

Removal of Sb-125 and Tc-99 from Liquid Radwaste by Novel Adsorbents

R.O. Harjula, R. Koivula, A. Paajanen
Helsinki University, Laboratory of Radiochemistry
PO Box 55, 00014
Finland

ABSTRACT

Novel proprietary metal oxide materials (MOM) have been tested for the removal of Sb-125 from simulated Floor Drain Waters of BWR. Antimony was present in the solutions as oxidized anionic form. Long term column experiment with simulated liquid that showed high Sb-125 removal at least up to 8000 bed volumes. One column experiments was carried out using non-radioactive Sb to exhaust the column. Leaching tests with 1000 ppm boric acid showed that 100 % of absorbed Sb remains in the sorbent material. Column experiments with real Fuel Pond Water from Olkiluoto NPP (BWR) 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, $5 \cdot 10^{-8} \mu\text{Ci/mL}$). Additional experiments have also been carried out with pertechnetate (Tc-99) ions. Results indicate that MOM materials are efficient also for the removal of Tc-99 from concentrated NaNO_3 solution.

INTRODUCTION

Selective ion media, e.g. inorganic adsorbents and ion exchangers, are increasingly used for the removal of key radionuclides such as Co-60, Sr-90 and Cs-137 from nuclear waste effluents due to their radiation stability, high processing capacity and high decontamination efficiency [1,2]. The materials used that are commercially available (e.g. zeolites, titanates, silicotitanates, hexacyanoferrates) are cation exchangers or adsorbents, which can remove efficiently cationic and neutral radioactive species. Inorganic anion exchange materials are quite rare and do not possess high selectivity.

Considering radiation doses to personnel and environment, Co-60,58 and Cs-137 are the most critical radionuclides in nuclear power plant (NPP) waste liquids and water streams. Improved processing systems have been able to reduce markedly the discharges of these radionuclides at many utility sites and further efforts have been directed to remove other radionuclides such as Cr-51, Ag-110m and Sb-125 that dominate in solution after cesium and cobalt elimination. Much attention has been paid recently to ^{125}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 [4]. These chemical features indicate that it is difficult to remove antimony from solution.

Recent tests showed that standard demineralizer resins and ion selective media are ineffective for the removal of Sb from liquid radwaste [5]. However, some commercially available inorganic cation exchangers, such as CoTreat, can remove Sb-125 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 have been shown to be effective method for Sb-125 removal in a test program conducted at Duke Power Company's Oconee plant [6]. Study of other methods such as electro-deionization and hollow-fiber filtration is underway e.g. in the EPRI Low-Level Waste program [7].

Recently, novel proprietary metal oxide materials (MOM) have been tested for the removal of Sb-125 from simulated Floor Drain Waters of PWR and BWR [8]. Antimony was present in the solutions as oxidized anionic form. Batch uptake experiments with the MOM materials showed 100 % uptake (below detection limit) of Sb-125 in many cases, and the measured distribution coefficients of Sb-125 exceeded 1,000,000 mL/g at best, indicating that very high dynamic processing capacities, in order of 1000 m³/kg might be achieved. Redox-measurement showed that the materials decrease the eH of the solution enhancing reducing chemical conditions, which may be the key for the high antimony uptake. Tentative dynamic column experiments showed efficient removal of Sb-125 (DF 300-600) from simulated BWR Floor Drain Water with no sign of column exhaustion when the test was discontinued at 2500 bed volumes [8].

PURPOSE OF WORK

Further experiments have been carried out to test the suitability of MOM materials for Sb-125 removal from NPP waste liquids. These experiments include long term column experiment with simulated liquid of higher salt content in which exhaustion of the column for Sb-125 was sought. As no column exhaustion was observed, the MOM material was “challenged” by using non-radioactive Sb (antimonate) at millimolar level. Leaching tests with 1000 ppm boric acid were conducted to confirm that absorbed Sb remains in the sorbent material. Column experiments with Fuel Pond Water from Olkiluoto NPP (BWR, Finland) were carried out to evaluate the material in real conditions.

Additional experiments have also been carried out with pertechnetate (Tc-99) ions in order to see if the MOM materials could have a wider range of applications in the removal of oxo-anionic radionuclides.

TEST PROCEDURES

Novel proprietary metal oxide materials (MOM) were prepared for the tests. The materials contained different metal oxide functionalities doped with reducing agents to convert anionic Sb species to neutral or cationic ones that could be captured by the base metal oxide functionality. First tests for the removal of Sb-125 were carried out using simulated NPP Floor Drain Waters (Table 1). Sb-125-tartrate was used as a precursor for antimonate (Sb(OH)₆⁻) tracer. The tartrate was oxidized using H₂O₂ and the oxidized solution was loaded on an anion exchange resins (86 % uptake of Sb-125 activity). Antimonate activity was then eluted from the resin using the simulated Floor Drain Waters as an eluant.

In addition, non-radioactive SbCl_3 was used as a precursor to prepare an antimonate solution of higher concentration (1 mmol/l) to determine the exhaustion capacity of the MOM material and to obtain exhausted material for leaching tests. Oxidation and chemical separation of $\text{Sb}(\text{OH})_6^-$ was carried out in similar way as for the ^{125}Sb -tartrate tracer above.

Table I. Chemical Compositions of Simulated Floor Drain Waters

Component mg/L	BWR1	BWR2
Na	90.1	230
K	nd	20
Mg	nd	12
Ca	29.8	40
pH	6.2	

^{125}Sb (antimonate) tracer added to yield 9000-15000 cpm/10 mL.

Dynamic column experiments were carried out using small minicolumns (bed volume $\text{BV} = 0.5$ mL, packed with MOM-1B, grain size 0.1-0.3 mm). Simulated Floor Drain Water (BWR2, Table 1) was traced with Sb-125 as described above to yield a count rate of about 1000 cpm/mL. The simulant was fed to the column using a peristaltic pump with a flow rate of about 5 mL/min (10 BV/h) initially and the flow rate was increased gradually to 25 mL/h (50 BV/h) towards the end of the experiments. The outlet solution was collected in fractions and counted for Sb-125. The decontamination factor (DF) for the outlet solution was calculated as the ratio of the count rates in the outlet and feed solution, respectively. The column experiment with real Fuel Pond Water (Table II) was conducted in similar manner except that the flow rate was kept constant at 10 mL/h (20 BV/h)

Table II. Composition of Fuel Pond Water from Olkiluoto-1 BWR, Finland

Component	Value	Unit
Conductivity	1	$\mu\text{Sv/cm}$
SO_4^{2-}	4	$\mu\text{g/L}$
Oxalate	1.5	$\mu\text{g/L}$
Cl^-	2	$\mu\text{g/L}$
Sb-125	396	Bq/L
	1.07E-05	$\mu\text{Ci/mL}$
Cs-137	8.6	Bq/L
	2.32E-07	$\mu\text{Ci/mL}$
Co-60	11.1	Bq/L
	3.00E-07	$\mu\text{Ci/mL}$

A column experiment for Tc-99 removal was conducted using a similar minicolumn. The feed solution was 1 M NaNO_3 that was traced with ^{99}Tc tracer obtained from MAP Medical Technologies, Finland.

The exhaustion test was carried out likewise using the 1 mmol/l antimonate solution traced with ^{125}Sb . After exhaustion, the column was first washed with water to remove feed solution and then eluted with 500 ml of 1000 ppm boric acid solution.

RESULTS

The column packed with MOM-1B removed Sb-125 from the simulated Floor Drain Water (BWR2) with a good efficiency (Fig. 1), the decontamination factor DF was above 100 most of the time. The DF dropped slightly to a value of 80 during the experiments, obviously due to increasing flow rate. The test was discontinued when close to 8000 BV of solution had been fed as the feed solution was depleted. There was no sign of column exhaustion (i.e. strong drop in DF) at this point. However, the level of DF was clearly lower ($DF \approx 100$) than in previous short-term experiment with BWR1 simulant ($DF 300-600$)(8), obviously due to increased salt content of the feed solution.

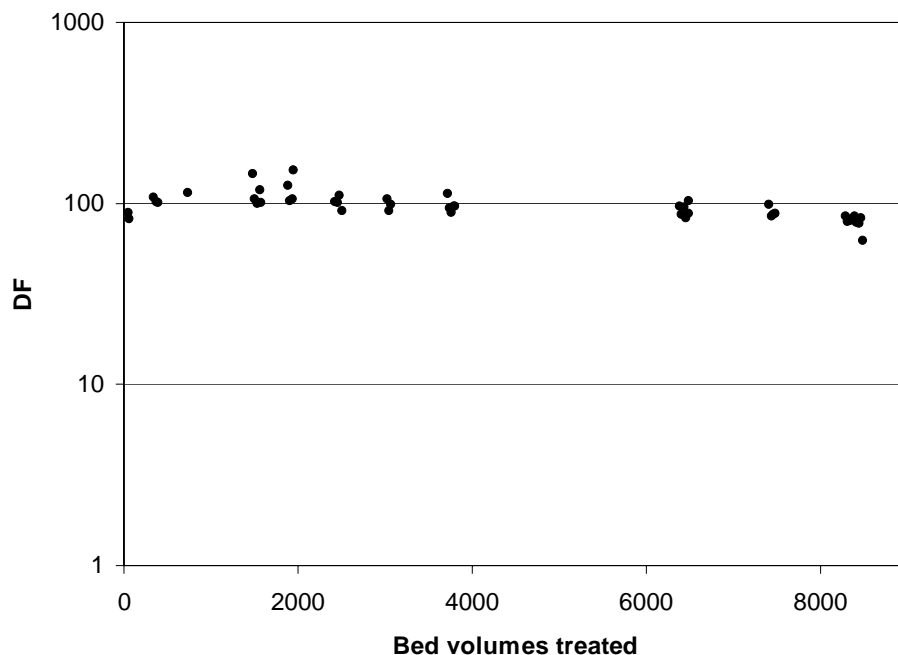


Fig. 1. Column uptake of Sb-125 by MOM-1B material in simulated Floor Drain Water BWR2. Bed volume 0.7 mL, flow rate 10-50 BV/h.

In the exhaustion test, when 1 mmol/L antimonate solution (traced with Sb-125) was fed into the column, exhaustion of MOM material was observed at 500 bed volumes. At this point, 0.7 mmol of antimonate had been loaded per 1 gram of MOM material. The exhausted column was eluted with 500 ml of boric acid (1000 ppm) and the eluant was collected as small fractions. All collected fractions were counted for Sb-125 but were found to be at background level. Thus boric acid was unable to leach any Sb-125 from the material.

Table III. Column Removal of Radionuclides from the Fuel Pond Water (see Table II)

No. of BV treated	DF		
	Sb-125	Cs-137	Co-60
360	>230	1.7	2.7
861	>230	1.5	1.7
1354	>230	1.4	1.4
1831	>230	1.3	1.0

BV = bed volumes, DF = decontamination factor

In the column test, 1 L (2000 BV) of Fuel Pond Water was fed through the column of MOM material. No Sb-125 was detected in the outlet solution (Table III). Calculated from the minimum detectable activity (MDA) of 1.7 Bq/L, the decontamination factor for Sb-125 was greater than 230.

The column test for Tc-99 removal showed very high uptake initially (DF > 1000) but the efficiency decreased sharply (DF < 100) when about 500 bed volumes of 1 M NaNO₃ had been treated (Fig. 2). However, it appeared that the DF stabilized to a level of about 20 when 1700 bed volumes had been treated with no sign of column exhaustion. This may indicate that there is first rapid uptake in the surface of MOM material, followed by a slower process inside the granules of the material.

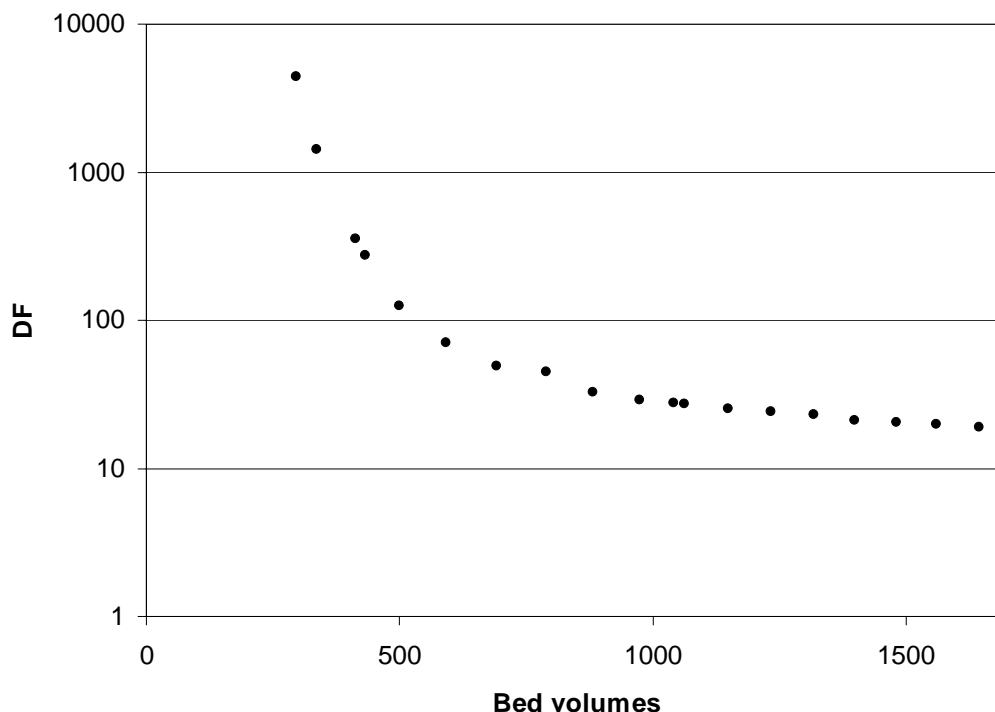


Fig. 2. Column uptake of Tc-99 by MOM-1B material in 1 M NaNO₃. Bed volume 0.7 mL, flow rate 20 BV/h

CONCLUSION

The novel MOM materials appear highly effective for the removal anionic forms of Sb-125 from simulated NPP Floor Drain Water. Short-term test with NPP Fuel Pond Water indicated that the material is applicable also in real conditions. The materials also show good ability to remove Tc-99 from concentrated salt waste but the uptake rate needs to be optimized.

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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. K. M. Krupka and R. J. Serne, Geochemical Factors Affecting the Behavior of Antimony, Cobalt, Europium, Technetium, and Uranium in Vadose Sediments, *PNNL-11485, Pacific Northwest Laboratory, Richland, Washington, 2002*.
5. Electric Power Research Institute, Analysis of Advanced Liquid Waste Minimization Techniques at a PWR, *TR-109444, 1998*.
6. Electric Power Research Institute, Improved Antimony Removal Using a Chemical Treatment and Microfiltration Process, *TR-109443, 1998*.
7. Electric Power Research Institute, Enhanced Liquid Radwaste Processing Using Ultrafiltration and Chemical Additives: Results of Pilot Scale and Media Testing, *TR-1009562, 2004*.
8. 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*.