METAL ANTIMONATES – HIGHLY EFFECTIVE ION EXCHANGERS FOR RADIONUCLIDE REMOVAL FROM ACIDIC AND NEUTRAL WASTE SOLUTIONS

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ABSTRACT

Several metal antimonates MSbO (M = Si, Ti, Mn, Sn) have been studied for the removal of several key radionuclides (^{60}Co, ^{90}Sr and ^{137}Cs) from nuclear waste solutions. Special emphasis was the removal of radionuclides from acidic effluents and from effluents of high Ca content. Synthesis and initial screening test indicated that increasing the degree of substitution of other metals (M) for Sb increases the uptake of divalent cations (Sr, Co) in acidic media. Some of the synthesised compounds also showed considerable tolerance for Ca ions in Sr removal. Column tests with granular silicon antimonate gave very good decontamination factors (DF) for ^{85}Sr (DF up to 10000) and ^{134}Cs (DF up to 600) in nitric acid solution (0.1 M) and for ^{57}Co (up to 5000) ^{85}Sr (up to 3000) in neutral simulated pond water. Precoat tests with manganese antimonate powder gave high decontamination factors for ^{57}Co (DF up to 600) in simulated NPP floor drain water. In general, the performance of the metal antimonates was considerably better than that of commercial materials (zeolite, titanate, and silicotitanate) that were tested in parallel for reference.

INTRODUCTION

Due to their high selectivity and radiation stability, inorganic ion exchangers lend themselves ideally for the treatment of nuclear waste effluents. A good number of effective inorganic exchangers are commercially available today. Natural and synthetic zeolites are used in several nuclear power plants for the removal of ^{137}Cs from low-salt effluents. In high- and medium-salt effluents more selective medias are used. These include different titanium oxide-based compounds (removal of ^{90}Sr and TRU-nuclides), silicotitanates (removal of ^{90}Sr and ^{137}Cs) and hexacyanoferrate compounds (removal of ^{137}Cs)(1-5). However, the water chemistry often limits the use of highly selective inorganic medias. A major challenge is the removal of ^{90}Sr from acidic or mildly acidic liquids, since the materials that are selective for ^{90}Sr are weakly acidic in nature and do not thus perform efficiently below pH = 5. Commercially available materials have practically no ^{90}Sr uptake in acidic medium (Table I). Another challenge is the removal of ^{90}Sr from Ca-bearing waste liquids since Ca ions usually interfere strongly with Sr uptake.

Considerable research has been carried out by the authors to study and develop acidic inorganic ion exchangers for the removal of ^{90}Sr and other key radionuclides from nuclear waste effluents.

Several promising groups of compounds have been identified and developed. These include titanium antimonates, which take up efficiently several important radionuclides present in nuclear wastes (Table I). In addition, these compounds tolerate considerable levels of Ca ions in the solution. Tungsten-doped silicon antimonates (6) show even higher radionuclide uptakes, but their Ca-tolerance is somewhat lower than that of titanium antimonate compounds. This paper describes some initial screening test results that have been obtained with the metal antimonate materials. In addition, recent dynamic column and precoat test results with simulated waste liquids are presented.

EXPERIMENTAL

Materials And Batch Tests

The metal antimonates $M_XSb_YO_Z$ x wH_2O (M = Si, W, Ti, Mn, Sb) of varying M/Sb- ratio (10-0.1) were synthesised by proprietary methods at the Laboratory of Radiochemistry (Finland) and at Crosfield Ltd. (UK). The synthesised products were first introduced to initial screening tests, which comprised the determination of radionuclide distribution coefficients (k_d) in 0.1 M HNO_3 and 0.01 M $Ca(NO_3)_2$ solutions: a sample of ion exchanger (in H^+-form or Ca^{2+}-form, m = 0.050-0.070 g) was contacted for three days with the solution (7-50 mL) traced simultaneously with ^{57}Co, ^{85}Sr and ^{134}Cs, after which the solution was centrifuged, filtered (0.2 um) and analysed for the radionuclide activities using a Canberra Ge-detector and multichannel analyser (DSA 2000) and Genie2000 software. Some commercial ion exchangers, i.e. silicotitanate CST (UOP, USA), titanate (Selion Oy, Finland) and clinoptilolite zeolite (BNFL) were tested in parallel for reference. The k_d-values were calculated using the formula:

$$k_d = \frac{\overline{A}}{A} = \frac{A_0 - A}{A}\frac{V}{m} \qquad \text{(Eq. 1)}$$

where $\overline{A}$ is the equilibrium radionuclide acvtivity concentration in the exchanger (Bq/g) and A_0 and A are the initial and equilibrium activity concentrations in the solution Bq/mL, respectively. The ratio V/m is that of solution volume (mL) to exchanger mass (g). The radionuclide k_d-values may be used to estimate the total processing capacity, in terms of solution volume (L) that can be purified with unit mass of ion exchanger (kg) under the conditions that prevail in the test. The k_d-value can also be used to measure the selectivity of the ion exchanger relative to the exchanging counter-ion B (charge z_B), i.e.

$$k_{A/B} = \frac{[\overline{A}]^{z_B}\,[B]^{z_A}}{[A]^{z_B}\,[\overline{B}]^{z_A}} = k_d^{\;z_B}\,\frac{[B]^{z_A}}{[\overline{B}]^{z_A}} \qquad \text{(Eq. 2)}$$

where [B] and $[\overline{B}]$ are the concentrations of counter-ion B in solution and in the ion exchanger, respectively.

Based on the initial screening test results, selected samples were tested further by determining the radionuclide distribution coefficients as a function of pH. These experiments were carried out by batch titration of the H-form exchangers with NaOH in $NaNO_3$ solutions (concentration 0.01-1

M) that were traced with a radionuclide ion. After a three-day contact time the solution was centrifuged, filtered and analysed for the radionuclide activity and pH. The k_d value was calculated as before (Eq. 1).

Dynamic Tests

Most promising materials were submitted to dynamic column and precoat tests. Column tests were carried out using small-scale (bed volume BV = 0.5 cm^3) columns packed with granular (0.30-0.15 mm) ion exchange material. Two types of simulated waste solution were used, 0.1 M HNO_3 solution and a simulated pond water (Na 100 ppm, Ca 1.5 ppm, Mg 0.7 ppm), which were traced with ^{57}Co, ^{85}Sr and ^{134}Cs with an activity level of 10000 Bq/L. The traced solutions (radionuclide activity A_0) were pumped through the columns at a flow rate of 10 mL/h (20 BV/h) and fractions were collected from the outlet for the determination of outlet activity A. The decontamination factors for the radionuclides were calculated as $DF = A_0/A$.

Precoat tests were carried out using a planar Millipore filter unit (Fig. 1) housing a 92 mm diameter filter membrane (filtration area 125 cm^2). The ion exchanger (m = 8-10 g, grain size < 0.15 mm) was slurried in water in a packing cylinder that was placed on top of the membrane. After the ion exchange material was settled on the membrane by the aid of suction, the top lid of the filter unit was closed. The feed solutions simulated NPP Floor Drain waters and contained a constant amount of Na (100 ppm) and varying amounts of Ca (0.5-25 ppm) were used in the precoat tests. Solution was circulated through the filter unit via a stirred 60-L feed tank. Concentrated solutions of radioactive tracer ions (^{134}Cs or ^{57}Co) were fed continuously into the feed tank to replenish the radioactivity taken up by the precoat filter and to keep the radioactive feed level approximately constant at 100 Bq/L. Feed solution flow rate was maintained at 0.3-0.6 L/h, which corresponds 1800-3600 exchanger "bed" or mass volumes per hour. Because of high throughput rate, the activity in the 60-L feed tank had to be kept low at the 100 Bq/L to avoid excessive build-up of radioactivity in the filter unit. In order to study the effect of feed activity on the precoat performance, the filter was fed for short periods using smaller feed vessel of much higher activity levels (10,000 – 100,000 Bq/L). The radionuclide activities were analyzed in the feed solution (A_0) and in the filter outlet solution (A), and the decontamination factor for the radionuclides was calculated as $DF = A_0/A$.

Fig. 1. The Millipore filter unit used in the precoat tests.

RESULTS AND DISCUSSION

Initial Screening Tests

Many of the tested metal antimonates took up efficiently ^{57}Co, ^{85}Sr and ^{134}Cs from acidic solution (Table I). Uptake of ^{57}Co and 85Sr in titanium antimonates increased with the increasing amount of Sb (ratio M/Sb decreases) in the compound, while ^{134}Cs uptake had a maximum when the Ti/Sb-ratio was 0.5-1.0. The manganese antimonates and tungsten doped silicon antimonates (W-$Si_XSb_YO_Z$) behaved similarly, except that the latter group of materials had a high uptake for ^{134}Cs and ^{85}Sr over a broader M/Sb-ratio than the titanium or manganese antimonates. The level of ^{134}Cs uptake was also somewhat higher in the W-doped silicon antimonates than in the other metal antimonates. This was a specific effect of doping tungsten into the silicon antimonate compound. Commercial Sr-selective Na-titanate exchanger did not work in the acid test solution (Table I.). Silicotitanate, which is known to be selective for both Cs and Sr, did not take up any ^{85}Sr, or ^{57}Co, from the acid solution. However, uptake of ^{134}Cs from the acid solution by CST was rather effective.

Table I. A selection of screening test results: radionuclide distribution coefficients for metal antimonates ($M_XSb_YO_Z$) in 0.1 M HNO_3.

Ion Exchanger		**k_d (L/kg)**		
M	M/Sb	Cs-134	Sr-85	Co-57
Ti	3.9	230	7	2
	1.2	41 000	370	3 500
	0.9	69 000	1 500	8 500
	0.6	76000	45 000	14 000
	0.19	5200	168 000	47300
Si, W	1.73	182000	1720000	14500
	0.76	110000	7570000	75000
	0.25	270000	6500000	2700
Mn	2	440	4100	5600
	1	19000	580000	22000
	0.65	65000	7100000	5800
	0.2	48000	11000000	4000
Na-titanate		0	4	5
Silicotitanate CST		51 500	10	0.2

The new metal antimonates had a reasonable uptake of ^{85}Sr from 0.01 M $Ca(NO_3)_2$ solution (Table II). It can be estimated using Eq. 2. that the selectivity coefficients $k_{Sr/Ca}$ between Sr and Ca were in the range of 14-82. Na-titanate had no specific selectivity for Sr over Ca ($k_{Sr/Ca} \approx 1$) while CST had a similar Sr/Ca selectivity ($k_{Sr/Ca} = 47$) as the best metal antimonate materials.

Table II. A selection of screening tests results: ^{85}Sr distribution coefficients k_d (Eq. 1) and Sr/Ca selectivity coefficients $k_{Sr/Ca}$ (Eq. 2) for metal antimonates ($M_XSb_YO_Z$) determined in 0.01 M $Ca(NO_3)_3$ solution.

Ion Exchanger		**K_d (L/kg)**	**$K_{Sr/Ca}$**
M	M/Sb	Sr-85	Sr-85
Ti	1.2	8200	82
	0.9	6 100	61
	0.6	3 300	33
Si, W	1.73	n.d.	
	0.76	2360	24
Mn	1	3000	30
	0.65	1400	14
Na-titanate		200	1
Silicotitanate CST		7000	47

Effect Of pH On Radionuclide Uptake

Regarding ^{85}Sr, the general trend for titanium antimonates was that the uptake in acidic solution increased as the proportion of antimony in the compound increased (Fig. 2). The uptake curves crossed over in neutral pH range so that some of the high-Sb products had somewhat lower uptake than the low-Sb compounds in neutral and slightly alkaline solution. For ^{57}Co and ^{134}Cs uptake, there was no steady increase in the uptake with increasing Sb content, but the uptake had a maximum at about Ti/Sb =1-2. The behaviour of ^{85}Sr uptake was similar in the silicon and manganese antimonates, but the maxima of the ^{57}Co and ^{134}Cs uptakes was not as strong as in titanium antimonates. The uptake of ^{85}Sr in Na-titanate (Fig. 2) and CST (not illustrated) was similar to that of low-Sb metal antimonates; i.e. the uptake was low in the acidic solution.

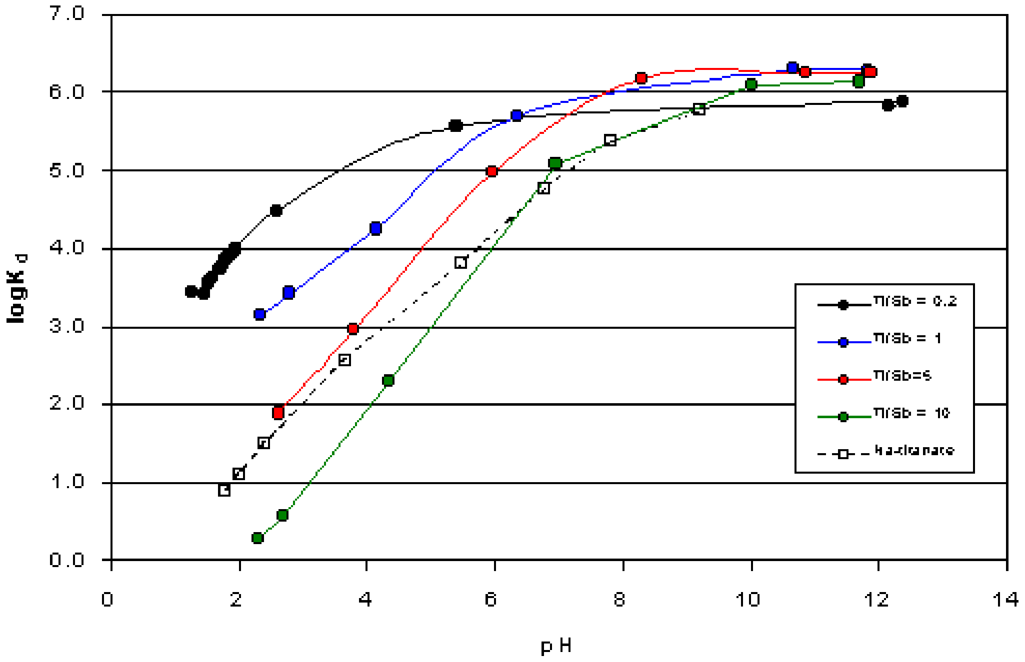

Fig. 2. Distribution coefficient k_d of ^{85}Sr for titanium antimonates of different Ti/Sb-ratio as a function of pH in 0.1 M $NaNO_3$. Data for Na-titanate shown for comparison.

Column Tests

Column experiments have been carried out using a granular W-doped silicon antimonate compound (WSiSb, Si/Sb = 0.76). This material removes efficiently both ^{85}Sr (DF up to 1000) and ^{134}Cs (DF up to 600) from HNO_3 solution (Fig. 3). Also the processing capacity is high for ^{134}Cs and ^{85}Sr, the column had considerable capacity left when the test was terminated at about 17000 BV. The level of ^{57}Co removal was only about 50 % (DF $\approx$ 2) most of the time and the ^{57}Co-capacity was exhausted at about 8000 BV, which is rather unexpected considering the relatively high k_d-value (Table I). This data indicate that the kinetics of ^{57}Co exchange in WSiSb is very low.

In neutral simulated pond water, the removal efficiency of WSiSb for ^{85}Sr was again very high (DF up to 3000). Also ^{57}Co is removed with a high efficiency (DF up to 5000) but ^{134}Cs was taken up with reasonable efficiency (DF > 10) only during the early stages of the column run. The capacity for ^{134}Cs was exhausted at about 3000 BV, while ^{85}Sr and ^{57}Co were still taken up when the test was terminated at 17000 BV. The removal efficiency of WSiSb for ^{57}Co and ^{85}Sr was considerably better than that of clinoptilolite zeolite (Fig. 4).

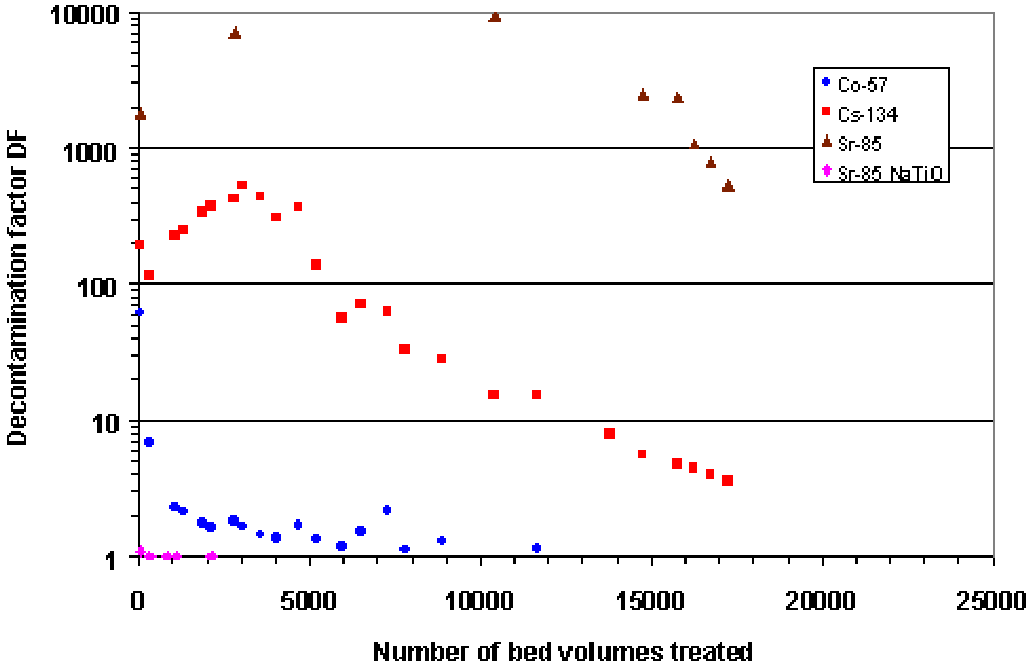

Fig. 3. Column decontamination factors DF of ^{57}Co, ^{85}Sr and ^{134}Cs for W-doped silicon antimonate (Si/Sb = 0.76, see Table I) and for a titanate (^{85}Sr) in 0.1 M HNO_3-solution. Radionuclide feed activities 10 kBq/L.

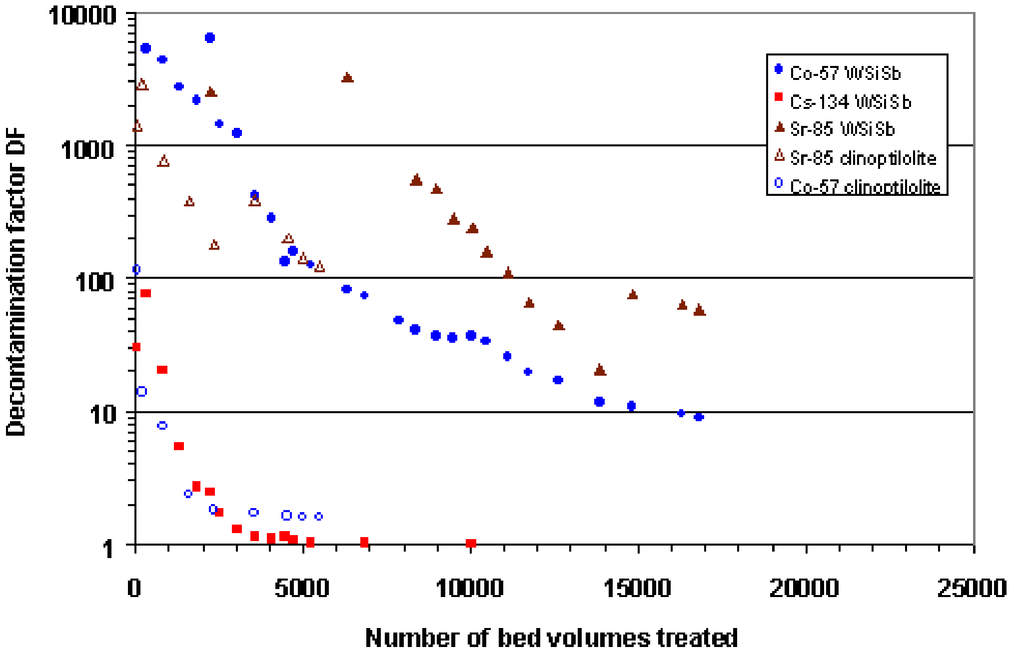

Fig. 4. Column decontamination factors DF of ^{57}Co, ^{85}Sr and ^{134}Cs for W-doped silicon antimonate (Si/Sb = 0.76, see Table I) and clinoptilolite zeolite in simulated pond water (Na 100 ppm, Ca 1.5 ppm, Mg 0.7 ppm). Radionuclide feed activities 10 kBq/L.

Precoat Tests

First precoat experiments were carried out using a powder of manganese antimonate (Mn/Sb = 10) and a simulated NPP Floor Drain Water (Na 100ppm, Ca 0.5 –25 ppm) spiked with ^{57}Co and ^{134}Cs (50-10000 Bq/L). The experiment was started using a solution with 0.5 ppm Ca content and a ^{57}Co feed activity of about 50 Bq/L. The observed DF for ^{57}Co was about 10 under these circumstances (Fig. 6). When the ^{57}Co feed activity was increased to about 10000 Bq/l, the DF's increased considerably to about 500. Similar strong dependence of DF on the feed activity has been observed earlier in the precoat tests of CsTreat and CoTreat ion exchange medias (4). Increasing the Ca content in the feed stepwise first to 5 ppm and then to 25 ppm (^{57}Co feed activity about 10000 Bq/L) did not decrease the DF noticeably, but the DF remained in a high level (400-600). At this stage 100 L of solution had been processed. The test was continued using the low ^{57}Co feed level of about 50 Bq/l and 0.5 ppm Ca level and the DF's decreased again to about 10 and remained at this level till the test was terminated at 530 L. The processing capacity was thus at least 77500 L/kg (exchanger dose 7 g) even though the solution contained considerable amount of Ca, which usually decreases strongly the uptake of divalent radionuclides in ion exchangers. Further experiments are underway using the silicon and titanium antimonate materials.

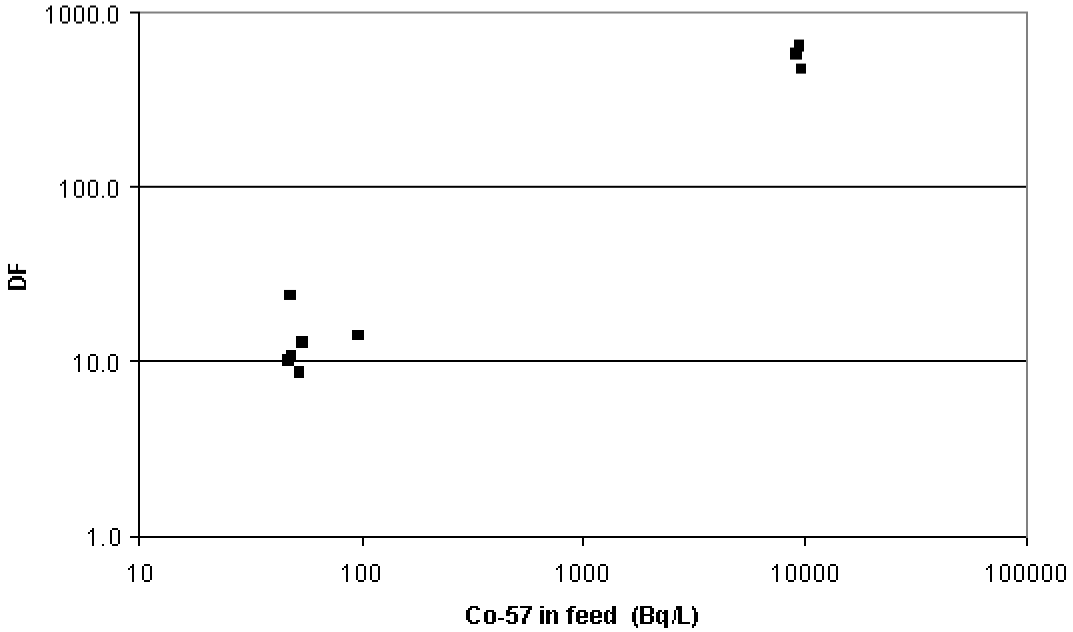

Fig. 5. Decontamination factor DF for ^{57}Co as a function of ^{57}Co feed activity in precoat test of manganese antimonate (Mn/Sb = 10).

CONCLUSIONS

The new metal antimonate compounds show great promise for the removal of ^{90}Sr and several other key radionuclides from acidic and neutral waste liquids. Static radionuclide uptakes are considerably higher than those obtained with commercial reference materials. Laboratory scale column experiments indicate that ^{85}Sr and ^{134}Cs can be removed with high DF from acidic waste with the W-doped silicon antimonate exchanger. This material also removes ^{57}Co and ^{85}Sr efficiently from neutral pond water simulant. Further work is necessary to evaluate the column performance of other types of metal antimonates. Application of the metal antimonates as powders on filter systems (precoat operation) appears a highly promising technique that allows much higher throughput rates than the conventional column operation.

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