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Removal of ^{85}Sr, ^{134}Cs, and ^{57}Co Radionuclides from Acidic and Neutral Waste Solutions by Metal Doped Antimony Silicates

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ABSTRACT

Antimony silicates doped with a metal, $(M)_{x,y}Sb_{2-x}Si_{2-y}O_7$ (M = W, Ti, Nb), were studied for the removal of the key radionuclides ^{85}Sr, ^{134}Cs, and ^{57}Co from nuclear waste solutions. Emphasis was given to the removal of radionuclides from acidic effluents for which no efficient commercial exchangers are available. Initial screening tests showed that the undoped antimony silicates (Sb:Si molar ratio ~1:1) are highly selective for ^{85}Sr. Distribution coefficients (K_D) of 35,500 $mL\,g^{-1}$ were obtained in 0.1-M HNO_3. The antimony silicates also have high or reasonable selectivity for ^{57}Co, ^{59}Fe, and ^{241}Am; but the selectivity for ^{134}Cs is low. An attempt to increase the selectivity for ^{134}Cs was conducted by doping the antimony silicate

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with Ti^{4+}, Nb^{5+}, or W^{6+}. Best results were obtained with a material doped with tungsten, which resulted in an almost ten-fold increase in cesium selectivity in acid. The pyrochlore structure of the materials was also expected to have an effect in creating cesium selectivity. The granular antimony silicate doped with tungsten performed very well in column tests, and high-breakthrough capacities were observed for ^{85}Sr ($> 17,000$ BV with 1% breakthrough) and ^{134}Cs (5,000 BV) in 0.1-M HNO_3, and for ^{57}Co (5,200 BV) and ^{85}Sr (11,000 BV) in neutral simulated pond water. In general, the performance of the metal doped antimony silicates was considerably better than that of commercial materials such as a zeolite, a sodium titanate, and a silicotitanate, which function effectively only in neutral or alkaline conditions and were tested in parallel for reference.

Key Words: Ion exchange; Pyrochlore; Hydrous metal oxide; Nuclear waste; Strontium; Cesium; Cobalt.

INTRODUCTION

There is a project underway that deals with the development of highly selective inorganic ion exchangers for the removal of radionuclides from nuclear waste solutions.[1–4] Selective ion exchange as a separation method for radioactive nuclides, present in trace concentrations, from effluents that usually contain large amounts of inactive metals, is effective and desirable for the minimization of waste volumes for final disposal and solidification. The chemical conditions in these waste solutions vary widely, and materials with different properties are needed to treat the liquids. The pH of the solution is often a limiting factor in the utilization of many inorganic ion exchangers. The commercially available materials selective for ^{90}Sr [crystalline silicotitanate (CST), sodium titanate (SrTreat)[5–8]] are weakly acidic exchangers, and are not efficient at low pH. Similarly, zeolites have a very narrow functioning pH range, because of the dissolution of silicon and aluminum at pH extremities. Several effective materials for ^{137}Cs removal in acidic conditions are available [transition metal hexacyanoferrate (CsTreat), ammonium molybdophosphate (AMP),[9,10] but they often cannot be applied in highly alkaline media; for instance, AMP starts to dissolve already at pH > 6. Also, separation of activation corrosion products (e.g., ^{63}Ni, $^{58,\,60}Co$, ^{51}Cr, ^{65}Zn, and ^{59}Fe) from floor drain and pond waters from nuclear power plants (NPP) is an increasingly important aspect. So far, only the activated carbons have shown reasonable affinity for cobalt.[11] Because of the large volumes of effluents generated by the reprocessing plants (France, UK, Russia, Japan), the removal of ^{90}Sr from acidic waste is of urgency, as well.

The aim of this study was to develop materials for efficient removal of the three key nuclides (^{90}Sr, ^{137}Cs, and ^{60}Co) from acidic solutions. Special attention was given to hydrous metal oxides, and, especially, to those of antimony. The hydrous antimony pentoxide $(H_3O)_2Sb_2O_6O'$ is known to be highly selective for strontium in acid[12–15] but is rather ineffective in the presence of the common inactive macro components (Ca^{2+}, Na^+, K^+). Therefore, our attention was given to the development of an antimony silicate, a structural analogue of the antimony pentoxide and, also, selective for strontium in acid.[1–2,16] The structure in these materials is that of a pyrochlore[17] when prepared by acidic hydrolysis with pentavalent antimony. The antimony silicate was first evaluated for the ability to remove a wide range of radionuclides commonly found in nuclear waste solutions (^{90}Sr, ^{137}Cs, $^{57,\,60}$Co, ^{65}Zn, ^{59}Fe, ^{51}Cr, ^{236}Pu, and ^{241}Am). To obtain an increase in the low affinity for cesium, the antimony silicate was doped with another metal. The dopants chosen were Ti^{4+}, Nb^{5+}, and W^{6+} on the basis of the effective ionic radii of the cations (0.60 ± 0.04 Å) and the closeness of this value to the effective radius of Sb^{5+}. Therefore, the metals were expected to substitute for antimony in the pyrochlore structure.

The synthesis of the SbSi doped with W^{6+} was optimized, and this product prepared in large scale. If production is taken further to industrial-scale manufacture, the estimation of the effect of large-scale preparation on the ion-exchange properties is important. The processing capacity of the SbSi-W compound was evaluated in breakthrough column operations. These experiments showed that the material could be applied for efficient removal of strontium and cobalt from acidic decontamination solutions and neutral nuclear power plant pond waters.

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).

Syntheses of the Materials

The crystalline antimony silicate was prepared in a simple acidic hydrolysis reaction. $SbCl_5$ (99%) in 4-M HCl was mixed with a silicate solution $Na_2Si_3O_7$ ($SiO_2 \sim 27\%$) in an Sb:Si mole ratio of 1:1 in distilled water so that the final concentration of HCl was 0.8 M.[1−2] A precipitate formed while the mixture was heated at 60°C for 1 day, which was then washed with distilled water and dried at 77°C. The metal dopants were introduced into the Sb–Si mixture as aqueous solutions of $Na_2WO_4{\cdot}2H_2O$, $NbCl_5$ and $TiCl_4$ (99%) in Sb:Si:M mole ratios 1:1:0.5, 1.1:0.1, and 1:1:0.5, respectively.

For the optimization of the antimony silicate doped with tungsten, the reaction conditions were slightly altered. The sodium silicate solution was Crystal 0503 (with ~ 50% SiO_2) and the synthesis temperature was 45°C.

Characterization

X-ray diffraction (XRD) patterns of the products were collected with a Philips (The Netherlands) PW1710 powder x-ray diffractometer operating at 40 kV and 50 mA. Relative crystallinity of the compounds was determined by the observed peak widths and intensities in the patterns. The water content in each sample was determined by thermogravimetry (TGA) with a Mettler-Toledo TA800 unit at a heating rate of 10°C min^{-1} under a nitrogen atmosphere. The elemental analyses were performed by x-ray fluorescence (XRF) from solid samples.

Ion-Exchange Experiments

The selectivities of the materials for the three key nuclides (^{134}Cs, ^{85}Sr, ^{57}Co), several corrosion products (^{65}Zn, ^{59}Fe, ^{51}Cr, ^{63}Ni), and the actinides, ^{241}Am and ^{236}Pu, were estimated by determining the radionuclide distribution coefficients (K_D) by the batch method. The test solutions were 0.1-M HNO_3 and 0.1-M $NaNO_3$, which were traced with the radioactive nuclide. The powder-like exchangers were equilibrated with 6 mL of solution with a solution volume to exchanger mass ratio of 100 to 200 mL g^{-1} for 3 days at ambient temperature using constant rotary mixing. It was assumed that adequate equilibrium was reached during this time considering the intended application of the exchangers. The solids were separated from solution by centrifugation (Beckman (USA) L8-M Ultracentrifuge; 20 min at 30,000 rpm) and filtered with 0.22-μm Minispike PVDF Bulk Acrodisk 13 filters. Five-mL aliquots of the filtered samples were measured for the activities (cpm) with a gammacounter Wallac 1480 Wizard 3 (^{134}Cs, ^{85}Sr, ^{57}Co, ^{65}Zn, ^{59}Fe, ^{51}Cr, and ^{241}Am) and with a liquid scintillator Wallac LKB 1217 Rackbeta (^{236}Pu and ^{63}Ni). The distribution coefficient (K_D) values were calculated according to

$$K_D = \frac{\bar{A}}{A} = \frac{\text{concentration in exchanger}}{\text{concentration in solution}} = \frac{(A_0 - A_{eq})}{A_{eq}} \frac{V}{m} \qquad (1)$$

where $\overline{A}$ and A are the concentrations in the exchanger and the solution, respectively. A_0 and A_{eq} are the activities of the tracer initially and at equilibrium, respectively, and $V\,m^{-1}$ is the solution volume to exchanger mass ratio (batch factor, $mL\,g^{-1}$).[1,18]

The column experiments were carried out with 0.5-mL columns ($i.d = 4\,mm$; $l = 40\,mm$), and solution flow rate of $20\,BV\,h^{-1}$. The grain size of the exchanger was 0.3 to 0.85 mm. The solutions were 0.1-M HNO_3 and a neutral simulated pond water with 100-ppm Na^+, 1.5-ppm Ca^{2+}, and 0.7-ppm Mg^{2+} at pH 6.75, traced with ^{134}Cs, ^{85}Sr, and ^{57}Co. The breakthrough was calculated as usual (activity at exit/activity of feed).

RESULTS AND DISCUSSION

Uptake of Radionuclides by Antimony Silicate

The antimony silicates (SbSi) have been found to have significantly higher affinity for strontium in acid, as well as in the presence of the macro component sodium at acidic pH, than several commercially available ion exchangers, such as the sodium titanate SrTreat, a sodium titanosilicate (CST) and the natural zeolite clinoptilolite.[1] Upon evaluation for uptake of several other radionuclides in acid, SbSi was found to be highly selective most notably for ^{59}Fe and the actinides ^{236}Pu and ^{241}Am (Table 1). The distribution coefficient (K_D) values for ^{57}Co were also reasonably high, being $4300\,mL\,g^{-1}$ in 0.1 M HNO_3. The interference of the monovalent sodium was strong on ^{134}Cs uptake as typical but not as significant on cations of higher

Table 1. Distribution coefficients (K_D, $mL\,g^{-1}$) of several radionuclides for antimony silicate.

Nuclide	0.1-M HNO_3	0.1-M $NaNO_3$
^{85}Sr	35,500	15,900
^{134}Cs	3,700	350
^{57}Co	4,300	12,700
^{65}Zn	2,200	3,100
^{51}Cr	680	4,100
^{59}Fe	74,500	170,500
^{63}Ni	1,000	230
^{241}Am	26,500	12,900
^{236}Pu	7,300	8,500

charge (e.g. Fe^{2+} and Am^{3+}). The observed increase in ^{59}Fe K_D value in 0.1-M $NaNo_3$ can be explained by the almost immediate oxidation of Fe^{2+} to Fe^{3+} and the consequent formation of iron species, which were removed in the filtration. However, as the conditions in the 0.1-M $NaNO_3$ solutions were slightly acidic, the equilibration pH being 3 to 4, no precipitation of the cations is expected to have happened.

Ion-Exchange Properties of Antimony Silicate Doped with Tungsten

To improve the low cesium affinity (^{134}Cs $K_D = 3,700\,mL\,g^{-1}$ in 0.1-M HNO_3), the antimony silicate was doped with metals Ti^{4+}, Nb^{5+}, or W^{6+}. The element of higher charge was expected to increase the acidity of the material, thus making the exchanger more effective in acidic solutions. However, the substitution of Sb^{5+} may have been random and resulted in vacancies in the structure, thus causing changes in the charge density of the exchanger. Slight distortion in the pyrochlore structure may also lead to changes in the ion-exchange properties of the material. However, the structural effects on ion-exchange properties were not investigated further.

No significant improvement in the selectivity for ^{134}Cs was observed with doping the antimony silicate with Ti^{4+} over that of the undoped material. In fact, the addition of Ti^{4+} causes the material to behave more like a weakly acidic exchanger, it not being efficient in acidic conditions. The ^{134}Cs distribution coefficient K_D was only 20 mL g^{-1} for SbSi–Ti in 0.1-M HNO_3 but increased to 250 mL g^{-1} at pH ~4 in 0.1-M $NaNO_3$.[1] On the other hand, doping the antimony silicate with niobium or tungsten resulted in an increase in cesium affinity. Addition of Nb^{5+} gave a K_D value of ~ 11,000 mL g^{-1} in 0.1-M HNO_3 and still a slightly higher value with tungsten. The ^{134}Cs K_D values were almost one order of magnitude higher for SbSi-W (~ 17,000 mL g^{-1} in 0.1-M HNO_3) than for the undoped material (3,700 mL g^{-1}).[1]

It was shown in titrations of SbSi1 and SbSiW1 that the Cs^+ capacity increases almost threefold upon tungsten incorporation into the structure. The capacity is 0.5 mmol g^{-1} for the antimony silicate SbSi1, but 1.3 mmol g^{-1} for SbSiW1 at pH 6 to 7 in $CsNO_3$.[19] The H^+ ion capacity determined for Na^+/H^+ exchange in the undoped antimony silicate (2.7 mEq g^{-1} at pH ~7) is only 53% of the capacity of the hydrous antimony pentoxide $(H_3O)_2Sb_2O_6O'$, 5.1 mEq g^{-1}.[1,14] This is presumed to result from the reduction in the amount of structural water, because of the addition of silicon into the structure. On the other hand, the increase in Cs^+ capacity observed with W^{6+} doping may also be thought to have resulted from the change in the charge density in the framework, which would create new exchange sites for univalent cations. This would also explain why the univalent Na^+ ion continued to be a detrimental interference in Cs^+ uptake.

Optimization of W^{6+}-Antimony Silicate

As doping with W^{6+} resulted in the greatest increase in the ^{134}Cs distribution coefficient in acid and also produced a harder product than the addition of titanium or niobium, this compound was chosen for further study. The preparative conditions strongly affect the ion-exchange properties of the hydrous metal oxides; and, therefore, a series of syntheses of the material with different W^{6+} amounts in reaction was conducted to find the optimum Sb:Si:W mole ratio for ^{134}Cs, ^{85}Sr, and ^{57}Co uptake in acid (Table 2). The synthesis procedure was performed as usual, with the exception that the effect of aging time was also studied by letting part of the mixture to sit in the mother liquor for another 5 days, giving products aged for 1 day and 6 days.

The increase in tungsten content led to a "step-wise" degradation of crystallinity of the pyrochlore phase until it was completely amorphous at a Sb:Si:W mole ratio of 1:0.98:0.52 in product (P 6). With the decrease in crystallinity, the K_D values tended to decrease as well (see Table 2). The selectivity for ^{134}Cs increased with the increasing tungsten content until the start of degeneration of crystallinity in product P 5. The trend is similar for ^{57}Co, while the highest affinity for ^{85}Sr was obtained with the undoped SbSi or a material with very little tungsten product P 2. Aging clearly improved the selectivities in general, but particularly for ^{57}Co. As observed for product P 3, the ^{57}Co K_D value was 2,300 $mL\,g^{-1}$ in 0.1-M HNO_3 after the usual 1 day of reaction time but 33,800 $mL\,g^{-1}$ after 6 days of aging (see Table 2). This increase could not be explained by the crystallinity of the samples as no significant differences were observed in the powder XRD patterns. Studies to elucidate the effect of aging have been continued.

As the maxima for ^{134}Cs, ^{85}Sr, and ^{57}Co, K_D values were obtained with different elemental compositions, an average for the optimal product was chosen. The synthesis conditions for product P 3, with Sb:Si:W mole ratio of $\sim$1:1:0.1 in reaction were used in further experiments.

Preparation of the Optimized Product in Large Scale

Synthesis reaction volume is also one of the factors that generally affects the crystallinity and the ion-exchange properties of the final inorganic product. Therefore, the synthesis of the optimized antimony silicate doped with

Table 2. Optimization of antimony silicate doped with tungsten for ^{134}Cs, ^{85}Sr, and ^{57}Co uptake in acid.

Sample	Sb:Si:W mole ratio in product	Phase	K_D (aged 1 d)/K_D (aged 6 d), mL g^{-1} in 0.1-M NO_3		
			^{134}Cs	^{85}Sr	^{57}Co
P 1	1:0.81:0	Pyrochlore	12,400/36,300	584,500/605,500	2,000/12,000
P 2	1:0.85:0.03	Pyrochlore	18,100/45,000	554,420/885,000	3,500/33,700
P 3	1:0.9:0.1	Pyrochlore	35,700/86,400	231,000/459,100	2,300/33,800
P 4	1:0.94:0.26	Pyrochlore	36,500/126,000	28,600/50,000	1,900/10,850
P 5	1:0.97:0.36	Semicrystalline pyrochlore	16,800/63,600	16,600/20,900	510/3,030
P 6	1:0.98:0.52	Amorphous	14,600/30,200	9,000/8,800	380/580
P 7	0.45:0.6:1	Amorphous	940/1,040	70/70	20/110
P 9	0:0.74:1	Tungstite $WO_3 \cdot n\,H_2O$	9,250/77,600	20/60	5/90
P 10	1:0.29:0.32	Semicrystalline pyrochlore	9,800/55,000	5,860/13,650	180/1,230
P 11	(1:0:1)[a]	Amorphous	3,400/—	1,110/—	155/—
P 12	0.3:1:0.12	Pyrochlore	20,400/45,000	23,700/3,700	720/530

[a] Mole ratio in rection.

tungsten (P 3) was scaled up by a factor of 35 from labs-scale (to a reaction volume of 7 L), with the view of possible industrial scale manufacture. Because of exothermic nature of the reaction, special care has to be taken when handling the large amounts of reactants. When the usual yield from the synthesis in laboratory scale was only about 2 to 3 g, 180 g was obtained from a reaction indicated as follows:

Scale-up of Product 3 (P 3)
A) 268.4 g $SbCl_5$ in 2.6 L of 4-M HCl
B) 105.6 g Crystal 0503 ((50% silica) in 2.2 L H2O
C) 29.0 g $Na_2WO_4(2H_2O$ in 2.2 L H_2O
Total volume: 7 L, Sb:Si:W mole ratio 1:1:0.1

B and C were mixed together with a prompt addition of A. The mixture was placed in a 45°C oven for 1 day, after which it was filtered after 4 days and dried at 77°C.

The product prepared in large scale was only slightly less crystalline than the material obtained in laboratory scale. This was not significant enough to affect the ^{134}Cs selectivity in 0.1-M HNO_3 compared to "P 3-lab" aged for 6 days (Table 3). The distribution coefficient of ^{57}Co decreased slightly, which may be explained by the clear effect of the aging time on the affinity for cobalt as seen earlier (see Table 2). The large-scale P 3 was aged for 4 days, thus the ^{57}Co K_D value of 15,000 mL g^{-1} almost linearly falls between the values of "P 3-lab"aged for 1 day (2300 mL g^{-1}) and 6 days (33,800 mL g^{-1}) (see Table 3). On the other hand, the exceptionally high ^{85}Sr K_D value may indicate a presence of an amorphous phase of the highly strontium selective antimony pentoxide undetected in the powder XRD pattern. Further optimization

Table 3. ^{134}Cs, ^{85}Sr, and ^{57}Co distribution coefficients (K_D) for antimony silicate doped with tungsten (P 3) prepared in laboratory-scale and in large-scale.

	Distribution coefficient K_D in 0.1-M HNO_3, mL g^{-1}		
Sample (aging time)	^{134}Cs	^{85}Sr	^{57}Co
Undoped SbSi	590	19,700	2,000
P3 (1 day)	35,700	230,700	2,300
P3 (6 days)	86,400	459,000	33,800
35 × scale-up (4 days)	86,900	1,200,000	15,000

of the synthesis procedure and the product has been continued at industrial level by INEOS Silicas Ltd., UK.

Breakthrough Capacity of SbSi-W

As batch experiments and K_D values only give an indication of the selectivity and the processing capacity of the exchanger, SbSi-W (P 3) was also evaluated for "real" processing capacity in column runs. SbSi-W performed extremely well for ^{85}Sr in 0.1-M HNO_3, it had a breakthrough capacity as high as 17,000 BV (1% breakthrough) (Fig. 1). The breakthrough capacity (1%) for ^{134}Cs was also very good, 5000 BV. SbSi-W performed very well in simulated neutral pond water, with no significant breakthrough at 16,000 BV for ^{85}Sr (Fig. 2). It was appreciably efficient for ^{57}Co as well, while the natural zeolite clinoptilolite, which was run for reference, had almost immediate breakthrough. The clinoptilolite column clogged at 5500 BV. The curve for ^{134}Cs is not shown because of poor performance of SbSi-W in the presence of Na^+ (100 ppm) in the feed. It may be expected based on the results obtained by Harjula et al on a hexacyanoferrate exchanger[20] that in full-scale columns the breakthrough capacities would be even higher.

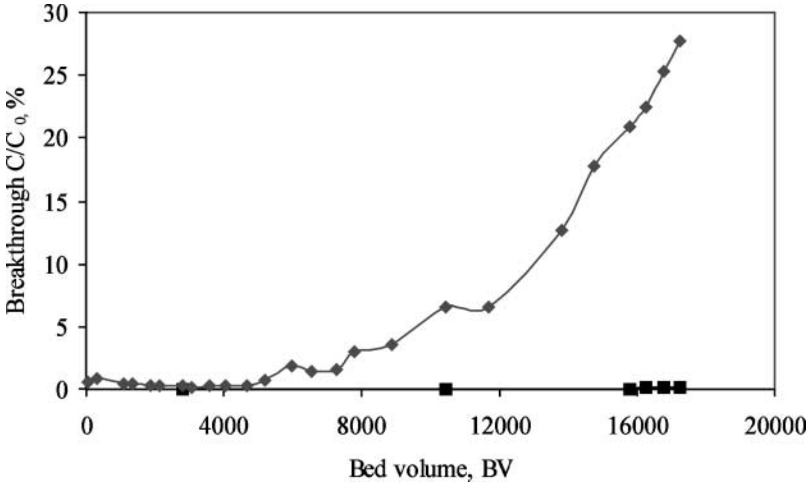

Figure 1. Breakthrough curves for ^{85}Sr (■) and ^{134}Cs (◆) in 0.1-M HNO_3 on antimony silicate doped with W^{6+}.

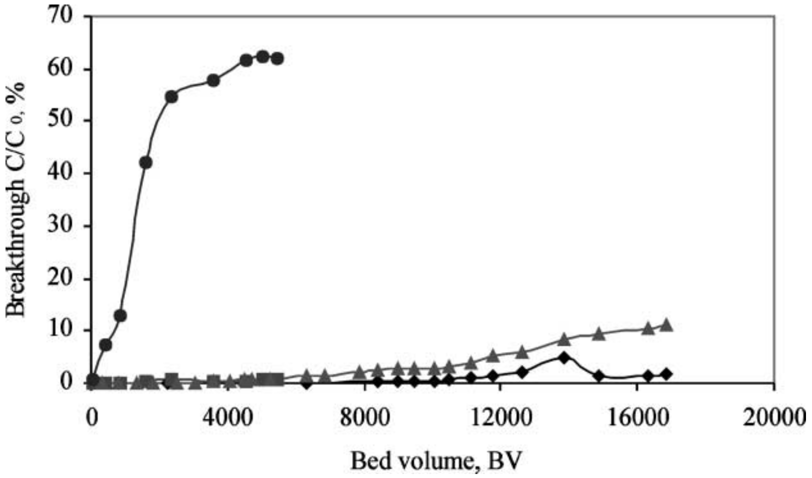

Figure 2. Breakthrough curves for ^{85}Sr and ^{57}Co in neutral simulated pond water on SbSiW (^{85}Sr : ◆, ^{57}Co : ▲) and clinoptilolite (^{85}Sr : ■, ^{57}Co : ●).

CONCLUSION

Antimony silicate prepared in an acidic hydrolysis reaction was found to be highly selective for ^{85}Sr, ^{59}Fe, and ^{241}Am, and reasonably efficient for ^{57}Co and ^{236}Pu removal in 0.1-M HNO_3 and $NaNO_3$. However, selectivity for ^{134}Cs is low. This property was successfully improved by doping SbSi with Nb^{5+} or W^{6+}. The optimal material that has high selectivity for the three key nuclides ^{134}Cs, ^{85}Sr, and ^{57}Co in 0.1-M HNO_3 was doped with tungsten in an Sb:Si:W mole ratio ~1:1:0.1 in reaction (1:0.9:0.1 in product P 3). Although tungsten improves the affinity for Cs^+ in acid, the inactive macrocomponent Na^+ continues to be a detrimental interference. However, the high-breakthrough capacities obtained in column runs for ^{85}Sr and ^{57}Co show promise for possible applications of this material in the removal of radioactive strontium and activation corrosion products from acidic and neutral nuclear wastewaters.

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