Selective Uptake of Cesium Ions on AMP-loaded Silica Gels

*Yusuke Endo, Yan Wu, Hitoshi Mimura and Yuichi Niibori
Graduate School of Engineering, Tohoku University,
Aramaki–Aza–Aoba 6–6–01–2, Aoba–ku, Sendai 980–8579, JAPAN
Masaki Ozawa
O–arai Engineering Center, Japan Atomic Energy Agency, O–arai, Narita–cho 4002, Ibaraki 311–1393, JAPAN

(Manuscript submitted March 25, 2007; accepted July 2, 2007)

Abstract
Ammonium molybdophosphate (AMP) was incorporated in the porous silica gels by successive impregnation with H₃Mo₁₂O₄₀P and NH₄NO₃. The selective uptake properties of Cs⁺ on AMP-loaded silica gels (SGAMP) and the recovery of Cs⁺ have been studied by batch and column methods, respectively. The uniform incorporation of AMP in matrices was confirmed by the characterization with SEM/EPMA. The loading percentage of AMP crystals on silica gels increased with the repetition times of impregnation. The distribution coefficient of Cs⁺ on SGAMP was above 500 cm³/g even in the presence of 5 M (= mol/dm³) HNO₃, while other nuclides were less than 20, indicating high selectivity of SGAMP toward Cs⁺. This ion exchanger is effective for the selective isolation of Cs⁺ from simulated high-level liquid wastes.

Key words: cesium, AMP, silica gel, high-level liquid waste

1 Introduction
The selective isolation of ¹³⁷Cs from radioactive waste solutions has attracted great interest in recent years due to its application as a radiation source in the field of medicine and in industry [1]. Ammonium molybdophosphate (AMP), which shows high selectivity toward Cs⁺ ions, can act as one of the most promising adsorbents for this purpose [2]. However, AMP is still not employed on a large scale because of its fine powder form which hinders simple column operation. To overcome this handling problem, several impregnation methods have been proposed to fix AMP on different supporting matrices like asbestos [3], porous alumina [4], Amberlite XAD–7 [5], titanium phosphate [6], and polyacrylonitrile [7]. But none of these methods has led to real success because these preparation procedures are rather complicated and the results are often not reproducible because of losses in capacity due to washing out effects in the column and a diminishing crystal surface [2]. Among the above granulated AMPs, the titanium phosphate–AMP absorbent showed excellent hydrodynamic properties, acid resistance, thermal stability, and radiation stability, but Rb⁺ and several rare earth elements competed strongly at lower acidities [6].

The purpose of this report is to describe how to eliminate the above synthetic shortcomings and to produce high quality AMP granules using phosphomolybdic acid hydrate as the precursor material. The present
paper deals with the evaluation of Cs⁺ selectivity of AMP, preparation procedure of AMP-loaded silica gels, their characterizations and uptake properties of Cs⁺.

2 Experimental

2.1 Materials and Preparation Procedure

The synthesis of AMP-loaded silica gels (SGAMP) is as follows. Ten grams of the silica gel granule Wako–Gel C–100 (Wako pure chemical, 150–475 µm size, pore size 7 nm; SG) was dried at 110°C. These SGs were then added to 25 cm³ of 0.2 M phosphomolybdic acid hydrate (H₃Mo₁₂O₄₀P; Fluka Chemie; PMA) solution. The resulting solution was kept under reduced pressure and at room temperature for 30 min in order to impregnate the PMA into the SG. The excess PMA solution was removed by aspiration. The product was freeze-dried to precipitate PMA in the macropores of SG. In a similar manner, PMA–loaded SG was treated with 25 cm³ of 10 M NH₄NO₃ solution to convert the loaded PMA into AMP. The reaction of PMA with NH₄NO₃ to form AMP is as follows.

\[ \text{H}_3\text{Mo}_{12}\text{O}_{40}\text{P} + 3\text{NH}_4\text{NO}_3 \rightarrow (\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 + 3\text{HNO}_3 \]  

After freeze-drying, the product was sieved by using a 150 µm sieve to remove fine AMP particles and dried at 50°C for 12 h and finally stored in a sealed vessel. AMP-loaded silica gels treated with once and twice impregnation were abbreviated as SGAMP–1 and SGAMP–2, respectively.

2.2 Characterization

The surface morphologies of SGAMP–2 granules were examined by scanning electron microscopy (SEM). The structure of SGAMP–2 was determined by powder X–ray diffractometry (XRD) using monochromatized Cu–Ka radiation. The adsorbed metal ions on SGAMP–2 and energy dispersive spectroscopic (EDS) spectrum were determined by electron probe microanalysis (EPMA). The specific surface area of SGAMP–2 was measured by BET method. The thermal decomposition of SGAMP–2 was examined by infrared spectroscopy. The concentration of Cs⁺ was measured by atomic absorption spectrophotometry (AAS).

2.3 Determination of Distribution Coefficient

An aqueous solution (7 cm³) containing 10 ppm metal ion was contacted with 0.070 g of SGAMP–2 sample at 25 ± 1°C for 3 h, which was found to be sufficient for attaining equilibrium. The aqueous phase was separated by centrifugation at 10,000 rpm for 15 minutes. The concentration of different metal ions (Na⁺, K⁺, Rb⁺, Cs⁺, Sr²⁺, Co³⁺, Eu³⁺) in supernatant was measured by the atomic adsorption spectrometer Jarrel–Ash AA–890. The uptake percentage of metal ions removed from the solution, R (%), and the distribution coefficient, \( K_d \) (cm³/g), are defined as

\[ R = \frac{[(C_i - C_t)/C_i]}{100} \% \]  

\[ K_d = \frac{[(C_i - C_t)/C_i]}{V/m \ \text{(cm}^3/\text{g)}} \]  

where \( C_i \), \( C_t \), and \( C_f \) (ppm) are the concentration at the initial stage, at time \( t \), and at equilibrium, respectively; \( m \) (g) is the weight of the SGAMP–2 sample; and \( V \) (cm³) is the volume of the aqueous phase.

2.4 Column Test

The SGAMP–2 sample (3 g) was densely packed into a glass column (8 mm×300 mm long) with a jacket thermostated at 25°C. The column volume of SGAMP–2 was 4.0 cm³. A feed solution ([Cs⁺] = 500 ppm) was then passed through the column at a flow rate of 0.15 cm³/min. Every 1.6 cm³ of the effluent was taken by a fraction collector. A breakthrough curve was obtained by plotting the breakthrough ratio \( (C/C_0) \) against the
effluent volume, where \( C_0 \) and \( C \) (ppm) are the concentration of the initial solution and the effluent, respectively. Elution / regeneration of the column was carried out by using \( \text{NH}_4\text{NO}_3 \) solution as an eluant. A solution of 5 M \( \text{NH}_4\text{NO}_3 \) was passed through the column at the above-mentioned flow rate, every 2 cm\(^3\) of the eluant was taken by a fraction collector. An elution curve was obtained by plotting the eluted % [\% ratio of the concentration of the eluant to the initial concentration (ppm) of the \( \text{Cs}^+ \)-adsorbed column] against the elution volume.

![Apparatus for column experiments](image)

### 3 Results and Discussion

#### 3.1 X-ray diffraction analysis

From the X-ray diffraction (XRD) patterns presented in Fig. 2, the presence of AMP peaks [8] in the XRD patterns of SGAMP–1 and SGAMP–2 confirms the successful loading on SG. The peak intensity of AMP in SGAMPs increased with the repetition times of the impregnation of the PMA solution as shown in the pattern of SGAMP–2 prepared by double impregnation. The AMP content of SGAMP–2 is estimated to be about 10 wt% from its \( \text{Cs}^+ \)-exchange capacity (0.60 meq/g). The AMP content roughly estimated (10 wt\%) is relatively low, but further increase in the concentration of PMA and repetition times of impregnation lead to the loading of a higher concentration of AMP.

#### 3.2 EPMA and BET analysis

A cross section of the SGAMP–2 particles embedded in the acrylic resin was submitted to electron probe X-ray microanalysis (EPMA). An energy dispersive spectroscopic (EDS) spectrum for the inner part of this particle is shown in Fig. 3. The constitutional element of molybdenum was detected in the spectrum, indicating that the AMP crystals are loaded on the macro pores of SG. The EDS spectrum in the vicinity of the surface was similar to that of the inner part of the particle. Figure 4 shows the SEM image of the SGAMP–2 particles. The crystal size as roughly estimated from SEM image was about 200 \( \mu \text{m} \).

Figure 4 also shows the result of line analysis of Mo–L\( \alpha \) and Cs–L\( \alpha \) by EPMA for a SGAMP–2 granule after it was treated with SW–11E (simulated high-level liquid waste) [9]. The concentration profile of Mo-L\( \alpha \) was almost similar to that of Cs-L\( \alpha \), indicating the selective incorporation of \( \text{Cs}^- \) into AMP crystal. Figure 5 shows EPMA color map for SGAMP–2 granule after it was treated

![XRD patterns of silica gels (Wako–gel C–100) and SGAMPs](image)

![EDS spectrum, for SGAMP–2 particle](image)
with SW–11E. Uniform dispersion of Cs and Mo were confirmed by the line analysis and EPMA color map. This also indicates the successful loading of AMP crystals onto the pores of SG. In conclusion, synthesized granular AMP (SGAMP) can be used as an effective adsorbent for the isolation of Cs⁺ ions from a high–level radioactive waste solution due to its high selectivity and operational ease.

The specific surface area of SGAMP–2 was measured by BET method (Quantachrome NOVA 2000). Figure 6 shows specific surface area of silica gels (Wako–gel C–100) and SGAMP–2. The high porosity is still maintained even after the impregnation of AMP onto the inner pores of the silica gels. Figure 6 also shows the schematic view of SGAMP–2. Aggregates of AMP uniformly dispersed in matrices of porous silica gels.

![Fig. 4 SEM and line analysis of Mo–La and Cs–La of SGAMP–2 treated with SW–11E](image)

![Fig. 5 EPMA color map for SGAMP–2; SW–11E, 25°C, 1 week](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET specific surface area / m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica gel</td>
<td>373.6</td>
</tr>
<tr>
<td>SGAMP–2</td>
<td>375.2</td>
</tr>
</tbody>
</table>

![Fig. 6 BET specific surface areas and a schematic view of the cross section of SGAMP–2 granule](image)

3.3 Thermal Stability of SGAMP–2

The thermal decomposition of SGAMP–2 was examined by infrared spectroscopy. Figure 7 illustrated the effect of calcining temperatures on the optical density (D) of NH₄⁺ at 1,400 cm⁻¹ [10]. Relatively large D value above 1.0 was obtained at lower temperature below 250°C, beyond which it decreases markedly with calcining temperature. This indicates the thermal decomposition of NH₄⁺.

![Fig. 7 Effect of calcining temperature on optical density (D) of NH₄⁺ at 1,400 cm⁻¹](image)
3.4 Uptake Rate of Cs⁺

Figure 8 shows the uptake ability of SGAMP–2 for different metal ions in HNO₃ solution. $K_d$ values for all metal ions decreased with an increasing concentration of HNO₃. The separation factors of Cs⁺ and other metal ions ($\alpha_{Cs:M} = K_{d,Cs}/K_{d,M}$, M = Na, K, Rb, Sr, Co, Eu) were estimated to be about $10^2$ even in the presence of 5 M HNO₃. As there was no cesium uptake on SG in acid solution, the high selectivity of SGAMP–2 to Cs⁺ is totally due to the “steric” effect [11] of the structure of loaded AMP.

3.5 Ion–Exchange Isotherm for Cs⁺ Uptake

In order to clarify the ion-exchange mechanism, ion–exchange isotherms were obtained in a wide range of initial Cs⁺ concentrations. The equilibrium amounts of Cs⁺ adsorbed on SGAMP–2 approached a constant value at about 3 mM Cs⁺, suggesting that the uptake of Cs⁺ follows a Langmuir-type adsorption equation [7,9]. As seen in Fig. 10, a fairly linear relation between $C_{eq}/Q_{eq}$ and $C_{eq}$ was obtained from Langmuir plots. The estimated $Q_{max}$ values are summarized in Fig. 9.

3.6 Breakthrough Properties of Cs⁺ through SGAMP–2 Column

Fig. 11 (left) illustrates the breakthrough curve of Cs⁺ (feed solution [Cs⁺] = 500 ppm), which is a symmetrical S–shaped profile, suggesting no dislodgement of AMP from the matrix of SG. The break point of 5% breakthrough was estimated to be 40 cm³ [bed volume (BV) = 10]. The breakthrough capacity (B. T. Cap.) and total capacity (T. Cap.) were calculated to be 0.045 and 0.060 meq/g, respectively, resulting in a relatively high column utilization (B. T. Cap. / T. Cap.) of 75%. The column packed with SGAMP–2 was thus effective for the selective removal of Cs⁺. On the other hand, the adsorbed Cs⁺ on the column can be eluted by flowing the ammonium salt solution. The elution of Cs⁺ was performed with 87% recovery of the adsorbed Cs⁺ up to first 15 BV of effluent [Fig. 11 (right)].
Fig. 11 Breakthrough (left) and elution (right) curves of Cs⁺ ion from SGAMP−2 column.

Left: Column, 0.8×30 cm; SGAMP−2, 3 g; feed solution [Cs⁺] = 500 ppm, flow rate 0.20 cm³/min, 25°C.
Right: Column, 0.8×30 cm; SGAMP−2, 3 g; 0.19 mmol Cs⁺ adsorbed initially; eluant, 5 M NH₄NO₃, flow rate 0.20 cm³/min, 25°C.

Acknowledgement
The authors express appreciation to Mr. T. Kamaya and Mr. Y. Sato (Tohoku University) for their helpful discussions of SEM and EPMA data. This study was financially supported by JAEA.

References