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A New Granular Composite with High Selectivity for Cesium Ion Prepared from Phosphomolybdic Acid Hydrate and Inorganic Porous Material

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ABSTRACT

Ammonium molybdophosphate (AMP) was incorporated in the porous alumina matrix (JA) by successive impregnation with $H_3Mo_{12}O_{40}P$ and NH_4NO_3. The loading percentage of AMP crystals on JA increased with the repetition times of impregnation. The distribution coefficients of Cs^+ on AMP-loaded granular composite (JAAMP) was above 10^4 cm^3/g in the presence of 1 mol/dm^3 H^+, while those of other nuclides were less than 10, indicating high selectivity of JAAMP to Cs^+. The separation factor of ^{137}Cs to other nuclides (^{85}Sr, ^{60}Co, ^{152}Eu, ^{241}Am, ^{22}Na) ($\alpha_{\mathrm{Cs/Sr;Co;Eu;Am;Na}} = K_{\mathrm{d,Cs}}/K_{\mathrm{d,Sr;Co;Eu;Am;Na}}$) was estimated to be above 10^3. The breakthrough curve for Cs^+ through the column packed with JAAMP exhibited a symmetrical S-shaped profile, and this exchanger proved to be effective for the selective isolation of radiocesium from a simulated high-level liquid waste.

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Key Words. Ammonium molybdophosphate; Inorganic porous material; Impregnation; Loading; Cesium separating agent; Steric effect; Radioactive waste solutions

INTRODUCTION

The selective isolation of ^{137}Cs 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^+ ion, can act as one of the most promising adsorbent materials 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 chromatographic systems have been proposed to fix AMP on different supporting matrices like asbestos (3), silica gel (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). Furthermore, while the method of preparation of granulated AMP using organic materials as supporting matrices solves the problem of the flow characteristics of AMP, nevertheless the materials are of limited use when applications at higher temperatures are needed. Another disadvantage is be the lower radiation stability of the granules in comparison with the original AMP (4). Among the above granulated AMPs, the titanium phosphate–AMP compound 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.

EXPERIMENTAL

Preparation of Composite

The synthesis of a AMP-loaded granular composite (JAAMP) is as follows. Two grams of the porous alumina granule JRC-ALO-1 (8) (48–100 mesh size, pore volume 0.67 cm^3/g, specific surface area 160 m^2/g; JA), which is a reference catalyst of the Catalysis Society of Japan was dried at 110°C. To this was added to 5 cm^3 of 0.2 M (1 M = 1 $mol \cdot dm^{-3}$) phosphomolybdic acid hydrate ($H_3Mo_{12}O_{40}P \cdot aq$; Fluka Chemie; PMA) solution.

The resulting solution was kept under reduced pressure and at room temperature for 30 minutes in order to impregnate the PMA into the JA. The excess PMA solution was removed by aspiration. The product was freeze-dried to precipitate PMA in the pores of JA. In a similar manner, PMA-loaded JA was treated with 5 cm^3 of 10 M NH_4NO_3 solution to change the loaded PMA into AMP. After freeze-drying, the product was sieved (by using a 100-mesh sieve) in distilled water to remove fine AMP particles and dried at 50°C for 12 hours and finally stored in a sealed vessel over a saturated NH_4Cl solution.

Determination of Distribution Coefficient

The distribution coefficients of various elements were determined radiometrically by using radio tracers (^{137}Cs, ^{22}Na, ^{85}Sr, ^{60}Co, ^{152}Eu, ^{241}Am) following the procedure reported earlier (9). The distribution coefficient, K_d (cm^3/g), is defined as

$$K_d = [(A_i - A_f)/A_f] \times V/m \qquad (\mathrm{cm}^3/\mathrm{g})$$

where A_i and A_f are the counting rates at the initial stage and at equilibrium, respectively; m (g) is the weight of the JAAMP sample; and V (cm^3) is the volume of the aqueous phase.

Column Test

The JAAMP-2 (48–100 mesh) sample (3 g) was densely packed into a glass column (8 mm $\phi \times$ 80 mm long) with a jacket thermostated at 25°C. The column volume of JAAMP-2 was 4.0 cm^3. A feed solution, a simulated high-level liquid waste (SW-11E) (10) whose chemical composition as given in Table 1 was estimated by a computer program, ORIGEN-79, developed by the Power Reactor and Nuclear Fuel Development Corporation (PNC), was then passed through the column at a flow rate of 0.27 cm^3/min [space velocity (SV) = 4.1/h]. Every 3 cm^3 of the effluent was taken by a fraction collector, and then their γ-activities and pH were measured. A breakthrough curve was obtained by plotting the breakthrough ratio (C/C_0) against the effluent volume, where C_0 and C (cpm/cm^3) are the counting rates of the initial solution and the effluent, respectively.

Elution/regeneration of the column was carried out by using NH_4NO_3 solution as an eluant. A solution of 5 M NH_4NO_3 was passed through the column at the above-mentioned flow rate, every 3 cm^3 of the eluant was taken by a fraction collector, and then their γ-activities were measured. A elution curve was obtained by plotting the eluted % [% ratio of the counting rates of the eluant to the initial counting rates (cpm/cm^3) of the Cs-sorbed column] against the elution volume.

TABLE 1
Chemical Compositions of Simulated High-Level Liquid Waste, SW-11E (10)
(28,000 MWD/tU; 5 years storage after reprocessing)

Element	Concentration (M)	Element	Concentration (M)
H^{+} [a]	2.5	Pd	8.66×10^{-3}
Na	0.920	Ag	3.45×10^{-4}
P	1.27×10^{-2}	Cd	4.67×10^{-4}
Fe	7.77×10^{-2}	Sn	3.32×10^{-4}
Cr	3.95×10^{-3}	Se	5.41×10^{-4}
Ni	9.37×10^{-3}	Te	3.57×10^{-3}
Rb	3.64×10^{-3}	Y	4.87×10^{-3}
Cs	1.61×10^{-2}	La	7.92×10^{-3}
Sr	8.78×10^{-3}	Ce	1.51×10^{-2}
Ba	9.72×10^{-3}	Pr	7.46×10^{-3}
Zr	3.61×10^{-2}	Nd	2.50×10^{-2}
Mo	3.06×10^{-2}	Sm	5.10×10^{-3}
Mn	1.31×10^{-2}	Eu	7.96×10^{-4}
Ru	1.69×10^{-2}	Gd	3.86×10^{-4}
Rh	3.39×10^{-3}		

[a] HNO_3 solution.

RESULTS AND DISCUSSION

From the x-ray diffraction (XRD) patterns presented in Fig. 1, the presence of AMP peaks (11) in the XRD patterns of JAAMP-1 and JAAMP-2 confirm the successful loading on JA. The peak intensity of AMP in JAAMPs increased with the repetition times of the impregnation of the PMA solution as shown in the pattern of JAAMP-2 which was prepared by double impregnation. The AMP content of JAAMP-2 is estimated to be about 50% from its Cs^{+}-exchange capacity (0.51 meq/g) which was measured in 0.1 M $CsNO_3$. The AMP content estimated (50%) is lower than that of titanium phosphate-AMP (74%) (6), but further increases in the concentration of PMA and repetition times of impregnation leads to the loading of a higher concentration of AMP.

Figure 2 shows the uptake ability of JAAMP-2 for various nuclides in HNO_3 solution. Except for Na^{+}, K_d values for all metal ions decreased with an increasing concentration of HNO_3. A large difference between the K_d value of ^{137}Cs and those of other nuclides has been observed in the presence of HNO_3. The separation factors of cesium and other nuclides ($\alpha_{Cs/Sr;Co;Eu;Am;Na} = K_{d,Cs}/K_{d,Sr;Co;Eu;Am;Na}$) were estimated to be above 10^3 in the presence of 1 M HNO_3. As there was no cesium uptake on JA in acid solution, the high selectivity of JAAMP-2 to ^{137}Cs is totally due to the "steric" effect (12) of the structure of loaded AMP.

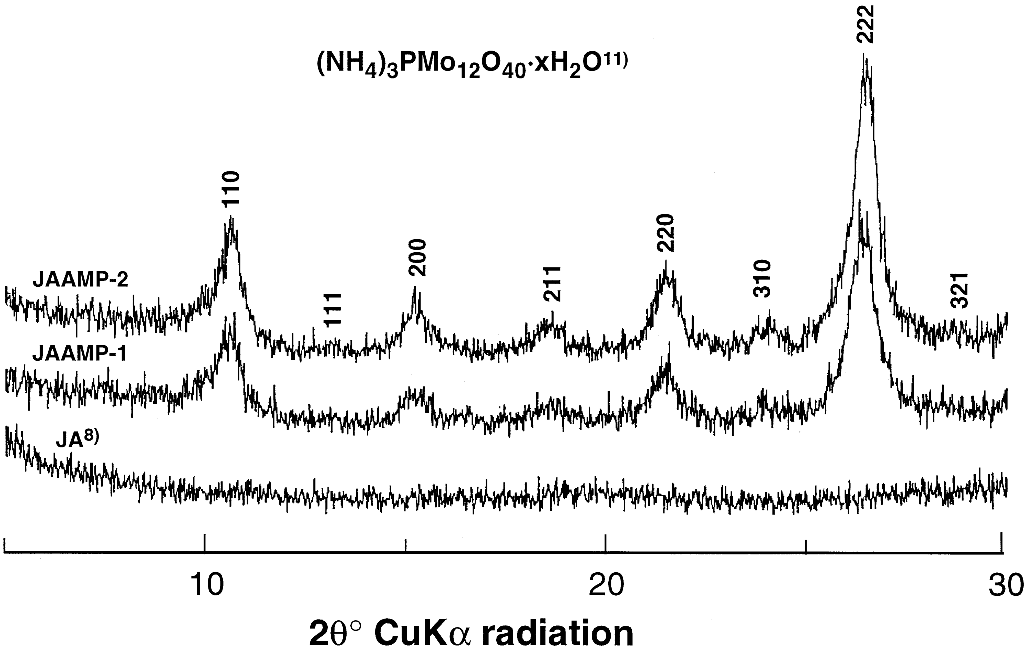

FIG. 1 XRD patterns of JA (JRC-ALO-1) (8) and JAAMPs.

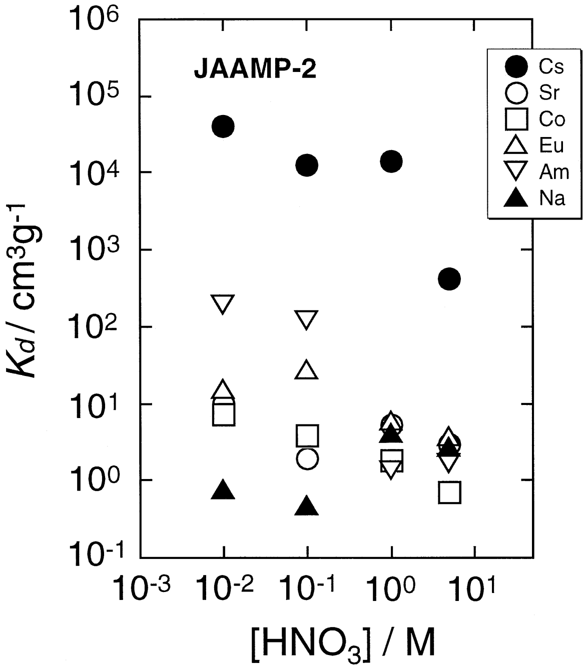

FIG. 2 Effect of HNO_3 concentration on distribution coefficient, K_d, of various nuclides. V/m, 100 cm^3/g; $[M^{n+}]$, 10 ppm; $[Am^{3+}]$, 2.1×10^{-9} M, 25°C, 7 days.

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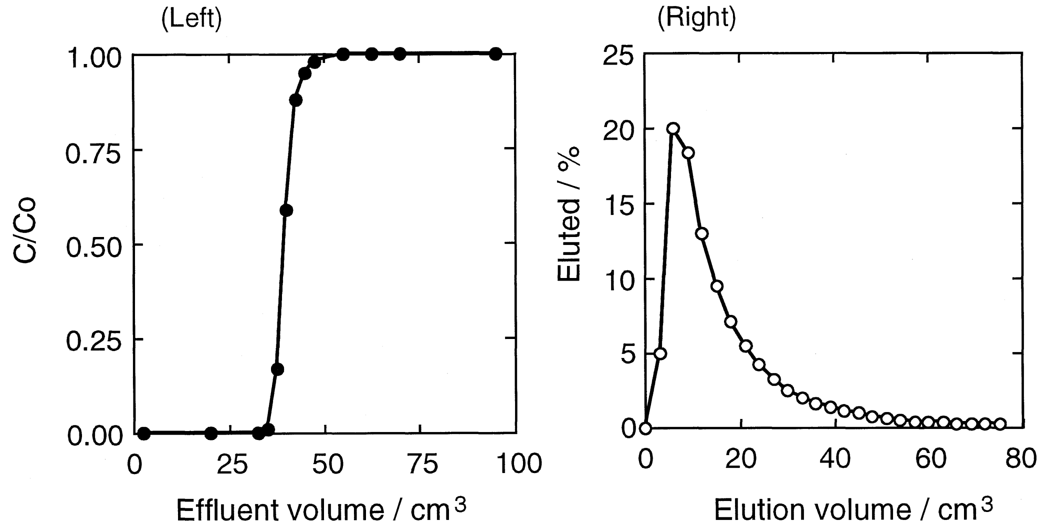

FIG. 3 Breakthrough (left) and elution (right) curves of Cs^+ ion from JAAMP-2 column. Left: Column, 0.8 × 8 cm; JAAMP-2, 3 g; feed solution, SW-11E (10); $[Cs^+]$, 1.61×10^{-2} M, flow rate 0.54 $cm^3 \cdot cm^{-2} \cdot min^{-1}$, 25°C. Right: Column, 0.8 × 8 cm; JAAMP-2, 3 g; 0.56 mmol Cs adsorbed initially; eluant, 5 M NH_4NO_3, flow rate 0.54 $cm^3 \cdot cm^{-2} \cdot min^{-1}$, 25°C.

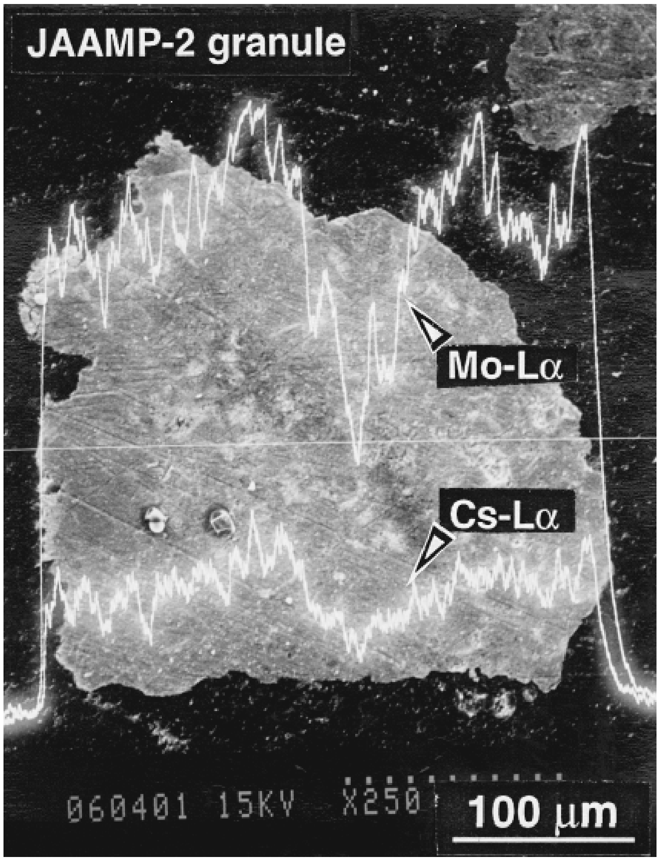

FIG. 4 Line analysis of Mo-Lα and Cs-Lα of JAAMP-2 treated with SW-11E (10).

Figure 3(left) illustrates the breakthrough curve for Cs^+, which is a symmetrical S-shaped profile, suggesting no dislodgement of AMP from the matrix of JA. The break point of a 5% breakthrough was estimated to be 35 cm^3 [bed volume (BV) = 8.8]. The breakthrough capacity (B.T.Cap.) and total capacity (T.Cap.) were calculated to be 0.19 and 0.21 meq/g, respectively, resulting in a relatively high column utilization (B.T.Cap./T.Cap.) of 90%. The column packed with JAAMP was thus effective for the selective removal of trace amounts of ^{137}Cs from the simulated high-level liquid waste SW-11E. On the other hand, JAAMP-2 released sorbed ^{137}Cs upon contact with an ammonium salt solution. The elution of ^{137}Cs was performed with 98.3% recovery of the sorbed cesium up to first 18.8 *BV* of effluent [Fig. 3(right)].

Figure 4 shows the result of line analysis of Mo-Lα and Cs-Lα by an electron probe x-ray microanalyzer on a JAAMP-2 granule after it was treated with SW-11E. Uniform dispersion of Cs and Mo were confirmed by the line analysis. This indicates the successful loading of AMP crystals onto the pores of JA.

In conclusion, synthesized granular AMP (JAAMP) can be used as an effective separating agent for the isolation of Cs^+ ions from a high level radioactive waste solution due to its high selectivity and operational ease. This work will be continued in a future study with the aim of establishing a firm understanding of the material.

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