TESTING OF NOVEL INORGANIC ION EXCHANGERS FOR THE REMOVAL OF RADIOCOBALT FROM NPP WASTE EFFLUENTS

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ABSTRACT

New antimonysilicate (SbSi) ion exchanger is being developed for industrial use. Tentative screening tests using simulated waste liquids have indicated that this material can remove most key radionuclides such as ^{60}Co, ^{90}Sr and ^{137}Cs in much broader pH-range than existing commercial materials. As a part of the development program, the material is being tested for the removal of ^{60}Co from real nuclear power plant waste waters. In this context, test with small-scale laboratory columns (bed volume 0.5 mL) have been carried out using a Floor Drain water samples from Ginna NPP and Diablo Canyon NPP, USA. More than 90 % of ^{60}Co in these liquids was removable by mechanical filtration (0.45 μm). SbSi columns removed more than 90 % of the soluble ^{60}Co that was left in the solutions after filtration. The tests were discontinued when about 2000 bed volumes were treated due to depletion of test liquids with no sign of column exhaustion.

INTRODUCTION

In terms of higher radiation stability and selectivity, inorganic ion exchangers are superior to organic ion exchange resins in the treatment of nuclear waste effluents. Several effective inorganic exchangers are available nowadays for industrial-scale applications. Natural and synthetic zeolites are used in several nuclear power plants (NPP) and other nuclear facilities for the removal of ^{137}Cs from low-salt effluents. For the treatment of effluents with higher salt content, more efficient inorganic medias are available. 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 these inorganic medias. In general, with the exception of ^{137}Cs, the inorganic materials available can be used efficiently in neutral and alkaline solutions only and the performance is often poor even in mildly acidic liquid (pH < 6). Another limitation is in the arsenal of inorganic ion exchange materials itself; few commercial materials are available for the removal of radionuclides other than ^{137}Cs and ^{90}Sr, i.e. for the activated corrosion product nuclides (e.g. ^{54}Mn, ^{59}Fe, ^{60}Co, ^{63}Ni).

Novel metal antimonate ion exchangers show great promise for efficient removal of a range of key radionuclides from neutral and acidic solutions. Tentative screening tests and trials with simulated waste solutions have shown that these materials can remove efficiently e.g. ^{137}Cs, ^{90}Sr, ^{60}Co and ^{125}Sb from neutral or even from acidic liquids[6-8]. One of these materials, silicon antimonate (SiSb), is being developed for large-scale manufacture and industrial use. So far, SbSi material has been tested using various simulated waste liquids. Good performance has been observed in acid solutions and in simulated pond water (for example, see Fig. 1)[8]. Testing work has is now being extended for real waste solutions. The first stage of the test comprises small-

scale column experiments in laboratory using real Floor Drain Waters obtained from several nuclear power plants (NPP). The tests will commence in July 2001, and are scheduled to run until November 2001. Results will be reported in the full paper.

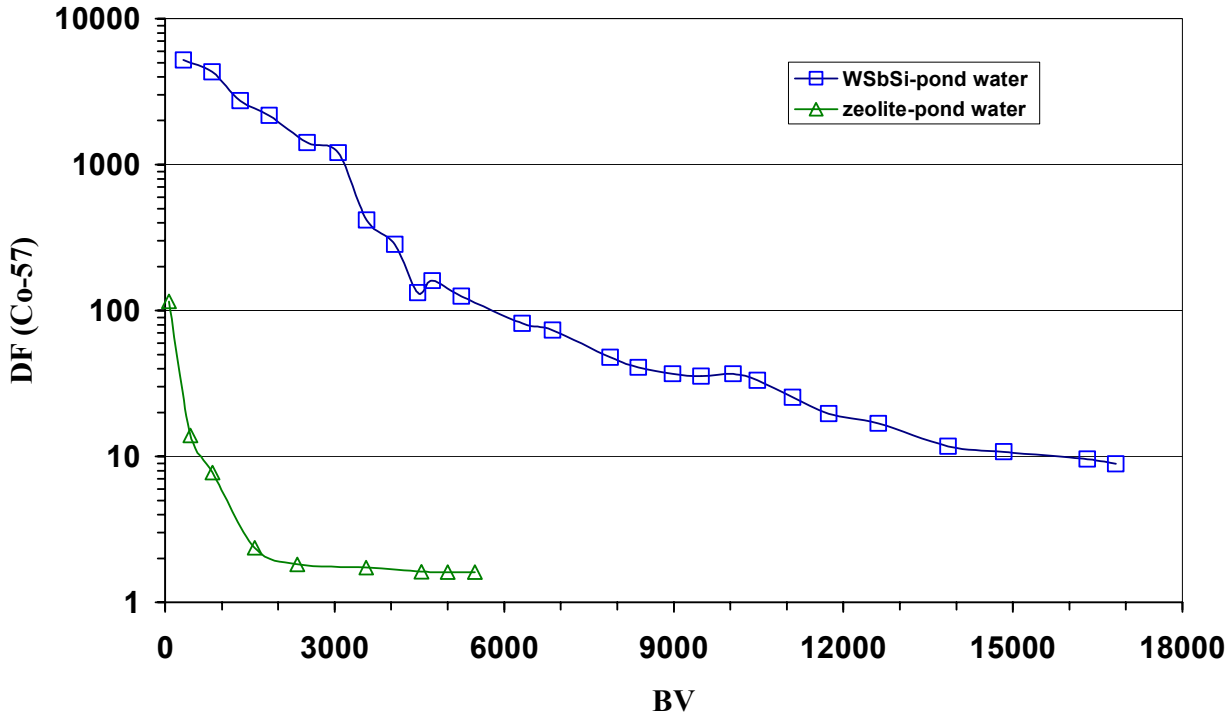

Fig. 1. Contamination factors DF obtained for ^{57}Co with SiSb and zeolite (Clinoptilolite) in column tests with simulated pond water.

EXPERIMENTAL

The antimonysilicate material used in the tests was obtained from INEOS Silicas Ltd (formerly Crosfield Ltd), Warrington, UK. Dynamic ion exchange column tests were carried out using small-scale (bed volume BV = 0.5 cm^3) columns packed with granular (0.25-0.85 mm) antimonysilicate material. The test solutions were a Floor Drain Water (FDW) obtained from Ginna NPP, USA, and an Equipment Drain Water (EDW), obtained from Diablo Canyon NPP, USA, in 1998 (for compositions, see Table 1). Most of these test solutions had been used in the testing of CoTreat and CsTreat ion exchange materials in 1998[9], but a few liters left for further studies was used in present trials. These test solutions were filtered prior to the column trials. Major proportion of ^{60}Co in the solutions was in a non-soluble form removable by 0.45 μm filtration. The decontamination factors (DF) obtained in filtration for ^{60}Co were 38 for the Ginna sample and 28 for the Diablo Canyon samples (Table 1). These DF's were considerably higher than what was measured for the same water samples in 1998 (12 and 8, respectively), indicating that increasing portion of ^{60}Co had converted to non-soluble form during the prolonged storage.

The test solutions (initial 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 factor for the radionuclides was calculated as $DF = A_0/A$.

Table I. Radiochemical composition of NPP Waste Waters used in the tests.

Sample Nuclide	**Activity concentration (Bq/L)**	
Ginna FDW	**Total**	**Soluble (<0.45 um)**
Co-60	24,800	646
Sb-125	1980	1,050
Ag-110m	280	45
Cs-134	730	730
Cs-137	8920	8564
Diablo Canyon EDW	**Total**	**Soluble (<0.45 um)**
Co-60	325,000	11,600
Sb-125	18,200	3870
Cs-137	2460	1616

RESULTS AND DISCUSSION

SbSi column removed ^{60}Co from both test solutions with a reasonable efficiency, the DF's being 12-22 for the Ginna sample and 12-15 for the Diablo Canyon sample. There was no sign of column exhaustion for ^{60}Co when the tests were stopped due to the depletion of liquid (Figs. 2-3). The columns removed practically no ^{125}Sb or ^{110m}Ag. The removal of ^{137}Cs was very efficient (DF > 100) during the early stages of the tests, but the columns had exhausted or showed signs of exhaustion for ^{137}Cs when the test was terminated.

Compared to earlier test data obtained for ^{60}Co with CoTreat[9], the decontamination factors were somewhat lower for the Ginna sample (CoTreat DF ≈ 35) and slightly higher for the Diablo Canyon sample (CoTreat DF = 10-8) than those measured for CoTreat. However, because considerable portion of ^{60}Co had converted to non-soluble form during prolonged storage between the two test series, the results between SbSi and CoTreat are not directly comparable. It is likely that SbSi would have performed somewhat better in fresh solutions that contain more soluble cobalt.

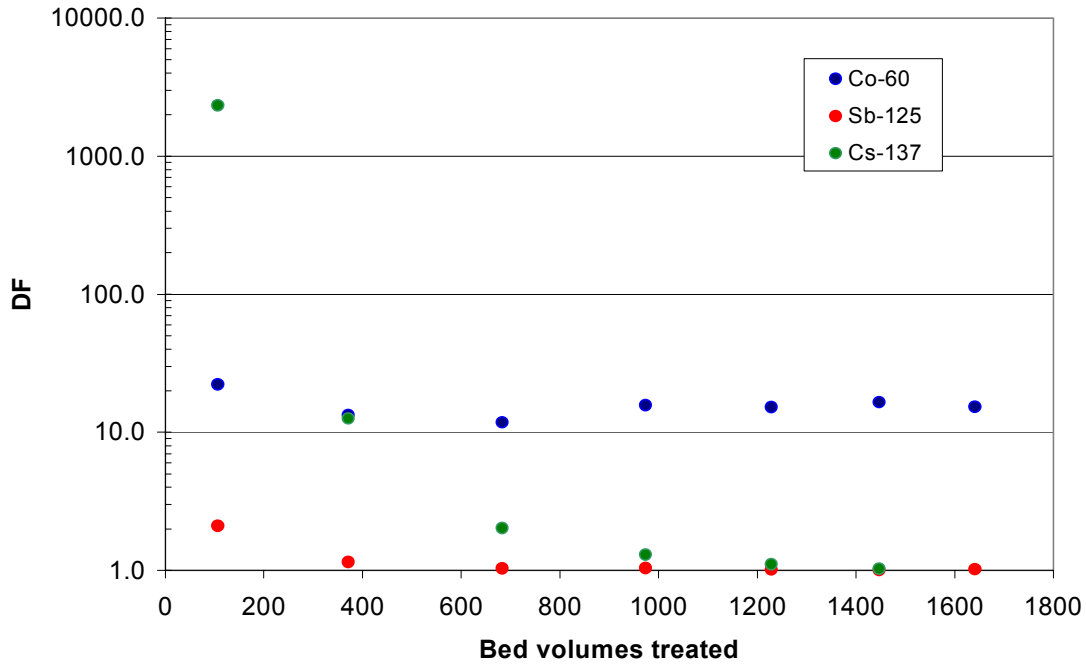

Fig. 2. Decontamination factors DF for Ginna sample after SbSi column ion exchange.

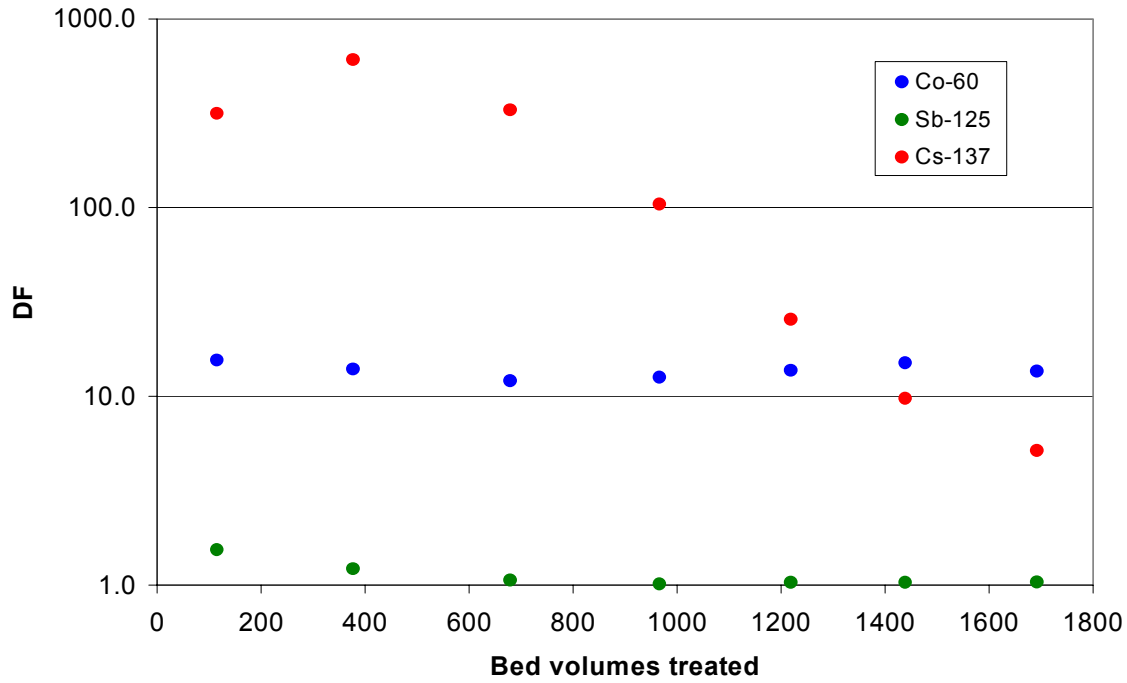

Fig. 3. Decontamination factors DF for Diablo Canyon sample after SbSi column ion exchange

CONCLUSIONS

The SbSi ion exchanger showed a good efficiency in the removal of ^{60}Co from neutral NPP waste effluents. The performance was similar to that of CoTreat, a commercial inorganic ion exchange media. The major advantage of SbSi compared to other Co-selective materials is its ability to function in acidic pH range. Further tests using real acidic waste effluents would thus be useful for the further evaluation of the new SbSi media.

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