PYROCHEMICAL PARTITIONING
OF ACTINIDES AND FISSION PRODUCTS
IN A MOLTEN CHLORIDE/LIQUID CADMIUM SYSTEM

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ABSTRACT

The distribution behaviours of actinides and fission products in a molten chloride/liquid cadmium system have been investigated in support of the development of a pyrochemical group partitioning process. The different distribution behaviours due to different group elements were clearly observed, indicating that the group partitioning is essentially feasible. However, the actinide and lanthanide elements were found to be less soluble in the cadmium phase and to form their solid intermetallics on reduction. A reductive extraction process combined with filtration of such intermetallics is proposed on the basis of the observations.

INTRODUCTION

Molten salts and liquid metals are highly radiation resistant and serve as high-density fluids at elevated temperatures. The use of these fluids makes it possible to develop the more compact processes and to decrease the amount of low-level radioactive wastes. The pyrochemical separation systems of these fluids are thus considered to be much useful for future nuclear engineering. A number of applications have been proposed and some of them are now being developed for the reprocessing of nuclear reactor fuels (1,2) and for the group partitioning of radioactive wastes (3,4).

In the present study, the distribution behaviours of actinides and fission products in a molten chloride/liquid cadmium system have been investigated in support of the development of a pyrochemical partitioning process. The results are analyzed by comparing with a theoretical prediction (5) and the feasibility of group partitioning of radioactive wastes is discussed on the basis of the distribution behaviours observed. The results obtained in the present study will also be important for the reprocessing of fast breeder metallic fuels (1,2).
EXPERIMENTAL

All the reagents were of reagent grade obtained from Nacalai Tesque, Co. The LiCl-KCl mixture of 50 mole% LiCl was prepared by melting the known amounts of LiCl and KCl. The reductant Li was prepared in the form of a Li-Cd alloy (25 mole% Li) to make the addition into the Cd phase easy. The radioactive tracers of Np-239, Pa-233, La-140, Ce-143, Eu-152m, Pd-109 and Zr-97 were produced by thermal neutron irradiation of U, Th, La, Ce, Eu, Pd and Zr metals, respectively, in Kyoto University Research Reactor. Non-irradiated metals were also used as solutes in some runs.

The experimental apparatus and general procedures employed in this study are much the same as in the previous ones for the salt/Bi systems (6-8). In a typical experiment, 1 mol of the LiCl-KCl, 2 mol of Cd metal and small amounts (less than 100 mg each) of the solute elements were loaded in a graphite crucible and dried by vacuum at 450 K in the extraction vessel of stainless steel. The system was then heated under an inert-atmosphere. In order to ensure the purification of the system, a H2-10 vol% HCl gas was bubbled for about 10 hours in some runs.

The distribution of the solutes was controlled by the incremental addition of the Li-Cd alloy to the system. After some equilibrations, the samples were taken out from each phase with a stainless steel sampling tube under a reduced pressure. The concentrations of the radioactive solutes were measured by direct Y-spectroscopy, and those of the reductant Li in the Cd phase and of non-radioactive solutes were determined by atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

1. Mechanism of equilibrium distributions

Fig. 1 shows a typical result of the measurement of distribution coefficients. The distribution coefficients are defined as

$$D_M = \frac{A_M(Cd)}{A_M(salt)} \quad (1)$$

$$D_{Li} = \frac{X_{Li(Cd)}}{X_{LiCl(salt)}} \quad (2)$$

where $A_M$ is the molar radioactivity of the element M, $X_{Li}$ and $X_{LiCl}$ are the mole fractions of Li and LiCl, respectively, and the subscripts (Cd) and (salt) denote the Cd phase and the salt phase, respectively. Fig. 1 also shows the distribution coefficients which are predicted with a thermodynamic model (5) by taking the reaction mechanism:
where $\text{Li}_{m-n} \text{MC}l_m + n \text{Li} + x \text{Cd} = \text{MC}d_x + m \text{LiCl}$

$$\text{(3)}$$

The similar mechanisms have well been established in the salt/Bi systems by observing the effects of salt and metal compositions on the equilibrium distributions (6-8). According to the model, the extractability $D_M^0/D_{Li}^0$ of each element is represented by

$$\log(D_M^0/D_{Li}^0) = -(2.3RT)^{-1}\left[ \Delta G_f(\text{MA}) + m \Delta G_f(\text{LiX}) - \Delta G_f(\text{Li}_{m-n} \text{MX}_m) \right]$$

$$+ x \log \chi_A - (m-n) \log \chi_{\text{LiX}} - \log \gamma_{\text{MA}} - m \log \gamma_{\text{LiX}}$$

$$+ \log \gamma_{\text{Li}_{m-n} \text{MX}_m} + n \log \gamma_{\text{Li}^0} + x \log \gamma_A$$

$$\text{(4)}$$

The terms in the right hand side in Eq. (4) are constant at a given temperature and composition and then the logarithm of $D_M^0$ is proportional to that of $D_{Li}^0$ with a slope of $n$. The thermodynamic data in Eq. (4) are taken from the literatures and estimated theoretically (5). Fairly good agreements between the experimental and predicted values are observed for lanthanide elements. The above mechanism is thus supported. However significant disagreements are found for actinides.

2. Effect of intermetallic compounds on equilibrium distributions

In order to know the behaviour of actinides, a careful measurement was made with uranium as a solute. The changes of uranium concentration in both phases with time are shown in Fig. 2 and the distribution coefficient is plotted in Fig. 3. Fig. 2 indicates that the uranium concentration in the salt phase rapidly decreases with the addition of reductant but that the concentration in the Cd phase does not increase so rapid. This suggests that most of the reduced uranium forms another phase in the system.

After the melt was frozen, the interface layer between both phases was inspected and the presence of a solid intermetallic compound, possibly $\text{UC}_{9}$, was inferred by a chemical analysis. The reduced uranium seems to remain at the interface as the solid intermetallics rather than to be dissolved into the Cd phase. Since a much higher solubility has been reported of uranium in liquid cadmium (9), this may be due to a very slow kinetics of dissolution of the compound or to an entrainment effect in the salt phase. A similar phenomenon has been observed in the salt/Bi system although the formation of solid intermetallics for a few hours is only temporary in that case (8). The distribution coefficient of uranium in Fig. 3 seems to be lowered by the entrainment of the solid intermetallics in the salt phase. The disagreements observed for the actinide elements in Fig. 1 can similarly be explained.
3. Systematics of equilibrium distributions

For applications, it is important to know some regularities in the equilibrium distributions. Fig. 4 shows the temperature dependences of the $D_{M}/D_{Li}^{n}$ value for each element. The values have been evaluated in several measurements for the species homogeneously dissolved into both phases. The datum of Nd is taken from the literature (10). All the $D_{M}/D_{Li}^{n}$ values decrease with the increasing temperature.

Fig. 5 shows the atomic number dependence of the normalized extractability, $(D_{M}/D_{Li}^{n})^{1/n}$, which are calculated from the experimental data in a LiF-BeF$_2$/Bi system (6,8,11). The analysis of this type is very useful not only to discuss the systematics of extractability but also to estimate the unknown $(D_{M}/D_{Li}^{n})^{1/n}$ values. Some regularities, possibly due to the f-electrons, can be seen for the actinide and lanthanide elements; it is interesting to note that such a tetradeffect(12) is observed for the actinide elements in Fig. 5. The data for the present system of LiCl-KCl/Cd are plotted in Fig. 6 and the similar regularities can be expected. As seen in Figs. 5 and 6, the extractabilities of the actinide elements are systematically different from and higher than those of the lanthanide. This supports the partitioning of both group elements in liquid-liquid extraction systems.

4. Group partitioning process

Fig. 7 shows the fractional distributions of typical solute elements in the molten LiCl-KCl, liquid Cd, and intermetallic compound phases. Palladium is always found in the Cd phase and cesium and strontium are in the salt phase. In the studied range, on the other hand, the distributions of actinide and lanthanide elements are much sensitive to the lithium concentration in the Cd phase, which is a measure of the redox potential of the system. In the case of the lower lithium concentration of $5 \times 10^{-4}$, most of uranium was reduced to form the intermetallic compound phase while only a part of lanthanum was reduced. At the higher lithium concentration of $9 \times 10^{-3}$, on the other hand, almost all of the lanthanide elements were reduced into the intermetallic compound phase. The actinide elements are reduced more easily than the lanthanide and most of both group elements seems to form their solid intermetallics on reduction.

In the present system, the actinide and lanthanide elements seem to be less soluble into the Cd phase and to form their solid intermetallics on reduction. The intermetallics would be dispersed into the salt phase, or sometimes into the metal phase, and then the recovery yields and separation/decontamination factors might be affected. This might be a problem for the development of the liquid-liquid extraction systems. In order to improve the situation, for example, it is suggested to combine the reductive extraction process with the
filtration of solid intermetallics as shown in Fig. 8. Sufficiently high separation factors may be achieved in such a combined process although those factors are much dependent on the efficiency of filtration.

CONCLUSIONS

The following conclusions can be drawn on the feasibility of the present pyrochemical separation system:

(1) Different distribution behaviours due to different group elements were clearly shown. The reduction of metal chlorides occurs in the order of platinum group elements, actinides, lanthanides, and strontium and cesium. The group partitioning in the system is thus essentially feasible.

(2) The actinide and lanthanide elements were less soluble in the Cd phase and remained at the interface as solid intermetallics on reduction. When the system is used for a liquid-liquid extraction, the recovery yields and separation/decontamination factors will be affected by the intermetallics.

(3) The performance might be improved significantly by combining the extraction process with the filtration of the solid intermetallics. Sufficiently high separation factors are expected in this case from the present distribution data.

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Fig. 1. Distribution coefficient of some typical elements in the LiCl-KCl/Cd system at 873K. Marks are experimental and curves are predicted (5).

Fig. 2. Changes of uranium concentration in molten LiCl-KCl and liquid Cd phases at 840K.
Fig. 3. Distribution coefficient of uranium in the LiCl-KCl/Cd system at 840K. Marks are experimental and curve is predicted (5).

Fig. 4. Temperature dependence of equilibrium distributions in LiCl-KCl/Cd system. Open marks are of the present study and closed is from the literature (10).

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Fig. 5. Atomic number dependence of equilibrium distributions in LiF-BeF₂/Bi system at 873K. Marks are taken from the literatures (6, 8, 11).

Fig. 6. Atomic number dependence of equilibrium distributions in LiCl-KCl/Cd system at 873K. Marks are taken from Fig. 4 and curves are for LiF-BeF₂/Bi system.
Fig. 7. Fractional distributions of typical solute elements among LiCl-KCl, Cd and intermetallic compound phases.
Fig. 8. A reductive extraction process combined with filtration of solid intermetallic compounds. PGM: platinum group elements; An: actinides; Ln: lanthanides.