Development and Testing of New Antimony Selective Media - 11183

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ABSTRACT

Antimony-124 (^{124}Sb) released from the fuel oxide layer into the Primary Coolant Water (PCW) during shutdown of the power plant can cause a major radiation dose to the personnel during annual maintenance period. A novel antimony selective media "SbTreat" is under development and the product format has been optimized for use as a finely divided filter material. New laboratory-scale test were conducted with the optimized product for the removal ^{124}Sb from the PCW of Loviisa Nuclear Power Plant (NPP), Finland, using small (volume ca. 1 cm^3) filtration capsules. The activity concentration of ^{124}Sb in the Loviisa PCW was 653,000 Bq/L initially and was decreased as low as 500 Bq/L after filtration with the SbTreat capsule (decontamination factor DF > 10,000).

INTRODUCTION

Radioactive antimony (^{124,125}Sb) exists in many Pressurized Water Reactor (PWR) and Boiling Water Reactor (BWR) water circuits and waste streams in activity concentrations comparable to that of radiocobalt (^{57,60}Co). Standard water treatment systems (demineralizers, chemical additives, and ion selective media) are effective for the removal of radiocobalt but generally inefficient for the removal of radioactive antimony [1, 2]. The difficulty of antimony removal stems from its complicated chemistry: antimony can exist in solution in two oxidation states (+3,+5) and in several hydroxyl species (e.g. $Sb(OH)_6^-$, $Sb(OH)_3$ (aq), $Sb(OH)_4^+$), depending on the pH and redox conditions. However, several new ion selective media have been developed recently, capable of extremely high removal of ^{124,125}Sb from PWR primary circuit and floor drain waters [2-5].

In Loviisa NPP (PWR, VVER-440, Finland) about 50% of the radiation dose received by personnel during the annual maintenance period is caused by antimony [2]. During the shut-down of the plant, ^{124}Sb is released from fuel oxide layer into the primary coolant water at levels greater than 100,000 Bq/L (> $3 \cdot 10^{-3}$ μCi/mL). The mixed-bed organic resin demineralizing

system used for activity removal under routine reactor operation is inefficient in removing the released antimony. Loviisa NPP has thus established a project to study and assess various antimony abatement technologies including identification of main sources and their elimination.

A new zirconium oxide based material, SbTreat [6], has been developed and tested for the removal of radioactive antimony from NPP waste liquids. Column experiments with real Fuel Pond Water from Olkiluoto NPP (BWR, Finland) showed a reduction of ^{125}Sb (feed level 400 Bq/L, $1 \cdot 10^{-5}$ $\mu Ci/mL$) below detection limit (MDA = 1.7 Bq/L, $5 \cdot 10^{-8}$ $\mu Ci/mL$) [5]. The material has also been tested for the removal of ^{124}Sb from the Primary Coolant Water (PCW) from Loviisa NPP (PWR, Finland) collected from service shutdown of Unit 1 that was stared on August 8, 2008. The level of soluble ^{124}Sb in the water was 600,000 Bq/L ($1.6 \cdot 10^{-2}$ $\mu Ci/mL$). Laboratory-scale column experiments conducted using granular (grain size 0.30-0.15 mm) SbTreat and PCW showed very high decontamination factors (DF) up to 30,000 for ^{124}Sb. However, in order to achieve such a high DF, the flow rate had to be kept very low at about 8 bed volumes (BV) per hour and increasing the flow rate to 22 BV/h caused the DF to drop to a level of 1000.

Attempts were made to improve antimony uptake kinetics [2] . Theoretically it can be expected that decreasing the material grain size would increase the uptake rate of ^{124}Sb on the material. Therefore, dynamic filtering tests utilizing powdered SbTreat (< 0.1 mm) material were also carried out using a planar filter holder (disc diameter 25 mm, filter surface area 3.5 cm^2). However, rather modest DF (about 10-100) were measured for ^{124}Sb. It appeared that it was difficult to produce material with small uniform sized granules and pack it evenly on the filter, which was obviously the reason for the modest DF-values.

Further work has been carried out to format the material to uniform powder and an easier manufacturing method has been developed. Static ^{124}Sb uptake experiments have shown good performance and column experiments were carried out with a new batch of PCW from Loviisa collected during the service shut-down of August 2010.

EXPERIMENTAL

Sorbent Material

The new zirconium-based sorbent material “SbTreat” was made from raw materials which avoid the presence of harmful anions such as chloride and sulphate in the product. Studies were made to produce a powdery product by varying the synthesis conditions. The obtained product showed very good static uptake of ^{124}Sb from the Loviisa PCW with distribution coefficients in the range of 20,000 – 1,000,000 L/kg ,depending on the solution pH.

Primary Coolant Water

PCW samples were obtained from Loviisa Unit 1 service shut-down on August 9, 2010. Temperature of the water was stable 57 ºC, but the pressure decreased during the sampling time from 25.7 bar (12:00) to 2.6 bar (20:00). The test samples (2 x 1 L) were taken on 14:05 and 17:55. The major burst of antimony occurs when the temperature of the circuit water starts to drop from 140ºC to 55ºC. The chemical composition of the PCW during sampling time is described in Table I. Chemical analysis shows that major constituent is boric acid (about 14 g/kg) and minor amounts of dissolved iron (65 µg/L) is present. The major gamma-emitting radionuclides in the samples were ^{58}Co (320 000 Bq/L) and ^{124}Sb (2 100 000 Bq/L) (Table II). The water used for the test was not filtrated in any way: earlier test had shown that only a minor fraction (7-8 %) of ^{58}Co and ^{124}Sb were filterable by a 0.45 micron filter [2].

Table I. Chemical composition of Primary Coolant Water from Loviisa NPP Unit 1 taken in August 9, 2010 at 12:05, 14:05, 16:00, 17:55 and 19:55. Temperature of water was stable 57 ºC, but the pressure decreased from 25.7 bar (12:00) to 2.6 bar (20:00). The test samples were taken on 14:05 and 17:55.

Sample point	**10TV04S0004**				
Sample date	**9.8.2010**				
Sample time	12:05	**14:05**	16:00	**17:55**	19:55
pH	4.89		5.00		4.79
Conductivity µS/cm	7.72		7.22		7.53
H_3BO_3 g/kg	14.08		13.90		13.74
SiO_2 µg/L	4704		4762		4736
Fe-sol µg/L	65.1		78.6		60.1
Fe-tot µg/L	94.5	109.0	217.0	102.0	88.6
Mn-tot µg/L	12.7	13.4	13.2	5.4	2.8
Co-tot µg/L	0.2	0.2	0.4	0.1	0.1
Ni-tot µg/L	89.8	94.8	121.0	54.2	38.2
Ag-tot µg/L	0.0	0.1	0.1	0.1	0.0
Sb-tot µg/L	1.3	1.7	1.4	1.0	0.6

Table II. Radiochemical composition of Primary Coolant Water from Loviisa NPP Unit 1 taken in August 9, 2010 at 14:05 and 17:55.

Radionuclide	date 9.8.2010 time 14:05		date 9.8.2010 time 17:55	
	kBq/m^3	% (2σ)	kBq/m^3	% (2σ)
^{54}Mn	13000	8	5100	13
^{58}Co	320000	5	140000	5
^{60}Co	7700	6	3800	8
^{76}As	150000	5	110000	5
^{110m}Ag	27000	4	19000	4
^{122}Sb	3070000	4	1500000	4
^{124}Sb	2100000	3	11000000	3
^{134}Cs			110000	3
^{137}Cs	31000	7	91000	7
Total γ	5700000		3100000	

Test Arrangement

Dynamic column experiments were carried out using a small acrylic filtration capsule (bed volume BV = 1.13 mL, id. 12 mm, packed with 1.40 g of SbTreat-material , grain size 74-149 microns). PCW was fed to the column inlet using a peristaltic pump. The pump was operated intermittently (6-8 h/d) and stopped for overnight. During the first test day the flow rate was about 10 ml/h (8.8 BV/h). For the second test day, the flow rate was doubled to 20 mL/h (17.7.BV/h) and then to 50 ml/h (44.2 BV/h) for the rest of the experiment (Table III). The experiment was discontinued on the 5th day when the available PCW had been consumed. The outlet solution was collected in fractions and counted for ^{124}Sb using a Ge-detector (Canberra GC4519) and a gamma spectrometer (Canberra DSA 1000/Genie 2000). The decontamination factor (DF) for the outlet solution was calculated as the ratio of the activity in the outlet and feed solution, respectively.

Table III: The conditions for the column test

Day	Run time (h)	Flow rate mL/h	Volume of water treated (mL)
1	6.5	10	73
2	6.25	20	142
3	4.75	50	264
4	8	50	449
5	3.75	50	208
		TOTAL	1136

RESULTS AND DISCUSSION

The initial DF obtained in the first test day for the SbTreat-column was about 1000 with the slow flow rate of 10 ml/h (8.8 BV/h). During the second day with the increased flow rate of 20 ml/h (17.7 BV/h), the DF remained in the same level. However, on the third test day, when the flow rate was further increased to 44.2 BV/h, a sharp increase of DF took place to a level of 10,000 and the DF remained in the high level till the end of the test. Theoretically it could have been expected that the DF would decrease with increasing flow rate as the contact time is decreased. Thus the increase of DF is related to some other factor than the residence time, e.g. to the delayed initial diffusion of Sb ions in the SbTreat crystals. This indicates that the material needs a few days to "wake up" to achieve the normal operational performance.

There was a dramatic improvement in the performance of the newer powder material compared to the older powder tested earlier [2]. The older powder material, although operated at somewhat higher flow rate of 100 BV/h, produced DF at a range of 100-10 only. The older granular material was able to produce a DF in the level of 10,000 at very low rate of 8 BV/h only.

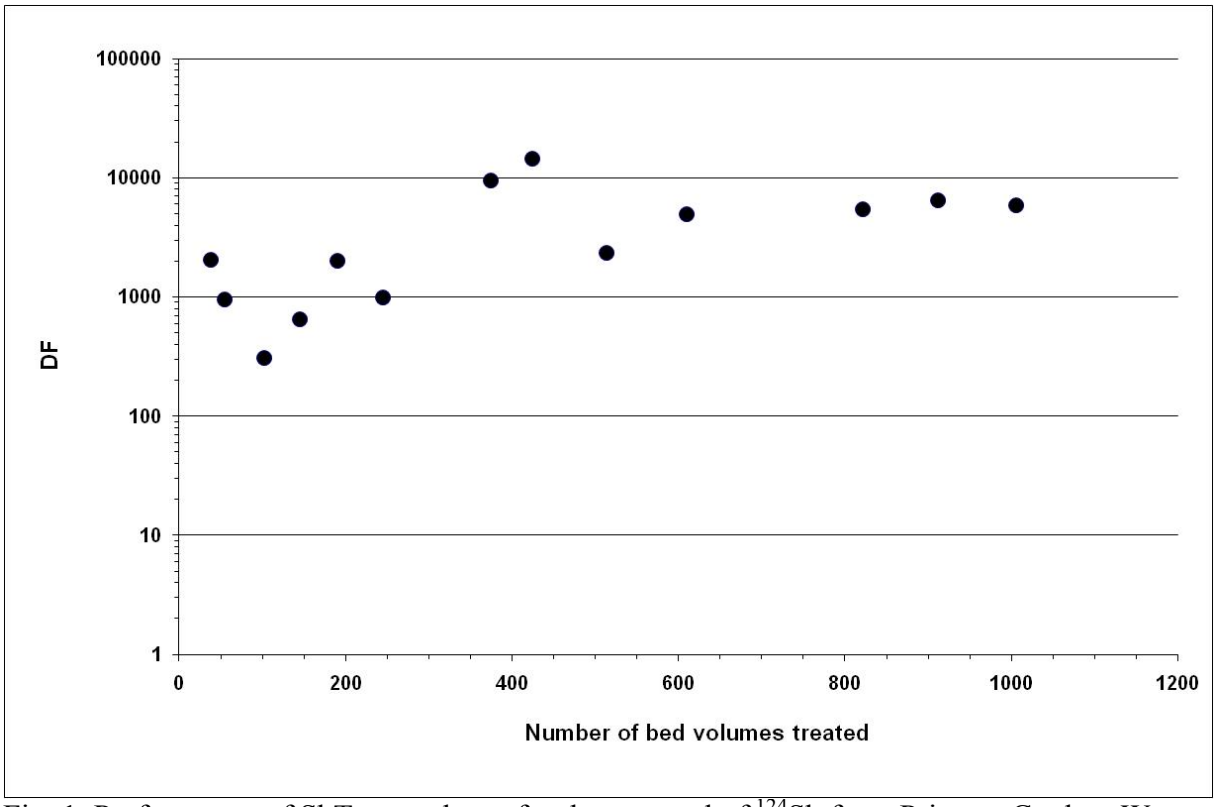

Fig. 1. Performance of SbTreat-column for the removal of ^{124}Sb from Primary Coolant Water of Loviisa NPP Unit 1.

CONCLUSION

Optimization of the synthesis conditions was successful in producing a suitable SbTreat product with small granule size. The new product format provides markedly improved flow rates and decontamination factors for the removal of radioactive antimony. Instead of conventional column use, the new SbTreat material shows promise to be used as a finely divided filter material in new types of contactors, e.g. as a filler in various cartridge filters.

Further test will be needed to challenge the processing capacity of the material. These tests will require larger amounts of radioactive water and need to be carried out at a NPP site.

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