caused a substantial increase in the measured K_d values (Table 1). This increase was believed to have two different origins: (i) a slight opening of the structure of the rigid pyrochlore materials and (ii) an increase in the electrostatic forces of the rutile structure materials.[22]

Nickel uptake from 0.1 M HNO_3 solution

The pyrochlore-structure antimony pentoxide has two different ion exchange sites (hydroxy groups), which are located at the surface and inside the material, in tunnels and cavities of the rigid three-dimensional structure. Most of these ion exchange sites are located inside the material.[25,26] The tunnels of pure Sb_2O_5 were too small for hydrated nickel ions to enter and reach the inner ion exchange sites[25] and this resulted in low nickel uptake. We assumed that substitution of Sb by more electropositive Sn ions would slightly distort and open up the tunnel structure of the pyrochlore antimony pentoxide. As a result of increasing Sn/Sb substitution in the tested pyrochlore structure materials, a shift in the most intensive XRD reflections (Fig. 1 and Table 2) and an increase in the nickel uptake from the 0.1 M HNO_3 solution was observed. The K_d values increased slowly with progressive metal substitution, reaching the highest value at a point where 38.5% of Sb was substituted by Sn, while the structure was retained as pyrochlore (Fig. 2). Higher substitution levels (between ~35 and 65%) resulted in an amorphous structure and lower K_d values.

Table 2 The most intensive XRD reflections of the pyrochlore structured materials

Material	*hkl* (111), *d*/Å	*hkl* (311), *d*/Å	*hkl* (222), *d*/Å
SnSb(**P$_1$**)	5.893	3.110	2.972
SnSb(**P$_2$**)	5.968	3.122	2.983
SnSb(**P$_3$**)	6.015	3.131	2.991

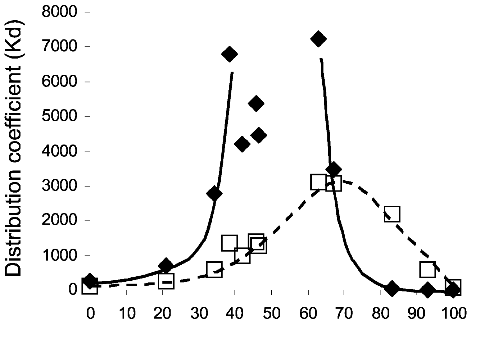

Fig. 2 Distribution coefficients (K_d as ml g^{-1}) for Ni in 0.1 M $Ca(NO_3)_2$ solution (□) and in 0.1 M HNO_3 solution (◆) as a function of Sn content (%).

The second assumption was that by substituting Sn from the lattice of rutile SnO_2 with Sb, which is a more electronegative ion, the p.z.c. of the material would be lower.[22,27] This would in turn result in enhanced cation exchange properties of the material in solutions of low pH. A decrease in the p.z.c. of the material was observed as a measured increase in the nickel uptake from 0.1 M HNO_3 solution after 17% metal substitution (Fig. 2). The highest K_d value for nickel was observed when 37% of Sn was substituted by Sb (SnSb(A_5)). This is near the highest reported substitution level (40%) of Sb into the lattice of rutile SnO_2.[7]

At a metal substitution range of 35–65% the tin antimonates were characterised as mixed metal oxides. Due to the heterogeneity within the structures of these materials, variation in nickel uptake was observed between the materials.

Nickel uptake from 0.1 M $Ca(NO_3)_2$ solution

The change in nickel uptake as a function of Sn/Sb substitution was somewhat similar in 0.1 M $Ca(NO_3)_2$ solutions to that in acidic (0.1 M HNO_3) solution. Earlier studies have demonstrated that calcium ions strongly interfere with the Sr uptake of Sb_2O_5.[23] This suggests that hydrated calcium ions are small enough, as are strontium ions, to reach the inner ion exchange sites of the pyrochlore structure Sb_2O_5. As a result of the 0.1 M $Ca(NO_3)_2$ media in our batch experiments, the pyrochlore structure of the exchangers was changed, at least partly, to calcium form. This change lowered the selectivity of the materials for ^{63}Ni and decreased the K_d values compared to ones from acidic solution. In addition, the change to calcium form is known to decrease the lattice constant of Sb_2O_5[26] and in this way narrows the tunnels and hinders nickel uptake.

For rutile-SnO_2-structured materials, the effect of Sb substitution on the p.z.c. was seen at a 7% substitution level (SnSb(**R$_3$**)) as an increase in the K_d value. The earlier increase in the K_d values as a function of metal substitution in 0.1 M $Ca(NO_3)_2$ solution was due to a higher equilibrium pH in the batch experiments compared with those in 0.1 M HNO_3 solution. The increase of K_d values was more or less linear as a function of Sb substituting Sn from the lattice of SnO_2 up to 33% substitution. The highest K_d value was measured at 37% substitution, after which the K_d started to decrease slowly. Due to this linear trend of uptake and rather small crystal size

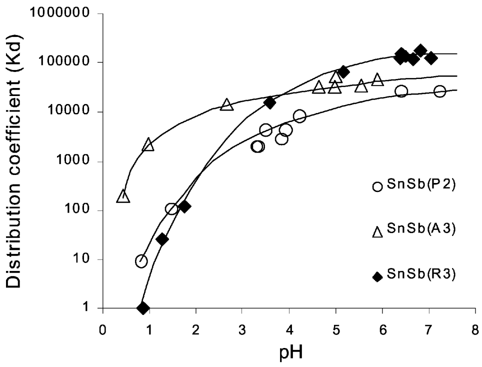

Fig. 3 The effect of pH on the distribution coefficient for Ni in 0.01 M $Ca(NO_3)_2$ solution, for three tin antimonates with different degrees of metal substitution.

($\sim$2 nm), plus the agglomerate particle character of hydrous SnO_2,[25] the increase in nickel uptake was associated with the increase in electrostatic forces of the material with increasing Sb content.

At the metal substitution range of 35–65%, the uptake of nickel was similar in 0.1 M $Ca(NO_3)_2$ solution to that in 0.1M HNO_3 solution, only at a lower K_d level.

Effect of pH on nickel uptake from floor drain simulate solution

In addition to the tolerance for competing ions, an ion exchanger should have a wide operating pH range. Since the synthesised materials showed good nickel uptake, even in a solution containing competing calcium ions, the pH dependence of the uptake was of great interest.

The K_d values of three tin antimonates, pyrochlore structure SnSb(**P$_2$**), rutile structure SnSb(**R$_3$**) and mixed metal oxide SnSb(**A$_3$**), were measured as function of pH (Fig. 3). A small Sn/Sb substitution in the lattice of SnO_2 (SnSb(**R$_3$**)) resulted in cation exchange properties for the material, even at fairly low pH ($\sim$1.5). An increase in the extent of deprotonisation of the ion exchange groups of the SnSb(**R$_3$**) occurred at neutral pH and excellent K_d values of over 175 000 ml g^{-1} resulted. The SnSb(**P$_2$**) exchanger was the most affected by interfering Ca ions, and it had the lowest nickel uptake, although the K_d values in the most acidic conditions were slightly higher than those of SnSb(**R$_3$**). Excellent nickel uptake was obtained with the SnSb(**A$_3$**) exchanger from acidic solutions. The exceptionally high selectivity for nickel from a solution of 0.01 M calcium and pH < 1 can only be explained by the fact that the exchanger had to consist mainly of metal oxide of high metal substitution (Fig. 2). Furthermore, the difference between the K_d values from 0.1 M HNO_3 and 0.1 M $Ca(NO_3)_2$ solutions for the SnSb(**A$_3$**) exchanger was very similar to that of the SnSb(**A$_5$**) exchanger. This could indicate that SnSb(**A$_3$**) was a mixture of high Sb-substituted SnO_2 and fairly low Sn-substituted Sb_2O_5, although XRD measurement could not verify this due to the low crystallinity of the product.

Conclusions

The synthesised tin antimonates showed good nickel uptake properties both in acidic and in competing calcium ion solutions. For the pyrochlore structure tin antimonates the substitution of Sb by Sn improved the nickel uptake in both 0.1 M HNO_3 and $Ca(NO_3)_2$ solutions. The increase of uptake from 0.1 M HNO_3 solution was somewhat surprising since substitution of Sb by more electropositive Sn should decrease the acidity of the metal oxide resulting in a lower uptake from acidic solution. The increase was associated with a slight distortion and an opening of the tunnels in the three dimensional structure of the pyrochlore Sb_2O_5. The nickel uptake from calcium solution was rather similar to that from acidic solution, but the level of uptake was lower. This was explained by the competition between Ca and Ni ions for the ion exchange sites of the exchanger and by the steric hindrance caused by the smaller lattice constant of the calcium form of the pyrochlore structure.

Rutile structure materials (SnO_2) of low Sn substitution by Sb had higher nickel uptake from the 0.1 M $Ca(NO_3)_2$ solution as compared to the 0.1 M HNO_3 solution. This *vice versa* nickel uptake character compared with the acidic solution can be explained by the p.z.c. of the material. At pH lower than the p.z.c. of the material, the exchanger does not have cation exchange properties (only a small uptake due to adsorption on the surface) but the p.z.c. of SnO_2 was lowered due to Sb substitution. A small Sb substitution into the lattice of SnO_2 resulted in an enhanced nickel uptake from the 0.1M $Ca(NO_3)_2$ solution. With a higher degree of metal substitution, nickel uptake from the 0.1 M HNO_3 solution was observed. This difference in metal substitution degree and nickel uptake between the two solutions was due to a higher equilibrium pH of the batch experiments in the calcium solution.

The effect of pH on the K_d values of the tin antimonates studied was significant, which is typical for hydrous metal oxides due to the weakly acidic nature of the materials. A strong increase in the K_d values for nickel with increasing equilibrium pH was observed. An excellent nickel uptake of over 175 000 ml g^{-1} was measured for the SnSb(**A$_3$**) exchanger from 0.01 M $Ca(NO_3)_2$ solution at neutral pH. A high degree of metal substitution had a positive effect on the nickel uptake from acidic solutions. The results obtained indicated good suitability of tin antimonates for decontamination of ^{63}Ni from floor drain waters at nuclear power plants.

The ion exchange properties of tin antimonates for nickel were so promising that additional work concerning their ion exchange properties as well as their chemical stability needs to be done. The relation between the structure and ion exchange needs further study, and a more powerful structure characterisation technique, such as EXAFS, should be applied because of the low crystallinity character of tin antimonates. The possibility of peptisation of the pyrochlore-structure materials and the solubility of tin from rutile-structure materials also need to be explored.

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