

REMOVAL OF ANTIMONY-125 FROM SIMULATED LIQUID RADWASTE BY NOVEL ADSORBENTS

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ABSTRACT

Novel proprietary metal oxide materials (MOM) have been tested for the removal of ^{125}Sb from simulated Floor Drain Waters of PWR and BWR. Antimony was present in the solutions as oxidized anionic form. Batch uptake experiments with the MOM materials showed 100 % uptake (^{125}Sb below detection limit) of Sb-125 in many cases, and the measured distribution coefficients of ^{125}Sb 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. Dynamic column experiment that was carried out with one of the materials showed good uptake kinetics with a decontamination factor of 300-600.

INTRODUCTION

Selective ion media, e.g. inorganic adsorbents and ion exchangers, are increasingly used for the removal of key radionuclides such as ^{60}Co , ^{90}Sr and ^{137}Cs 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, $^{58,60}\text{Co}$ and ^{137}Cs 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 ^{51}Cr , $^{110\text{m}}\text{Ag}$ and ^{125}Sb 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 (Fig. 1). 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 (4). However, some commercially available inorganic cation exchangers, such as CoTreat, can remove ^{125}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}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).

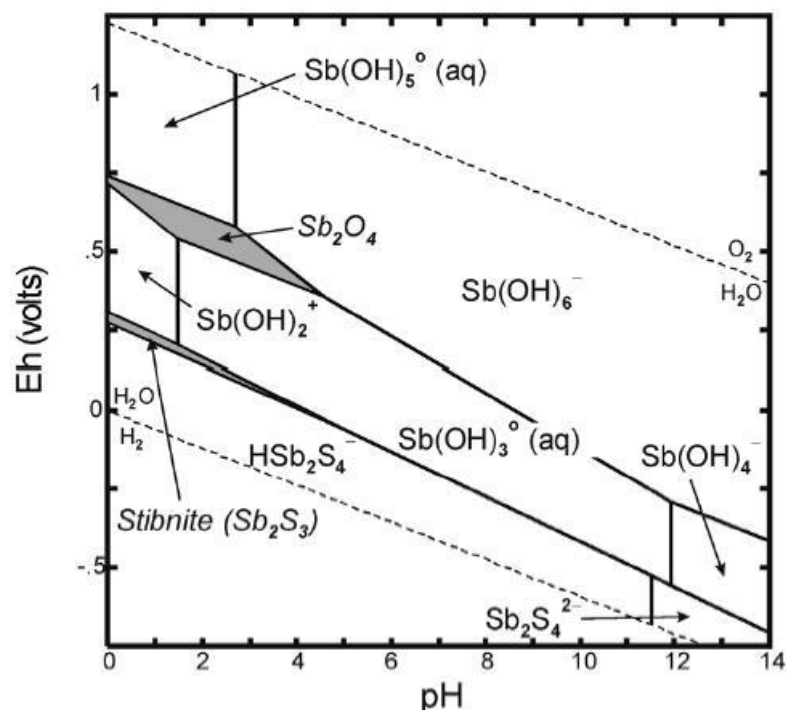


Fig. 1. Chemical speciation of antimony in solution at different pH and Eh (7).

Purpose of Work

The laboratory of radiochemistry at the University of Helsinki has extensive experience in the development of ion selective medias. These include commercial materials CsTreat[®], SrTreat[®] and CoTreat[®], developed jointly with Fortum Nuclear Services Oy, that have found industrial applications worldwide. The latest research project is aimed to develop selective ion medias for the separation harmful oxo-anions such as antimonate, arsenate, dichromate and pertechnetate ions. Some tentative results for ¹²⁵Sb removal are presented in this paper.

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 ¹²⁵Sb were carried out using simulated NPP Floor Drain Waters (Table 1) to tentatively screen the prepared materials. ¹²⁵Sb-tartrate was used as a precursor for antimonate (Sb(OH)_6^-) tracer. The tartrate was oxidized using H_2O_2 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. Batch experiments were carried out to measure the distribution coefficients (k_d) of Sb-125 in the simulated waste solutions. These experiments were carried out by contacting 20 mg of MOM material with 10 mL of simulated Floor Drain Water for 3 days. Thereafter the

solution was centrifuged and filtrated with a 0.2 µm disc filter and counted for ¹²⁵Sb activity using Wallac 1480 Wizard gamma-analyzer. The distribution coefficient k_d for ¹²⁵Sb was calculated from:

$$k_d = \frac{{}^{125}\text{Sb concentration in solid}}{{}^{125}\text{Sb concentration in solution}} = \frac{\text{cpm}_0 - \text{cpm}_{eq}}{\text{cpm}_{eq}} \frac{V}{m}$$

where cpm_0 and cpm_{eq} are the ¹²⁵Sb count rates in solution before and after contact with the MOM material, respectively. V is the solution volume (10 mL) and m is the mass of MOM (20 mg) contacted with the solution.

Table I. Chemical Compositions Of Simulated Floor Drain Waters

Component mg/L	PWR1	PWR2	BWR1
Na	36.8	43.3	90.1
K	7.7	75.0	nd
Ca	0.86	290	29.8
H ₃ BO ₃	160	120	nd
pH	8.7-9.0	na	6.2

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

The pH of the Floor Drain solutions changed during the contact with the MOM materials and the magnitude of the change depended on the individual characteristics of the material. Therefore the results obtained for the different materials were not directly comparable. In order to obtain representative results, the dependence of Sb-125 uptake of solution pH was studied using 0.1 M NaNO₃ as a test solution in a similar fashion.

The redox-potential of 0.1 M NaNO₃ solution dosed with different amounts of MOM materials was measured with Thermo Orion Model 97-78 Platinum electrode to check the redox functionality of the materials.

A dynamic column experiment was carried out using a small minicolumn (bed volume BV = 0.7 mL, packed with MOM-1B, grain size 0.1-0.3 mm) and simulated Floor Drain Water BWR1, 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 7 mL/min (10 BV/h) initially and the flow rate was increased gradually to 35 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.

Results

Selected test results in the Simulated Floor Drain Water for some of the best MOM materials are presented in Table 2. After contact with the MOM materials the activity of Sb-125 in the simulated Floor Drain Waters was very low and in some cases below the detection limit (Table 2). When measurable, the values of k_d exceeded 1,000,000 mL/g for MOM-1, indicating that extremely high dynamic processing capacities, in order of 1000 m³/kg, could be obtainable. The simulated liquids became slightly acidic after contact with the MOM materials (Table 2).

Table II. Distribution Coefficients K_d (ML/G) Of Sb-125 In Simulated Floor Drain Waters.

Simulant/Metal oxide	Distribution coefficient k_d for Sb-125 (mL/g)		
	MOM-1A	MOM-1B	MOM-2
PWR1	6502700	nd	59100
PWR2	nd	5059700	64700
BWR1	nd	nd	56100
Equilibrium pH	3,31 – 3,39	3,48 – 3,54	2,58 – 2,62

Further experiments in NaNO_3 solutions at different pH showed that ^{125}Sb uptake (k_d) for MOM-1B was constant and at high level ($k_d > 100,000 \text{ L/kg}$) in mildly acidic to neutral range (pH = 2-7) but decreased linearly with pH ($\log k_d/\text{pH}$) in alkaline solution (Fig. 2). At pH=10 however, the uptake was still reasonable ($k_d = 20,000 \text{ mL/g}$). A reference test that was carried out using the ^{125}Sb -tartrate precursor directly as a tracer showed 100 % uptake of Sb-125 indicating that the MOM-1 materials could also remove efficiently reduced (cationic) forms of antimony. MOM2 material had slightly lower uptake of ^{125}Sb at pH = 2 at uptake decreased linearly with pH (Fig. 2).

Redox-measurements for different MOM-1B doses (g/10 mL solution) showed that the eH-value of the solution decreased with increasing dose of solid material in the solution (Fig. 3), indicating that the MOM-1B material contained reducing functionality. However, the eH-value obtained at 20 mg/10 mL was about 470 mV which is not low enough to reduce $\text{Sb}(\text{OH})_6^-$ (see Fig. 1). The eH-value in the pore water of the material is likely to be much lower, though. This can be concluded from Fig.3 by extrapolating the curve to very large doses (50 % internal porosity would roughly correspond a dose of 10 g/10 mL of solution). In the internal pores the eH is likely to be low enough to convert antimony to neutral $\text{Sb}(\text{OH})_3$ species which could be trapped or adsorbed within the pores.

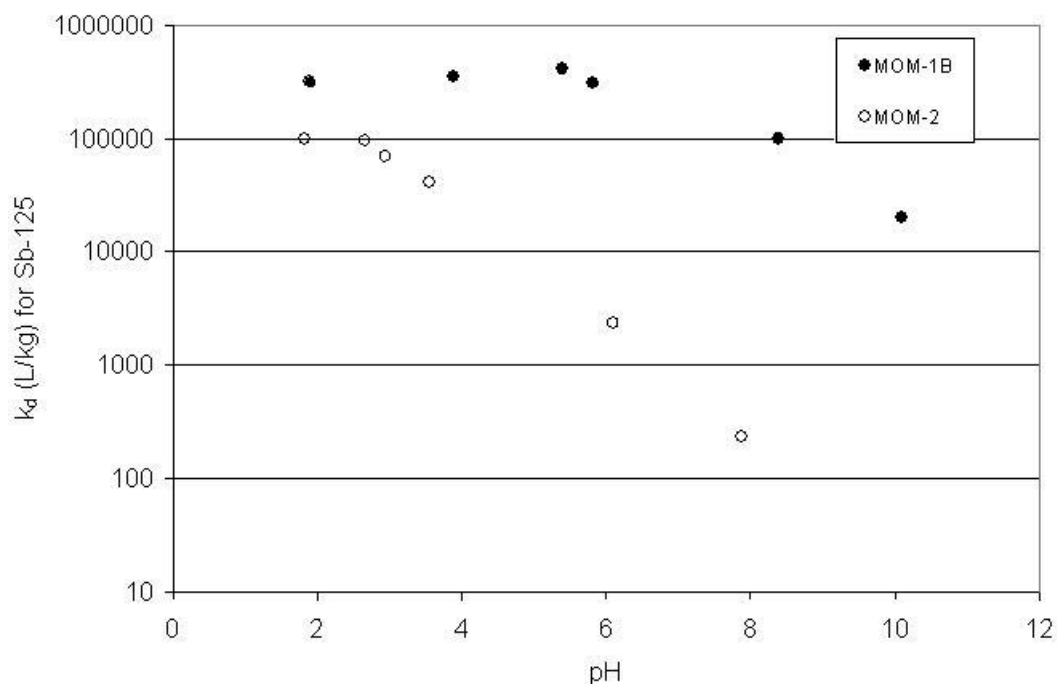


Fig. 2. Uptake (distribution coefficient k_d) of ^{125}Sb by MOM-1B and MOM-2 materials in 0.1 M NaNO_3 as a function of pH.

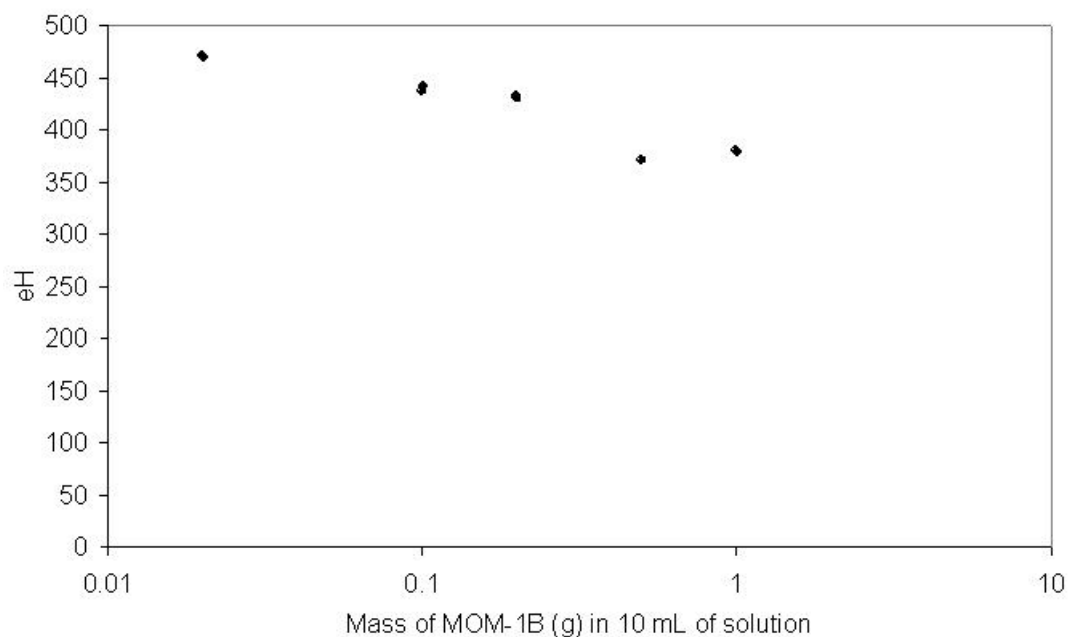


Fig. 3. Redox potential (eH) in 0.1 M NaNO_3 solution contacted with different doses (g/10 mL) of MOM-1B material. Values have been corrected for the changes of solution pH.

The column packed with MOM-1B removed Sb-125 from the simulated Floor Drain Water (BWR1) with a good efficiency, the decontamination factor DF was about 300-600 most of the time. The DF remained at this constant level and did not thus depend on the flow rate which was increased stepwise from 10 BV/h to 50 BV/h during the experiment. The test was

discontinued when 2500 BV of solution had been fed due to time constraints. There was no sign of column exhaustion (i.e. Drop in DF) at this point.

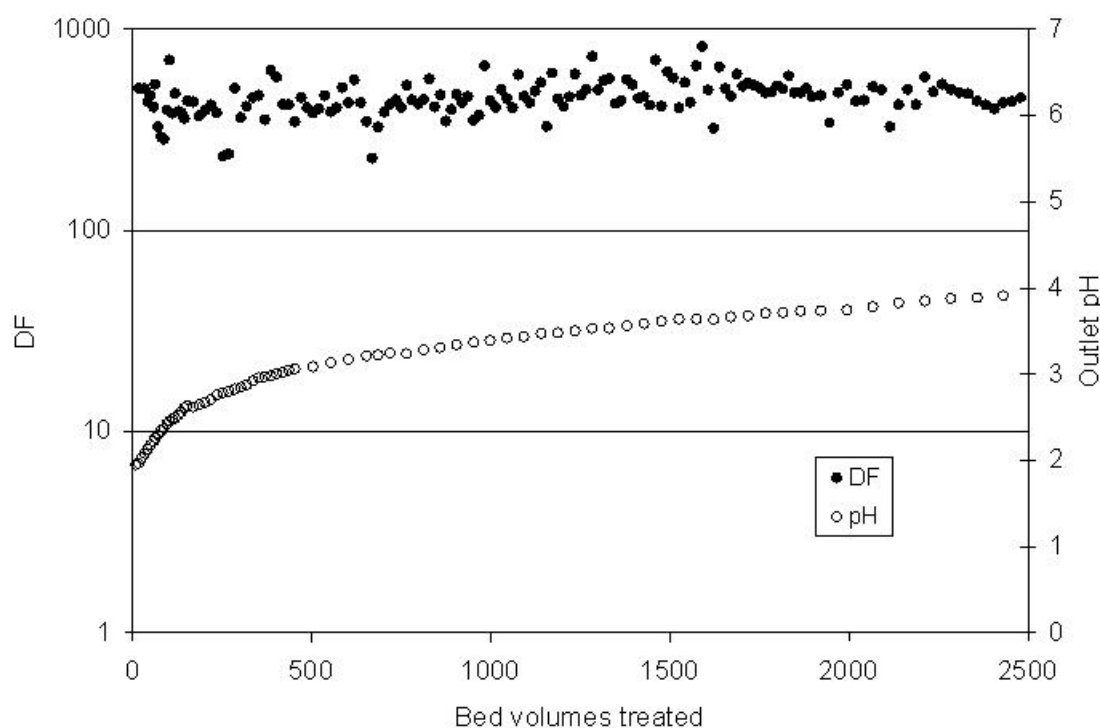


Fig. 4. Column uptake of ^{125}Sb by MOM-1B material in simulated Floor Drain Water BWR1. Bed volume 0.7 mL, flow rate 10-50 BV/h.

CONCLUSIONS

The novel MOM materials appear highly effective for the removal of both cationic and anionic forms of ^{125}Sb from solution over a wide pH-range. Estimated from the static k_d -experiments, the processing capacities may be in the order of $1000 \text{ m}^3/\text{kg}$ even in high-conductivity Floor Drain Waters. Column experiments showed rapid kinetics for Sb-125 removal with decontamination factors from 300 to 600. Long-term column experiments are necessary to confirm the high processing capacities estimated from the k_d -experiments and to assess the stability of the material in extended column use.

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