REMOVAL OF RADIOACTIVE NUCLIDES BY MULTI-FUNCTIONAL MICROCAPSULES ENCLOSING INORGANIC ION-EXCHANGERS AND ORGANIC EXTRACTANTS

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ABSTRACT

The microcapsules enclosing two kinds of functional materials, inorganic ion-exchangers and organic extractants, were prepared by taking advantage of the high immobilization ability of alginate gel polymer. The fine powders of inorganic ion-exchanger and oil drops of extractant were kneaded with sodium alginate (NaALG) solution and the kneaded sol readily gelled in a salt solution of $CaCl_2$, $BaCl_2$ or HCl to form spherical gel particles. The uptake properties of various nuclides, ^{137}Cs, ^{85}Sr, ^{60}Co, ^{88}Y, ^{152}Eu and ^{241}Am, for thirty-four specimens of microcapsules in the presence of 10^{-1}-10^{-4} M HNO_3 were evaluated by the batch method. The distribution coefficient (K_d) of Cs^+ above 10^3 cm^3/g was obtained for the microcapsules enclosing CuFC or AMP. The K_d of Sr^{2+} around 10^2 cm^3/g was obtained for the microcapsules containing clinoptilolite, antimonic acid, zeolite A, zeolite X or titanic acid. The microcapsules enclosing DEHPA exhibited relatively large K_d values of trivalent metal ions above 10^3 cm^3/g; for example, the K_d values of Cs^+, Sr^{2+}, Co^{2+}, Y^{3+}, Eu^{3+} and Am^{3+} for a favorable microcapsule (CuFC/clinoptilolite/DEHPA/CaALG) were 1.1×10^4, 7.5×10, 1.1×10, 1.0×10^4, 1.4×10^4, 3.4×10^3 cm^3/g, respectively. The uptake rates of Cs^+, Y^{3+}, Eu^{3+} and Am^{3+} for this microcapsule were rather fast; the uptake percentage above 90% was obtained after 19 h-shaking and the uptake equilibrium was attained within 1 d. The AMP/CaALG exhibited high uptake ability for Cs^+ even after irradiation of 188 kGy, and DEHPA/CaALG microcapsule had similar K_d values of Cs^+, Sr^{2+}, Co^{2+}, Y^{3+}, Eu^{3+} and Am^{3+} ions before and after irradiation. The microcapsules with various shapes such as spherical, columnar, fibrous and filmy forms were easily prepared by changing the way of dipping kneaded sol into gelling salt solution. The microcapsules enclosing inorganic ion-exchangers and extractants have a potential possibility for the simultaneous removal of various radioactive nuclides from waste solutions.

INTRODUCTION

The rapid decontamination of accidental liquid wastes containing various radioactive nuclides is important from the standpoint of radiation exposure reduction and radiation protection. For this purpose, the development of "multi-functional" microcapsules with high uptake ability for different radioactive nuclides is required for this treatment. In order to remove radioactive nuclides from the waste solutions, a large number of selective inorganic ion-exchangers and extractants have been

developed (1-5). Since most of these materials are very fine powder or oily, they have some difficulties in handling for the practical applications.

The granulation of these materials with organic polymers seems to be very effective for the rapid decontamination and safety handling. (6) The organic binding polymers for the encapsulation have a number of advantages such as the simplicity of preparation procedure, high porosity, high content of active component and mechanical strength. (7) The gel network of the polymeric materials is further expected to prevent the exchangers and extractants from leaching out. (8)

Alginic acid is a biopolymer, which occurs in brown seaweeds and has carboxyl groups capable of forming complexes with calcium ions. (9) Recently, the gel-forming property of this polymer has led to its extensive use in biomedicine and biotechnology industry to immobilize or encapsulate enzymes, subcelluler organelles and living cells. (9) Thus, the prominent immobilizing ability of alginates seems to be applicable to the encapsulation of inorganic ion exchangers and organic extractants. (6)

In this study, we have attempted to enclose various inorganic ion-exchangers and organic extractants with the alginate gel polymers to form microcapsules. The present study deals with the preparation procedure of microcapsules, their characterizations and the uptake properties of different radioactive nuclides.

EXPERIMENTAL

Materials and Preparation of Microcapsules

Various types of inorganic ion-exchangers and organic extractants were used as active components for the uptake of radioactive nuclides. The ion exchangers and extractants used in this study are listed in **Table I**. Here the inorganic ion-exchangers, Cu-ferrocyanide (CuFC), heteropolyacids (AMP, AWP) and zeolites (mordenite, clinoptilolite), were used for the uptake of Cs^+. The inorganic ion-exchangers, zeolites (zeolite A, zeolite X and clinoptilolite), titanic acid and antimonic acid, were used for the uptake of Sr^{2+} and Co^{2+}. Trivalent metal ions, Y^{3+}, Eu^{3+} and Am^{3+}, were extracted with organic extractants, DEHPA, CYANEX 301, CMP and β-diketones, etc.

The preparation procedure for alginate microcapsules is as follows. Viscous sodium alginate (NaALG) solutions were kneaded with both fine powders of inorganic ion-exchangers and oil drops of extractants at prescribed mixing ratio. The content of exchanger and extractant was varied from 0.2 to 1.0 g in the NaALG solution (100 cm^3). Thirty-four kinds of specimens of microcapsules were prepared by varying the combination of the inorganic ion-exchanger and extractant as shown in Table I. The kneaded sol was then added dropwise to either 0.5 M $CaCl_2$, 0.5 M $BaCl_2$ or 1 M HCl solution (gelling agent) with stirring at room temperature to form spherical gel particles. After overnight standing, the gel particles were separated from the solution and washed with deionized water. Air-drying at 40˚C was performed to obtain the granular microcapsules. The microcapsules with different contents and combinations of inorganic ion-exchangers and extractants were thus obtained by simple preparation procedure.

The surface morphology and physicochemical property of microcapsules were examined by scanning electron microscopy (SEM, Hitachi 4100-L) and electron probe microanalysis (EPMA, Hitachi X-650S). The specimens of microcapsule for SEM were air-dried at 40˚C and coated with platinum. The accelerating voltage of electron beam was 10.0 keV. The microcapsule specimens dried at 40˚C

were embedded in the acrylic acid resin and coated with carbon for EPMA analysis. The accelerating voltage and incident current were 15.0 keV and 10^2 pA, respectively. The accumulating time and energy range for energy dispersive spectroscopy (EDS) were 10^2 sec and 0~10.24 keV, respectively.

Determination of Uptake

The uptake percentage and distribution coefficient of Cs^+, Sr^{2+}, Co^{2+}, Y^{3+}, Eu^{3+} and Am^{3+} ions were determined by the batch method. An aqueous solution (7 cm^3) containing 10 ppm metal ion in the presence of $10^{-1} - 10^{-4}$ M HNO_3 was contacted with 70 mg of granular microcapsule at 25±1ºC for 3 d. After equilibration, the γ-activities of ^{137}Cs, ^{85}Sr, ^{60}Co, ^{88}Y, ^{152}Eu and ^{241}Am in the aqueous phase were measured by NaI(Tl) scintillation counter (OKEN, Model RC-101A). Here the radioisotopes of ^{85}Sr and ^{88}Y were produced on the reaction of $^{86}Sr(\gamma, n)^{85}Sr$ and $^{89}Y(\gamma, n)^{88}Y$ by bremsstrahlung from LINAC, Tohoku Univ., respectively.

The uptake percentage, R (%), and the distribution coefficient, K_d (cm^3/g), are defined as

$$R = [(A_i - A_t)/A_i] \times 100 \qquad (\%), \qquad\qquad\qquad (Eq.\ 1)$$

$$K_d = [(A_i - A_f)/A_f] \times V/m \qquad (cm^3/g), \qquad\qquad\qquad (Eq.\ 2)$$

where A_i, A_t and A_f (cpm/cm^3) are the counting rates at the initial stage, at time t, and at equilibrium, respectively; m (g) the weight of microcapsule; V (cm^3) the volume of aqueous phase.

Table I. Inorganic Ion-exchangers and Organic Extractants Enclosed in the Microcapsules

[Inorganic ion-exchangers for Cs uptake]
- Ammonium molybdophosphate(AMP): $(NH_4)_3PMo_{12}O_{40} \cdot 3H_2O$
- Ammonium tungustophosphate(AWP): $(NH_4)_3PW_{12}O_{40} \cdot 3H_2O$
- Cu-ferrocyanides(CuFC): $K_{2-x}Cu_{x/2}[CuFe(CN)_6] \cdot nH_2O$, x=1.22
- Mordenite(Synthetic zeolite, SM): $Na_{8.7}[(AlO_2)_{8.7}(SiO_2)_{39.3}] \cdot 24H_2O$
- Clinoptilolite(Natural zeolite, CP)[a]: $Na_6[(AlO_2)_6(SiO_2)_{30}] \cdot 24H_2O$
[Inorganic ion-exchangers for Sr-Co uptake]
- Zeolite A (A): $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27H_2O$
- Zeolite X (X): $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}] \cdot 264H_2O$
- Antimonic acid (IXE 300): $Sb_2O_5 \cdot nH_2O$
- Titanic acid (TiO_2): $TiO_2 \cdot nH_2O$
[Organic extractants for Y-Eu-Am extraction]
- DEHPA: di-(2-ethylhexyl) phosphoric acid
- CYANEX 301: (bis (2,4,4,-trimetylpentyl) dithiophosphinic acid
- CYANEX 272: (bis (2,4,4,-trimetylpentyl) phosphinic acid
- CMP: dihexyl-N,N-diethylcarbamoylmethyl- phosphonate
- β-diketones: LIX 51, LIX 54
- α-hydroxyoximes: LIX 65N, LIX 64N

[a]   Two kinds of natural clinoptilolite were obtained from Itaya (CP(I)) and Futatsui (CP(F)), Japan.

RESULTS AND DISCUSSION

Surface Morphology and Structure of Microcapsules

In most cases, the inorganic ion-exchangers and extractants were well enclosed in the alginate matrices, while the combinations of AMP and extractants (CYANEX, CMP and LIX) were unsuitable for the encapsulation; for example, the coexistence of AMP and CYANEX led to the destruction of AMP structure and dislodgment of Mo in the solution. The microcapsules with various shapes such as spherical, columnar and fibrous forms were easily prepared by changing the way of dipping of kneaded sol into salt solution. **Figure 1** shows the SEM image of spherical microcapsule (AMP-CP-DEHPA-CaALG) prepared from the kneaded sol consisting of 0.2 g AMP- 0.2 g CP- 0.2 g DEHPA and 100 cm^3 of NaALG solution (1.5 wt.%, 500~600 cP). The aggregates of inorganic ion-exchangers around 30μm and a number of oil drops of DEHPA around 5μm in diameter are seen to be encapsulated in the calcium alginate gel matrices. Here the aggregates and oil drops are encapsulated in the alginate gel matrices cross linked with Ca^{2+} ions, and the cross section of gel matrices has been reported to exhibit "egg-box junction" which brings about high porosity and mechanical strength of microcapsule (9). The encapsulation of extractant at higher mixing ratio over 1.5/100 g/cm^3 resulted in an ooze of extractant through the wall of gel matrices.
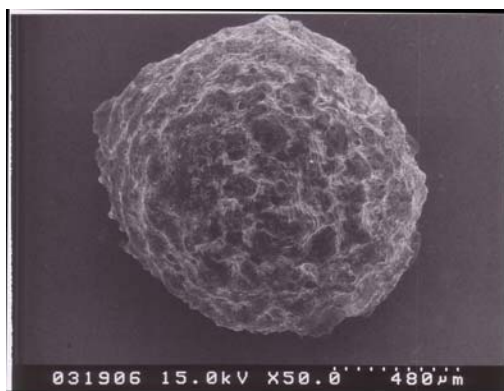

031906 15.0kV X50.0 480μm

Fig. 1. SEM image of spherical microcapsule (AMP/CP/DEHPA/CaALG) prepared from the kneaded sol consisting of 0.2 g AMP- 0.2 g CP- 0.2 g DEHPA and 100 cm^3 of NaALG solution (1.5 wt.%, 500~600 cP)

Distribution of Various Metal Ions

The distribution coefficient (K_d) of various metal ions for microcapsules with different gel matrices, BaALG, CaALG and HALG, was determined by the batch method. This experiment was a screening test for the selection of the favorable microcapsules with high K_d values of various ions.
Table II summarizes the K_d values of various metal ions for barium alginate (BaALG) microcapsules in the presence of 10^{-2} M HNO$_3$. The encapsulation of AMP crystals and DEHPA extractant resulted in an enhancement of K_d values of Cs$^+$ and trivalent metal ions. The K_d values of Sr^{2+} and Co^{2+} were around 10-10^2 cm^3/g. Zeolite A is well known to have relatively high selectivity for Sr^{2+} and Co^{2+}, while in this case the eluted Ba^{2+} ions seem to compete with these ions, resulting in a lowering of

their K_d values. The structure of AMP crystals were destroyed in the presence of CYANEX 301 and CMP extractants, resulting in a lowering of K_d value of Cs^+.

Table III summarizes the K_d values of various metal ions for calcium alginate (CaALG) microcapsules in the presence of 10^{-2} M HNO_3. The encapsulation of AMP and CuFC crystals led to an enhancement of K_d value of Cs^+ over 10^3 cm^3/g. The K_d values of Sr^{2+} and Co^{2+} were around

Table II. Distribution Coefficients of Various Metal Ions for Barium Alginate (BaALG)
Microcapsules in the Presence of 10^{-2} M HNO_3

Microcapsule (BaALG gel)	Exchanger(g)/ Extractant(g)	K_d (cm³/g)					
		Cs^+	Sr^{2+}	Co^{2+}	Y^{3+}	Eu^{3+}	Am^{3+}
AMP/DEHPA	0.5/0.5	$1.4x10^3$	$1.3x10$	$1.8x10$	$2.1x10^3$	$1.8x10^3$	$1.1x10^3$
AMP/A/DEHPA	0.2/0.2/0.2	$2.3x10^3$	$2.3x10$	$4.9x10$	$7.0x10^2$	$9.1x10^2$	$1.1x10^3$
AMP/A/DEHPA/CMP	0.2/0.2/0.2/0.2	$8.7x10$	$2.5x10$	$4.1x10$	$6.0x10^2$	$1.0x10^3$	$8.8x10^3$
AMP/C301	0.5/0.5	$1.6x10^2$	7.3	$4.4x10^2$	$1.5x10^2$	$2.8x10^2$	$4.9x10^2$
AMP/A/C301/DEHPA	0.2/0.2/0.2/0.2	$4.0x10$	$1.6x10$	$7.4x10^2$	$1.0x10^3$	$5.2x10^2$	$1.3x10^3$

V/m 100 cm^3/g; carrier concn. 10 ppm, [Am^{3+}]: $2.1x10^{-9}$ M; 25ºC; 3d.

Table III. Distribution Coefficients of Various Metal Ions for Calcium Alginate (CaALG)
Microcapsules in the Presence of 10^{-2} M HNO_3

Microcapsule (CaALG gel)	Exchanger(g)/ Extractant(g)	K_d (cm³/g)					
		Cs^+	Sr^{2+}	Co^{2+}	Y^{3+}	Eu^{3+}	Am^{3+}
AMP/A/DEHPA	0.2/0.2/0.2	$5.2x10$	$9.2x10$	$1.7x10$	$1.8x10^3$	$1.7x10^3$	$1.7x10^3$
AMP/A/DEHPA	0.5/0.5/0.5	$8.6x10^2$	$6.2x10$	$1.7x10$	$9.9x10^2$	$5.0x10^2$	$1.7x10^3$
AMP/A/DEHPA	1.0/1.0/1.0	$1.9x10^3$	$3.4x10$	$1.3x10$	$4.0x10^2$	$3.4x10^2$	$1.2x10^3$
AWP/A/DEHPA	0.2/0.2/0.2	$1.0x10$	$1.1x10^2$	$2.4x10$	$3.2x10^2$	$2.5x10$	$5.2x10$
SM/A/DEHPA	0.2/0.2/0.2	$1.8x10^3$	$5.4x10$	$2.0x10$	$3.5x10^3$	$2.0x10^3$	$2.1x10^3$
<u>CuFC/A/DEHPA</u>	0.2/0.2/0.2	$1.1x10^4$	$8.1x10$	$4.1x10$	$1.1x10^3$	$1.6x10^3$	$2.8x10^3$
CP(I)/DEHPA	0.2/0.2	$1.5x10^3$	$1.0x10^2$	$2.0x10$	$7.5x10^3$	$8.5x10^3$	$3.3x10^3$
AMP/X/DEHPA	0.2/0.2/0.2	$1.3x10^3$	$5.4x10$	$3.5x10$	$2.5x10^3$	$1.6x10^3$	$1.7x10^3$
AMP/A/C272	0.2/0.2/0.2	$6.4x10^2$	$7.3x10$	$3.0x10$	$1.9x10^2$	$1.6x10^3$	$2.4x10^3$
AMP/IXE300/DEHPA	0.2/0.2/0.2	$6.2x10^3$	$9.2x10$	$2.7x10$	$1.2x10^4$	$7.8x10^3$	$2.0x10^3$
AMP/TiO2/DEHPA	0.2/0.2/0.2	$6.4x10^3$	$7.6x10$	$3.0x10$	$5.3x10^3$	$6.0x10^3$	$8.3x10^2$
AMP/A/LIX51	0.2/0.2/0.2	$5.0x10$	$7.1x10$	$1.8x10$	$1.5x10^2$	$4.3x10^2$	$2.4x10^3$
AMP/A/LIX54	0.2/0.2/0.2	$6.2x10$	$6.7x10$	$1.9x10$	$1.2x10^2$	$3.2x10^2$	$2.1x10^3$
AMP/A/LIX65N	0.2/0.2/0.2	$3.4x10$	$6.0x10$	$1.8x10$	$1.2x10^2$	$2.9x10^2$	$1.9x10^3$
AMP/A/LIX64N	0.2/0.2/0.2	$4.8x10$	$6.6x10$	$1.4x10$	$1.0x10^2$	$2.4x10^2$	$1.2x10^3$
<u>CuFC/CP(I)/DEHPA</u>	0.2/0.2/0.2	$7.1x10^3$	$6.3x10$	$1.4x10$	$7.6x10^3$	$1.8x10^4$	$3.3x10^3$
<u>CuFC/CP(I)/DEHPA</u>	0.2/0.2/0.2	$1.1x10^4$	$7.5x10$	$1.1x10$	$1.0x10^4$	$1.4x10^4$	$3.4x10^3$
<u>AMP/CP(I)/DEHPA</u>	0.2/0.2/0.2	$5.8x10^3$	$6.1x10$	$1.2x10$	$1.2x10^4$	$7.2x10^3$	$1.2x10^4$
<u>AMP/CP(F)/DEHPA</u>	0.2/0.2/0.2	$3.6x10^3$	$6.5x10$	$1.4x10$	$3.0x10^4$	$1.3x10^4$	$4.4x10^3$
CuFC/IXE300/DEHPA	0.2/0.2/0.2	$7.5x10^3$	$6.8x10$	$1.3x10$	$2.8x10^3$	$9.6x10^3$	$3.9x10^3$

V/m 100 cm^3/g; carrier concn. 10 ppm, [Am^{3+}]: $2.1x10^{-9}$ M; 25ºC; 3d.

10-10^2 cm^3/g. Zeolite A and X are well known to have relatively high selectivity for Sr^{2+} and Co^{2+}, while in this case the eluted Ca^{2+} ions seem to compete with these ions. The combination of AMP and LIX resulted in a considerable lowering of K_d value of Cs$^+$. As for CuFC/CP(I)/DEHPA/CaALG microcapsule, similar K_d values were obtained by the second batch experiment.

Table IV summarizes the K_d values of various metal ions for alginic acid (HALG) microcapsules in the presence of 10^{-2} M HNO$_3$. In this case, the equilibrium pH was lowered by the ion exchange of H$^+$ in the alginic acid matrices and the metal ions in the solution (10); in this experiment, the equilibrium pH was around 1.4-1.8. The lowering of equilibrium pH resulted in a decrease of K_d values, especially in the case of trivalent metal ions; for example, the K_d values of Am^{3+} for all specimens were around 10^2 cm^3/g, which was about one order of magnitude lower than those for CaALG microcapsules.

Table IV. Distribution Coefficients of Various Metal Ions for Alginic Acid (HALG) Microcapsules in the Presence of 10^{-2} M HNO$_3$

Microcapsules (HALG gel)	Exchanger(g)/ Extractant(g)	K_d (cm^3/g)					
		Cs$^+$	Sr^{2+}	Co^{2+}	Y^{3+}	Eu^{3+}	Am^{3+}
CuFC/X/DEHPA	0.2/0.2/0.2	7.0×10^3	3.1×10	1.4×10	9.7×10^2	2.1×10^3	3.4×10^2
AMP/X/DEHPA	0.2/0.2/0.2	3.4×10^3	3.3×10	1.7×10	2.7×10^2	1.8×10^2	6.5×10^2
SM/X/DEHPA	0.2/0.2/0.2	3.9×10^2	2.3×10	4.9	9.2×10^2	3.8×10^3	1.3×10^2
CP(I)/DEHPA	0.2/0.2	3.4×10^2	3.0×10	1.2×10	2.0×10^4	8.2×10^3	5.3×10^2
CuFC/X/DEHPA	0.5/0.5/0.5	3.7×10^4	2.2×10	1.2×10	1.5×10^3	1.0×10^3	2.0×10^2
AMP/X/DEHPA	0.5/0.5/0.5	4.5×10^3	3.2×10	1.4×10	4.6×10^2	2.2×10^2	2.6×10^2
CuFC/X/C301	0.2/0.2/0.2	2.9×10^3	4.8×10	5.6×10	2.2×10^2	5.9×10^2	8.6×10^2
CuFC/A/C301	0.2/0.2/0.2	4.9×10^3	3.9×10	2.8×10	2.0×10^2	4.8×10^2	7.7×10^2
CuFC/A/DEHPA/C301[a]	0.2/0.2/0.2/0.2	1.7×10^3	1.6×10	2.2×10	4.9×10^2	3.0×10^3	1.2×10^2
CuFC/A/DEHPA/C301[b]	0.2/0.2/0.2/0.2	2.6×10^3	2.6×10	7.0×10	7.9×10^3	4.3×10^3	4.1×10^2

[a] Prepared by using 2.5 wt% NaALG with 100-150 cP.
[b] Prepared by using 1.5 wt% NaALG with 500-600 cP.
V/m 100 cm^3/g; carrier concn. 10 ppm, [Am^{3+}]: 2.1×10^{-9} M; 25ºC; 3d.

Table V summarizes the K_d values of various metal ions for BaALG and CaALG microcapsules in the presence of 10^{-4} M HNO$_3$. The K_d values are similar to those in Table II and Table III. In the case of AMP/A/DEHPA/CaALG microcapsules, the K_d values of Sr^{2+}, Co^{2+} and trivalent metal ions tended to slightly increase with decreasing HNO$_3$ concentration. As for the HNO$_3$ concentration dependency of K_d, the microcapsules enclosing CuFC and AMP exhibited relatively large K_d values of Cs$^+$ above 10^3 cm^3/g in the presence of 10^{-1}-10^{-4} M HNO$_3$, while the K_d values of divalent and trivalent metal ions markedly decreased with increasing HNO$_3$ concentration over 10^{-2} M.

From the above results, the favorable combinations of inorganic ion-exchangers and extractant yielding relatively high K_d values are found to be CuFC/A/DEHPA/CaALG, CuFC/CP/DEHPA/CaALG and AMP/CP/DEHPA/CaALG. The improvement of the uptake of

divalent metal ions is the subject for a future study. The uptake behavior (uptake rate and characterization) for these microcapsules was further investigated in the subsequent experiments.

Table V. Distribution Coefficients of Various Metal Ions for CaALG Microcapsules
in the Presence of 10^{-4} M HNO$_3$

Microcapsules (BaALG, CaALG)	Exchanger(g)/ Extractant(g)	K_d (cm^3/g)					
		Cs$^+$	Sr^{2+}	Co^{2+}	Y^{3+}	Eu^{3+}	Am^{3+}
AMP/DEHPA[a]	0.5/0.5	1.1×10^3	2.7×10	2.4×10	8.5×10^2	3.8×10^3	1.3×10^2
AMP/A/DEHPA[b]	0.2/0.2/0.2	7.1×10	5.8×10	7.8×10	1.7×10^3	1.3×10^4	4.5×10^3
AMP/A/DEHPA	0.2/0.2/0.2	3.8×10	1.6×10^2	2.7×10	1.6×10^4	3.7×10^4	4.7×10^3
AMP/A/DEHPA	0.5/0.5/0.5	2.4×10^2	1.0×10^2	2.9×10	5.0×10^3	4.7×10^4	1.0×10^4
AMP/A/DEHPA	1.0/1.0/1.0	6.1×10^2	8.7×10	2.2×10	4.3×10^3	2.3×10^4	2.4×10^3
SM/A/DEHPA	0.2/0.2/0.2	3.7×10^3	1.5×10^2	4.7×10	2.8×10^3	6.4×10^3	2.9×10^2
CuFC/A/DEHPA	0.2/0.2/0.2	8.4×10^3	1.1×10^2	7.4×10	1.9×10^3	4.9×10^4	8.3×10^2
CP/DEHPA	0.2/0.2	1.6×10^3	1.0×10^2	2.8×10	3.1×10^4	4.3×10^3	2.3×10^3
AMP/X/DEHPA	0.2/0.2/0.2	2.9×10^2	1.0×10^2	2.6×10	2.3×10^3	2.5×10^3	5.2×10^3
AMP/IXE300/DEHPA	0.2/0.2/0.2	3.3×10^4	9.4×10	2.3×10	1.2×10^4	1.7×10^4	5.5×10^2
AMP/TiO2/DEHPA	0.2/0.2/0.2	4.5×10^3	9.3×10	2.4×10	1.7×10^4	1.4×10^4	2.2×10^2

[a]   AMP/DEHPA/BaALG microcapsule.
[b]   AMP/A/DEHPA/BaALG microcapsule.
V/m 100 cm^3/g; carrier concn. 10 ppm, [Am^{3+}]: 2.1×10^{-9} M; 25ºC; 3d.

Uptake rate

The uptake rate of Cs$^+$, Sr^{2+}, Co^{2+}, Y^{3+}, Eu^{3+} and Am^{3+} ions for the microcapsules of CuFC/A/DEHPA/CaALG, CuFC/CP/DEHPA/CaALG and AMP/CP/DEHPA/CaALG was examined at regular time intervals. **Figure 2** shows the effects of shaking time on the uptake percentage, *R* (%), of the above metal ions for CuFC/CP/DEHPA/CaALG microcapsule in the presence of 10^{-2} M HNO$_3$. The uptake of Cs$^+$, Y^{3+}, Eu^{3+} and Am^{3+} ions attained equilibrium within 1 d and relatively large *R* values above 90 % were obtained. As for Sr^{2+} and Co^{2+} ions, the *R* values were around 40 and 10 %, respectively. Similar tendency was observed for the other microcapsules.
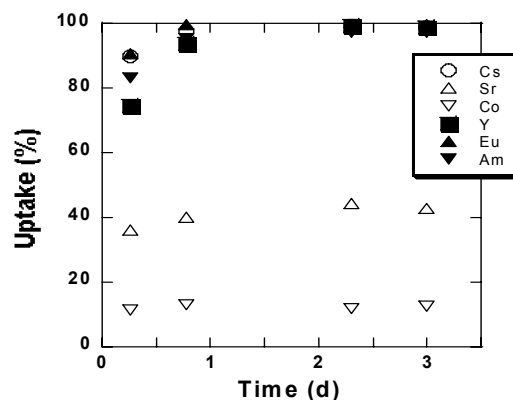

Fig. 2. Uptake rate of various metal ions for CuFC/CP/DEHPA/CaALG microcapsule in the
presence of 10^{-2} M HNO$_3$. *V/m* 100 cm^3/g; carrier concn. 10 ppm, [Am^{3+}]: 2.1×10^{-9} M; 25˚C.

EPMA Observation of Various Metal ions in Microcapsules

The granule of microcapsule was contacted with a solution containing 2×10^2 ppm Cs^+, Sr^{2+}, Co^{2+}, Y^{3+} and Eu^{3+} ions. The treated specimen was embedded in the acrylic acid resin and the cross section of microcapsule was analyzed with EPMA. Here the acrylic resin was only used for the fixation of the treated specimen for EPMA analysis.

Figure 3 shows the SEM image of the cross section of the granule of CuFC/CP/DEHPA/CaALG microcapsule. In the cross section, relatively large aggregates of CuFC crystals for size 50-200μm, small aggregates of CP and oil drops of DEHPA below 10μm are seen to be encapsulated in the granule. **Figure 4** shows the energy dispersive spectrum (EDS) for the cross section of the granule. In
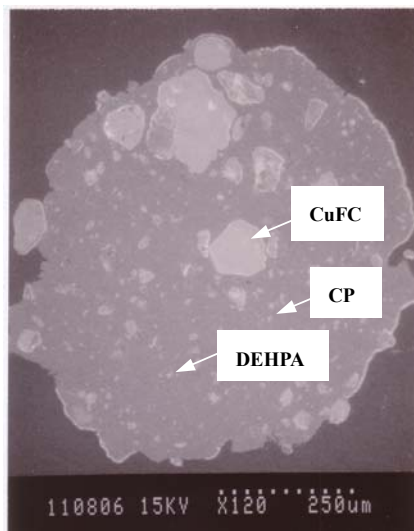

Fig. 3. SEM image of the cross section of CuFC/CP/DEHPA/CaALG microcapsule
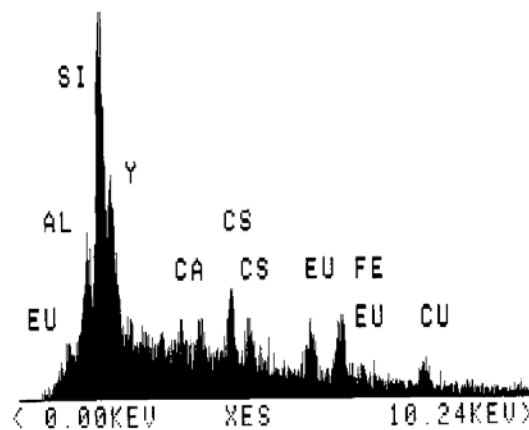

Fig. 4. EDS spectrum of metal ions adsorbed on CuFC/CP/DEHPA/CaALG microcapsule

EDS spectrum, Cu, Fe, Ca, Si and Al are the constitutional elements for CuFC, alginate and CP. The elements of Cs, Y and Eu are the metal ions adsorbed on the microcapsule. The classification of the distribution of metal ions for each material enclosed in the microcapsule was as follows:
CuFC: Cs^+; CP: Cs^+; DEHPA: Y^{3+}, Eu^{3+}; CaALG: Sr^{2+}, Y^{3+}, Eu^{3+}.

Radiation Resistance

The radiation stability of alginate polymer enclosing inorganic ion exchanger (AMP/CaALG) and extractant (DEHPA/CaALG) was examined by irradiation with a ^{60}Co-source. The absorbed dose was varied between 24–188 kGy.

Table VI summarizes the distribution coefficients of Cs^+ for AMP/CaALG after irradiation (^{60}Co-sourse) with various doses. The K_d value of Cs^+ was almost constant, irrespective of the dose, and the AMP/CaALG still exhibited a high uptake ability for Cs^+ even after irradiation of 188 kGy.

Table VI. Distribution Coefficient of Cs^+ for AMP/CaALG after Irradiation (^{60}Co-sourse) with Various Doses

Irradiation dose (kGy)	K_d (Cs^+, cm^3/g)	
	After 6.2 h-shaking	After 19 h-shaking
0	$2.3x10^4$	$7.3x10^3$
24	$4.2x10^3$	$1.5x10^4$
47	$1.3x10^3$	$3.2x10^4$
96	$2.5x10^4$	$9.8x10^4$
188	$6.9x10^3$	$2.0x10^4$

V/m 100 cm^3/g; 10 ppm Cs^+; 25°C.

Table VII summarizes the distribution coefficient of various metal ions for DEHPA/CaALG and the specimen irradiated with188 kGy. The DEHPA/CaALG microcapsule had similar K_d values of Cs^+, Sr^{2+}, Co^{2+}, Y^{3+}, Eu^{3+} and Am^{3+} ions before and after irradiation, indicating a high radiation stability.

Table VII. Distribution Coefficient of Various Metal Ions for DEHPA/CaALG and the Specimen Irradiated with188 kGy (^{60}Co-sourse)

Microcapsule	K_d (cm^3/g)					
	Cs^+	Sr^{2+}	Co^{2+}	Y^{3+}	Eu^{3+}	Am^{3+}
DEHPA-CaALG	$3.2x10$	$2.2x10$	5.7	$2.8x10^3$	$1.4x10^3$	$2.0x10^3$
Irradiated specimen	1.3	$1.6x10^2$	$1.7x10$	$2.1x10^4$	$5.2x10^3$	$8.6x10^2$

V/m 100 cm^3/g; carrier concn. 10 ppm, [Am^{3+}]: $2.1x10^{-9}$ M; 25°C; 3 d.

CONCLUSIONS

The microcapsules enclosing two kinds of functional materials, inorganic ion-exchangers and organic extractants, were well prepared by taking advantage of the high immobilization ability of alginate gel polymer. The fine powders of inorganic ion-exchanger and oil drops of extractant were kneaded with sodium alginate solution and the kneaded sol readily gelled in a salt solution of $CaCl_2$, $BaCl_2$ or HCl to form spherical particles. The uptake properties of various nuclides, ^{137}Cs, ^{85}Sr, ^{60}Co, ^{88}Y, ^{152}Eu and ^{241}Am, for thirty-four specimens of microcapsules in the presence of 10^{-1}-10^{-4} M HNO_3 were evaluated by the batch method. The distribution coefficient (K_d) of Cs^+ above 10^3 cm^3/g was obtained for the microcapsules enclosing CuFC or AMP. The K_d of Sr^{2+} around 10^2 cm^3/g was obtained for the microcapsules containing clinoptilolite, antimonic acid, zeolite A, zeolite X or titanic acid. The microcapsules enclosing DEHPA exhibited relatively large K_d values of trivalent metal cations above 10^3 cm^3/g. For example, the K_d values of Cs^+, Sr^{2+}, Co^{2+}, Y^{3+}, Eu^{3+} and Am^{3+} for a favorable microcapsule (CuFC/clinoptilolite/DEHPA/CaALG) were $1.1x10^4$, $7.5x10$, $1.1x10$, $1.0x10^4$, $1.4x10^4$, $3.4x10^3$ cm^3/g, respectively. The uptake rates of Cs^+, Y^{3+}, Eu^{3+} and Am^{3+} for this microcapsule were rather fast; the uptake percentage above 90% was obtained after 19 h-shaking and the uptake equilibrium was attained within 1 d. The AMP/CaALG exhibited high uptake ability for Cs^+ even after irradiation of 188 kGy, and DEHPA/CaALG microcapsule had similar K_d values of Cs^+, Sr^{2+}, Co^{2+}, Y^{3+}, Eu^{3+} and Am^{3+} ions before and after irradiation. The microcapsules with various shapes such as spherical, columnar, fibrous and filmy forms were easily prepared by changing the way of dipping kneaded sol into gelling salt solution. The microcapsules enclosing inorganic ion-exchangers and extractants seem to have a potential possibility for the simultaneous removal of various radioactive nuclides from waste solutions. In order to use the microcapsules as the matrix for long-term immobilization of the contaminants, a lot more testing is required (e.g., leach testing, biostability, mechanical stability, etc.) to determine their predicted behavior under disposal conditions.

ACKNOWLEDGEMENT

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