

## Removal of Antimony-124 from PWR Coolant Water -9111

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### ABSTRACT

Antimony-124 ( $^{124}\text{Sb}$ ) released from the fuel oxide layer into the Primary Coolant Water (PCW) during shutdown of the power plant causes a major radiation dose to the personnel during annual maintenance period at Loviisa NPP (PWR, VVER-440), Finland. Novel proprietary metal oxide materials (MOM) have been tested for the removal of  $^{124}\text{Sb}$  from Loviisa PCW collected from service shutdown of Unit 1 that was started on August 8, 2008. The level of soluble  $^{124}\text{Sb}$  in the water was 600,000 Bq/L ( $1.6 \cdot 10^2 \mu\text{Ci/mL}$ ). Static uptake test showed a high uptake of  $^{124}\text{Sb}$  by the MOM materials with the distribution coefficients ( $k_d$ ) exceeding values of 1,300,000 L/kg, indicating that processing capacities in order of 1000 m<sup>3</sup>/kg (5 Mgal/ft<sup>3</sup>) could be obtainable. Laboratory-scale column experiments conducted using granular (grain size 0.30-0.15 mm) MOM material and PCW showed very high decontamination factors (DF) upto 30,000 for  $^{124}\text{Sb}$ . Further experiments conducted with powdered MOM material on a filter allowing higher throughput rates gave markedly lower DF-values, most probably due to uneven packing of the material.

### INTRODUCTION

Highly selective inorganic adsorbents and ion exchangers are increasingly used for the removal of key radionuclides such as  $^{60}\text{Co}$ ,  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  from nuclear waste effluents due to their radiation stability, high processing capacity and high decontamination efficiency (1,2). The commercially available inorganic materials (e.g. zeolites, titanates, silicotitanates, hexacyanoferrates) are cation exchangers or adsorbents, which can remove efficiently cationic and neutral radioactive species. Improved processing systems utilizing inorganic materials have been able to reduce markedly the discharges of cationic radionuclides such as  $^{137}\text{Cs}$  and  $^{60}\text{Co}$  radionuclides at many utility sites and further efforts have been directed to remove other radionuclides such as  $^{51}\text{Cr}$ ,  $^{110\text{m}}\text{Ag}$  and  $^{124,125}\text{Sb}$  that dominate in solution after cesium and cobalt elimination.

Much attention has been paid recently to  $^{125}\text{Sb}$ . It may exist completely in soluble form in the Floor Drain Waters (3). In solution, antimony can exist in two oxidation states (+3,+5) and in several hydroxyl species (e.g.  $\text{Sb}(\text{OH})_6^-$ ,  $\text{Sb}(\text{OH})_3$  (aq),  $\text{Sb}(\text{OH})_4^+$ ), depending on the pH and redox conditions (Fig. 1). These

chemical features indicate that it is difficult to remove antimony from solution. Especially the removal of anionic species,  $\text{Sb}(\text{OH})_6^-$ , is difficult as highly selective anion exchange materials are not available.

Recent tests have showed that standard demineralizer resins and ion selective materials are ineffective for the removal of Sb from liquid radwaste (4). However, some commercially available inorganic cation exchangers, such as CoTreat, can remove  $^{125}\text{Sb}$  from NPP Floor Drain water with good efficiency (3) in some cases, but their utilization is obviously restricted to cationic antimony species. Regarding other methods, chemical additives coupled with ultra filtration has been shown to be effective method for  $^{125}\text{Sb}$  removal in a test program conducted at Duke Power Company's Oconee plant (5). Study of other methods such as electro-deionization and hollow-fiber filtration is underway e.g. in the EPRI Low-Level Waste program (6). Novel proprietary metal oxide materials (MOM) have shown ability for efficient removal of  $^{125}\text{Sb}$  from simulated Floor Drain Waters of PWR and BWR achieving decontamination factors (DF) in range of 300-600 for  $^{125}\text{Sb}$  (7). Laboratory-scale column experiments with real Fuel Pond Water from Olkiluoto NPP (BWR, Finland) showed reduction of Sb-125 (feed level 400 Bq/L,  $1 \cdot 10^{-5} \mu\text{Ci/mL}$ ) below detection limit (MDA = 1.7 Bq/L,  $5 \cdot 10^{-8} \mu\text{Ci/mL}$ ), which corresponds to a DF > 270 (8).

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

## PURPOSE OF STUDY

A joint project (Laboratory of Radiochemistry at University of Helsinki, Loviisa NPP and Fortum Nuclear Services Oy) has just initiated to study the removal of antimony from borated waters at the power plant. At the first stage, the novel MOM materials are evaluated for  $^{124}\text{Sb}$  removal at small laboratory-scale using samples obtained after Loviisa 1 service shutdown in August 2008.

## EXPERIMENTAL

### PCW Samples

Primary Coolant Water samples were obtained from Loviisa Unit 1 service shut-down that started on August 8, 2008. Four 1 L samples were taken during August 10-11 at 4 hour intervals at the temperature drop from 140 °C to 55 °C, when the major burst of antimony occurs. Chemical analysis showed that major constituent in PCW was boric acid (14 g/L) and that minor amounts of dissolved iron (68 µg/L) were present (Table 1).

Table I. Chemical composition of Primary Coolant Water from Loviisa NPP Unit 1. Sample No. 1 Taken on August 10 at 14:00.

Unit	LO1		
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<b>Sample Date Time</b>	<b>10TV04S0004 10.8.2008 14:00</b>		
<b>pH</b>	4,89	<b>Co-tot</b>	0,2 µg/L
<b>Conductivity</b>	9,5 µS/cm	<b>Ni-tot</b>	57,2 µg/L
<b>H<sub>3</sub>BO<sub>3</sub></b>	13,97 g/kg	<b>SiO<sub>2</sub></b>	1764,1 µg/L
<b>Fe-tot</b>	71,6 µg/L	<b>Ag-tot</b>	0,1 µg/L
<b>Fe-sol</b>	67,8 µg/L	<b>Sb-tot</b>	0,5 µg/L
<b>Mn-tot</b>	10,1 µg/L		

The major gamma-emitting radionuclides in the PCW were <sup>58</sup>Co (240,000 Bq/L) and <sup>124</sup>Sb (637,000 Bq/L)(Table 2). These radionuclides were mainly in soluble form; filtration (0.45 µm) removed only 7.4 % of <sup>58</sup>Co and 8.2 % of <sup>124</sup>Sb.

TableII. Radiochemical Composition of Primary Coolant Water from Loviisa NPP Unit 1.

<b>Radionuclide Bq/L</b>	<b>Non-filtered</b>	<b>Filter cake</b>	<b>Filtrate</b>
<b>Cr-51</b>		2,159E3	
<b>Mn-54</b>	8,768E3	2,413E2	7,497E3
<b>Co-58</b>	2,431E5	2,618E3	2,258E5
<b>Fe-59</b>		2,638E2	
<b>Co-60</b>	3,716E3	2,089E2	3,519E3
<b>As-76</b>		3,426E3	
<b>Nb-95</b>	1,633E3	2,140E3	
<b>Zr-95</b>		1,634E3	
<b>Ag-110m</b>	4,091E3	1,582E3	1,481E3
<b>Sb-122</b>	7,053E5	7,747E3	6,563E5
<b>Te-123m</b>	5,685E2	1,808E2	1,370E2
<b>Sb-124</b>	6,373E5	6,649E3	5,853E5
<b>Sb-125</b>	6,800E3		
<b>Total-gamma</b>	1,611E6	2,920E4	1,483E6

#### Antimony-124 Uptake Experiments

Static batch experiments were carried out to measure the distribution coefficients ( $k_d$ ) of <sup>124</sup>Sb for MOM in the PCW. These experiments were carried out by contacting 20 mg of MOM material with 20 mL of PCW for 3 days. Thereafter the solution was centrifuged and filtrated with a 0.2 µm disc filter and counted for <sup>124</sup>Sb activity using Canberra Genie2000 multi-gamma analyzer. The distribution coefficient  $k_d$  for <sup>124</sup>Sb was calculated from:

$$k_d = \frac{{}^{124}\text{Sb concentration in solid}}{{}^{124}\text{Sb concentration in solution}} = \frac{A_0 - A_{eq}}{A_{eq}} \frac{V}{m}$$

where  $A_0$  and  $A_{eq}$  are the activity concentrations of  $^{124}\text{Sb}$  (Bq/L) in solution before and after contact with the MOM material, respectively.  $V$  is the solution volume (20 mL) and  $m$  is the mass of MOM (20 mg) contacted with the solution.

As the chemical and radiochemical composition of all four (1 L) PCW samples was practically identical, samples were combined to yield a 4 L master sample for dynamic  $^{124}\text{Sb}$  removal tests.

Dynamic column experiments were carried out using small minicolumns (bed volume  $BV = 0.5$  mL, packed with 0.6 g of MOM, grain size 0.1-0.3 mm). About 1.5 liters PCW was fed to the column using a peristaltic pump with an initial flow rate of about 11 mL/h (22 BV/h). The flow rate was decreased to about 4 mL/h (8 BV/h) at midway of the run in order to see the effect of residence time on column performance. The outlet solution was collected in fractions and counted for  $^{124}\text{Sb}$ . The decontamination factor (DF) for the outlet solution was calculated as the ratio of the activity in the outlet and feed solution, respectively.

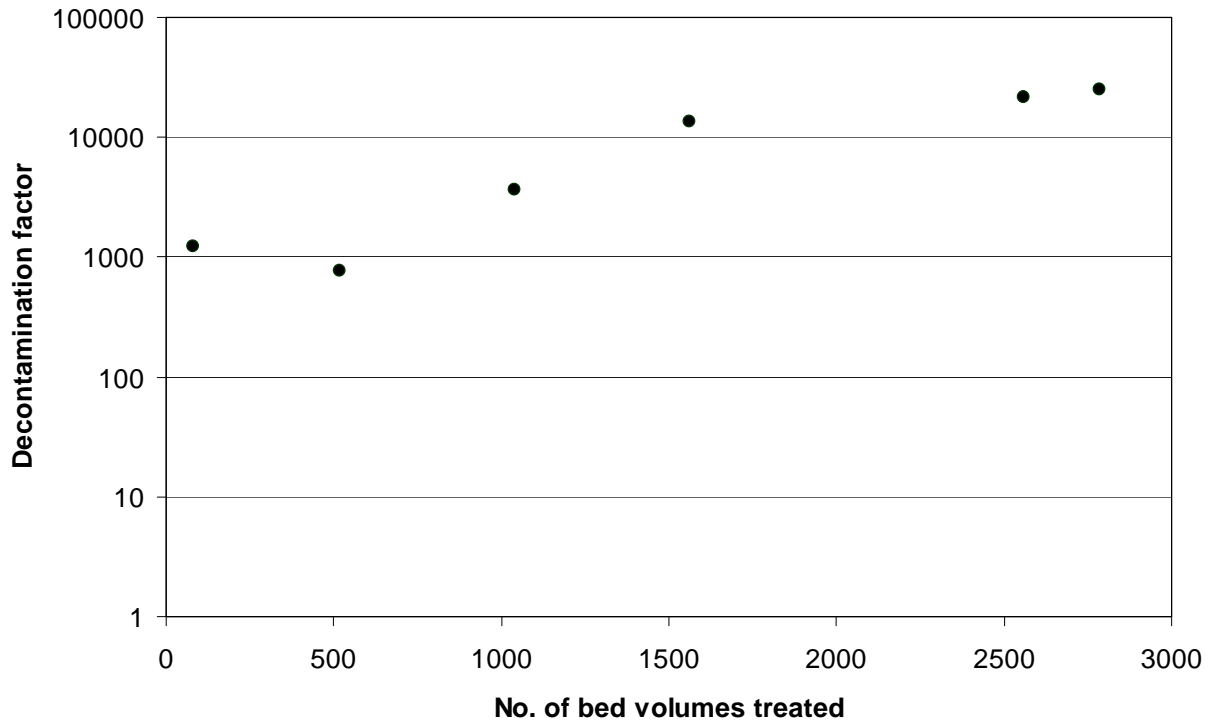
Theoretically it can be expected that decreasing the MOM grain size would increase the uptake rate of  $^{124}\text{Sb}$  on the material. Therefore, dynamic filtering tests utilizing powdered MOM ( $< 0.1$  mm) material were also carried out using a planar Millipore Swinnex Filter Holder (katalogissa oleva nimi) of disc diameter 25 mm (filter surface area 3,5 cm<sup>2</sup>). 200 mg of MOM powder (dose ca. 60 mg/cm<sup>2</sup>) was packed on the filter by using a packing cylinder filled with water. The powder was slurred in the packing cylinder and allowed to settle on top of the filter (Millipore SMWP with 5.0 μm pore size). Water was removed by suction from below after which the packing cylinder was replaced by the upper lid of the filter housing. PCW was run once through to the filter unit via a 1-L feed vessel with a flow rate of 20 mL/h. As the bulk density of the MOM material was 1.0 cm<sup>3</sup>/g, the flow rate was 100 bed volumes per hour in terms of MOM material volume on the filter. Filter effluent was sampled regularly and analysed for  $^{124}\text{Sb}$ . The decontamination factor DF for  $^{124}\text{Sb}$  was calculated as  $DF = A_0/A$ , where  $A_0$  and  $A$  are the activity concentrations of  $^{124}\text{Sb}$  (Bq/L) in the filter influent and effluent, respectively.

## RESULTS

Static uptake test showed a high uptake of  $^{124}\text{Sb}$  by the MOM materials with the distribution coefficients ( $k_d$ ) in range of 1,300,000-1,800,000 L/kg (Table 3). These  $k_d$ -values indicate that processing capacities in order of 1000 m<sup>3</sup>/kg (5 Mgal/ft<sup>3</sup>) could be obtainable under dynamic conditions.

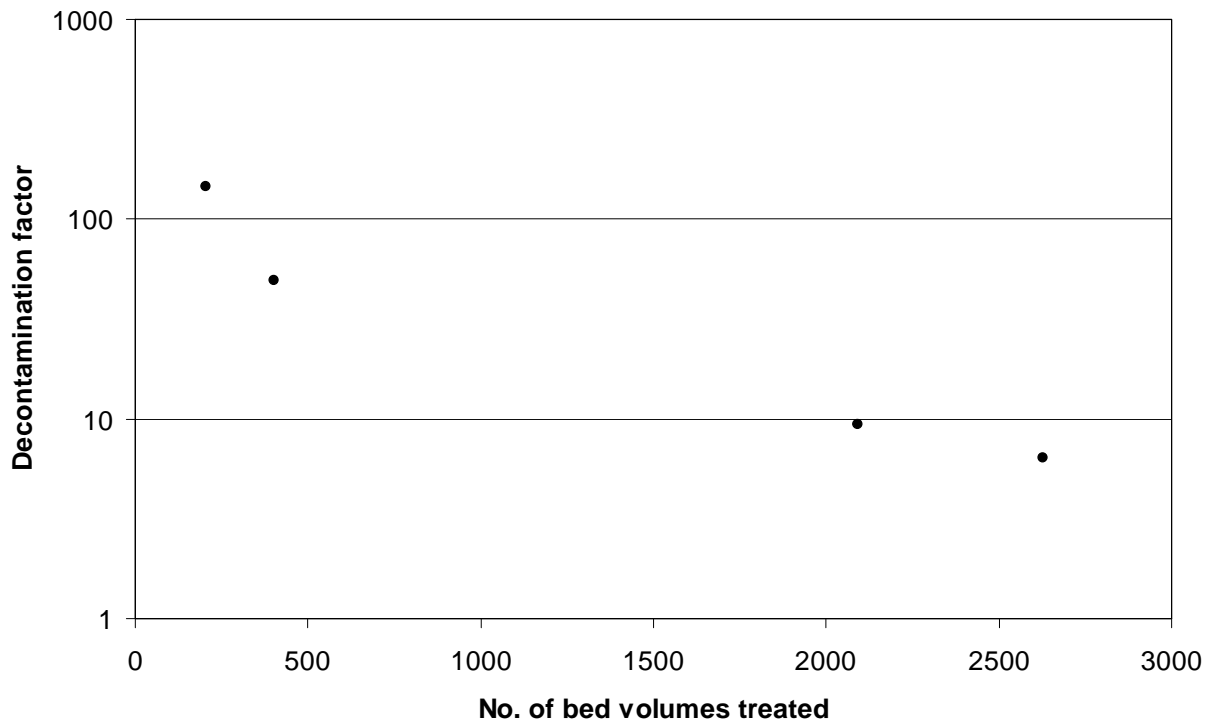
Table III. Distribution Coefficients ( $k_d$ ) for  $^{124}\text{Sb}$  and MOM Material in the Primary Coolant Water Samples from Loviisa Unit 1

SAMPLE	$K_d$ (ave)	$\square K_d$ (ave)
	L/kg	L/kg
Lo1-10TV04-14	1299589	59267
Lo1-10TV04-18	1557497	60499
Lo1-10TV04-22	1835111	63035
Lo1-10TV04-02	1312835	52301



**Figure 1. Uptake of  $^{124}\text{Sb}$  in MOM column. Initial flow rate 22 BV/h changed to 8 BV/h at 780 bed volumes.**

As it could be expected from the high batch uptake  $k_d$ -values, the column packed with MOM material was very effective for  $^{124}\text{Sb}$  removal from the PCW. At higher flow rate of 22 BV/h, the decontamination factors (DF) were in the order of 1,000 (Fig. 1). When the flow rate was decreased to 8 B/h, the DF's increased markedly and DF-values as high as 30,000 were measured. In one effluent sample,  $^{124}\text{Sb}$  was below the detection limit. The test was stopped when about 2800 BV of water was treated due to the small sample amount. There was no indication of exhaustion of the MOM column when the test was stopped, as could be predicted from the very high  $k_d$ -values.



**Figure 2. Uptake of  $^{124}\text{Sb}$  in MOM filter packed with 0,2 g (0.2 mL) of powdered material. Flow flow rate 10 mL/h (corresponding 100 BV/h). Decontaminatiuon factor is low due to poor packing of material on the filter.**

In the test carried out with the powdered material, the decontamination level for  $^{124}\text{Sb}$  was dramatically lower than in the column test with granular material (Fig. 2). The DF-value for  $^{124}\text{Sb}$  was only 146 in the first effluent sample and fell below 10 at the enf of the test. These values are markedly lower than what has been observed in earlier tests of powdered inorganic materials (9-10). Inspection after the test run revealed that the layer of MOM material on the filter was highly uneven and practically empty spots of filter surface could be observed. The relative low DF's are thus most like due to inadequate packing of the material, or alternatively, the MOM layer on the filter has been disturbed by the water flow during the test.

## CONCLUSIONS

In granular form in an ion exchange column, the novel MOM material appears highly effective for the removal of  $^{124}\text{Sb}$  from PWR Primary Coolant Water. Testing with powdered MOM material in a filter showed only modest performance, which is likely due to the poor packing of the thin layer of material on the filter. Further test with the powdered material will be carried out after the packing problem has been solved.

## REFERENCES

1. R. HARJULA, J. LEHTO, “Selective Separation of Radionuclides from Nuclear Waste Solutions with Inorganic Ion Exchangers”, *Radiochim. Acta*, 86(1999)65.
2. R. HARJULA, A.PAAJANEN, J.LEHTO, E. TUSA, R. SMITH AND P. STANDRING, “Additional Testing Of CoTreat Inorganic Ion Exchange Media For The Removal Of Co-60 From Thorp Pond Water”, *Proceedings of Waste Management 2004 Conference*, February 29- March 4, 2004, Tucson, AZ.
3. R. HARJULA, J. LEHTO, A. PAAJANEN AND L. BRODKIN AND E. TUSA, “Testing of highly selective CoTreat ion exchange media for the removal of radiocobalt and other activated corrosion product nuclides from NPP waste waters”, *Proceedings of Waste Management '99*, Tucson, AZ, February 28-March 4, 1999.
4. Electric Power Research Institute, “Analysis of Advanced Liquid Waste Minimization Techniques at a PWR”, TR-109444, 1998.
5. Electric Power Research Institute, “Improved Antimony Removal Using a Chemical Treatment and Microfiltration Process”, TR-109443, 1998.
6. Electric Power Research Institute, “Enhanced Liquid Radwaste Processing Using Ultrafiltration and Chemical Additives: Results of Pilot Scale and Media Testing”, TR-1009562, 2004.
7. R. HARJULA, H. MYLLYMAA AND R. KOIVULA, “Removal of antimony-125 from simulated liquid radwaste by novel adsorbents”, *Proceedings of Waste Management 2005 Conference*, February 27- March 3, 2005, Tucson, AZ.
8. R. HARJULA, A. PAAJANEN AND R. KOIVULA, “Removal Of Sb-125 And Tc-99 From Liquid Radwaste By Novel Adsorbents”, *Proceedings of Waste Management 2006 Conference*, February 26 – March 2, 2006, Tucson, AZ.
9. R.HARJULA, J. LEHTO, A. PAAJANEN, E. TUSA AND P. YARNELL, “Use Inorganic Ion Exchange Materials As Precoat Filters For Nuclear Waste Effluent Treatment”, *Reactive & Functional Polymers*, 60(2004)85.
10. P. A. YARNELL, T. EDWARDS AND J. PORE, “Development Of Composite Filters For Selective Removal Of Radionuclides”, *Proceedings of WM'04 Conference*, February 29 – March 4, 2004 Tucson, AZ, WM-4228.