Selective uptake of caesium by mordenite enclosing AMP microcapsules

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Abstract

The selective separation and recovery of a heat-generating nuclide (^{137}Cs) from high-level liquid waste (HLLW) containing highly concentrated HNO_3 and $NaNO_3$ are vital in relation to reducing the volume of radioactive waste and partitioning of nuclides. Ammonium molybdophosphate ($(NH_4)_3PO_4 \cdot 12MoO_3$, AMP), which shows high selectivity toward Cs^+ ions, can be one of the most promising adsorbents for this purpose. 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. However, none has allowed real success because the preparation procedures are relatively complicated and the results often not reproducible because of losses in capacity associated with washing-out effects in the column and the diminishing crystal surface. In this study, we have attempted to prepare the mordenite enclosing fine AMP crystals and alginate gels (AMP-M), types of inorganic and organic composites, in order to enhance the Cs^+ uptake rate and selectivity of mordenites. The present paper deals with the preparation of AMP-M, their characterisation, and the uptake behaviour of Cs^+ ions in the presence of highly concentrated HNO_3 and $NaNO_3$.

The AMP-M composites were prepared by the successive impregnation of: i) PMA ($H_3Mo_{12}O_{40}P$); ii) kneaded sol of NH_4NO_3 and sodium alginate (NaALG) into the macro pores of mordenites. In this procedure, the synthesis of AMP crystals and their loading are simultaneously accomplished in the macropores. The synthetic reaction of AMP in mordenites was expressed by the precipitation of $H_3Mo_{12}O_{40}P + 3NH_4NO_3 \leftrightarrow (NH_4)_3PO_4 \cdot 12MoO_3 + 3HNO_3$, and the X-ray diffraction intensities of AMP were almost constant after the initial loading. Here the AMP-M composites obtained by one to three cycles were abbreviated as AMP-M-1, AMP-M-2 and AMP-M-3, respectively.

The uptake of Cs^+ for AMP-M from HNO_3 and $NaNO_3$ solutions was examined by the batch method. The uptake of Cs^+ for AMP-M in the presence of 1 M HNO_3 attained equilibrium within 5 h, and a relatively large uptake percentage above 99% was obtained; the uptake rate and uptake (%) of Cs^+ ions for AMP-M were remarkably enhanced compared to those for mordenite. The AMP-M-3 composite exhibited a relatively large distribution coefficient (K_d) above 10^3 cm^3/g for Cs^+, even in the presence of 1-5 M HNO_3, which was close to the HNO_3 concentration in HLLW. The order of K_d value was $Cs^+ >> Rb^+ > Ag^+$; a significant difference in K_d value for Cs^+ and Rb^+ was observed and the maximum separation factor of Cs^+ and Rb^+ ($K_{d,Cs}/K_{d,Rb}$) was estimated at 18. The uptake isotherm of Cs^+ for AMP-M-1 followed a Langmuir-type adsorption equation, and the maximum adsorption capacity was estimated at 0.24 mmol/g. The Cs^+ ions were uniformly dispersed in the composites.

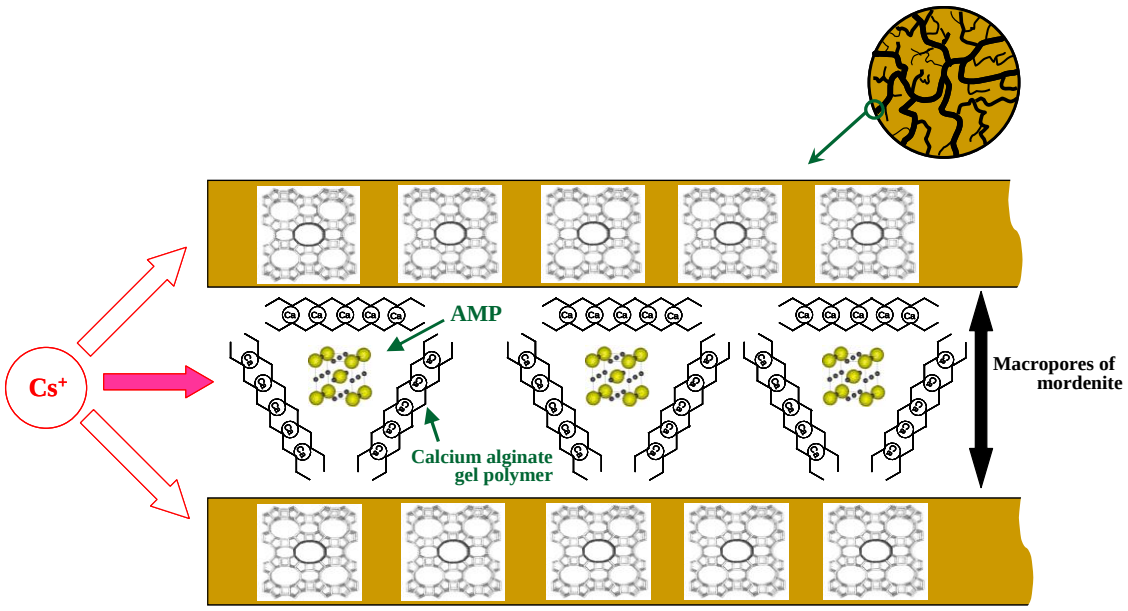
Thus, the AMP-M exchangers are found to be effective for the selective separation and recovery of Cs^+ from HLLW.

Introduction

The selective separation and recovery of ^{137}Cs from radioactive liquid wastes containing highly concentrated HNO_3 and $NaNO_3$ are of great interest in recent years for the application to volume reduction of radioactive wastes and partitioning of nuclides [1,2]. Ammonium molybdophosphate (AMP) with a high selectivity for Cs^+, can act as one of the most promising inorganic ion-exchanger for this purpose [3,4]. However, microcrystalline AMP exchanger is still not employed on a large scale because of its fine powder morphology which is unsuitable for the successive separation such as column operations. In order to overcome the handling problem, a mixture of AMP exchanger and asbestos was employed as a column bed [5], while this led to a marked lowering of bed density and uptake capacity.

The mordenite is useful for column operations, because it can be granulated easily and has many macropores. Moreover, it has high Cs^+-selectivity. By the loading of AMP crystals into macropores of mordenites, the enhancement of Cs^+ selectivity will be expected. In this study, calcium alginate gel polymer was used as immobilising matrices. Alginate gel polymer prevents the leakage of AMP fine crystals from the macropores of mordenites. The schematic diagram of mordenite enclosing AMP microcapsules (AMP-M composite) is shown in Figure 1. The fine crystals of AMP and calcium alginate gel polymer are loaded into macropores of mordenite as AMP microcapsules. Both mordenites and AMP contribute to the uptake of Cs^+ ions.

Figure 1: Schematic diagram of AMP-M composites



Experimental

Materials and preparation procedure of AMP-M composites

The synthesis of the mordenite enclosing AMP microcapsules (AMP-M) is as follows. First, three grams of the mordenites (natural mordenite, Kawarago, Miyagi Pref.) was converted to Ca-type by the conditioning with 5 M $Ca(NO_3)_2$ (Wako Pure Chemical Ind.) solution. These mordenites were dried at 80°C, and then added to 25 cm^3 of 0.2 M phosphomolybdic acid hydrate ($H_3Mo_{12}O_{40}P$; Wako Pure Chemical Ind.; PMA) solution. The resulting solution was kept under reduced pressure and at room temperature for 1 h in order to impregnate the PMA into the mordenite. The excess PMA solution was removed by filtration. The product was freeze-dried to impregnate PMA in the macropores of mordenite. In a similar manner, mordenites impregnating PMA was then treated

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with 25 cm^3 of kneaded sol of NH_4NO_3 and sodium alginate (NaALG, 80-120 cP; Wako Pure Chemical Ind.) for the precipitation of AMP crystals. The synthetic reaction of AMP is as follows:

$$H_3Mo_{12}O_{40}P + 3NH_4NO_3 \rightarrow (NH_4)_3PO_4{\cdot}12MoO_3 + 3HNO_3 \quad (1)$$

After freeze-drying, the product was sieved by using a 150 μm sieve to remove fine AMP particles and finally stored in a sealed vessel. AMP-M obtained by the repeated impregnation (once to three times) were abbreviated as AMP-M1, AMP-M2 and AMP-M3, respectively.

Surface morphology and structure of AMP-M composites

The structure of fine AMP crystals was checked by powder X-ray diffractometry (XRD, Rigaku MiniFlex) using monochromatised Cu-Kα radiation. The surface morphology and chemical composition were examined by scanning electron microscopy (SEM, Hitachi Miniscope TM-1000) equipped EDS system.

Determination of distribution coefficient

The distribution coefficients of various metal ions were determined by the batch method. An aqueous solution (4 cm^3) containing 10 ppm metal ion was contacted with 0.040 g of adsorbents (mordenites, AMP-M1, AMP-M2 and AMP-M3) at 25±1°C for 24 h, which was found to be sufficient for attaining equilibrium. After equilibration, the concentration of caesium ions in supernatant was measured by the atomic adsorption spectrometer (Nippon Jarrell-Ash AA-890). The uptake (%) of metal ions removed from the solution, R (%), and the distribution coefficient, K_d (cm^3/g), are defined as:

$$R = [(C_i - C_t)/C_i] \times 100 \ (\%) \quad (2)$$

$$K_d = [(C_i - C_f)/C_f] \times V/m \ (cm^3/g) \quad (3)$$

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 adsorbents; and V (cm^3) is the volume of the aqueous phase.

Column test

Two grams of AMP-M1 adsorbent were packed into the glass column (5 mmϕ × 200 mm long) with a jacket thermostated at 25±1°C (Figure 2). 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 and regeneration of the column were carried out by using NH_4NO_3 eluent. An elution curve was obtained by plotting the elution(%) [% ratio of the amount of eluted metal ions to that of initial loaded ones] against the elution volume.

Results and discussion

Surface morphology and structure of AMP-M composites

The fine powders of AMP with high Cs^+-selectivity were loaded into the macropores of mordenite using the calcium alginate gel polymer as immobilising matrices. The SEM images of AMP-M1 and the magnification of its surface are shown in Figures 3(a) and 3(b). In Figure 3(b), the aggregates of AMP crystals are observed on the surface of AMP-M composite; EDS for the cross-section of adsorbent (AMP-M3) saturating with Cs^+ ions shows the uniform distribution of Cs, Mo and P, suggesting the adsorption of Cs^+ on AMP crystals (Figure 4).

The XRD patterns of mordenite, AMP-M1, AMP-M2 and AMP-M3 are shown in Figure 5. The typical peaks of AMP are shown in XRD patterns of AMP-M composites indicating that the fine crystals of AMP are loaded into the mordenite. The estimated lattice constants of AMP crystals in AMP-M composites are listed in Table 1. As the repeated run of loading increased, the lattice constant gradually approached to that of original fine crystals of AMP.

Figure 2: Apparatus for column experiments

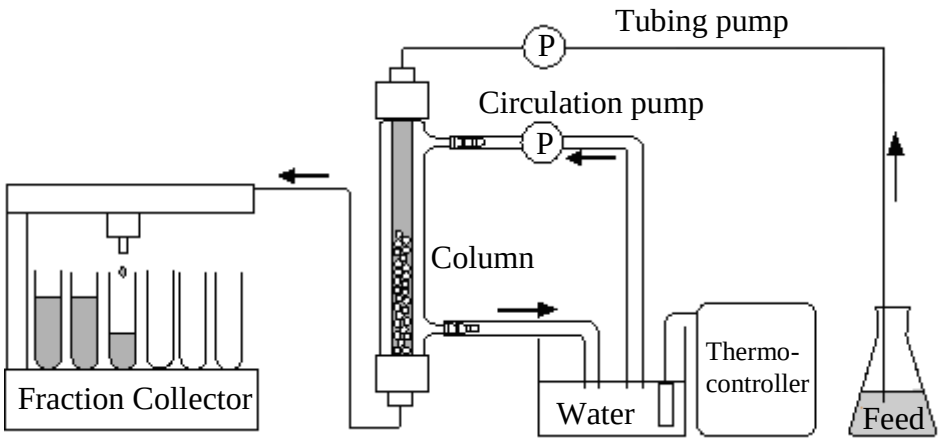


Figure 3: SEM images of AMP-M1

(a) AMP-M1 (b) Magnification image

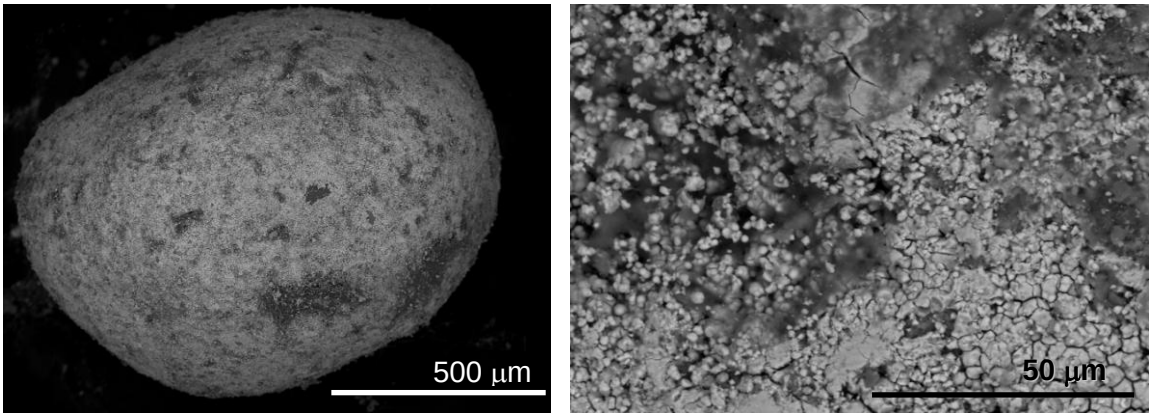


Figure 4: Mapping of Cs, Mo and P in AMP-M3

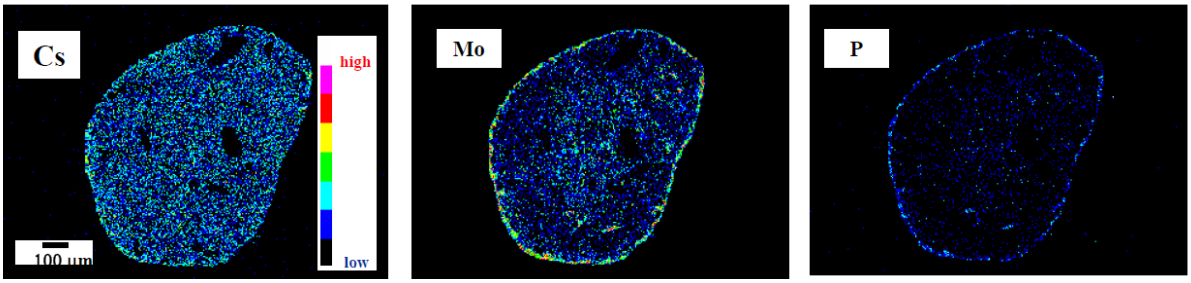


Figure 5: XRD pattern of adsorbents

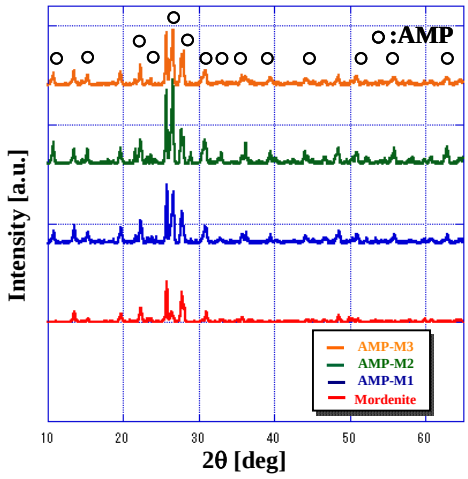


Table 1: Lattice constants (Å) of AMP crystals in AMP-M

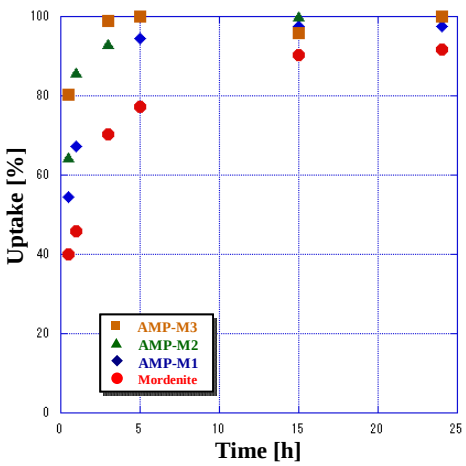
AMP-M1	11.621±0.005
AMP-M2	11.630±0.006
AMP-M3	11.636±0.013
Original fine crystals of AMP	11.655±0.000

Uptake rate of Cs^+ for AMP-M composites

Figure 6 shows the effect of equilibration time on the uptake (%) of Cs^+ for AMP-M composites in the presence of 1 M HNO_3. Here the uptake (%) of Cs^+ for AMP-M composites was compared with that for mordenite. The initial uptake (%) of Cs^+ for AMP-M composites was fairly fast; the uptake (%) increased markedly within 3 h. The uptake equilibrium for mordenite attained within 10 h, while the uptake equilibrium for AMP-M composites attained within 5 h; the uptake rate of Cs^+ for AMP-M composites was higher than that for mordenite. In particular relatively large uptake (%) above 99% was obtained for AMP-M2 and AMP-M3, indicating that the repetition of loading of AMP enhanced the uptake (%).

Figure 6: Uptake rate of Cs^+

V/m = 100 cm^3/g; 25±1°C



Effect of HNO_3 concentration on K_d of Cs^+ for AMP-M composites

The effects of HNO_3 concentration on $K_{d,Cs}$ of the AMP-M composites and mordenite are shown in Figure 7. The $K_{d,Cs}$ for mordenite remarkably lowered in the presence of HNO_3 above 0.1 M, while relatively large $K_{d,Cs}$ values was obtained for AMP-M composites; in the presence of 10^{-2}-5 M HNO_3, the $K_{d,Cs}$ value of AMP-M3 was almost constant over 10^3 cm^3/g, indicating that the repetition of loading of AMP enhanced the $K_{d,Cs}$ value.

Figure 7: Effects of HNO_3 concentration on $K_{d,Cs}$

V/m = 100 cm^3/g; [Cs^+]: 10 ppm; 25±1°C

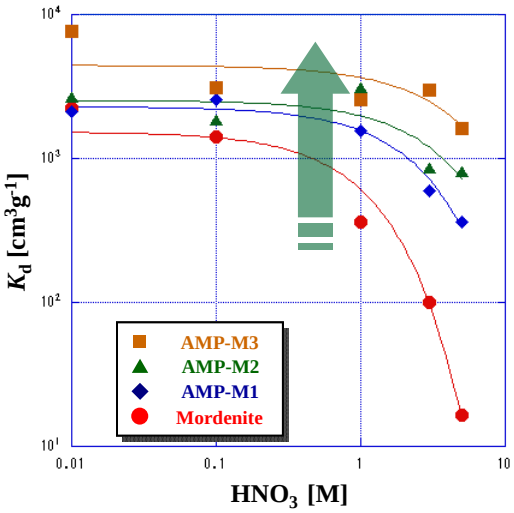
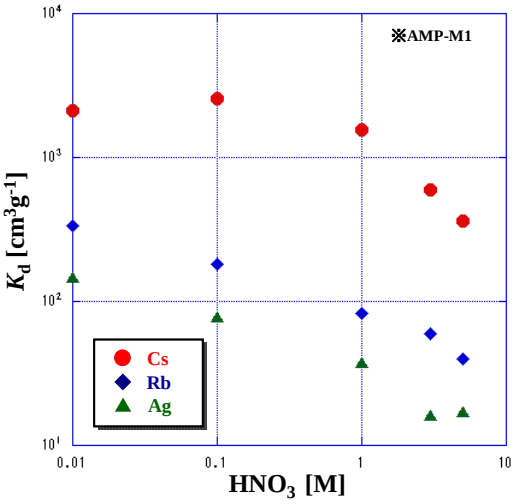


Figure 8 shows the comparison of uptake ability of different metal ions for AMP-M1 in the presence of HNO_3. The order of K_d value was $Cs^+ >> Rb^+ > Ag^+$, and a large difference in K_d value was observed for Cs^+ and Rb^+. The separation factor of Cs^+ and Rb^+ ions ($\alpha_{Cs/Rb} = K_{d,Cs}/K_{d,Rb}$) was estimated to be 18 in the presence of 1 M HNO_3. These finding suggests that the Cs^+ ions can be separated from other metal ions by using the column chromatography.

Figure 8: K_d of different metal ions for AMP-M1

V/m = 100 cm^3/g; [M^{n+}]: 10 ppm; 25±1°C



Uptake isotherm of Cs^+ for AMP-M composites

The uptake isotherms of Cs^+ for AMP-M composites and mordenite were obtained in a wide range of initial Cs^+ concentration from 10 to 900 ppm. The equilibrium amount of Cs^+ adsorbed on the adsorbents approached a constant value with increasing Cs^+ concentration, suggesting that the uptake of Cs^+ follows a Langmuir adsorption equation [6]. The Langmuir equation is given by:

$$C_{eq}/Q_{eq} = 1/KQ_{max} + (1/Q_{max})C_{eq} \text{ (g/dm}^3\text{)} \quad (4)$$

where C_{eq} (mol/dm^3) and Q_{eq} (mol/g) are the equilibrium concentrations of Cs^+ in the aqueous and solid phases, respectively; Q_{max} (mol/g) is the maximum amount of Cs^+ taken up; K (dm^3/mol) is the Langmuir constant. The uptake isotherm of Cs^+ on AMP-M1 and Langmuir-plot are shown in Figures 9 and 10. The results for other adsorbents (mordenite, AMP-M2 and AMP-M3) were similar to that for AMP-M1. As seen in Figure 10, a fairly linear relation between C_{eq}/Q_{eq} and C_{eq} was obtained from Langmuir-plots for the AMP-M1. The Q_{max} value was calculated from the Langmuir plot as listed in Table 2. The largest Q_{max} value was estimated to be 0.24±0.008 mmol/g for AMP-M1.

Figure 9: Uptake isotherm of Cs^+ on AMP-M1

V/m = 100 cm^3/g; 25±1°C

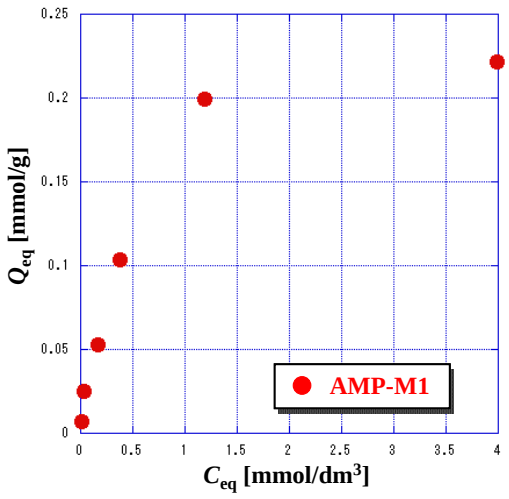


Figure 10: Langmuir-plot

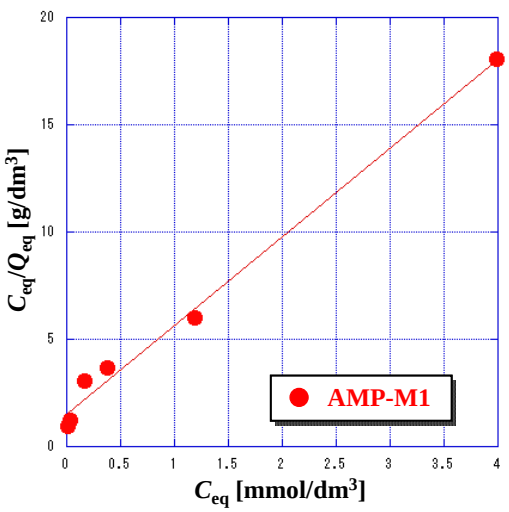


Table 2: Q_{max} values of adsorbents

Adsorbent	Mordenite	AMP-M1	AMP-M2	AMP-M3
Q_{max} [mmol/g]	0.22±0.010	0.24±0.008	0.21±0.021	0.21±0.009

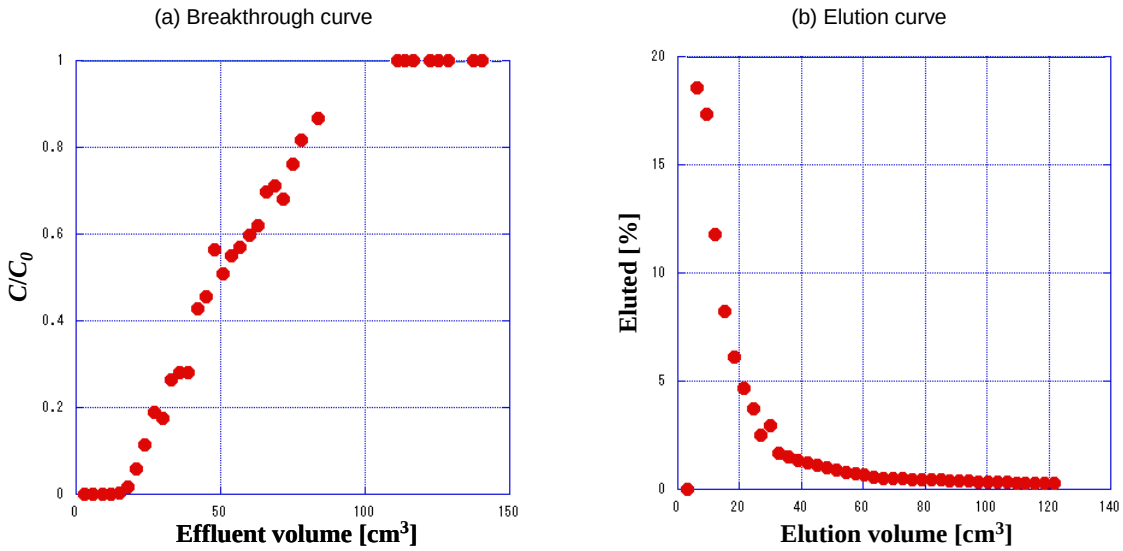
Breakthrough and elution properties of Cs^+ through AMP-M1 column

Figure 11(a) illustrates the breakthrough curve of Cs^+ for AMP-M1 column. The curve had a symmetrical S–shaped profile, suggesting no dislodgement of AMP from the matrix of mordenite. The breakpoint of 5% breakthrough was estimated to be 20 cm^3. The breakthrough capacity (*B. T. Cap.*) and total capacity (*T. Cap.*) were calculated to be 0.051 and 0.17 mmol/g, respectively. The column packed with AMP-M composite was thus effective for the selective removal of Cs^+. Further, the adsorbed Cs^+ on the column can be eluted by passing the eluent of NH_4NO_3 solution. The elution (%) of Cs^+ adsorbing on the column was estimated to be 95%.

Figure 11: Breakthrough and elution curves of Cs^+ for AMP-M1 column

Column: 0.5 cm ϕ × 20 cm, AMP-M1: 2 g; flow rate: 0.22 cm^3/min; 25±1°C

(a) Feed solution [Cs^+] = 1 000 ppm; (b) loaded amount of Cs^+: 0.34 mmol; eluent: 5 M NH_4NO_3



Conclusions

The fine crystals of AMP exchanger were loaded into the macropores of mordenite using the calcium alginate gel polymer as immobilisation matrices. The uptake rate of Cs^+ for the AMP-M composites was fairly fast and the uptake equilibrium was attained within 5 h. The uptake rate of Cs^+ for AMP-M composites was enhanced compared with that for mordenite. The K_d value of Cs^+ for AMP-M3 was over 10^3 cm^3/g in the presence of 10^{-2}-5 M HNO_3, while the K_d value for mordenite remarkably decreased in the presence of HNO_3 above 0.1 M. The order of K_d value was $Cs^+ >> Rb^+ > Ag^+$, and the maximum separation factor of Cs^+ and Rb^+ ($K_{d,Cs}/K_{d,Rb}$) was estimated to be 18. The uptake of Cs^+ followed a Langmuir adsorption isotherm, and the maximum uptake capacity of Cs^+ was estimated to be 0.24±0.008 mmol/g for AMP-M1. As for the column experiments, the breakthrough curve had a symmetrical S-shaped profile, and relatively large elution (%) of 95% was obtained for the AMP-M1 column. Thus the AMP-M composites are effective for the selective separation of Cs^+ ions from the simulated high-level liquid wastes.

References

[1] *IAEA Technical Rep. Ser.*, No. 356, IAEA, Vienna (1993).

[2] Kubota, M., *et al.*, *Actinide and Fission Product Partitioning and Transmutation, 5th Information Exchange Meeting*, OECD/NEA, Paris, 131 (1998).

[3] Pekarek, V., V. Vesely, *Talanta*, 19, 1245-1248 (1972).

[4] Qureshi, M., K.G. Varshney, *Inorganic Ion Exchangers in Chemical Analysis*, CRC Press Inc., Boston, 57-90 (1991).

[5] Smit, J. van R., W. Robb, J.J. Jacobs, *J. Inorg. Nucl. Chem.*, 12, 104 (1959).

[6] Benes, P., V. Majer, *Trace Chemistry of Aqueous Solutions*, Elsevier Sci. Publ., Amsterdam, 199 (1980).