Adsorption Behavior of Cesium on Hybrid Microcapsules in Spent Fuel Solution

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Abstract

Hybrid microcapsules (H-MCs) are being developed for the column separation of Cs from high-level radioactive liquid waste (HLLW). In this paper, adsorption behavior of H-MCs has been evaluated by a batch method in single-element solution and a spent fuel solution prepared from irradiated MOX fuel. The spent fuel solution contains FPs and minor actinide (MAs), not containing U and Pu. Distribution coefficients \(K_d\) of various metal ions including Cs were determined for three types of H-MCs (AMP-SG (silica gel enclosing ammonium molybdophosphate), AMP-ALG (calcium alginate gel enclosing ammonium molybdophosphate) and AWP-ALG (calcium alginate gel enclosing ammonium tungstophosphate)) in the spent fuel solution. The three types of H-MCs exhibited higher \(K_d\)'s for Cs than those for the other elements in spent fuel solution. The difference of \(K_d\) for the specific element (Cs) and the other elements was larger than one order of magnitude. Therefore, chromatographic separation of Cs in the spent fuel solution using a column packed with H-MCs will be achieved. It was the similar tendency between the spent fuel solution and the single-element solution that the \(K_d\) value for Cs of AWP-ALG was the largest among those of three gels. Thus, the mechanism of adsorption of Cs onto these H-MCs would not be changed in the presence of FPs and MAs. Therefore, these types of H-MCs can be effective for separation of Cs in the spent fuel solutions.

Keywords: calcium alginate gel, silica gel, ammonium molybdophosphate, ammonium tungstophosphate, cesium, spent fuel

1. Introduction

All elements, except for U and Pu, will be disposed of as high-level radioactive liquid waste (HLLW) in the form of vitrified blocks in the Japanese reprocessing system presently under discussion. However, their potential toxicity of all elements except U and Pu, and the disposal cost of the vitrified blocks pose challenges. Therefore, separation of particular fission products (FPs) from HLLW is proposed as a means of reducing the potential toxicity and environmental load as well as achieving the effective use of resources\(^1\).

Cesium-137 and strontium-90 are major heat-generating nuclides present in spent fuel. Separation of heat-generating elements leads to the reduction of heat generated in a vitrified block and allows minimization of the disposal area\(^2\). The separated Cs and Sr are expected to be utilized as radiation or heat sources.

Mimura \textit{et al.}\(^3\)\textendash\(^12\) and Wu\(^13\) have proposed separation methods based on hybrid microcapsules (H-MCs). H-MCs are composed of a carrier matrix (e.g. alginate gel polymer, silica gel) and extractants (e.g. AMP (ammonium molybdophosphate), AWP (ammonium tungstophosphate), TOA (tri-octyl amine) etc.). Hybrid microcapsules are suitable for column operation because they form granular material. Specific elements can be adsorbed and separated by using column packed with H-MCs. Mimura \textit{et al.}\(^3\)\textendash\(^12\) and Wu\(^13\) have also examined the selective uptakes of Cs using three types of H-MCs (AMP-SG (Silica gel enclosing AMP), AMP-ALG (alginate gel enclosing AMP) and AWP-ALG (alginate gel enclosing AWP)) in both single-element solution and spent fuel solution. The spent fuel solution contain FPs and minor actinide (MAs), not containing U and Pu. These H-MCs will be exposed to heat and radiation in actual separation process. Thermal stability
of AMP-SG and AWP-ALG have been investigated and these
H-MCs are stable up to 300 and 190°C, respectively.5,10
Below 190°C, these H-MCs show high ability to adsorb Cs.

The design of separation procedures using a column is
based on the distribution coefficient (Kd), defined as the ratio
of the volume of aqueous phase to the weight of adsorbent.
The distribution coefficient is a pseudo-thermodynamic
parameter and it is unlikely to depend on the solid-to-solution
ratio before saturation.14 Although uptake of Cs for H-MCs in
spent fuel solution has been reported,15 Kd of various
ions for H-MCs have not been evaluated. Comparison of Kd
for each type of H-MCs in spent fuel solution has also not
been conducted. Comparison of Kd in single-element solution
has also not been conducted, although uptake and Kd of Cs for
H-MCs in single-element solution have been reported.15
Considerations about Kd in single-element solution and spent
fuel solution have also not been made.

Thus, in the present study, effects of irradiation and co-existing FPs and minor actinides (MAs) on adsorption
behavior were evaluated based on Kd. First, Kd of various
ions for AMP-SG, AMP-ALG and AWP-ALG in the spent fuel
solution were evaluated by batch method. Second, Kd of Cs
for AMP-SG, AMP-ALG and AWP-ALG were compared in
both the single-element solution and the spent fuel solution.
Finally, variation of Kd of Cs in the single-element solution
and the spent fuel solution was discussed. An outline of
the past experiments using the single-element solution is
included in the experimental section.

2. Experimental
2.1 Preparation of hybrid microcapsules
H-MCs used in the experiments are listed in Table 1. The
preparation of the H-MCs in a condition where alginate gel
was used as gel material was as follows: The sodium alginate
(NaALG) solution was kneaded with adsorbent and fully
dispersed. The well-kneaded sol was injected dropwise into
calcium nitrate (Ca(NO3)2) solution to form gel. The preparation
of the H-MCs in a condition where silica gel was used as gel
material was as follows: Dried silica gel was brought into
contact with the solution of phosphomolybdic acid hydrate
(H3Mo12O40P) under reduced pressure for several hours and
then dried. Silica gel impregnated with phosphomolybdic acid
hydrate was reacted with a solution of ammonium nitrate
(NH4NO3) to form AMP precipitates in the macropores of silica
gel. The details of the preparation method were presented
previously.5,7,9,13

Amounts of heteropoly acid (AMP or AWP) are different in
each H-MC. Maximum adsorption capacity of each H-MC are
also different. These data were shown in Table 1.

2.2 Preparation of spent fuel solution
In actual reprocessing process, FPs and MAs solution after
removing U and Pu are HLLW. In this study, spent fuel solution
as a simulant of HLLW prepared from mixed oxide (MOX)
fuel irradiated in the experimental fast reactor Joyo was used
for adsorption experiments as shown in Fig. 1. The MOX fuel
including 29.98 wt% Pu (in 8.03 wt% enriched U), namely
PFC030, was irradiated from the 9th to the 23rd cycles in
the 2nd or 3rd row of the Joyo. The effective full power days
(EFPDs) were 836.7, and the peak burnup and maximum
neutron fluence were 119 GWd/MTM and 1.78 × 1027 (n/m²)
(E ≥ 0.1 MeV), respectively.15

First, the spent fuel was dissolved using nitric acid. Next,
U and Pu were removed by an anion exchange method. Although
Kd of U(VI) for anion exchange resin in nitric acid solution
are relatively low and about 10 cm3/g,9,10,12,17,18 99% of the U
was removed from the original solution by the described
procedure. As components of cladding or fission products,
the concentrations of Fe, Sr, Zr, Mo, Cs, Ba, La, Ce, Pr, Nd
and Sm in the prepared solution were relatively high and
determined quantitatively. The concentrations of those
elements were shown in Table 2. The concentrations of
those elements including Cs were almost within the same
order of magnitude. The elemental concentration of Cs was
derived from the concentrations of Cs-137 and the Cs isotopic
composition calculated from ORIGEN2.19 Elution of much
Mo from AMP-SG and AMP-ALG, however, was confirmed
and precipitation of Zr with Mo may occur. Thus, adsorption
behaviors of Mo and Zr were evaluated only for AWP-ALG.

2.3 Determination of distribution coefficients
Methods of adsorption tests in the both single-element
solution and spent fuel solution are described below, although
Kd of Cs in single-element solution were obtained by Mimura

| Adsorbent sample | Solid supports | Amount of ion exchanger in H-MC (wt%) | Maximum adsorption amount (mmol/g) | Element | Reference |
|------------------|----------------|---------------------------------------|-----------------------------------|--------|-----------|
| AMP-SG           | Silica gel (Davisil 646) | 24 (Ammonium molybdophosphate) | 0.241 | Cs | 5) |
| AMP-ALG          | Calcium alginate | 43 (Ammonium molybdophosphate) | 0.43 | Cs | 6, 10) |
| AWP-ALG          | Calcium alginate | 52 (Ammonium tungstophosphate) | 0.34 | Cs | 7, 9, 11–13) |
Adsorption tests in spent fuel solution was conducted once, because volume of spent fuel solution was small. The adsorption of Cs from the spent fuel and single-element solutions was examined by the batch method using each type of H-MCs. Single-element (Cs) solution was obtained by diluting standard solution (1,000 mg/dm$^3$, Wako Pure Chemical Ind.). The nitric acid concentration of the experimental sample solution was adjusted to 1 or 2 mol/dm$^3$ (M). Solid-to-solution ratios were adjusted to 10 or 100 cm$^3$/g by adding sample solution and each H-MC into plastic vials or glass beakers at the prescribed amounts. After addition, the beakers were gently shaken a few times every 30 min over a period of 5 h for the experiments using spent fuel solution. When using a Lab shaker, the vials were shaken for 3, 24 or 72 h. Experimental conditions are summarized in Table 3.

The concentrations of metal ions in the supernatant were then measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin Elmer OPTIMA 3000 RL or Seiko Instruments Inc. SPS7800) and gamma-ray spectrometry. The gamma-ray spectrometry system was mainly composed of.

### Table 2 Concentrations of major elements in spent fuel solution

| Elements | Concentration (mg/dm$^3$) |
|----------|---------------------------|
| Fe       | 2.5                       |
| Sr       | 0.9                       |
| Zr       | 4.3                       |
| Mo       | 3.2                       |
| Cs$^a$   | 5.6                       |
| Nd       | 8.0                       |
| (Cs-137) | (1.3)                     |
| Sm       | 2.5                       |

$^a$ The elemental concentration of Cs was derived from the concentrations of Cs-137 and the Cs isotopic composition calculated from ORIGEN2.

### Table 3 Experimental conditions for batch adsorption tests

(a) In the spent fuel solution

| H-MC  | Solution phase | Solid-to-solution ratio (cm$^3$/g) | Time (h) | Stirring method | Temperature |
|-------|----------------|-----------------------------------|----------|-----------------|-------------|
| AMP-SG | [HNO$_3$] (mol/dm$^3$) | [Cs-137] (mg/dm$^3$) | 10 | 5 | Manual | R. T.$^a$ |
| AMP-ALG | 2 | 1.3 | 10 | 5 | Manual | R. T.$^a$ |
| AWP-ALG | 2 | 1.3 | 10 | 5 | Manual | R. T.$^a$ |

$^a$ Room Temperature

(b) In single-element solution

| H-MCs  | Solution phase | Solid-to-solution ratio (cm$^3$/g) | Time (h) | Stirring method | Temperature | Reference |
|--------|----------------|-----------------------------------|----------|-----------------|-------------|-----------|
| AMP-SG | [HNO$_3$] (mol/dm$^3$) | [Cs] (mg/dm$^3$) | 100 | 3$^a$ | Lab shaker | 25 ± 1 | 5 |
| AMP-ALG | 1 | 10 | 100 | 72$^a$ | Lab shaker | 25 ± 1 | 6, 10 |
| AWP-ALG | 1 | 10 | 100 | 24$^a$ | Lab shaker | 25 ± 1 | 9, 12, 13 |

$^a$ Equilibrium adsorption was attained.
of a multi-channel pulse height analysis system (MCA, ORTEC Model 7600-000) and a coaxial thin window type high germanium detector (ORTEC Model GMX-20P4).

The uptake percentage \( R, \% \) of each metal ion removed from the solution, distribution coefficient \( K_d, \text{cm}^3/\text{g} \) and separation factor of metal ion A to metal ion B \( \alpha_{A/B} \) are defined as:

\[
R = \frac{C_0 - C_f}{C_0} \times 100 \, \% 
\]
\[
K_d = \frac{C_0 - C_f}{C_f} \times \frac{V}{m} \, \text{cm}^3/\text{g} 
\]
\[
\alpha_{A/B} = \frac{K_{d,A}}{K_{d,B}} 
\]

where \( C_0 \) and \( C_f \) are the measured concentrations (mg/dm\(^3\)) or activities of metal ions initially and at equilibrium, respectively; \( m \) (g) is the weight of H-MCs or heteropoly acid (AMP or AWP) in the H-MCs; and \( V \) (cm\(^3\)) is the volume of the aqueous phase.

3. Results and discussion

The \( R_s \) of various elements for the three types of H-MCs (AMP-SG, AMP-ALG and AWP-ALG) are plotted in Figs. 2, 3 and 4. Distribution coefficients for metal ions including Cs are also plotted in Figs. 2, 3 and 4, because the \( K_d \) is a pseudo-thermodynamic parameter and unlikely to depend on the solid-to-solution ratio. The difference in \( K_{d,B} \) between Cs and some other ions were much clearer than the difference in \( R_s \).

The \( K_s \) of Cs for the three types of H-MCs were above 240 cm\(^3\)/g and higher than those of almost all the other elements by one order of magnitude. Alginate gel and silica gel as matrices of H-MCs can adsorb some metal cations including Fe, Zr and lanthanides\(^{11} \). Consequently, some \( K_s \) of the elements other than Cs for the H-MCs were a few dozen cm\(^3\)/g, but much lower than those of Cs. These large differences of \( K_d \) between the specific element (Cs) and the other elements make chromatographic separation of Cs possible. In future, chromatographic separation of Cs in the spent fuel solution using AMP-SG and AMP-ALG is expected to be achieved soon. Comparison of \( K_s \) of Cs for AWP-ALG, AMP-ALG and AMP-SG in the spent fuel solution and single-element solution are shown in Fig. 5. Distribution coefficients of Cs
were evaluated based on not the total weight of H-MCs, but the net weight of AMP or AWP. In the spent fuel solutions, $K_d$ for AWP-ALG was the highest. $K_{ds}$ of Cs for these types of H-MCs became smaller in the order: AWP-ALG $\approx$ AMP-ALG $\lesssim$ AMP-SG. The difference of the $K_{ds}$ between AMP-ALG and AMP-SG seems to be reflected on their amounts of heteropoly acid. However, there seems to be effect of difference of silica gels and calcium alginate. AWP-ALG has lower adsorption capacity than AMP-ALG. Therefore, higher $K_{ds}$ of AWP-ALG is thought to be reflected on the intrinsic ability of AWP.

The slight difference of the distribution coefficients between AMP-ALG and AMP-SG could have been caused by the opposite charges of the adsorbents. Zeta potentials of silica gel are positive in solutions for pH of 2 or less. The positive charge around the silica gel interfered with the adsorption of Cs$^+$ on AMP-SG. On the other hand, zeta potentials of alginate
gel are negative even in a solution of pH 1\textsuperscript{21}. The negative charge around the alginate gel did not affect the adsorption behaviors of Cs\textsuperscript{+}. Hence, \( K_d \) of Cs on AMP-ALG could have been larger than that on AMP-SG. Zeta potentials of silica gel are derived from adsorbed water on the surface of the silica gel. Since radiation causes radiolysis of water\textsuperscript{22}, difference of zeta potential between AMP-ALG and AMP-SG could have become larger by radiation. However, under the experimental conditions with the spent fuel solution, zeta potential did not seem to be affected by radiation because the relation of \( K_d \) of Cs for AMP-ALG and AMP-SG was not changed.

The slight difference in uptake ability toward Cs between AWP and AMP appeared to be caused by the slight difference of lattice constants of their secondary structures. After completing the ion exchanges between Cs\textsuperscript{+} and NH\textsubscript{4}\textsuperscript{+}, AMP and AWP form cesium molybdophosphate (CsMP) and cesium tungstophosphate (CsWP), respectively. Secondary structures of AMP, CsMP, AWP and CsWP are all cubic structures. The change of lattice constants accompanying ion exchange reactions in AWP is slightly smaller than that of AMP\textsuperscript{23,24}. Thus, the free energy (\( \Delta G^\circ \)) of the ion exchange (NH\textsubscript{4}\textsuperscript{+} ↔ Cs\textsuperscript{+}) for AWP is −13.2 kJ/mol and more negative than that for AMP (−9.7 kJ/mol)\textsuperscript{6,7}. For these reasons, Cs\textsuperscript{+} was likely to be adsorbed in the order of AWP-ALG, AMP-ALG and AMP-SG. Although some heteropolyanions (phosphomolybdic acid, [\( H_3\text{PMo}_{12}\text{O}_{40} \]) were reported to be reduced by radiation and converted to another heteropolyanion, [\( H_2\text{PMo}_{12}\text{O}_{40} \])\textsuperscript{25}, obvious structural changes including variation of lattice constants of AMP and AWP might not have occurred under the experimental conditions with the spent fuel solution because the relation of \( K_{s} \) of Cs for AWP-ALG and AMP-ALG was not changed.

While, in the single element solution obtained by Mimura \textit{et al.}\textsuperscript{5,6,9,10,12} and Wu\textsuperscript{13}, \( K_{s} \) for AWP-ALG was the highest. \( K_{s} \) of Cs for these types of H-MCs became smaller in the order: AWP-ALG > AMP-ALG > AMP-SG. In the single element solution, there are slight difference of adsorption amount of Cs between AMP-SG and AMP-ALG. Because other metal ions in the solution were absent, adsorption amount of Cs was thought to be same value to the amount of AMP in H-MCs (24 wt\% in AMP-SG and 43 wt\% in AMP-ALG). Therefore, the difference were affected by the adsorption to alginate gel. H-MCs containing much amount of alginate gel was thought to adsorb Cs (mono-valent cation).

In the spent fuel solutions, adsorption amount of Cs are same to AMP-SG and AMP-ALG. Because alginate gel can adsorb various metal cation in the spent fuel solutions, adsorbability of alginate gel to Cs was diminished.

Amount of rare earth elements to H-MCs were in the order of AWP-ALG > AMP-ALG > AMP-SG. Separation factor based on Cs were shown in Fig. 6. Separation factor of rare earth elements were in the same order among these H-MCs. These H-MCs have similar ability to selective separation of Cs.

Although the batch method experiments in the single-element solution were conducted until equilibrium was attained, shaking time in the spent fuel solutions was limited to 5 h. Furthermore, the stirring method in the experiments with spent fuel solution was less vigorous than that with single-element solution. Those differences were due to the handling of radioactive materials. Hence, difference of \( K_{s} \) values between the spent fuel solution and the single-element solution occurred. However, it was the similar tendency between both solutions that the \( K_{s} \) value of AWP-ALG was the largest among those of three gels. When the equilibriums are attained in the spent fuel solution, \( K_{s} \) of Cs for these types of H-MCs will further increase over 1000 cm\( ^3 \)g\textsuperscript{−1}. Therefore, these types of H-MCs can be effective for separation of Cs in the spent fuel solutions.

4. Conclusion

The \( K_{s} \)s of various metal ion including Cs for three types of H-MCs (AMP-SG, AMP-ALG and AWP-ALG) were evaluated based on batch adsorption test in the spent fuel solution. The three types of H-MCs exhibited higher \( K_{s} \)s for Cs than those for the other elements in spent fuel solution. The difference of \( K_{s} \) for the specific element (Cs) and the other elements was larger than one order of magnitude. Therefore, chromatographic separation of Cs in the spent fuel solution using a column packed with H-MCs will be achieved. Distribution coefficients of Cs for the three types of H-MCs were compared. The \( K_{s} \) became smaller in the order: AWP-ALG > AMP-ALG ≥ AMP-SG. Distribution coefficients of Cs in the spent fuel solution and the single-element solution were compared and effects of radiation, FPs and MAs were considered. It was the similar tendency between the spent fuel solution and the single-element solution that the \( K_{s} \) value for Cs of AWP-ALG was the largest among those of three gels. Thus, the mechanism of adsorption of Cs onto these H-MCs would not be changed in the presence of FPs and MAs. Therefore, these types of H-MCs can be effective for separation of Cs in the spent fuel solutions. As future work, design of Cs separation process from HLLW using column packed with H-MCs will be planed, considering the temperature inside the column, because Cs-137 is major heat source in HLLW.

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