Adsorption and Elution Behavior of Cesium and Rubidium on Ammonium Tungstophosphate (AWP)-CaALG Alginate Microcapsules - 9180

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ABSTRACT

Fine crystals of ammonium tungstophosphate (AWP) exchanger having high selectivity toward Cs^+ were encapsulated in the biopolymer matrices (calcium alginate, CaALG). The characterization of AWP-CaALG microcapsule was examined by scanning electron microscope (SEM), and the uptake and recovery of Cs^+ and Rb^+ were investigated by batch and column methods. Spherical and elastic microcapsules were obtained, and the particle size of microcapsules was about 700 μm. A relatively high uptake (%) of Cs^+ and Rb^+ above 70% was obtained in the presence of 2.5 M HNO_3 – 1 M $NaNO_3$ solution, and the uptake equilibrium was attained within 5 h. The distribution coefficient of Cs^+ ($K_{d,Cs}$) and Rb^+ ($K_{d,Rb}$) decreased in the order of coexisting ions, $H^+ > Na^+ >> NH_4^+$. In a wide HNO_3 concentration range of 10^{-2} - 3 M, $K_{d,Cs}$ value for the microcapsule was above 10^5 cm^3/g, while the $K_{d,Rb}$ value was around 500 cm^3/g even in the presence of 3 M HNO_3. The uptake of Cs^+ and Rb^+ followed a Langmuir-type adsorption equation, and the maximum uptake capacity was estimated to be 0.096 and 0.071 mmol/g, respectively. A linear relationship with a slop of about -1 was obtained between log K_d and log $[NH_4^+]$ ($[NH_4^+] > 0.01$ M), and the retention volume (V_R) values of Cs^+ and Rb^+ in chromatography also decreased similarly to the K_d value. The V_R value can be predicted from the K_d value based on the linear relation, and the experimental V_R values were closed to the calculated ones. Well-resolved chromatogram with resolution (Rs) = 1 was obtained by flowing 0.6 M NH_4NO_3. In this case, the total elution percentage of Cs^+ and Rb^+ was estimated to be 71% and 83%, respectively. The loaded Cs^+ and Rb^+ on column were thus successfully eluted with NH_4NO_3 solution, yielding a large deference in V_R values.

INTRODUCTION

Recently, much attention has been given to the selective separation and recovery of Cs-137 from high level liquid wastes (HLLWs) in relation to the partitioning of radioactive nuclides and their effective utilization [1-4]. Cesium-137 having relatively long half-life of about 30 years exhibited high radioactivity and heat generation, and large amounts of Cs group (~3.6 kg/1tHU, 45 GWd/t) are contained in HLLWs[5]. Therefore, selective separation of Cs-137 from HLLWs is an important environmental issue for nuclear waste management. In addition, the purified Cs is also expected for the reuse as radiation and heat sources in the field of medicine and industry [6,7].

Many methods for the separation of Cs^+ such as ion exchange, solvent extraction and co-precipitation

have been studied[8-11]. In the ion-exchange process, heteropolyacids are well known to have selective uptake ability to Cs^+. Ammonium tungstophosphate (AWP), a kind of heteropolyacid, which shows a high selectivity toward Cs^+ and excellent radiation stability, can act as one of the most promising adsorbent for the uptake of Cs^+[3, 4]. However, AWP is still not applied to the practical separation process because of its fine powder form which is insufficient for the continuous treatment using packed column. In order to overcome this handing problem, the granulation of AWP powder with alginate gel polymers seems to be one of the most prominent techniques for the practical column operation[3, 4].

Microencapsulation is an unique technique for enclosing active component in a porous polymeric matrix[12-15]. It is well known that alginates (ALG), a kind of biopolymer, has high immobilization ability and this method has been extended to industrial, medical and agricultural fields. Alginate is a salt of alginic acid having carboxyl groups capable to form gels by crosslinking with multivalent metal ions. This immobilizing property of alginate has led to its extensive applications to the microencapsulation of enzymes, subcellular organelles, and living cells[16,17]. Thus, the granulation with alginate gel has several advantages such as simplicity for preparation, mechanical strength and strong acid resistance[12-15].

In this study, we have attempted to encapsulate the fine crystals of AWP exchanger into the biopolymer matrices (calcium alginate, CaALG) by using its high immobilizing ability for the selective separation of Cs^+ and Rb^+ from the waste solution containing highly concentrated HNO_3 and $NaNO_3$. The present paper deals with the preparation of microcapsules (MCs), characterization, uptake properties, and elution properties of Cs^+ and Rb^+ for the column packed with MCs.

EXPERIMENTAL

Materials

The AWP exchanger consisting of Keggin-type polyanions ($PW_{12}O_{40}^{3-}$) [18] and exchangeable NH_4^+ ions is used as an active component, and its unit cell composition was $(NH_4)_3PO_4 \cdot 12WO_3 \cdot 3H_2O$ (Wako Pure Chemical Ind.). Sodium alginate (NaALG, 500-600 cP) was purchased from Wako Pure Chemical Ind. The Cs^+ and Rb^+ solutions were obtained by diluting the standard solutions (10^3 ppm, Wako Pure Chemical Ind.).

Preparation of MCs

The alginate gel enclosing AWP was prepared as follows. AWP (0.5 g) was kneaded with the NaALG solution (50 cm^3, 1.5 wt%) and fully dispersed by using kneader equipped the function of rotation and revolution. The well-kneaded sol was injected dropwise into a 0.5 M $Ca(NO_3)_2$ solution using a medical needle under constant stirring at room temperature to form MCs. The MCs were stirred gently for one night to enhance the aging. The MCs were then separated from the solution, washed with distilled water and finally air-dried at 30°C for 2 d. The MCs prepared by gelation of kneaded sols of AWP/NaALG with $Ca(NO_3)_2$ solution were abbreviated as AWP-CaALG.

Characterization

The surface morphology MCs was observed by optical microscope and SEM (Hitachi TM-1000). In order to estimate the acid resistance, the AWP-CaALG specimens (50 mg) were treated with 2.5 M HNO_3 (5 cm^3) for 24 h and analyzed by SEM after drying.

Determination of Distribution Coefficient (K_d)

The distribution of Cs^+ and Rb^+ ions for MCs was estimated by batch method. An aqueous solution (5 cm^3) containing 10 ppm Cs^+ or Rb^+ ion was contacted with 50 mg of MCs at 25±1°C up to 1 d, which was found to be sufficient for attaining equilibrium. The concentrations of Cs^+ and Rb^+ ions were measured by atomic absorption spectrometer (AAS, Jarrell AA890)

The uptake percentage (R, %) of metal ions removed from the solution and the distribution coefficient (K_d, cm^3/g) are defined as :

$$R = (C_0 - C_t)/C_0 \times 100, \quad (\%) \qquad \text{(Eq. 1)}$$

$$K_d = ((C_0 - C_f)/C_f) \times V/m, \ (cm^3/g) \qquad \text{(Eq. 2)}$$

where C_0, C_t and C_f (ppm) are the concentration of metal ions at initial, at time t, and at equilibrium, respectively; m (g) the weight of microcapsules; V (cm^3) the volume of aqueous phase.

Column Chromatographic Separation of Cs^+ and Rb^+

The column was prepared by packing about 1.7g of MC in a glass column (5 mm in diameter ×100 mm long) with thermostatic water jacket. The column volume was estimated to be 1.8 cm^3. The Cs^+ and Rb^+ ions (250 μg) were loaded on the upper part of the column, respectively. The eluent used in this study were NH_4NO_3 - HNO_3 solutions. Here, the HNO_3 was used to restrain the swelling of MCs. The flow rate of eluent was maintained at 0.14 cm^3/min. The effluent was collected by a fraction collector, and concentration of Cs^+ and Rb^+ were determined by AAS. The operation runs were carried out at 25±1°C.

The elution chromatogram was obtained by plotting the elution percentage (Elution, %) against the elution volume (cm^3). The elution percentage is defined as the ratio of the eluted amount of Cs^+ or Rb^+ in each fraction to the initial amount loaded on the column. The retention volume (V_R) is defined as the total volume of eluent until the maximum of elution peak, and is given as:

$$V_R = V_m + \rho V_a K_d, \quad (cm^3) \qquad \text{(Eq. 3)}$$

where V_m (cm^3) and V_a (cm^3) are respectively the interstitial volume and the column volume of adsorbent, and ρ (g/cm^3) the density of adsorbent.

The separation parameters such as the number of theoretical plate (N), the tailing coefficient (S), and the resolution (Rs), were defined as follows:

$$N = 16(V_R/W)^2, \qquad \text{(Eq. 4)}$$

$$S = B/A, \qquad \text{(Eq. 5)}$$

$$Rs = 2(V_{R,2} - V_{R,1})/(W_1 + W_2), \qquad \text{(Eq. 6)}$$

where W is the peakwidth and the subscript numbers refer to eluted components; B and A are respectively the base width of right and left sides of the V_R value.

RESULTS AND DISCUSSION

Surface Morphology and Acid Resistance

Figures 1(a) and **(b)** show the SEM images of the surface of AWP-CaALG. The structure of CaALG gel

matrices is composed of crosslinked polymer networks with ionic bonding of Ca^{2+} and carboxyl groups. Obvious spherical and elastic granules were obtained. On the surface of AWP-CaALG, a numbers of fine AWP crystals (~ 1 μm in diameter) are seen to be encapsulated. Some creases were observed on the surface of AWP-CaALG. The practical sizes of MCs were estimated to be 0.7 mm in diameter by optical microscope and SEM image. The AWP content in MCs was estimated to be 14 wt%.

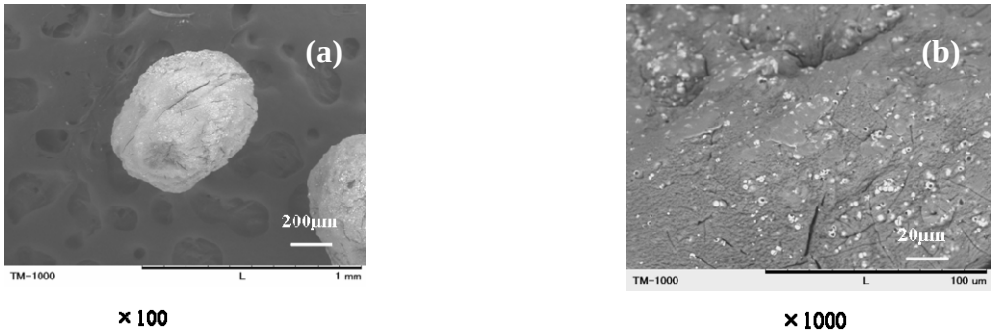

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Fig. 1. SEM images of the surface of AWP-CaALG.

The resistance against acid is one of the most important factors for the estimation of chemical stability. **Figures 2(a)** and **(b)** show the SEM images of the surface of AWP-CaALG treated with 2.5 M HNO_3. Distinct differences of the surface morphology are observed at higher magnification compared to the fresh AWP-CaALG. The surface of AWP-CaALG treated with acid is apparently more porous than that of the original granule and a number of creases are also observed on the surface. The effect of acid on AWP-CaALG may be realized by the rupturing of the ionic crosslinkage with Ca^{2+} ions; the structure of gel matrices treated with HNO_3 was maintained by the hydrogen bonding of H^+/carboxyl group. The treatment of AWP-CaALG with highly concentrated HNO_3 resulted in the alteration of gel matrices and hence care must be taken in the loss of AWP through the wall of gel matrices in the presence of highly concentrated HNO_3.

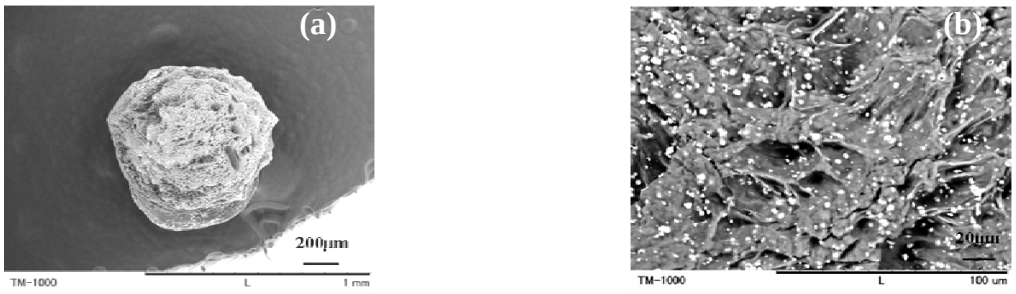

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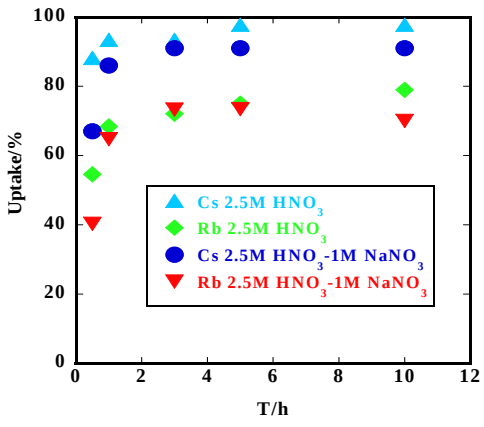
Fig. 2. SEM images of the surface of AWP-CaALG treated with 2.5 M HNO_3.

Uptake Rate

In order to check the equilibration time of Cs^+ and Rb^+ for AWP-CaALG, the effect of shaking time on uptake(%) was examined in the presence of 2.5 M HNO_3 or 2.5 M HNO_3 – 1 M $NaNO_3$ solutions by batch method (**Fig. 3**). The uptake rates of Cs^+ and Rb^+ for MCs in 2.5 M HNO_3 attained equilibrium rather fast in the initial stages



within 5 h, and relatively large *R* value above 70% was obtained. The uptake of Cs^+ and Rb^+ in the initial stage was probably due to the adsorption on the surface, followed by a step controlled by mass transfer through gel matrices[19]. On the other hand, in the presence of 2.5 M HNO_3 – 1 M $NaNO_3$, the initial uptake rates of Cs^+ and Rb^+ were tended to decrease. The reason may be due to the swelling of MCs in the presence of highly concentrated Na^+ ion resulted in the lowering of the uptake rate of Cs^+ and Rb^+.

Distribution of Cs^+ and Rb^+ in the Presence of Monovalent Cations

Figures 4 (a) and **(b)** show the K_d values of Cs^+ ($K_{d,Cs}$) and Rb^+ ($K_{d,Rb}$) for AWP-CaALG in the presence of different monovalent cations. The $K_{d,Cs}$ value was almost constant in the presence of HNO_3(10^{-3} ~ 3M). Relatively large $K_{d,Cs}$ value above 10^5 cm^3/g was obtained, indicating that AWP-CaALG has strong adsorption ability to Cs^+. The $K_{d,Rb}$ value was around 500 cm^3/g even in the presence of 3 M HNO_3. The uptake of Cs^+ and Rb^+ tended to slightly decrease in distribution of Cs^+ and Rb^+ shows a linearity with a slo NH_4^+, suggesting that the uptake of Cs^+ and Rb^+ or cation-exchange reaction of $NH_4^+ \rightleftharpoons Cs^+$ or $NH_4^+ \rightleftharpoons Rb$ or log $K_{d,Rb}$ and log [NH_4^+] was obtained as:

Fig. 3. Effects of shaking time on he uptake(%) of Cs^+ and Rb^+. *V/m* : 100 M cm^3/g; 10 ppm Cs^+ and Rb^+; 2.5 M a HNO_3; 2.5 M HNO_3-1M $NaNO_3$; 25ºC. Cs

$$\log K_{d,Cs} = 1.53 - 1.31 \log[NH_4^+], \qquad \text{(Eq. 7)}$$

$$\log K_{d,Rb} = 0.66 - 0.86 \log[NH_4^+]. \qquad \text{(Eq. 8)}$$

Thus, the calculated V_R values of Cs^+ and Rb^+ can be defined by substituting Eq. 7 or Eq. 8 into Eq. 3. The $K_{d,Cs}$ and $K_{d,Rb}$ decreased in the order of coexisting ions, $H^+ > Na^+ >> NH_4^+$. This result was similar to that of decreasing order of the size of hydrated cations[21].The effect of NH_4^+ on the uptake for MCs indicated that the chromatographic separation of Cs^+ and Rb^+ can be achieved by controlling the concentration of NH_4^+.

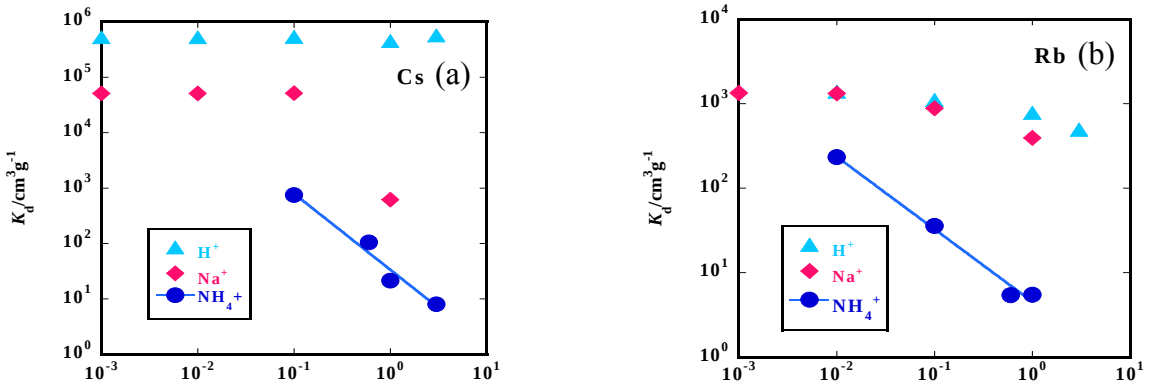


Fig. 4. Effects of monovalent cation concentration on $K_{d\ Cs}$ and $K_{d\ Rb}$. *V/m*=100 cm^3/g; 10 ppm Cs^+ and Rb^+; 25ºC, 1 d.

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The uptake isotherm of Cs^+ for AWP-CaALG was obtained in a wide range of initial Cs^+ concentration from 10 ppm to 800 ppm. The equilibrium amount of Cs^+ adsorbed on AWP-CaALG approached a constant value with increasing concentration, suggesting that the uptake of Cs^+ follows a Langmuir-type adsorption equation [22]. The Langmuir equation

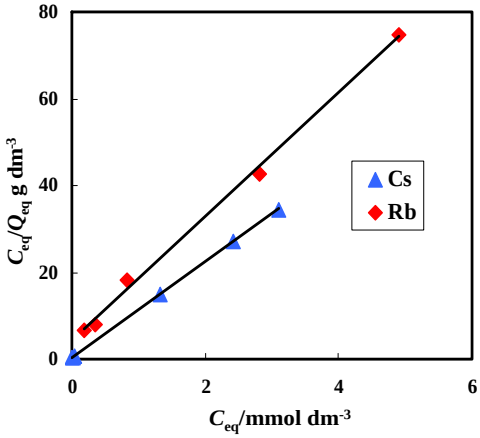


Fig. 5. Langmuir-plots of Cs^+ and Rb^+ uptake for AWP-CaALG. 2.5 M HNO_3-1M $NaNO_3$; 25°C; 1d.

can be rewritten as follows:

$$C_{eq}/Q_{eq} = 1/KQ_{max} + (1/Q_{max})C_{eq}\ (g/dm^3), \qquad \text{(Eq. 9)}$$

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.

As seen in **Fig. 5**, a fairly linear relation between C_{eq}/Q_{eq} and C_{eq} was obtained from Langmuir-plots for AWP-CaALG. The result shows that the Q_{max} value of Cs^+ for AWP-CaALG was estimated to be 0.096 mmol/g. The uptake of Rb^+ also followed a Langmuir adsorption isotherm, and the Q_{max} value of Rb^+ was estimated to be 0.071 mmol/g.

Chromatographic Separation of Cs^+ and Rb^+

Chromatographic separation was examined by varying the concentration of eluting reagent of NH_4NO_3 (0.6 – 3 M) -1 M HNO_3. **Figures 6 (a) ~ (c)** show the chromatograms obtained at different concentrations of NH_4NO_3 and their elution data are summarized in **Table I** and **II**.

Figure 6(a) illustrates the chromatogram of Cs^+ and Rb^+ eluted with 0.6 M NH_4NO_3-1 M HNO_3. Well-resolved chromatogram with the resolution (Rs) = 1 was obtained. A sharp elution curve of Rb^+ having N=24 was obtained, yielding the V_R value of 16 cm^3 which was close to the calculated one. The Cs adsorbing on AWP-MC was gently eluted from the column yielding the N=7.3 and larger V_R value of 87 cm^3. The recovery of Cs^+ and Rb^+ was estimated to be 71% and 83%, respectively.

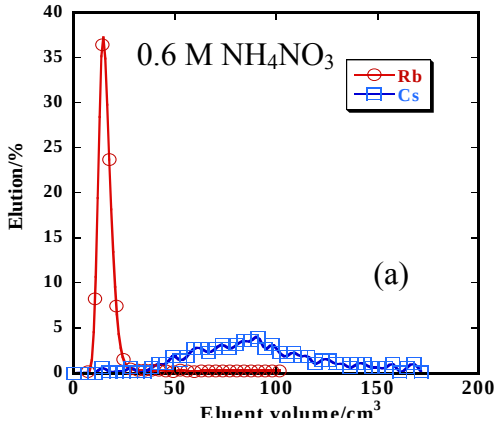
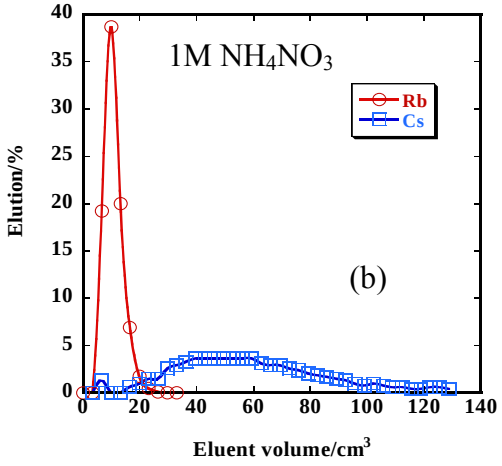


Fig. 6(a). Chromatographic separation of Cs^+ and Rb^+ through AWP-CaALG column. AWP-CaALG: 1.7 g; Cs^+:200 µg; Rb^+: 200 µg; eluent: 0.6 M NH_4NO_3-1 M HNO_3; flow rate: 0.14 cm^3/min; 25°C.

Figures 6 (b) and **(c)** show the elution chromatograms with 1 M NH_4NO_3-1 M HNO_3 and 3 M NH_4NO_3-1 M HNO_3, repectively. The R_s were calculated to be 0.62 and 0.16 at 1 and 3 M NH_4NO_3, respectively. A relatively sharp and symmetric profile was observed in the elution



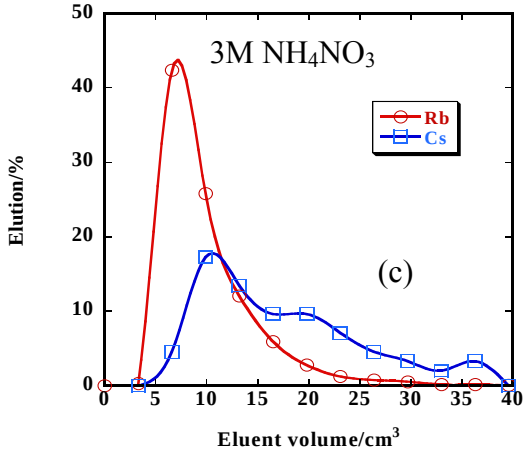


Fig. 6(b) and (c). Chromatographic separation of Cs^+ and Rb^+ through AWP-CaALG column. AWP-CaALG: 1.7 g; Cs^+:200 μg; Rb^+: 200 μg; eluent: 1 M NH_4NO_3-1 M HNO_3, 3 M NH_4NO_3 -1 M HNO_3; flow rate: 0.14 cm^3/min; 25°C.

curve of Rb^+, suggesting that the Rb^+ was readily eluted with NH_4NO_3. The increase in NH_4NO_3 concentration resulted in a shift of each elution curve to lower effluent volumes, and the V_R value of Cs^+ and Rb^+ in chromatography was lowered similarly to the K_d value. The N value was tended to decrease with increasing the concentration of NH_4NO_3. The S value was estimated to be 1.5 ~ 3.7, indicating a slight tailing in the chromatogram(**TableI** and **II**). In this case, the elution percentage was estimated to be above 70%.

Thus, the lowering of NH_4^+ concentration resulted in an enhancement of Rs value. The chromatographic separation of Cs^+ and Rb^+ was successfully accomplished by using the eluent of 0.6 M NH_4NO_3. In order to enhance the Rs and elution percentage, lower flow rate, smaller particle size and longer column are required for the practical operation.

Table I. Elution Data of Cs^+ with NH_4NO_3 Solutions

NH_4NO_3/M	V_R/cm^3	t_R/min	N	S	Elution/%	Calculated V_R/cm^3	Rs
0.6	87	670	7.3	0.9	71	117	1.0
1	46	351	3.5	1.5	70	59	0.62
3	24	185	2.5	3.4	75	16	0.16

Table II. Elution Data of Rb^+ with NH_4NO_3 Solutions

NH_4NO_3/M	V_R/cm^3	t_R/min	N	S	Elution/%	Calculated V_R/cm^3	Rs
0.6	16	124	24	1	83	15	1.0
1	11	85	11	1.8	87	11	0.62
3	9	71	4.4	3.7	92	6	0.16

CONCLUSIONS

The uptake properties of Cs^+ and Rb^+, characterization and dynamic adsorption properties were investigated by using AWP-CaALG. The uptake of Cs^+ and Rb^+ for AWP-CaALG was fairly fast in the initial stage and the uptake equilibrium attained within 5 h. The $K_{d,\,Cs}$ for AWP-CaALG was almost constant(10^5 cm^3/g) up to 3 M HNO_3. The $K_{d,Cs}$ and $K_{d,Rb}$ decreased in the order of coexisting ions, H^+ > Na^+ >> NH_4^+. The uptake isotherm of Cs^+ and Rb^+ followed a Langmuir-type adsorption equation. The adsorbed Cs^+ and Rb^+ can be successfully eluted with the NH_4NO_3, yielding an excellent peak resolution (Rs=1). The MCs enclosing AWP were thus effective for the selective separation and recovery of Cs^+ and Rb^+.

REFERENCES

1. Technical Report Series, No. 356, IAEA, Vienna, Austria (1993).
2. H. Mimura, M. Saito, K. Akiba and Y. Onodera, *Solvent Extr. Ion Exch.*, **18**(5), pp. 1015-1027(2000).
3. H. Mimura, M. Saito and K. Akiba, *J. Nucl. Sci. Technol.*, **38**, No. 10, pp. 872-878(2001).
4. H. Mimura and Y. Onodera, *J. Nucl. Sci. Technol.*, **39**, No. 3, pp. 282-285(2002).
5. R. Ando and T. Takano, JAERI-Rearch 99-004(1994).
6. H. Mimura and K. Akiba, *J. Nucl. Sci. Technol.*, **33**, No. 6, pp. 511-518(1996).
7. H. Mimura, K. Iijima and K. Akiba, *J. Nucl. Sci. Technol.*, **34**, No. 3, pp. 269-276(1997).
8. R. P. Buch and G. J. K. Acres, AERE-R-12830(1987).
9. M. L. Dietz, E. P. Horwitz, S. Rhoads, R.A. Bartsch and J. Krzykawski, *Solvent Extr. Ion Exch.* **14,** 1, pp.1-12(1996).
10. R. Chiarizia, E. P. Horwitz, R. A. Bauvais and S. D. Alexandratos, *Solvent Extr. Ion Exch.*, **16**, 3, pp. 875-898(1998).
11. A. F. Reguillon, B. Dunjic, M. Lemaiue , and R. Chomel, *Solvent Extr. Ion Exch.*, **19,** 1, pp. 181-191(2001).
12. H. Mimura, T. Sakakibara, Y. Niibori and K. Tanaka, *J. Ion Exchange*, **16**, pp. 29-33(2005).
13. M. Outokesh, H. Mimura, Y. Niibori and K. Tanaka, *Ind. & Eng. Chem. Res.*, **45**, pp. 3633-3643(2006).
14. Y. Wu, H. Mimura and Y. Niibori, *J. Ion Exchange*, Vol. **18**, No. **4**, pp. 396-401(2007).
15. Y. Wu, M. Outokesh, H. Mimura and Y. Niibori, *Progress in Nuclear Energy*, **50**, pp. 487-493(2008).
16. H. Watari and S. Hatakeyama , *Analytical Science*, **7**, pp. 487-489(1991).
17. E. Kamio and K. Kondo, *Journal of Chemical Engineering of Japan*, **35**, pp. 574-581 (2002).
18. J. F. Keggin, Roc. Roy. Soc., London, A144, 75(1934).
19. F. Sebesta, J. John and A. Motl, IAEA-TECDOC-947, Vienna, Austria, p.79(1997).
20. V. Pekarek and V. Vesely, *Talanta*, **19**, 11, pp.1285-1293(1972).
21. H. A. Laitinen and W.E. Harris, “Chemical Analysis”, McGraw-Hill Kogakusha, Ltd., Tokyo, p.14(1975).
22. P. Benes and V. Majer, “Trace Chemistry of Aqueous Solutions”, Elsevier Scientific Publishing Company, Amsterdam, p. 199(1980).