Selective adsorption of caesium by hybrid microcapsules enclosing AWP

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Abstract

Recently, there has been significant focus on the selective separation and recovery of ¹³⁷Cs from high-level liquid waste (HLLW) in relation to the partitioning of radioactive nuclides and their effective utilisation. Many separation methods for Cs⁺ ions such as ion exchange, solvent extraction and co-precipitation have been studied. In the ion-exchange process, heteropolyacids are well known to have selective uptake ability to Cs⁺. In particular, ammonium tungstophosphate ((NH₄)₃PO₄·12WO₃·3H₂O, AWP), a kind of heteropolyacid, which shows a high selectivity toward Cs⁺ and excellent radiation stability, can act as one of the most promising adsorbents for the uptake of Cs⁺. However, AWP is still not applied to the practical separation process because of its fine powder form, which renders it insufficient for continuous treatment using a packed column. 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. The present paper deals with the preparation of microcapsules enclosing AWP (AWP-CaALG), characterisation and Cs⁺ uptake properties in simulated HLLW.

Spherical and elastic AWP-CaALG microcapsules were obtained, the particle size of which was about 700 µm. The elemental distribution of the sixty-seven kinds of ions for AWP-CaALG was determined by the batch method in the presence of HNO₃ up to 9 M. The monovalent ions of Cs⁺, Rb⁺ and Ag⁺ were adsorbed on AWP-CaALG in the order of Cs⁺ >> Rb⁺ > Ag⁺. In contrast, the K_d values of other ions were considerably lowered. Within the lower concentration range of HNO₃ below 1 M, lanthanoids ions and ZrO²⁺ were adsorbed on AWP-CaALG; these ions were probably adsorbed on the alginate matrices by ion exchange with Ca²⁺. However, the K_d values of these ions are markedly dependent on the co-existing HNO₃ concentration, and can be easily eluted with highly concentrated HNO₃.

The selective uptake of Cs^+ from two types of simulated HLLW (SW-11E (HNO₃ and HCl type): $[Cs^+] = 2.22 \text{ g/L}$, $[HNO_3] = 2 \text{ N}$, [HCl] = 2 N, 28 components solution, JAEA) was examined by the batch method. The uptake (%) of metal ions for CaALG was also determined. The uptake (%) of Cs^+ in SW-11E (HNO₃ type and HCl type) at V/m of 5 cm³/g and 25°C were estimated to be 80.2% and 80.0%, respectively. The Rb⁺ ions were also adsorbed similarly to the above results of elemental distribution. The uptake (%) of rare metals (Ru, Rh, Zr, Mo, Te and Sn) exceeding 40% were obtained; Ru, Rh and Zr were adsorbed by the ion exchange with Ca^{2+} ions in alginate matrices, and hydrolysable Mo and Te were precipitated as zirconium molybdates and hydroxides due to the lowering of acidity. In addition, AWP-CaALG had slight adsorbability to the trivalent lanthanoids (Gd and Sm) and divalent metal ions (Sr and Ba) due to the ion exchange with Ca^{2+} ions in alginate. The incorporation of these metal ions in AWP-CaALG was confirmed by the wavelength dispersive spectrometry (WDS) for the cross-section.

Introduction

There has been considerable focus on the selective separation and recovery of ¹³⁷Cs from HLLW, in relation to the partitioning of radioactive nuclides and their effective utilisation [1,2]. ¹³⁷Cs, with a relatively long half-life of about 30 years, exhibited high radioactivity and heat generation, and a large amount of Cs group (~3.5 kg/MTU, 45 GWd/t) are contained in HLLW. Therefore, the selective separation of ¹³⁷Cs from HLLW is a key environmental issue for nuclear waste management. Further, the reuse of purified Cs is expected for radiation and heat sources in the fields of medicine and industry. Many methods have been studied [3] for the separation of Cs⁺ such as ion exchange, solvent extraction and co-precipitation. In the ion-exchange method, heteropolyacids are well known to have selective uptake ability toward Cs⁺; in particular, ammonium tungstophosphate (AWP), a kind of heteropolyacids, which shows a high selectivity toward Cs⁺ and excellent radiation stability, can act as one of the most promising absorbents for the uptake of Cs⁺ [4]. However, AWP is not yet applied to the practical separation process because of its fine powder form, which is insufficient for continuous treatment using the packed column.

In order to overcome this handling problem, the granulation of AWP powder by alginate gel polymers seems to be one of the most prominent techniques for the practical column operation [4]. Microencapsulation is a unique technique for enclosing an active component in a porous polymeric matrix [5]. It is well known that alginates (ALG), which are a kind of biopolymer, have a high immobilisation ability and this methods has been extended to industrial, medical and agricultural fields. Alginate is a salt of acid, with carboxyl groups capable of forming gels by cross-linking with multivalent metal ions. This immobilising property of alginate has spawned extensive applications, including the microencapsulation of enzymes, sub-cellular organelles, and living cells [6,7]. Granulation with alginate gel therefore has several advantages such as simplicity of preparation, mechanical strength and strong acid resistance.

In this study, we have attempted to encapsulate the fine crystals of the AWP exchanger into the CaALG matrices using its high immobilising ability for the selective separation of Cs⁺ and Rb⁺ from waste solutions containing highly concentrated HNO₃ and NaNO₃ [4]. The present paper deals with the preparation of AWP-CaALG microcapsules (MC), characterisation, uptake properties, and elution properties of Cs⁺ for the column packed with AWP-CaALG MC.

Experimental

Materials

Figure 1 shows the structure of AWP. AWP exchanger consists of Keggin-type polyanions $(PW_{12}O_{40}^{3-})$ [4] and the exchangeable NH_4^+ ions which can be exchanged with Cs⁺ ions. The unit cell composition of AWP was $(NH_4)_3PO_4\cdot 12WO_3\cdot 3H_2O$ (Wako Pure Chemical Ind.). Figure 2 shows the SEM image of AWP particles. The sodium alginate (NaALG, 500-600 cP) was purchased from Wako Pure Chemical Ind. The Cs⁺ and Rb⁺ solutions were obtained by diluting standard solutions (10³ ppm, Wako Pure Chemical Ind.).

Preparation of MC

The AWP-CaALG MC were prepared as follows (Figure 3). The fine AWP powders (0.5 g) were kneaded with sodium alginate (NaALG) solution (50 cm³, 1.5 wt.%) and fully dispersed using a kneader equipped with the functions of rotation and revolution. The well-kneaded sol was then injected dropwise into a 0.5 M Ca(NO₃)₂ solution via a medical needle under constant stirring at room temperature to form MC. The MC (hydrogel type) were then stirred gently for one night to enhance aging, and separated from the solution, washed with distilled water and finally air-dried at 30°C for 2 d. The MC (xerogel type) prepared by the gelation of kneaded sols of AWP/NaALG with Ca(NO₃)₂ solution were abbreviated as AWP-CaALG. The CaALG matrices without AWP were also prepared by the similar manner.

Figure 1: Structure of AWP exchanger



Figure 2: SEM image of AWP particles



Figure 3: Preparation procedure of AWP-CaALG (xerogel polymer)



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Characterisation

The surface morphologies of AWP-CaALG and CaALG matrices were checked by scanning electron microscopy (SEM, Hitachi, TM-1000). The adsorbed metal ions on AWP-CaALG and their wavelength dispersive spectroscopic (WDS) spectra were determined by electron probe microanalysis (EPMA, JEOL, JXA-8200WD/ED).

Determination of distribution coefficient (K_d)

The distribution of Cs⁺ ions for MC was determined by batch method. As for the elemental distribution for 67 kinds of ions using AWP-CaALG and CaALG matrices, the batch experiment was carried out under the following conditions: metal ion concentration of 10 ppm, coexisting HNO₃ concentration of 0.1~9 M, $V/m = 10 \text{ cm}^3/g$, and at 25±1°C for 1 d, which was found to be sufficient for attaining equilibrium. The uptake (%) of different ions containing in simulated HLLW (SHLLW) was also determined using AWP-CaALG and CaALG matrices under the conditions: $V/m = 5 \text{ cm}^3/\text{g}$ and at $25\pm1^\circ\text{C}$ for 1 d. Here the simulated HLLW ([Cs⁺]: 2 220 ppm, [HNO₃]: 2 N, [HCl]: 2 N, 28 components solution, SW-11, JAEA)[8] was obtained from KAKEN Co. Ltd. The concentrations of different ions in SHLLW are listed in Table 1; this composition was estimated by a computer program ORIGEN-79 and corresponded to the waste stored for 5 years after reprocessing spent fuels cooled for 6 months after discharge at burn-up of 28 000 MWd/tU from a light water reactor [8]. The concentrations of Cs⁺ and other metal ions were measured by atomic absorption spectrophotometry (AAS, Thermo Fisher Scientific K.K., AA-890), ¹³⁷Cs tracer method, and inductively coupled plasma atomic emission spectrometry (ICP-AES, SII, SPS7800). The uptake percentage $(R, \sqrt[3]{b})$ of metal ions removed from the solution and the distribution coefficient (K_a , cm³/g) are defined as:

$$R = \frac{C_0 - C_f}{C_0} \cdot 100$$
 (%) (1)

$$K_d = \frac{C_0 - C_f}{C_f} \cdot \frac{V}{m} \text{ (cm}^3/\text{g)}$$
⁽²⁾

where C_o and C_f (ppm) are the concentrations of metal ions at initial and equilibrium, respectively; (g) the weight of MC; and V (cm³) the volume of the aqueous phase.

28-component solution, SW-11E, JAEA				
	Element	Concentration [g/L]	Element	Concentration [g/L]
_	Na	21.600	Pd	0.884
	Р	0.290	Ag	0.037
	Fe	4.120	Cd	0.064
	Cr	0.211	Sn	0.035
	Ni	0.548	Se	0.044
	Rb	0.277	Те	0.434
	Cs	2.220	Y	0.408
	Sr	0.750	La	1.150
	Ba	1.450	Ce	2.030
	Zr	2.970	Pr	1.140
	Mo	2.940	Nd	3.570
	Re	0.840	Sm	0.811
	Ru	1.810	Eu	0.124
	Rh	0.341	Gd	0.072

Table 1: Chemical composition of SHLLW

Results and discussion

Surface morphology of AWP-CaALG MC and Ca-ALG matrices

Figures 4 and 5 show the SEM images of the surface of AWP-CaALG and CaALG matrices. Spherical and elastic granules were obtained. On the surface of AWP-CaALG, a number of fine crystals of AWP are seen to be encapsulated, and many creases were clearly observed. The size of MC was estimated to be about 500~700 μ m in diameter by optical microscope and SEM image. The structure of CaALG gel matrices is composed of cross-linked polymer networks with ionic bonding between Ca²⁺ ions and carboxyl groups.

Figure 4: SEM image of AWP-CaALG



Figure 5: SEM image of CaALG matrices



Elemental distribution of various ions for AWP-CaALG and CaALG in the presence of HNO3

Since various ions are contained in HLLW, the elemental distribution of the 67 kinds of ions for AWP-CaALG was determined by batch method in the presence of HNO₃ up to 9 M. As shown in Figure 6, monovalent ions of Cs⁺, Rb⁺ and Ag⁺ are adsorbed on AWP-CaALG in the order of Cs⁺ >> Rb⁺ > Ag⁺. From the results by batch experiments, the separation factor of Cs⁺ and Rb⁺ was estimated to be above 10², indicating the possibility of mutual separation by chromatography. In contrast, the K_d values of other ions were considerably lowered. In lower concentration range of HNO₃ below 1 M, lanthanoids ions and ZrO²⁺ tended to be adsorbed on AWP-CaALG; these ions were probably adsorbed on the alginate matrices by ion exchange with Ca²⁺. However, the K_d values of these ions are markedly lowered at higher acidity; they can be easily eluted with highly concentrated HNO₃. Figure 7 shows the elemental distribution for CaALG matrices. Some metal ions, Zr(IV), Ru(III), Ag(I) and W(VI) were found to be adsorbed on the alginate matrices; selective uptake of RuNO³⁺ for CaALG was reported by Mimura, *et al.* [9].



Figure 6: Elemental distribution in the presence of HNO₃ using AWP-CaALG

Figure 7: Elemental distribution in the presence of HNO₃ using CaALG matrices

 $V/m = 10 \text{ cm}^3/\text{g}; [M^{n+}] = 10 \text{ ppm}; [HNO_3] = 0.1 \sim 9 \text{ M}; 25^{\circ}\text{C}; 24 \text{ h}$



Uptake properties of Cs⁺ from simulated HLLW

The selective uptake of Cs⁺ from simulated HLLW (SHLLW, [Cs⁺]: 2 200 ppm, [HNO₃]: 1.92 M, 28 component solution, SW-11, JAEA) was examined by batch method. The uptake (%) of various metal ions is shown in Figure 8. The uptake (%) of Cs⁺ in SW-11E (HNO₃ type and HCl type) at V/m of 5 cm³/g and 25°C were estimated to be 80.2% and 80.0%, respectively, which were considerably larger than that for mordenites [10]. The Rb⁺ ions were also adsorbed similarly to the above results of elemental distribution. The uptake (%) of rare metals [Ru(III), Rh(III), Zr(IV), Mo(VI), Te(VI), Se(VI) and Sn(IV)] exceeding 40% were obtained; Ru(III), Rh(III) and Zr(IV) were adsorbed by the ion exchange with Ca²⁺ ions in alginate matrices, and hydrolysable Mo(VI), Te(VI) and Sn(IV) were precipitated as zirconium molybdates and hydroxides probably due to the lowering of acidity.



Figure 8: Uptake percentage of various metal ions in SHLLWs for AWP-CaALG

In addition, AWP-CaALG had slight adsorbability to the trivalent lanthanoids [Gd(III) and Sm(III)] and divalent metal ions [Sr(II) and Ba(II)] probably due to the ion exchange with Ca²⁺ ions in alginate matrices [11]. The incorporation of metal ions into AWP-CaALG MC after treatment with SHLLW is shown in Figure 9; the colour of the surface of microcapsules was changed to brown and dark brown for HNO₃-SHLLW and HCl-SHLLW, respectively. The uptake behaviour of metal ions in SHLLWs for CaALG matrices is shown in Figure 10. Compared to the AWP-CaALG MC, the uptake(%) of Cs⁺ ions was considerably lowered for CaALG matrices. Other metal ions [Ru(III), Zr(IV), Rh(III), Ag(I) and Rb(I)] were also adsorbed on CaALG matrices, and hydrolysable Mo(VI) and Te(VI) were precipitated as zirconium molybdates and hydroxides probably due to the lowering of acidity. The colour change after treatment with SHLLWs was similar to that for microcapsules (Figure 11).











After treatment with HCI-SHLLW





 $V/m = 5 \text{ cm}^3/\text{g}; \text{SW-11E}; 25^\circ\text{C}; 24 \text{ h}$

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Figure 11: Colour change of CaALG matrices after treatment with SHLLW

SEM images of CaALG



Before treatment



After treatment with HNO₃-SHLLW



After treatment with HCI-SHLLW

Incorporation of metal ions into AWP-CaALG and precipitates

Metal incorporation into AWP-CaALG was examined by SEM/EPMA. Figure 12 shows the wavelength dispersive spectra (WDS spectra) and SEM images of AWP-CaALG and precipitates after treatment with HNO_3 -SHLLW. In AWP-CaALG, Cs and the constitutional element of W for AWP were detected, and other metal ions (Ru (III), Mo(VI) and Zr(IV)) were incorporated into alginate phase and partly precipitated on the surface. Further, the adsorption of Cs⁺ ions on AWP crystals was confirmed by line analyses as shown in Figure 13: the WDS spectra of Cs were close to those of W and P. The precipitates formed after batch experiments contained Te(IV), Mo(VI), Zr(IV) and P(V).

Incorporation of metal ions into CaALG matrices and precipitates

Figure 14 shows the WDS spectra and SEM images of CaALG matrices and precipitates after treatment with HNO_3 -SHLLW. In CaALG matrices, Ba(II), Ru (III), Zr(IV), Pd(II) and Mo(VI) were incorporated and partly precipitated on the surface. The precipitates formed after batch experiments contained Te(IV), Mo(VI), Zr(IV) and P(V), similarly to the case of AWP-CaALG.







Figure 13: Line analyses of W, P and Cs for AWP-CaALG after treatment with HNO₃-SHLLW

Figure 14: WDS spectra (left) and SEM images of CaALG and precipitates (right) after treatment with HNO₃-SHLLW



Conclusions

Fine crystals of ammonium tungstophosphate (AWP) exchanger, which have high selectivity towards Cs^+ , were readily encapsulated in the biopolymer matrices (calcium alginate, CaALG) and AWP-CaALG microcapsules were prepared by sol-gel methods; spherical MC with particle size of about 500~700°C were obtained, Monovalent ions of Cs^+ , Rb^+ and Ag^+ were adsorbed on AWP-CaALG in the order of $Cs^+ >> Rb^+ > Ag^+$. The uptake percentage of Cs^+ in SHLLW for

AWP-CaALG were above 80% at $V/m = 5 \text{ cm}^3/\text{g}$. On the other hand, Ru(III) and Zr(IV) ions tended to be adsorbed on CaALG matrices. After treatment with SHLLW, the precipitates containing Te(IV), Mo(VI), Zr(IV) and P(V) were detected. The Cs⁺ ions can be separated from other metal ions by stepwise elution chromatography. Thus, AWP-CaALG microcapsules are effective for the selective uptake of Cs⁺ from SHLLW.

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