



Ion-Exchange Properties of Microporous Tungstates: Novel Adsorbents for Nuclear Waste Management Applications

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SUMMARY. A hydrothermally prepared tungsten oxide-based phase, ATS-1 (ANSTO Tungstate Sorbent), of nominal composition, $\text{Na}_{0.3}\text{Mo}_{0.1}\text{W}_{0.9}\text{O}_3 \cdot x\text{H}_2\text{O}$, has been shown to display promising selectivity for both Cs^+ and Sr^{2+} cations from acidic simulant, indicative of the Intermediate Level Liquid Waste (ILLW) produced from ^{99}Mo radioisotope production at the ANSTO site. The development of an inorganic ion-exchanger that displays such selectivity for both Cs^+ and Sr^{2+} in acidic solutions has previously eluded researchers in the field of inorganic ion-exchangers. The ATS-1 adsorbent also displays exquisite selectivity for lead (and polonium) in low to high acidity solutions, and as such is being further investigated as a method to reduce the radiological hazard from ^{210}Pb and ^{210}Po during the processing of uranium ore bodies. The adsorption of Cs^+ , Sr^{2+} and Pb^{2+} cations by ATS-1 has been extensively investigated with respect to the kinetics of adsorption, capacity and the effect of competing cations *viz.* Na^+ , K^+ . The ATS-1 adsorbent has also been successfully granulated with an inert, organic matrix, which has consequently allowed the study of cation adsorption using more application-based, column separations. The results of these investigations suggest that these materials have potential application in several nuclear waste management issues in Australia at the present.

INTRODUCTION

The nuclear industry as a whole is dogged by the issue of disposing of radioactive waste streams. One option for dealing with these waste streams is to remove the problematic radionuclides with an ion-exchanger. However, the viability of such an approach is highly dependent on the stability of the ion-exchanger in the relevant medium, the radionuclide/s of interest, selectivity of the ion-exchanger employed, complexity and volume of the waste stream etc. Our research on such radioactive waste management issues at ANSTO has principally centered on developing novel tungsten oxide-based inorganic adsorbents (Figure 1) which display selectivity for radionuclides with ionic radii of *ca.* 1.2 (^{90}Sr , ^{210}Pb) and 1.7 Å (^{137}Cs , ^{210}Po).[1]

The radionuclides ^{137}Cs and ^{90}Sr constitute the majority of the radioactivity present in wastes arising from spent fuel reprocessing, weapons manufacture and ^{99}Mo (^{235}U irradiation) radioisotope production after *ca.* 5 years.[2] This last source of ^{137}Cs and ^{90}Sr is where ANSTO's interest in this issue lies. Through the use of a selective inorganic ion-exchanger, the bulk of the radioactivity from such sources can potentially be concentrated onto a small volume of adsorbent, thus allowing the bulk of the effluent to be disposed of as low level waste. Although, a number of inorganic sorbents have shown excellent selectivity for cesium in acidic

solutions most have little or no selectivity for strontium.[3-14] However, a tungsten oxide-based inorganic ion-exchanger, ATS-1 (ANSTO Tungstate Sorbent), with a structure based on hexagonal tungsten bronze, and of nominal composition, $\text{Na}_{0.3}\text{Mo}_{0.1}\text{W}_{0.9}\text{O}_3 \cdot x\text{H}_2\text{O}$, developed at ANSTO displays selectivity for both cesium and strontium from acidic solutions (Figure 1).

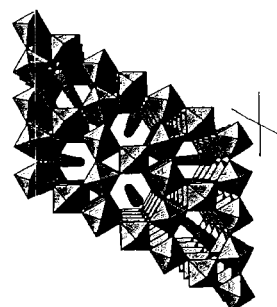


Figure 1. ATS-1; Tungsten oxide-based, inorganic adsorbent developed at ANSTO.

Aside from the obvious implications of elevated levels of radionuclides in our natural environment, ^{210}Pb (and ^{210}Po) are radionuclides that attract interest for their potential radiological hazard during the processing of uranium ore bodies. The ATS-1 inorganic ion-exchanger also displays exquisite selectivity for both lead and polonium in low to high acidity solutions, and as such this technology could

have application in a number of mineral processing streams in Australia.

Any application of this adsorbent technology would however require the engineering of a granulated form of the microcrystalline ATS-1 material that would be suitable for deployment in a fixed-bed column separation.

This article will outline our studies of the sorption of Cs^+ , Sr^{2+} and Pb^{2+} by the tungsten oxide adsorbent, ATS-1, and will be presented in two parts. The first section will deal with the general performance of ATS-1 in adsorbing Cs^+ , Sr^{2+} and Pb^{2+} , and the second will deal with fixed bed column separations of these cations.

RESULTS AND DISCUSSION

Cs^+ , Sr^{2+} and Pb^{2+} Ion Exchange Properties

A program of research concerned with developing and assessing novel inorganic ion-exchangers for the pretreatment of Intermediate Level Liquid Waste (ILLW) produced from ^{99}Mo radioisotope production commenced at ANSTO in 1998. Initial studies revealed that the molybdenum-doped, hexagonal tungsten bronze phase, $\text{Na}_{0.3}\text{Mo}_{0.1}\text{W}_{0.9}\text{O}_3 \cdot x\text{H}_2\text{O}$ (ATS-1), displays appreciable selectivity ($>2000 \text{ mL.g}^{-1}$) for Cs^+ , Sr^{2+} and Pb^{2+} in 1M HNO_3 . Furthermore, preliminary studies have indicated that the adsorbent displays selectivity for ^{210}Po , comparable with that of Pb^{2+} (^{210}Pb).^[15] In essence, the structural sites within the ATS-1 structure involved in ion-exchange exhibit a strong preference for cations with ionic radii of *ca.* 1.70 Å (Cs^+ - 1.67 Å) and 1.20 Å (Sr^{2+} - 1.18 Å; Pb^{2+} - 1.19 Å) over hydronium ions.

The ATS-1 adsorbent is easily prepared by pH adjustment of sodium tungstate/molybdate solutions followed by hydrothermal treatment.^[16-18] The hexagonal phase produced by these methods differs from the classical hexagonal tungsten bronze produced by high temperature methods in that they have a microcrystalline fibrous morphology and the materials are in an oxidised rather than a reduced state. It is well known that the sodium A cations initially situated within the *c*-axis tunnels (Figure 1) can be completely replaced by other alkali metal cations such as Cs^+ , K^+ and Rb^+ by ion exchange using concentrated solutions.^[19] However, our group is the first to explore in detail the ion-exchange properties of these materials.

In addition to high selectivity for Cs^+ , Sr^{2+} and Pb^{2+} , the time dependence of the ion-exchange mechanism is of prime importance for most practical applications. Investigations conducted using batch contact experiments revealed that for the ATS-1

adsorbent, maximum sorption of Cs^+ , Sr^{2+} and Pb^{2+} occurred after 30 – 60 minutes of contact (Figure 2) (*ca.* 100 ppm $\text{Cs}^+/\text{Sr}^{2+}$; 10 ppm Pb^{2+} in 1M HNO_3). These rapid exchange results demonstrate that the kinetics of exchange are not affected by the crystalline nature of the phase, as has been reported for numerous antimony-based sorbents investigated by Harjula and co-workers.^[21-23]

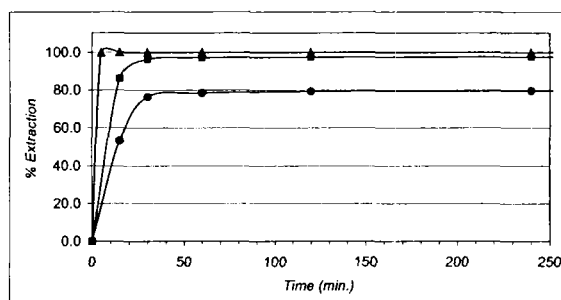


Figure 2. Time dependent uptake of Cs^+ , Sr^+ and Pb^{2+} by ATS-1 (-■-, -●- and -▲- respectively).

Another important property of any ion-exchange material is the capacity for a given ionic species. The ATS-1 adsorbent possesses a *theoretical* capacity of 0.3 mmol.g^{-1} for a monovalent cation such as Cs^+ , and 0.15 mmol.g^{-1} for a divalent cation such as Sr^{2+} (Pb^{2+}), in the fully oxidised state.^[16,18] Compositional data obtained by electron dispersion spectroscopy (either *via* TEM or SEM), indicates that most of the Na^+ present in the adsorbent is exchanged under conditions sufficient to saturate the adsorbent *viz.* in the presence of high levels of the given cation. Monitoring the Na^+ liberated during batch contact experiments also confirms this assertion. The Cs^+ , Sr^{2+} and Pb^{2+} equilibrium isotherm curves for ATS-1 are presented in Figure 3 and were obtained *via* multiple batch contact experiments conducted with increasing concentrations of Cs^+ , Sr^{2+} or Pb^{2+} in acidic (1M HNO_3) solutions. The dashed lines represent regressed Langmuir fits to the experimental data and allow the theoretical maximum capacity, or asymptotic capacity (q_o), for a given metal cation to be calculated using the formulae;

$$\frac{q}{q_o} = \frac{KC_f}{(1 + KC_f)} \quad (1)$$

where q_o is the maximum asymptotic capacity ('capacity'; mmol.g^{-1}); q is the number of moles of cation present in the sorbent (mmol.g^{-1}); K is the Langmuir coefficient; C_f is the equilibrium Cs^+ , Sr^{2+} or Pb^{2+} solution concentration (mg.L^{-1}).

The *asymptotic* capacity for Cs^+ , Sr^{2+} and Pb^{2+} of the ATS-1 adsorbent is $0.592 \text{ mmol.g}^{-1}$ (78.7 g.kg^{-1}), $0.255 \text{ mmol.g}^{-1}$ (22.3 g.kg^{-1}) and $0.252 \text{ mmol.g}^{-1}$ (52.2 g.kg^{-1}), respectively. The higher than theoretical *asymptotic* capacities may be due to the

reduction of some of the Mo^{6+} centres, and hence an increase in the overall negative charge on the metal oxide framework. Indeed the blue-green colouration of the ATS-1 adsorbent supports this view, although the extent of framework reduction that this colouration represents is yet to be quantified.

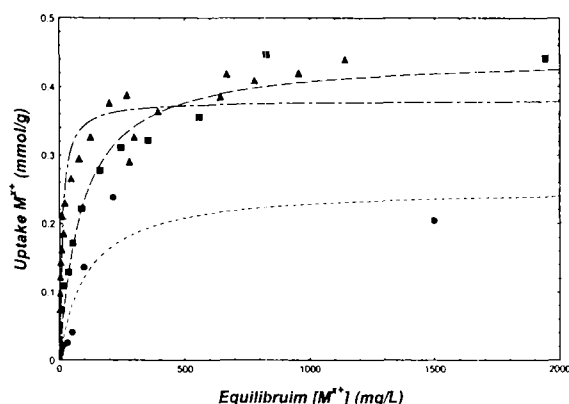


Figure 3. Equilibrium Cs^+ , Sr^{2+} and Pb^{2+} adsorption isotherm curves (-■-, -●- and -▲-, respectively) for the ATS-1 adsorbent.

Whether one is concerned with pretreatment of radioactive waste streams or treating uranium processing streams, the effect that varying levels of competing cations, such as Na^+ , K^+ etc, have upon the selectivity of an adsorbent towards a given metal cation/s is an extremely important aspect of adsorbent performance. It should be noted that preliminary investigations on the selectivity of ATS-1 for ^{210}Pb (and ^{210}Po) in the presence of a range of alkali metal, alkali earth and transition metal cations has revealed little to no effect on the sorption of these nuclides. Additionally, the ILLW stream at ANSTO only contains ppm concentrations of Al and Fe, and ppb concentrations of numerous radioisotopes, and no appreciable quantities of alkali metal cations. The effect that these cations have on the selectivity of the ATS-1 adsorbent was investigated to ascertain its suitability towards other waste streams that might contain such cations.

In Figures 4 and 5 are presented Cs^+ and Sr^{2+} (*ca.* 100 ppm in 1M HNO_3) adsorption isotherms for the ATS-1 adsorbent, in the presence of Na^+ and K^+ , respectively. It is apparent from Figure 4 that extraction of Cs^+ (-■-) by ATS-1 is moderately efficient *ca.* 75% at the maximum concentration of Na^+ . Conversely, the inclusion of Na^+ has an immediate negative impact on Sr^{2+} extraction (-●-), decreasing to only *ca.* 10% at the highest Na^+ concentration studied. Similar trends in Cs^+ and Sr^{2+} uptake by ATS-1 are observed with increasing K^+ concentration.

In Figure 6 is presented the Cs^+ , Sr^{2+} and Pb^{2+} adsorption isotherms for the ATS-1 adsorbent for low to high acidity solutions. For both Cs^+ (-■-) and

Pb^{2+} (-▲-), the percentage of cation extracted does not vary greatly across the $[\text{H}^+]$ range studied, except for Pb^{2+} at extremely high $[\text{H}^+]$ (15.4M). This is especially impressive in the case of Pb^{2+} given the high $[\text{H}^+]$ solutions employed and wide range of $[\text{H}^+]$ investigated. Few conventional inorganic adsorbents can tolerate such acidity without decomposition. The lower selectivity of the ATS-1 adsorbent for Sr^{2+} in medium acidity solutions is particularly evident, with a *ca.* 100% increase in percentage extraction when $[\text{H}^+]$ is decreased from just 2M to 0.1M.

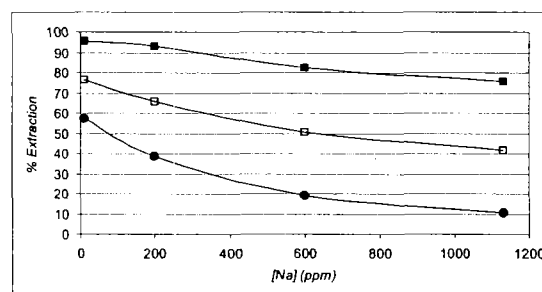


Figure 4. Uptake of Cs^+ and Sr^{2+} (-■- and -●-, respectively) by ATS-1 adsorbent as a function of $[\text{Na}^+]$. Combined uptake of Cs^+ and Sr^{2+} is represented by -□-.

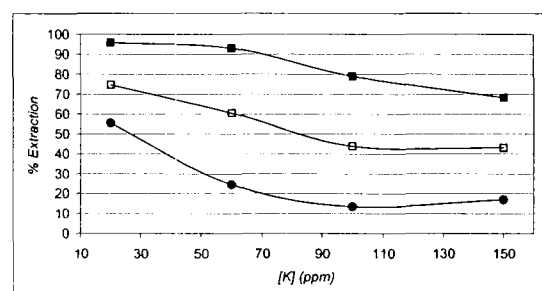


Figure 5. Uptake of Cs^+ and Sr^{2+} (-■- and -●-, respectively) by ATS-1 adsorbent as a function of $[\text{K}^+]$. Combined uptake of Cs^+ and Sr^{2+} is represented by -□-.

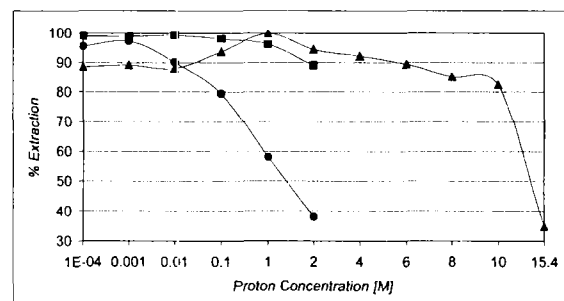


Figure 6. Uptake of Cs^+ , Sr^{2+} and Pb^{2+} (-■-, -●- and -▲-, respectively) by ATS-1 adsorbent as a function of $[\text{H}^+]$.

Fixed-bed Column Separations of Cs^+ , Sr^{2+} and Pb^{2+} .

The microcrystalline nature (powder) of the ATS-1 adsorbent makes its direct use in any column-based

application impossible, and as such a suitable 'engineered form' of the adsorbent was pursued. In conjunction with researchers at the Czech Technical University in Prague, a granular form (60% w/w ATS-1) of the adsorbent has been prepared using an inert, organic matrix. An electron micrograph of a cross section of the composite adsorbent material is shown in Figure 7. The high degree of internal macroporosity present in these composite materials is the key to their success as a support. Furthermore, the organic matrix has been shown to be extremely robust to radiation fluxes of 1×10^{10} Gy, and as such is very amenable to the nuclear applications presented herein.[24] Efforts are continuing in preparing materials with a higher weight loading of the ATS-1 adsorbent, so as to increase the capacity for Cs^+ and Sr^{2+} per unit mass of composite adsorbent.

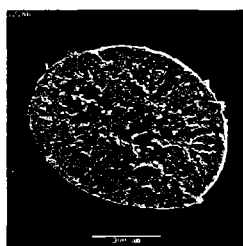


Figure 7. Electron micrograph of a cross section of the ATS-1 composite adsorbent.

Cs^+ and Sr^{2+} – ANSTO ILLW

To evaluate the potential of the composite adsorbent to remove Cs^+ and Sr^{2+} from ILLW simulant in a fixed bed system, bench-scale (2 ml bed volume - BV) column tests were undertaken to obtain kinetic and loading capacity data. Figure 8 shows the cesium and strontium breakthrough curves generated for a flowrate of 20 BV.h^{-1} . This data allows the calculation of Cs^+ and Sr^{2+} column capacity (q_0) and column exhaustion rate constants (k_l) using theory developed by Thomas and others.[25,26] Typical q_0 and k_l values for Cs^+ obtained using ANSTO ILLW simulant were 14.43 g.kg^{-1} and $0.0252 \text{ L.h}^{-1}.\text{g}^{-1}$, respectively.

Modeling the adsorption kinetics of Cs^+ and Sr^{2+} to the fixed bed of composite adsorbent was conducted by application of Equation 2;

$$\frac{C_0}{C} = 1 + e^{\frac{k_l}{F}(q_0 M - C_0 V)} \quad (2)$$

where C = cation effluent concentration (mg.L^{-1}); C_0 = cation feed concentration (mg.L^{-1}); k_l = column exhaustion rate constant ($\text{L.h}^{-1}.\text{mg}^{-1}$); F = flowrate (L.h^{-1}); q_0 = equilibrium adsorbent phase cation concentration (mg.g^{-1}); M = mass of adsorbent (g); V = eluant volume (L). The validity of this modeling approach has been confirmed at other flowrates *ca.* 15 BV.h^{-1} .

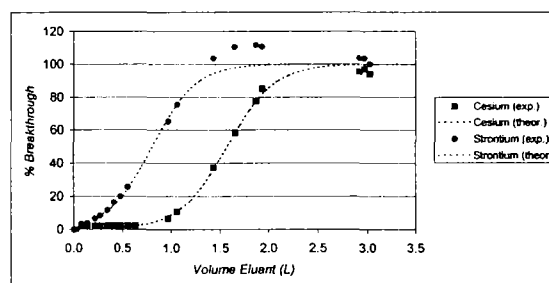


Figure 8. Cesium and strontium breakthrough curves using ANSTO ILLW simulant (2ppm Cs^+ and 0.6ppm Sr^{2+} in 1M HNO_3).

The theoretical breakthrough curve for Cs^+ shows a high degree of correlation with the experimentally determined breakthrough curve; however, there is a distinct deviation from the predicted behaviour for Sr^{2+} . The higher than 100% breakthrough observed suggests that some of the adsorbed Sr^{2+} 'bleeds' from the column over the course of the elution with ANSTO ILLW feed. Efforts are presently underway to quantify this 'bleed' of Sr^{2+} and discern whether it is due to a competitive desorption involving Cs^+ or continual elution with $[\text{H}^+]$.

The theory used to model column performance may also be utilised to design large scale separations. If a number of columns of defined bed volume, and known column performance (q_0 and k_l), are placed in series, the breakthrough ($C_0/C = 100000$) and exhaustion ($C_0/C = 1.05$) points for each column may be calculated. Figure 9 shows a plot of these breakthrough and exhaustion points for Cs^+ and Sr^{2+} as a function of eluant volume for the ATS-1 composite adsorbent.

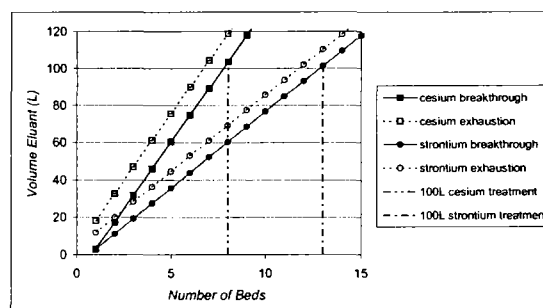


Figure 9. Predicted breakthrough and exhaustion volumes for treatment of 100L of ILLW simulant.

As an example, this theoretical approach defines that in order to treat 100L of ILLW simulant 8 and 13 columns (30 ml bed volume) would be required to remove Cs^+ and Sr^{2+} , respectively, to a level of $C_0/C = 100000$. The greater number of columns required to remove Sr^{2+} from the 100L of simulant is a reflection of the lower selectivity and capacity of the ATS-1 composite adsorbent for the cation. Furthermore, this approach can be extended to

predict the amount of composite adsorbent needed to treat the entire *ca.* 6000L of ILLW stored at the ANSTO site, with a predicted total volume of 22L of composite adsorbent sufficient to remove both ^{137}Cs and ^{90}Sr radionuclides.

Pb^{2+} - preliminary studies

Similar studies to that with Cs^+ and Sr^{2+} have been undertaken with Pb^{2+} in 1M HNO_3 with the experimental and theoretical breakthrough curves presented in Figure 10. Initial column evaluation studies of the ATS-1 composite with Pb^{2+} -containing acidic solutions have shown behaviour which is consistent with the theory proposed by Thomas.[25] The q_0 and k_f values for Pb^{2+} obtained were 13.66 g.kg^{-1} and $0.0526 \text{ L.h}^{-1}.\text{g}^{-1}$, respectively, but assume ideal behavior beyond the *ca.* 20% breakthrough point. Efforts are currently underway to follow column breakthrough through to exhaustion and thereby confirm the validity of the Thomas model in predicting column performance.

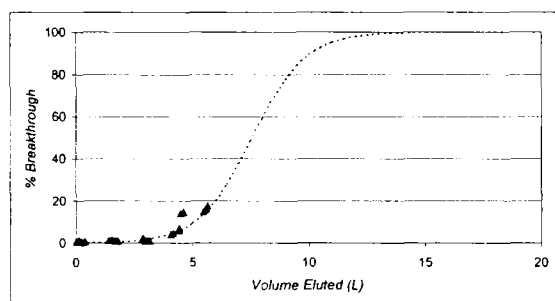


Figure 10. Lead breakthrough curves using 1ppm Pb^{2+} in 1M HNO_3 feed solution.

Studies have also commenced with ^{210}Pb and ^{210}Po -containing solutions indicative of uranium ore processing streams *viz.* 2M H_2SO_4 and containing various metal cations. These results will be treated in a manner similar to that of the Cs^+ and Sr^{2+} results with ANSTO ILLW to design a larger scale separation of ^{210}Pb and ^{210}Po .

Conclusions

The unique ability of the ATS-1 adsorbent to sorb both Cs^+ and Sr^{2+} from acidic radwaste simulant has been demonstrated, and presents itself as a potential technology for the pretreatment of ANSTO ILLW. Other ^{137}Cs and ^{90}Sr -containing radioactive waste streams with low to medium levels (<500ppm) of alkali metal and alkali earth cations could be treatable with the ATS-1-based technology.

The exquisite selectivity of the ATS-1 adsorbent for Pb^{2+} across a wide range of pH indicates that this adsorbent could have application in removing ^{210}Pb (or Pb^{2+}) and ^{210}Po from a number of areas, namely, uranium ore processing, uranium ore tailings leachates and groundwater treatment/testing.

Acknowledgements

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