Uptake of [85]Sr, [134]Cs and [57]Co by antimony silicates doped with Ti^{4+}, Nb^{5+}, Mo^{6+} and W^{6+}

Teresia Möller,*[a] Risto Harjula,[a] Martyn Pillinger,[b] Alan Dyer,[b] Jon Newton,[b] Esko Tusa,[c] Suheel Amin,[d] Maurice Webb[e] and Abraham Araya[e]

[a]Laboratory of Radiochemistry, Department of Chemistry, University of Helsinki, P.O. Box 55, FIN-00014 Helsinki, Finland. E-mail: teresia.moller@helsinki.fi
[b]Chemistry Division, Science Research Institute, Cockcroft Building, University of Salford, Salford, UK M5 4WT
[c]Selion OY, Rajatorpantie 8, FIN-01600 Vantaa, Finland
[d]British Nuclear Fuels plc., Risley, Warrigton, Cheshire, UK WA3 6AS
[e]Crosfield Ltd., Warrington, UK WA5 1AB

Antimony silicate ion exchangers were prepared by precipitation using two different procedures. A crystalline product with a pyrochlore structure (SbSi) was obtained by mixing SbCl$_5$ in HCl with sodium silicate solution (pH$_{final}$ < 1) and heating it at 60 °C overnight. An amorphous material (KSbSi) formed when KSb(OH)$_6$ was mixed with tetraethylorthosilicate (TEOS) in acidic conditions and heated overnight at 77 °C. In both cases the Sb : Si molar ratio was 1 : 1 in the starting mixture. The products showed high [85]Sr selectivity in acidic conditions, distribution coefficients (K_D) being 35 500 mL g^{-1} for SbSi and 19 700 mL g^{-1} for amorphous KSbSi in 0.1 M HNO$_3$. They are very selective for [85]Sr over a wide pH range, making them superior to other strontium selective ion exchangers such as zeolites, sodium titanates and silicotitanates, which function effectively only in neutral or alkaline conditions. The antimony silicate products had also a high or reasonable selectivity for [57]Co, ^{59}Fe and [63]Ni, but the selectivity for [134]Cs was low. An attempt was made to increase the selectivity for [134]Cs by doping the antimony silicates with Ti^{4+}, Nb^{5+}, Mo^{6+} or W^{6+}. The best results were obtained by doping SbSi with W, which resulted in a 10-fold increase in caesium selectivity. The original pyrochlore structure was retained in the W-doped SbSi.

Introduction

Due to their radiation stability and high selectivity, inorganic ion exchange materials lend themselves ideally to the treatment of nuclear waste solutions. The major radionuclides in these solutions include fission products such as ^{90}Sr and [137]Cs. In addition, neutron activation products, e.g.. [60]Co and [63]Ni, are relevant in some waste types. The selective separation of radionuclides from nuclear waste solutions is a highly effective method for the minimization of nuclear waste volumes for final disposal. Several inorganic ion exchangers such as zeolites, sodium titanates,[1,2] silicotitanates[3,4] and hexacyanoferrates[5,6] are in use in nuclear sites for the separation of ^{137}Cs and [90]Sr. However, the pH of the waste solution is often a limiting factor in the use of the materials. Zeolites can only be used in neutral solutions due to the dissolution of aluminium at pH extremities. Other caesium selective materials (hexacyanoferrates, silicotitanates) usually have a wide operational pH-range (from 0–1 to 13–14), but the strontium selective materials (titanates, silicotitanates) have a poor performance even in slightly acidic solutions. There is a demand for ion exchangers that tolerate acidic solutions and are selective simultaneously to the most important waste radionuclides, e.g. for ^{137}Cs, ^{90}Sr and ^{60}Co, in these difficult conditions.

The hydrous metal oxides are a group of ion exchangers that have been investigated extensively since the 1960's for these applications. The structure and ion exchange properties of the hydrous antimony pentoxide (antimonic acid) Sb$_2$O$_5$·4H$_2$O[7–11] is particularly well known. It has a theoretical ion exchange capacity of 5.1 meq g^{-1}[9,10] and its high affinity for strontium in acidic conditions is also well established.[12,13] In general, the

crystallinity of the hydrous metal oxides has a strong effect on the ion exchange properties. Abe et al. showed that by aging in acid a crystalline hydrous antimony pentoxide could be prepared.[7,8] Three crystalline phases are known to exist, one of which is the pyrochlore structure type, which is cubic and has a space group of Fd3m with $a \approx 10.3$ Å. The dimensions of the unit cell vary slightly with the synthesis method. Factors that influence the crystallization of the pyrochlore structure (general formula A$_2$B$_2$O$_6$O′) include the effective ionic radii ratio of atoms A and B (A having a radius of 0.87 Å < r_A < 1.51 Å and B with 0.40 < r_B < 0.78 Å) and the charge balance, the most typical charge combinations being (A^{3+}, B^{4+}) and (A^{2+}, B^{5+}). The pyrochlore structure has a three dimensional framework and, in the case of (H$_3$O)$_2$Sb$_2$O$_6$·nH$_2$O (the more accurate composition for the pyrochlore antimonic acid), it is built up from corner sharing SbO$_6$ groups that form a three-dimensional Sb$_2$O$_6$ network. The water molecules and the protons are located in the tunnels and cavities of the framework structure.[14] A fine review of the oxide pyrochlores was given by Subramanian et al. in 1983.[15]

More recently, antimony silicates[16,17] have attracted some interest as ion exchangers for strontium separations. When silicon is added to antimonic acid in low temperature reactions it does not necessarily change the pyrochlore structure, but affects the ion exchange properties by creating vacancies.[18,19] In this work, antimony silicate materials have been prepared using two different procedures[16,20] that lead to two products: an amorphous and a crystalline product with a pyrochlore structure. The crystalline one was given a tentative molecular formula of [Sb$_2$O$_5$(H$_2$SiO$_3$)$_6$]·nH$_2$O.[16] These materials showed high selectivity for strontium in acidic solutions, but the

selectivity for caesium and cobalt was low. Thus an attempt was made to increase the selectivity of antimony silicates for Cs^+ and Co^{2+} by adding a metal dopant.

The hydrous oxides of W^{6+}, Nb^{5+} and Ti^{4+} are commonly prepared in hydrolysis reactions at low temperature and are often amorphous, although it is possible to obtain crystalline materials *via* solid state reactions at high temperatures (800–1200 °C). However, materials prepared at such high temperatures seldom have significant ion exchange capacities and even heating the metal oxides over 400 °C generally lessens their capacities. Hydrothermal treatment usually improves the crystallinity while permitting the products to retain their ion exchange properties. Recently, a $WO_3 \cdot 0.5H_2O$ with a defect pyrochlore structure was prepared hydrothermally at 155 °C at pH 3.5[21] and a correction to an earlier report[22] that caesium could not be exchanged into the WO_3 pyrochlore was made. Hydrous niobium(v) oxide has also shown reasonable caesium selectivity.[23] Most of these materials do not tolerate a very wide pH range. Tungstic acid prepared by precipitation dissolves in alkaline media (pH > 6), whereas the hydrous titanium oxides are relatively weakly acidic and cannot be applied in most acidic conditions.[7,24]

The effective ionic radii of Ti^{4+}, Mo^{6+}, Nb^{5+} and W^{6+} are about the same as that of Sb^{5+} (0.60 ± 0.04 Å). Therefore, it could be expected that these metals would substitute for some of the antimony in the framework of the antimony silicate even in the mild conditions (low temperature and hydrolysis) used for the antimony silicate syntheses. Incorporation of a dopant in the $A_2B_2O_6O'$ structure may lead to changes in the unit cell dimensions and even cause defects and vacancies in the structure. These effects were not investigated in this work.

Indication of selectivity of the ion exchanger for radionuclides can be obtained by determining the distribution coefficient (K_D). In this report batch experiments have been carried out in several "model" solutions (0.1 M HNO_3, 0.1 M $NaNO_3$, 0.1 M $NaNO_3$/0.1 M NaOH) and as a function of pH for ^{134}Cs, ^{85}Sr and ^{57}Co with the antimony silicates and the materials doped with niobium, molybdenum, titanium and tungsten. The effect of the macro ion Ca^{2+} on strontium uptake of some of the materials doped with W^{6+} has been studied as well.

Experimental

Reagents

All reagents were of analytical grade (Fluka, Riedel-de Haën, Merck) and used without further purification. The radioactive tracers used in ion exchange experiments were obtained from Amersham International (UK).

Characterisation

X-Ray diffraction (XRD) patterns of the materials were collected with a Philips PW1710 powder X-ray diffractometer with Cu K_α radiation (1.54 Å). Elemental analysis of the materials was carried out by X-ray fluorescence (XRF) and/or direct-coupled plasma (atomic emission spectrometry) (DCP-AES). Solid samples were used for XRF analysis. For DCP (SpectraSpan VI spectrometer) the samples were dissolved by heating 50 mg of sample with 0.8 g of NaOH pellets in a platinum crucible at 585 °C. The melt was dissolved in deionized water and acidified with 6 mL of concentrated HCl after which 1 mL of 30% H_2O_2 was added. Finally the sample was diluted to 100 mL with deionized H_2O. The water contents of the samples were determined thermogravimetrically (TGA) at a heating rate of 10 °C min^{-1} under oxygen using a DuPont Thermal Analyst 2000. Rough particle size determinations were carried out with scanning electron microscopy (SEM).

Syntheses of the materials

The materials were prepared by hydrolysis reactions at low temperatures. Generally, the antimony source was mixed with sodium silicate solution and the metal dopant solution at pH < 1 at room temperature. The mixture was then placed in a 60–77 °C oven for one day. The resulting white precipitate was filtered off, washed with distilled water, and dried at 25–77 °C or calcined at 100–1100 °C.

Antimony silicates. The antimony silicates were prepared using two different procedures. (1) A crystalline product (code: SbSi) was obtained when $SbCl_5$ (99%) in 4 M HCl was mixed with $Na_2Si_3O_7$ solution ($SiO_2 \sim 27$ wt% in $Na_2Si_3O_7$) as a 1 wt% mixture at pH < 1 with Sb : Si molar ratio of 1 : 1. The mixture was heated at 60 °C overnight.[16] (2) An amorphous material (code: KSbSi) formed when $KSb(OH)_6$, dissolved in distilled water, was mixed with $Si(OC_2H_5)_4$ (TEOS, 98%) in ethanol (Sb : Si molar ratio 1 : 1). The pH was set below 1 with concentrated HNO_3. When the obtained material was calcined at 1100 °C, a crystalline product, different from a pyrochlore, formed.[20] This product did not practically remove any ^{85}Sr from solution. Materials that were heated below 450 °C had significant affinity towards several radionuclides, the product with the maximum affinity was dried at 100 °C.[25] The products heated and dried at 77 °C were chosen for further experiments.

Antimony silicates with a metal dopant. Titanium(IV), molybdenum(VI), tungsten(VI) and niobium(V) were doped into antimony silicate by carrying out the syntheses in a similar fashion as for SbSi or KSbSi with $TiCl_4$ (99%), $(NH_4)_2MoO_4$, $Na_2WO_4 \cdot 2H_2O$ or $NbCl_5$ added to the reaction. The molar ratios of the elements in the starting mixture are given in Table 1 and Table 5 (for niobium).

Tungsten was doped into antimony silicate using both preparative procedures (KSbSi and SbSi). A crystalline material was obtained using the SbSi method (1). 0.02 mol of $SbCl_5$ (99%) in 4 M HCl was added to a solution of 0.02 mol of SiO_2 ($\sim 27\%$ in $Na_2Si_3O_7$) in H_2O and 0.01 mol of $Na_2WO_4 \cdot 2H_2O$ in H_2O (Sb : Si : W molar ratio 1 : 1 : 0.5 (code: WSbSi6)). An additional 200 mL of H_2O was quickly added so that the final volume was 500 mL and the concentration of HCl 0.8 M.

Samples of tungsten silicate and antimony tungstate were prepared as described above, leaving antimony and silicon, respectively, out of the reactions.

Ion exchange studies

All synthesized products were first evaluated by measuring the radionuclide distribution coefficients (K_D) by the batch method in test solutions simulating common types of nuclear waste liquids. The test solutions were 0.1 M HNO_3, 0.1 M $NaNO_3$ and a mixture of 0.1 M $NaNO_3$ and 0.1 M NaOH. The solutions were traced with a radioactive isotope and equilibrated with the finely ground ion exchanger in 8 mL polypropylene centrifuge tubes (Du Pont Sorvall) with a solution volume to exchanger mass ratio of 100–200 mL g^{-1} for 1 or 4 days at ambient temperature using constant rotary mixing. The ion exchanger samples were then separated from the solutions by centrifugation (Beckman L8-M Ultracentrifuge; 20 min at 30000 rpm) and filtered through 0.22 μm Minispike PVDF Bulk Acrodisk 13 filters. 5 mL aliquots of the filtered samples were measured for their ^{134}Cs, ^{85}Sr, ^{57}Co and ^{59}Fe activities (cpm) with a gamma-counter Wallac 1480 Wizard™ 3. ^{63}Ni activity was measured with a liquid scintillation counter Wallac LKB 1217 Rackbeta.

The distribution coefficient (K_D) values were calculated according to

Table 1 Chemical data for the antimony silicates and the antimony silicates doped with Ti^{4+}, Mo^{6+}, W^{6+}

	Sample name	Sb:Si:M molar ratio in reaction	Powder XRD (phase)	Sb/Si/M in product/mmol g^{-1}	~Sb:Si:M molar ratio in product	Water content (%) <350 °C
1	KSbSi	1:1:1	A	4.1/3.6/3.8	1:0.9:0.9	13.0
2	SbSi	1:1	P	2.8/7.8	1:2.8	16.4
3	TiSS	1:1:0.6	A	1.7/7.5/1.8	1:4.2:1	20.3
4	MoSS	1:1:1	AMP	2.3/1.6/3.8	1:0.7:1.6	10.6
5	MoSS2	1:1:0.2	A	3.4/2.5/1.1	1:0.8:0.3	13.7
6	WKSbSi1	1:1:0.5	A	3.0/3.4/0.9	1:1:0.3	12.0
7	WKSbSi4	1:1:0.1	A	3.8/3.6/0.3	1:1:0.1	15.6
8	WSbSi2	1:1:1	P	2.6/2.4/1.6	1:1:0.6	8.7
9	WSbSi6	1:1:0.5	P	2.9/3.0/1.1	1:1:0.4	9.9
10	WSbSi7	1:2.5:1.7	P	1.6/6.3/1.1	1:4:0.8	8.0
11	WSi	0:1:1	T	—/2.8/3.9	—:1:1.4	7.4
12	WSb	1:0:1	A	1.6/—/1.9	1:—:1.2	7.4

A = amorphous, P = pyrochlore, AMP = ammonium molybdenum phosphate, T = tungstite.

$$K_D = \frac{\bar{A}}{A_{eq}} = \frac{(A_0 - A_{eq})}{A_{eq}} \frac{V}{m} \quad (1)$$

where $\bar{A}$ is the activity concentration of the radionuclide in the exchanger (Bq kg^{-1}), A_0 and A_{eq} are the activity concentrations in the solution initially and at equilibrium, respectively, V is the solution volume (mL) and m the mass of the exchanger (g).

Based on the initial evaluations in the test solutions, samples were chosen for further experiments to study the effect of pH on the uptake of ^{134}Cs, ^{85}Sr and ^{57}Co. These experiments were carried out by the batch technique described above in 0.1 M NaNO$_3$ background solution. The pH of solution was adjusted by adding varying amounts of HNO$_3$ or NaOH prior to equilibration with the ion exchanger sample.

The pH values of the sample solutions were measured after equilibration with the exchanger. The experiments were carried out on materials in hydrogen form obtained from the syntheses with no pre-treatments.

Considerable amounts of calcium, which frequently interfere with the uptake of radionuclide ions, are often present in nuclear waste. The effect of the macro ion Ca^{2+} on the uptake of ^{85}Sr was studied in three Ca(NO$_3$)$_2$ concentrations, 0.01 M, 0.1 M and 1 M. For these experiments the exchanger was first equilibrated with 1 M Ca(NO$_3$)$_2$ for 3 days with a batch factor of 200 mL g^{-1} in order to obtain the Ca^{2+} form of the material. A fresh salt solution was changed three times before washing with a small amount of distilled water.

Determination of ion-exchange capacity by titration

Ion-exchange capacities of an antimony silicate SbSi and a W^{6+}-doped product were determined by titration in 0.1 M NaNO$_3$ + NaOH solutions. The materials were first converted to the H$^+$-form by equilibrating 0.5–1.0 g of exchanger with 20 mL of 0.1 M HNO$_3$. Fresh HNO$_3$ was changed several times until a pH of about 1.3 was reached. Titrations were carried out in successive batch equilibrations by adding varying amounts of NaOH into 0.1 M NaNO$_3$. A 0.02 g portion of the exchanger was equilibrated with 5 mL of 0.1 M NaNO$_3$ + NaOH solution for 6 days.

After equilibration, the solution and the exchanger were separated by centrifugation and filtration through a 0.2 μm filter and the pH of the solution was measured.

Theory

The selectivity of a binary ion exchange in the reaction between ions A and B can be measured by the selectivity coefficient $k_{A/B}$,[26] i.e.

$$k_{A/B} = \frac{[\bar{A}]^{z_B}[B]^{z_A}}{[A]^{z_B}[\bar{B}]^{z_A}} \quad (2)$$

where $[\bar{A}]$, $[\bar{B}]$ refer to the ion concentrations in the exchanger,

[A] and [B] to those in solution and z_A and z_B are the respective ion charges. Combining eqn. 1 and 2 yields for $k_{A/B}$

$$k_{A/B} = K_D^{z_B} \frac{[B]^{z_A}}{[\bar{B}]^{z_A}} \quad (3)$$

In the case where A is present in trace amounts ($[\bar{A}] \ll [\bar{B}]$, $[A] \ll [B]$), and $[\bar{B}]$ is practically constant and equal to the ion exchange capacity Q ($[\bar{B}] \approx Q$) of the exchanger, one obtains from eqn. 3 for K_D, in logarithmic form:

$$\log K_D = (1/z_B)\log(k_{A/B}Q^{z_A}) - (z_A/z_B)\log[B] \quad (4)$$

Then the K_D of the trace ion A depends only on the concentration of ion B (in dilute solutions the selectivity coefficient is practically independent of the ionic strength of the solution, therefore the activity correction is unnecessary), and plotting log K_D as a function of log [B] gives a straight line with a slope of $-(z_A/z_B)$ when sorption of the ion is pure ion exchange.

Results

The powder XRD patterns of SbSi and WSbSi6 (Fig. 1) are similar to that of the hydrous antimony pentoxide, exhibiting a typical pattern for a pyrochlore structure ($Fd3m$). The sample doped with Ti^{4+} (code: TiSS) is poorly crystalline, with weak peaks at about 6.00 Å and 3.13 Å, typical of the pyrochlore phase. A more crystalline product could probably have been prepared by modifying the synthesis conditions. The material doped with molybdenum (code: MoSS), on the other hand, has a similar pattern (not illustrated) to that of the ammonium 12-molybdophosphate (AMP) (reference data from the Joint Committee on Powder Diffraction Standards (JCPDS)), although the bright yellow MoSS is less crystalline than AMP.

The amorphous materials have an average weight loss of 13% by 350 °C whereas the crystalline ones lose ~9% with the exception of SbSi (Table 1). This discrepancy may be attributed to the fact that the locations for H$_3$O$^+$ ions in the cavities and tunnels of the pyrochlore structure are fewer than the adsorption sites on the surface of the amorphous material. The elemental molar ratios of antimony and silicon in the reaction and in the product of KSbSi are approximately equal (Table 1), indicating that most of the silicon has reacted with the antimony. An excess of silicon is present in SbSi (Sb:Si molar ratio 1:2.8), which also leads to a higher water/proton content (16.4%). This was observed by Polevoi et al. as well.[18] The material doped with titanium has four times more silicon relative to antimony in the product than the other samples (with the exception of WSbSi7). This again leads to a water content (20% up to 350 °C) that is almost twice the amount found in the other samples. The smaller weight loss in WSbSi7 (8.0%) relative to the amount of silicon in the product is a result of the product being calcined prior to the TGA measurement.
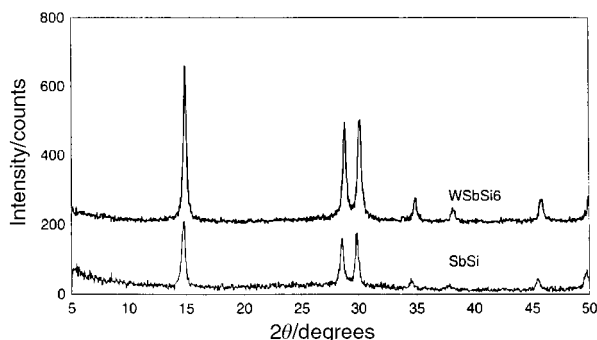
Fig. 1 The powder X-ray diffraction patterns of antimony silicate (SbSi) and antimony silicate doped with W^{6+} (WSbSi6).

Fig. 2 The titration curves for antimony silicate SbSi (■) and antimony silicate doped with W^{6+} WSbSi6 (▲) in H^+-form as a function of added NaOH (meq g^{-1}).

The elemental analyses show that all the samples contain the metal dopant. The maximum amount of tungsten incorporated into the antimony silicate, still retaining the pyrochlore structure, is 60% with an antimony to silicon ratio of 1. According to the powder XRD pattern (Fig. 1), the pyrochlore phase does not have peaks caused by an impurity phase *e.g.* $WO_3 \cdot 1/3H_2O$ or split peaks that might be due to the presence of a pyrochlore $WO_3 \cdot 0.5H_2O$. Therefore, it can be concluded that tungsten had been doped into the framework structure. In the case of the amorphous materials it is not completely certain that the samples are not mixtures. KSbSi is expected to be a single phase on the basis of its ion exchange behaviour, which is very similar to that of the crystalline SbSi. Also, the similarity of the elemental compositions of the amorphous materials to those with the pyrochlore phase would indicate that we have a single phase. However, the possible presence of an impurity phase in the amorphous samples cannot be ruled out.

The SEM analyses indicate that the samples doped with tungsten (WSbSi2 and WSbSi6) contain irregularly shaped particles that range in size from 10–100 μm. More precise particle size determination will be carried out on samples that have been prepared for column applications.

H^+-Ion exchange capacities

H^+-Ion exchange capacities were determined graphically from the inflection points of the titration curves (Fig. 2) for the antimony silicate SbSi and the tungsten doped antimony silicate WSbSi6. The two materials behave rather similarly and the clear inflection indicates that they are monofunctional and strongly acidic in character. The undoped SbSi has a slightly
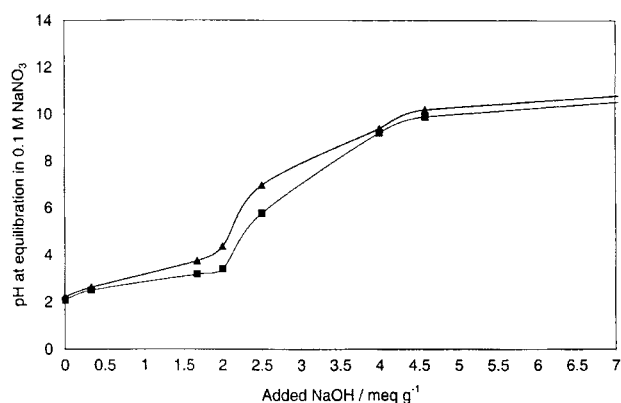
higher capacity, 2.7 meq g^{-1} (at pH ~ 7), than the material doped with W^{6+}, which has a capacity of 2.4 meq g^{-1} at the same pH. These are only 53% and 47% of the theoretical capacity of antimonic acid, ~ 5.1 meq g^{-1}.[7,9] Because the inflections are not very sharp, the capacities obtained here may be too low and ion uptake may still occur after these points.

Uptake of ^{85}Sr, ^{134}Cs, ^{57}Co, ^{59}Fe and ^{63}Ni

The antimony silicates SbSi and KSbSi showed a very high selectivity for ^{85}Sr in 0.1 M HNO_3, the K_D values being 35 500 mL g^{-1} and 19 700 mL g^{-1}, respectively (Table 2). Indication of the high affinity for strontium of these materials could be anticipated based on results obtained for the hydrous antimony pentoxide $(H_3O)_2Sb_2O_6 \cdot 2H_2O$[7,13] and the antimony silicate in reference 16. None of the materials tolerate highly concentrated acid solutions, though, as the K_D values were generally < 60 mL g^{-1} in 4 M HNO_3. The presence of the macro component Na^+ does not drastically interfere with strontium or cobalt uptake for KSbSi or SbSi, and K_D values of over 10 000 mL g^{-1} are observed in 0.1 M $NaNO_3$ (pH 2.5). The amorphous KSbSi performs better than the crystalline SbSi, having ^{85}Sr and ^{57}Co K_D values of 44 300 mL g^{-1} and 34 000 mL g^{-1}, respectively (Table 2). This difference again can be explained by the additional adsorption sites on the surface of the amorphous material. Both antimony silicate materials have much higher ^{85}Sr uptake compared to the commercial ion exchangers in acidic pH (pH < 6) (Fig. 3).

Table 2 ^{134}Cs, ^{85}Sr and ^{57}Co distribution coefficients (K_D/mL g^{-1}) for antimony silicates and antimony silicates doped with Ti^{4+}, Mo^{6+} and W^{6+}

|	4 M HNO_3	0.1 M HNO_3	0.1 M $NaNO_3$	0.1 M $NaNO_3$/0.1 M NaOH	Dist. H_2O
^{134}Cs					
KSbSi	30	590	280	25	2 500
SbSi	35	3 700	350	5	14 000
TiSS	5	20	250	103 000	2 600
MoSS	5	400	430	20	1 100
MoSS2	25	470	330	20	1 200
WKSbSi1	35	700	380	35	2 000
^{85}Sr					
KSbSi	70	19 700	44 300	56 000	13 500
SbSi	520	35 500	16 000	315 000	—
TiSS	1	190	180	20	7 800
MoSS	10	360	5 000	51 500	4 750
MoSS2	55	2 000	4 400	740	3 400
WKSbSi1	20	8 200	9 000	48 000	32 000
^{57}Co					
KSbSi	—	2 000	34 000	6 200	270
SbSi	1	4 300	13 000	60	320 000
TiSS	1	1	5	180	25
MoSS	45	290	1 500	180	1 500
MoSS2	55	20	4 400	740	3 400
WKSbSi1	350	14 300	114 000	1 300	4 300
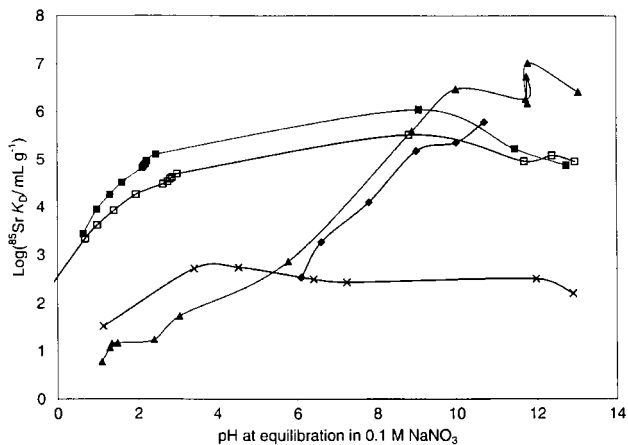
Fig. 3 [85]Sr distribution coefficient as a function of equilibration pH in 0.1 M NaNO$_3$ for antimony silicates KSbSi ($\square$), SbSi ($\blacksquare$), sodium silicotitanate ($\blacktriangle$), sodium titanate ($\blacklozenge$) and clinoptilolite ($\times$).

Neither of the antimony silicate materials takes up [134]Cs significantly (Table 2). Doping with titanium or molybdenum does not increase the caesium selectivity either (Table 2), whereas clear improvement was seen when the SbSi was doped with tungsten (WSbSi2 and WSbSi6 in Table 3). The caesium K_D values were almost one order of magnitude higher in 0.1 M HNO$_3$ for the WSbSi materials ($>17\,000$ mL g^{-1}) than for the undoped antimony silicate SbSi (3 700 mL g^{-1}). Closer inspection of the data revealed that log K_D for [134]Cs increased almost linearly as a function of the relative amount of tungsten in the products (Fig. 4). Likewise, the logarithmic values of [85]Sr K_Ds were almost linear with the relative amount of antimony in the products. However, an amorphous product that contained only Sb^{5+} and W^{6+} had poor selectivity for both [134]Cs and [85]Sr in 0.1 M HNO$_3$ (WSb in Table 3). A combination of W^{6+} and Si^{4+} gave a crystalline product with a structure of tungstite that had a high selectivity for [134]Cs. These features show that the pyrochlore structure gives ion sieve properties to these materials and that silicon may have an important role, in addition to tungsten, in creating caesium selectivity.

The antimony silicates and the samples doped with tungsten are both highly selective for ^{59}Fe in 0.1 M HNO$_3$ (Table 4). WSbSi6 takes up iron especially well, the K_D being over 90 000 mL g^{-1}. In the presence of the macro component Na$^+$ (after equilibration the pH of the 0.1 M NaNO$_3$ solution is ~2.5) the [59]Fe K_D for WSbSi6 is still extremely high, 241 000 mL g^{-1}. At pH<3 precipitation of iron(III) oxide is not expected to happen. With the exception of WKSbSi1 none of the materials are particularly selective for [63]Ni. The amorphous WKSbSi1 also takes up cobalt better than the other products (Table 2). Selective removal of the neutron activation products [63]Ni and ^{60}Co from nuclear waste solutions is usually difficult and the selectivity of WKSbSi1 for both these radionuclides should be studied in more detail.

Table 3 [134]Cs, [85]Sr and [57]Co distribution coefficients (K_D/mL g^{-1}) in 0.1 M HNO$_3$ for antimony silicates doped with W^{6+} and antimony pentoxide

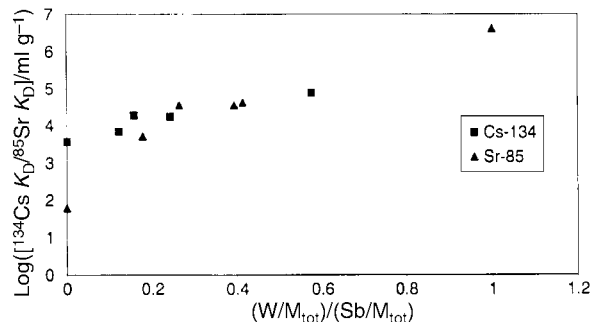| Sample	[134]Cs K_D/ mL g^{-1} in 0.1 M HNO$_3$	[85]Sr K_D/ mL g^{-1} in 0.1 M HNO$_3$	[57]Co K_D/ mL g^{-1} in 0.1 M HNO$_3$
WKSbSi4	1 300	41 400	1 800
WSbSi2	17 200	35 500	1 500
WSbSi6	18 700	42 200	1 450
WSbSi7	6 900	5 200	290
WSi	77 500	60	90
WSb	3 430	1 110	150
(H$_3$O)$_2$Sb$_2$O$_6$·xH$_2$O	1 800	4 200 000	200

Fig. 4 Distribution coefficients (K_D) for [85]Sr and [134]Cs in antimony silicates doped with W^{6+} as a function of W mole fraction W/M$_{tot}$ (K_D of [134]Cs) or Sb mole fraction Sb/M$_{tot}$ (K_D of [85]Sr) in the product.
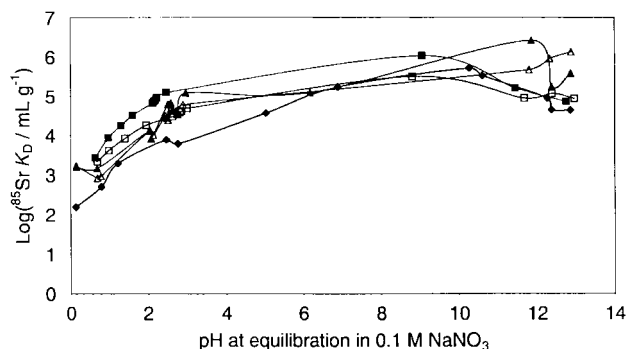

Fig. 5 [85]Sr distribution coefficient as a function of equilibration pH in 0.1 M NaNO$_3$ for antimony silicates KSbSi ($\square$), SbSi ($\blacksquare$) and antimony silicates doped with W^{6+}: WSbSi6 ($\blacktriangle$), WSbSi2 ($\triangle$) and WKSbSi1 ($\blacklozenge$).

When the antimony silicate is doped with niobium at ambient temperature, a considerable increase in the K_D values of ^{137}Cs in 0.1 M HNO$_3$ is seen at lower niobium doses (Table 5). However, when the Nb dose in the reaction mixture is further increased (Si : Nb >0.1, Si : Sb $=1$), the K_D values decrease dramatically.

The K_D values of ^{90}Sr/^{90}Y and [57]Co decrease on the whole with increasing niobium content. Aging the samples at room temperature for 3 days does not significantly improve the uptake of any of the isotopes. Heating at 75 °C and 200 °C, on the other hand, generally decreases the K_D values when the molar ratio of Sb : Si : Nb is $<1:1:0.1$. On the other hand, heating a sample with a higher molar ratio in reaction (1 : 1 : 1) to 200 °C increases the [137]Cs K_D from 260 mL g^{-1} (75 °C) to 47 000 mL g^{-1}. The heating increases the strontium and cobalt K_D values as well, although not as significantly. Heating the hydrous metal oxides above 400 °C typically causes a release of structural water irreversibly, which leads to a decrease in the ion exchange capacity. This was found to be the case for the undoped antimony silicate samples as well.[25]

Table 4 ^{59}Fe and [63]Ni distribution coefficients (K_D, mL g^{-1}) for antimony silicates and antimony silicates doped with W^{6+}

	K_D/mL g^{-1}			
Sample	[59]Fe in 0.1 M HNO$_3$	[59]Fe in 0.1 M NaNO$_3$	[63]Ni in 0.1 M HNO$_3$	[63]Ni in 0.1 M NaNO$_3$
SbSi	74 500	170 500	1 000	230
KSbSi	14 300	6 400	480	5 500
WKSbSi1	26 000	550	2 200	17 000
WSbSi2	74 000	8 300	800	540
WSbSi6	94 000	241 000	430	660

The effect of pH on ^{85}Sr, ^{134}Cs and ^{57}Co uptake

Regarding the effect of pH, the W^{6+} doped materials perform as well as SbSi and KSbSi at pH > 3, taking up ^{85}Sr selectively in 0.1 M NaNO$_3$ with K_D values of 100 000 mL g^{-1} (Fig. 5). Between pH 1–3, however, the crystalline SbSi is still superior.

WSbSi7 showed high ^{134}Cs K_D values at pH 1–5 after which they decreased rapidly when pH > 5. ^{134}Cs K_D values of about 35 000 mL g^{-1} were reached in 0.1 M NaNO$_3$ below pH 5 (Fig. 6), which is 1.5 orders of magnitude higher than for WSbSi2. This further supports the observation that in addition to tungsten, silicon enhances caesium selectivity. WSbSi7 has a silicon content that is four times higher than in the other W^{6+} doped samples (Table 1). The same property can be seen in the cases of the undoped antimony silicates as well. SbSi has an Sb : Si molar ratio of 1 : 2.8 when it is 1 : 0.9 in KSbSi. This leads to a slightly higher selectivity for caesium in SbSi (^{134}Cs K_D
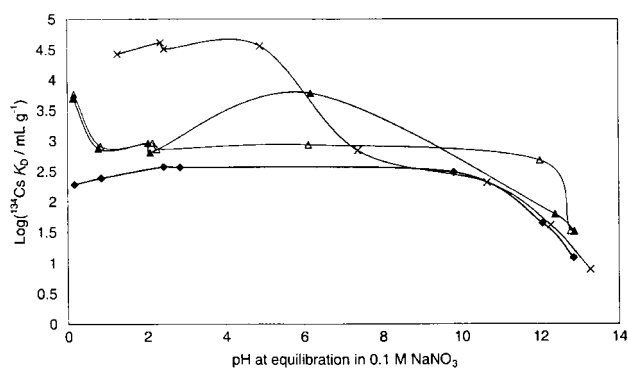
Fig. 6 ^{134}Cs distribution coefficient as a function of equilibration pH in 0.1 M NaNO$_3$ for antimony silicates doped with W^{6+}: WSbSi6 (▲), WSbSi2 (△), WSbSi7 (×) and WKSbSi1 (◆).

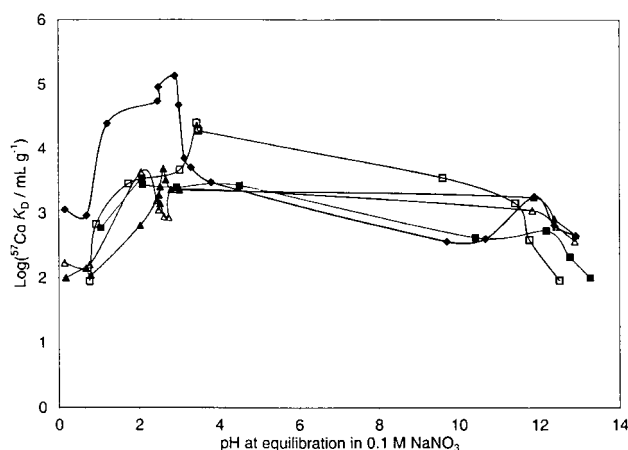**Fig. 7** ^{57}Co distribution coefficient as a function of equilibration pH in 0.1 M NaNO$_3$ for antimony silicates KSbSi (□), SbSi (■) and antimony silicates doped with W^{6+}: WSbSi6 (▲), WSbSi2 (△) and WKSbSi1 (◆).

Table 5 ^{137}Cs, ^{90}Sr/^{90}Y and ^{57}Co distribution coefficients (K_D/mL g^{-1}) in 0.1 M HNO$_3$ for antimony silicates doped with Nb^{5+}

Sample (Sb : Si : Nb in reaction)	^{137}Cs K_D/ mL g^{-1} in 0.1 M HNO$_3$	^{90}Sr/^{90}Y K_D/ mL g^{-1} in 0.1 M HNO$_3$	^{57}Co K_D/ mL g^{-1} in 0.1 M HNO$_3$
SSNb1 (1 : 1 : 0.01)	10 300	132 000	5 500
SSNb2 (1 : 1 : 0.1)	11 300	64 000	2 900
SSNb3 (1 : 1 : 0.5)	400	300	15
SSNb4 (1 : 1 : 1)	150	15	1

3 700 mL g^{-1} in 0.1 M HNO$_3$) than in KSbSi (^{134}Cs K_D 590 mL g^{-1}, Table 2).

An interesting feature clearly seen when approaching pH 0 from higher pH was the increase in the distribution coefficient values with both WSbSi2 and WSbSi6. The same effect can be observed in the ^{85}Sr (Fig. 5) and ^{57}Co (Fig. 7) exchanges, but not as strong. Additional experiments were carried out in 1 M HNO$_3$ for both WSbSi2 and WSbSi6 in order to clarify whether the K_D values would still increase below pH 0. The obtained ^{134}Cs K_D values of 4 900 mL g^{-1} for WSbSi6 and 5 800 mL g^{-1} for WSbSi2 show that the values start to decrease again soon when pH is just below 0, i.e. ^{134}Cs K_D has a strong maximum when the pH is slightly higher than 0.

As expected, the amorphous WKSbSi1 (Sb : Si : W molar ratio in product 1 : 1 : 0.3) shows the poorest performance for caesium exchange (Fig. 6), the K_D values level off at about 400 mL g^{-1} between pH 2–10. The W^{6+} doped materials were not compared to the undoped antimony silicates SbSi and KSbSi, as these are not very selective for caesium, and WKSbSi1 could be considered to represent them (Fig. 6).

WKSbSi1 was already found to be highly selective for ^{57}Co in 0.1 M HNO$_3$ with a K_D value of 14 300 mL g^{-1} (Table 2) and 114 000 mL g^{-1} in 0.1 M NaNO$_3$ at pH ~ 2.5. After pH > 3 in the presence of the macro component Na$^+$ the uptake decreases rapidly (Fig. 7). This unexpected maximum does not have a definite explanation, but it is assumed that it might arise from the selective uptake of cobalt to a different ion exchange site at this narrow pH range.

At pH 3.5 the antimony silicate KSbSi has the highest ^{57}Co K_D, which then also decreases from about 20 000 mL g^{-1} to 1 000 mL g^{-1} when reaching pH 12.

In conclusion, all the antimony silicate materials tolerate a wide pH range, but work extremely efficiently in acidic media. The exceptions were the materials doped with titanium and molybdenum. Clear improvement in caesium selectivity was obtained when the Sb : Si : W molar ratio in the product was 1 : 1 : 0.4 or 1 : 1 : 0.6.

The effect of Ca^{2+} on the ^{85}Sr K_D for antimony silicates doped with W^{6+}

The effect of Ca^{2+} on Sr^{2+} uptake is dramatic, and the ^{85}Sr distribution coefficients decrease considerably for all antimony silicate samples already in 0.01 M Ca(NO$_3$)$_2$ (Fig. 8). The K_D values are smaller than 1 000 mL g^{-1} in 0.01 M Ca(NO$_3$)$_2$, pH at equilibration 2.5–3.5, when they are over 40 000 mL g^{-1} in 0.1 M HNO$_3$ without interfering cations (Table 3) and close to 100 000 mL g^{-1} in 0.1 M NaNO$_3$ at pH 3 (Fig. 5). Bengtsson et al.[27] obtained strontium K_D values of about 4 300 mL g^{-1} at pH 7.4 in the presence of 0.01 M CaCl$_2$ for a S-28 antimony
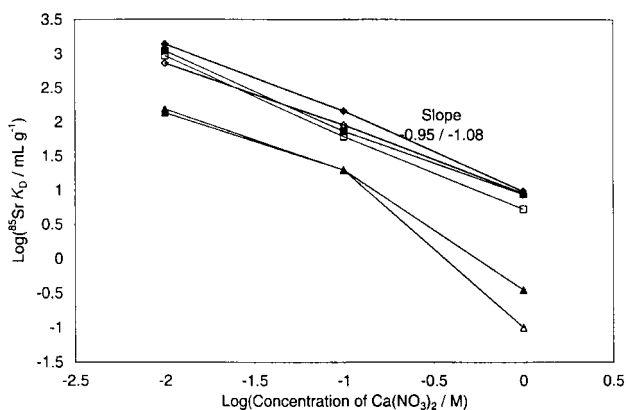
Fig. 8 ^{85}Sr distribution coefficient as a function of Ca(NO$_3$)$_2$ concentration for antimony silicates KSbSi (□), SbSi (■) and antimony silicates doped with W^{6+}: WSbSi6 (▲), WSbSi2 (△), WKSbSi1 (◆) and WKSbSi4 (◇).

silicate sample. This is four times higher than what we obtained for our materials at the same calcium concentration. However, this can most probably be explained by the difference in equilibration pHs. The fact that the slopes of the curves in Fig. 8 are approximately -1 indicates that sorption of strontium is equivalent exchange of Ca^{2+} for Sr^{2+}. At $pH > 7$, hydrolysation of strontium species $Sr(OH)^+$ may change this situation.

Doping with W^{6+} does not improve strontium selectivity over calcium. In the case of the crystalline WSbSi2 and WSbSi6 the K_D values are one order of magnitude smaller than those for the amorphous WKSbSi1 and WKSbSi4 or the undoped materials SbSi and KSbSi (Fig. 8). The fact that the undoped SbSi and KSbSi perform better in the presence of Ca^{2+} may be explained partly by the changes in the unit cell dimensions and the sizes of the openings of the tunnels in the structure caused by the doping. In the amorphous materials, the ion sieve effect is not as clear and in addition to ion exchange adsorption of Sr^{2+} on to the surface may take place. However, the structural properties were not studied in this work.

Conclusions

The aim of this work was to improve the selectivity of some antimony silicate materials for other radionuclides in addition to strontium. It is especially important to obtain high caesium selectivity in acidic conditions. The two synthesized antimony silicates, the crystalline SbSi and the amorphous KSbSi take up strontium extremely well in a wide pH range and perform better than many of the commercially available inorganic ion exchangers. Doping the antimony silicates with Ti^{4+} and Mo^{6+} does not significantly improve the selectivities of the materials. In fact, doping with titanium caused the material to perform more like a typical silicotitanate, having low affinity for any of the tested nuclides below pH 4. Molybdenum in the material did not increase the ^{134}Cs distribution coefficients either and this product was unstable at pHs higher than 8, where molybdenum was found to leach out of the material. No significant improvement in the ^{90}Sr and ^{57}Co distribution coefficients was obtained by doping with niobium. The K_D values were generally the same as those for the pure antimony silicates. However, a considerable increase in the K_D values of ^{137}Cs in 0.1 M HNO_3 was seen at lower niobium doses (Si:Nb < 0.1, Si:Sb = 1 in reaction). Increasing the niobium content to more than a Si:Nb molar ratio of 0.1 tends to decrease the affinity for ^{137}Cs.

Doping the antimony silicates with tungsten gave very promising results. In 0.1 M HNO_3 the ^{134}Cs K_D values were nearly one order of magnitude higher than those of the undoped antimony silicates. A linear dependence of ^{85}Sr and ^{134}Cs distribution coefficients upon antimony and tungsten contents in the products was clearly observed. As expected, materials with high Sb^{5+} content are more selective for strontium. The caesium selectivity could be improved until a maximum Sb:Si:W molar ratio of 1:1:0.6 was obtained in the product. It was found that in addition to tungsten, silicon in the pyrochlore structure also enhances caesium selectivity. No significant improvement in the cobalt selectivity has been seen yet, except in the case of an amorphous sample with a Sb:Si:W molar ratio of 1:1:0.3. This product was reasonably selective for ^{63}Ni as well.

The presence of the macro component Ca^{2+} dramatically interferes with strontium uptake in all tested conditions. In fact, the undoped SbSi samples seem to tolerate the presence of calcium slightly better than the samples doped with W^{6+}. Crystallinity of the product is a significant factor in obtaining separation of Sr^{2+} and Ca^{2+}. The amorphous W^{6+} doped materials take up strontium better than the ones with higher crystallinity (the pyrochlore structure) in the presence of calcium.

Doping with tungsten also produces a harder product, which could be processed more easily for column operations, whereas the undoped antimony silicates are powder-like. For strontium uptake at $pH < 6$ these materials perform better than many of the commercially available ion exchangers.

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