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Reductive extraction kinetics of actinide and lanthanide elements in molten chloride and liquid cadmium system

H. Moriyama [a,*], D. Yamada [a], K. Moritani [a], T. Sasaki [a], I. Takagi [a],
K. Kinoshita [b], H. Yamana [c]

[a] *Department of Nuclear Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan*
[b] *Central Research Institute of Electric Power Industry, Tokyo 201-8511, Japan*
[c] *Research Reactor Institute, Kyoto University, Osaka 590-0494, Japan*

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Abstract

For the development of reductive extraction process, the rate of extraction of actinide and lanthanide elements was measured in a two-phase system of molten LiCl–KCl eutectic salt and liquid cadmium at 723–873 K. The mass transfer coefficient of the elements was evaluated by applying a film theory. The obtained mass transfer coefficients were found to be as high as expected in the present system. In some cases, however, it was found that the rate of reductive extraction was affected possibly by the solubility of the solute elements in the metal phase.

Keywords: Reductive extraction; Actinide; Lanthanide; Chloride; Cadmium

1. Introduction

In recent years, there has been a renewed interest for new nuclear fuel cycles or new nuclear waste management strategies. This is mainly for efficient transmutation of long-lived radionuclides such as transuranic elements (TRUs) in order to minimize the radiological toxicity of nuclear wastes. A number of the studies on the partitioning and transmutation of nuclear wastes are thus being performed in several countries.

Reductive extraction process which has originally been developed for reprocessing molten salt reactor fuels is expected to be much useful for the separation and recovery of TRUs, as seen in a proposed pyrometallurgical partitioning method [1,2]. In this method, which uses molten salt and liquid metal as solvents, a reductive extraction process is combined with an electrochemical process for the recovery of U and TRUs from high level radioactive waste (HLW). Because of the high radiation resistance of the solvents, it is expected to reduce the quantity of the radioactive secondary waste and to downscale the size of requisite processing equipment. In spite of the importance from a practical point of view, however, little is still known on the kinetics of the process.

In the case of molten salt breeder reactor (MSBR), for example, a mechanically agitated two-phase extractor system was suggested in which the intermediate product of Pa-233 and the neutron poisons of rare earth fission products were removed from the fuel salt into liquid bismuth [3,4]. However, a critical problem was recognized for the kinetics in which the overall mass transfer coefficients were much lower than would be expected and any meaningful correlations were hardly observed between the overall mass transfer coefficient and the agitation speed [5]. In our previous study on this problem [6], the rate of reductive extraction of actinide and lanthanide elements was measured in the two-phase system of molten fluoride salt and liquid bismuth. Following the addition of the reductant, it was observed that the rate of transfer of solute elements into the bismuth phase was much slower

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[*] Corresponding author.
E-mail address: moriyama@nucleng.kyoto-u.ac.jp (H. Moriyama).

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than the rate of stripping from the salt phase. The formation of bismuthides of solute elements at the interface was inferred from the observation in this case. It is, thus, important to know its consequence on the performance of the extractor system.

Similarly to the previous one [6], the present study deals with the kinetic aspects of reductive extraction in another system. The rate of reductive extraction of actinide and lanthanide elements was measured in a two-phase system of molten LiCl–KCl eutectic salt and liquid cadmium at 723–873 K. The mass transfer coefficients are obtained and the extraction kinetics is discussed.

2. Experimental

The systems studied are shown in Table 1. The LiCl–KCl eutectic (Li:K = 59:41 in mole) and $CdCl_2$ were purchased from Anderson Physics Laboratory, rare earth metals and zirconium metal were from Furuuchi Chemical Co., thorium metal from Reactor Experiments Inc., and all other reagents were from Nacalai Tesque. The radioactive tracers were produced by neutron irradiation of metallic specimens. Using high-purity reagents, all experiments were performed in a glove box with argon atmosphere containing <0.5 ppm of O_2 and <0.2 ppm of H_2O.

The measurement of the rate of reductive extraction was performed in the same manner as for the $LiF–BeF_2$ and Bi system [6]. Together with radioactive tracers, cadmium metal, which were purified by the eutectic melt, and another eutectic salt were loaded in an alumina crucible, and were melted at a given temperature. The contact area of the two-phases was around 10 cm^2. In order to assure a complete dissolution of every solute in the salt phase, $CdCl_2$ was added to the system prior to reductive extraction. Then the extraction of the solutes from the salt phase into the metal phase was started by the addition of the reductant lithium in the form of a Li–Cd alloy. In some measurements, the inert gas was used for stirring the system with a rate of a few cm^3/s during the extraction. A small amount of the samples was taken out from each phase at fixed time intervals and subjected to the analysis. The concentration of the radioactive solutes was measured by direct γ-ray spectroscopy, and that of the reductant lithium by atomic absorption spectrophotometry.

3. Results and discussion

3.1. Mass balance

According to our previous study [7], the mechanism of the equilibrium distributions in the molten LiCl–KCl eutectic salt and liquid cadmium system is generally expressed as:

$$\mathrm{Li}_{m-n}\mathrm{MCl}_m + n\mathrm{Li} + i\mathrm{Cd} = \mathrm{MCd}_i + m\mathrm{LiCl} \quad (1)$$

where $Li_{m-n}MCl_m$ is the complex compound of the solute element M formed in the salt phase, MCd_i is the intermetallic compound in the cadmium phase. As shown in reaction (1), the solute element M in the form of $Li_{m-n}MCl_m$ is reduced by the reductant Li and transferred from the salt phase into the cadmium phase.

Fig. 1(a and b) show typical results of the measurements, in which the amounts of radioactive tracers in the two-phases are plotted as a function of time after the addition of the reductant. In some of the measurements, it has been observed that the rate of transfer of solutes into the cadmium phase is not equal to the rate of stripping from the salt phase, and that the mass balance in both phases is broken for several minutes after the addition of reductant. Thus, the formation of some intermetallic compounds may be inferred as observed in the $LiF–BeF_2$ and Bi system [6]. In the previous case, the formation of bismuthides of solute elements has been observed at the interface between both phases and the following reaction mechanism has been suggested:

$$\mathrm{Li}_{m-n}\mathrm{MF}_m(\mathrm{salt}) + n\mathrm{Li(Bi)} + y\mathrm{Bi(Bi)} \rightarrow \mathrm{MBi}_y(\mathrm{interface}) + m\mathrm{LiF(salt)} \quad (2)$$

$$\mathrm{MBi}_y(\mathrm{interface}) + (x-y)\mathrm{Bi(Bi)} \rightarrow \mathrm{MBi}_x(\mathrm{Bi}) \quad (3)$$

A similar reaction mechanism is thus considered to hold in the present system. According to the solubility data [8], in fact, some of solute elements such as zirconium seem not to be so highly soluble in the cadmium phase.

3.2. Extraction kinetics

By considering the above observation, two components are taken into account in the analysis of the present results, of which one is of a rapid transfer with no formation of any

Table 1
Experimental conditions

Run number	Temperature (K)	Stirring flow rate (cm^3/s)	Solvent weight (g)		Solute weight (mg)			
			LiCl–KCl	Cd	Zr	La	Ce	Th
1	773	–	50.2	100.9	56	11	16	10
2	773	–	48.5	93.6	Same as above			
3	873	3	49.9	96.8	100	10	10	10
4	723	3	46.8	93.4	Same as above			
5	773	3	50.4	101.5	98	11	12	9
6	823	3	49.6	93.1	Same as above			

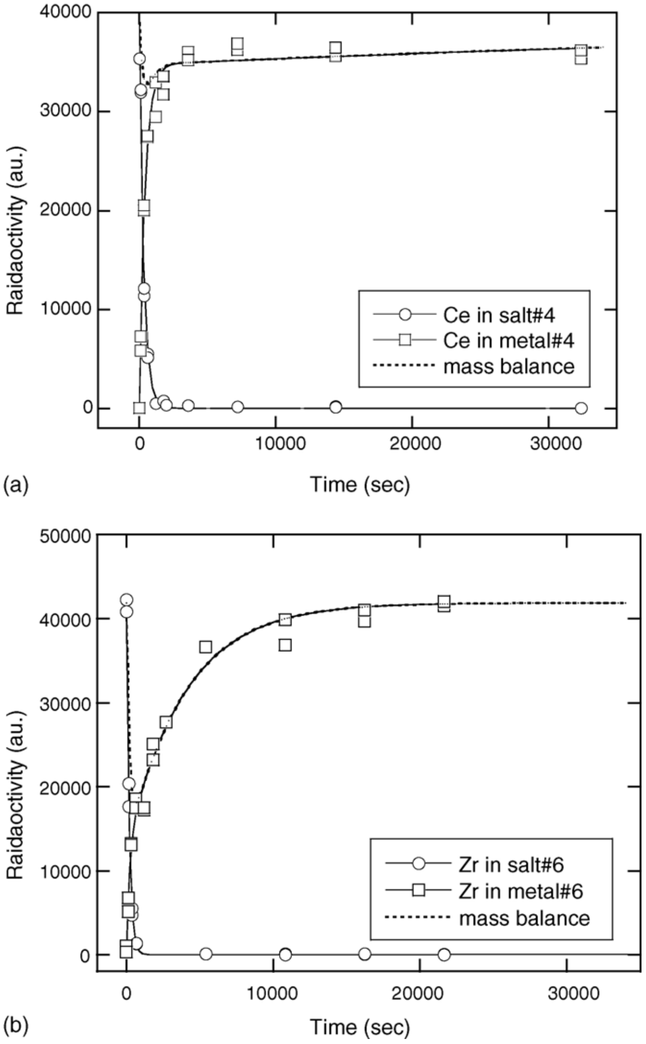

Fig. 1. Rate of reductive extraction from molten LiCl–KCl into liquid Cd with stirring: (a) cerium at 723 K and (b) zirconium at 823 K. Curves denote the best fits of the experimental data to eqs. (4) and (5).

intermetallic compounds and the other of a slow transfer with the formation of some intermetallic compounds. Taking a film theory and following our previous study [6], the equations of extraction kinetics are given by

$$C_{\mathrm{M(Salt)}} = \overline{C}_{\mathrm{M(Salt)}}\left[1-\exp\left(\frac{AK_{\mathrm{M(Salt)}}}{V_{\mathrm{Salt}}}t\right)\right] \tag{4}$$

$$C_{\mathrm{M(Cd)}} = \overline{C}_{\mathrm{M(Cd)}}\left[1-\exp\left(\frac{AK_{\mathrm{M(Cd)}}}{V_{\mathrm{Cd}}}t\right)\right] + \overline{C}'_{\mathrm{M(Cd)}}\left[1-\exp\left(\frac{AK'_{\mathrm{M(Cd)}}}{V_{\mathrm{Cd}}}t\right)\right] \tag{5}$$

where $K_{\mathrm{M(Salt)}}$, $K_{\mathrm{M(Cd)}}$ and $K'_{\mathrm{M(Cd)}}$ are the mass transfer coefficients of the element M in each phase, $C_{\mathrm{M(Salt)}}$ and $C_{\mathrm{M(Cd)}}$ the bulk concentrations, $\overline{C}_{\mathrm{M(Salt)}}$, $\overline{C}_{\mathrm{M(Cd)}}$ and $\overline{C}'_{\mathrm{M(Cd)}}$ the equilibrium concentrations, A the contact area, and V_{Salt} and V_{Cd} the volumes. The first and second terms in the right hand side of eq. (5) represent the two components of rapid and slow transfers into the Cd phase. In the present analysis, it has been assumed that the reaction itself is much faster than the mass transfer. Obtained results are summarized in Table 2 and the curves in Fig. 1 represent the best fit of the experimental data to eqs. (4) and (5).

Table 2
Mass transfer coefficients

Solute M	$K_{\mathrm{M}} = A\exp(-E/RT)$		K_{M} at 723 K (cm/s)
	log A (cm/s)	E (kJ/mol)	
Salt-side			
Zr	0.21 ± 0.36	30.3 ± 5.5	1.0×10^{-2}
La	-1.15 ± 0.17	11.8 ± 2.6	9.9×10^{-3}
Ce	-0.79 ± 0.34	16.9 ± 5.1	9.7×10^{-3}
Pa	0.02 ± 0.31	27.7 ± 4.7	1.0×10^{-2}
Metal-side (fast)			
Zr	-0.12 ± 0.49	33.3 ± 7.5	3.0×10^{-3}
La	-1.02 ± 0.62	21.1 ± 9.4	2.8×10^{-3}
Ce	-0.91 ± 0.63	22.4 ± 9.5	3.0×10^{-3}
Pa	-0.20 ± 0.77	31.3 ± 11.7	3.4×10^{-3}
Metal-side (slow)			
Zr	-0.11 ± 1.79	57.4 ± 27.2	5.5×10^{-5}
La	2.92 ± 1.06	108.2 ± 16.1	1.3×10^{-5}
Ce	3.31 ± 0.98	111.0 ± 14.9	1.9×10^{-5}
Pa	0.66 ± 1.03	66.3 ± 15.1	7.4×10^{-5}

3.3. *Mass transfer coefficients*

In the measurements, it was found that the rate of reductive extraction is much sensitive to stirring by argon gas and that the rate of extraction with stirring is much higher than that with no stirring. With stirring (run number 3–6), the evaluated mass transfer coefficients are found to be in the order of 10^{-2} cm/s in the salt phase, as shown in Fig. 2. These values are much higher than those in the LiF–BeF$_2$ and Bi system [6]. This difference may be explained by considering the difference in solvent viscosity.

By using the Stokes–Einstein equation for the diffusion coefficient, the experimental data can be fitted to the following equation:

$$K \propto D^n \propto \left(\frac{T}{\mu}\right)^n \tag{6}$$

where D is the diffusion coefficient, T the temperature and μ is the solvent viscosity. By taking the literature values for μ [9,10], it is found that the salt-side mass transfer coefficient is proportional to the diffusion coefficient with an exponent of 0.5–1.0, as suggested by Higbie's model [11] and Whitman's model [12].

Some differences may be found in the mass transfer coefficients of different solute elements. It can be seen in Fig. 2 that the values of the mass transfer coefficients for tetravalent Zr and Pa are rather larger than those for the others of lower valence. This trend is well consistent with the observations in the electrolysis experiments, in which the mass transfer coef-

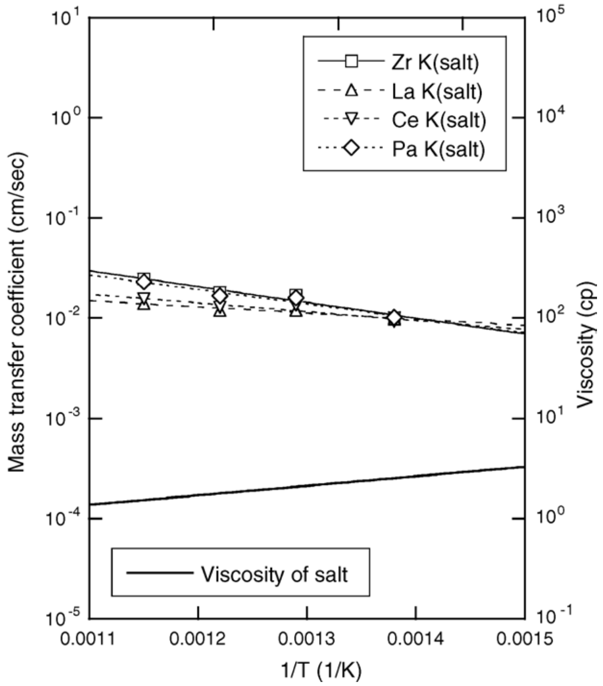

Fig. 2. Arrhenius plots of mass transfer coefficients in molten LiCl–KCl phase. Bold line denotes the viscosity of molten LiCl–KCl [5] and other lines the best fits of the experimental data to Arrhenius type equations.

ficients increase with the increasing ionic charge of solute elements [13]. However, a reverse trend has been reported in the LiF–BeF$_2$ and Bi system in which the mass transfer coefficients increase with the decreasing ionic charge of solute elements [6]. It is interesting to understand different trends in different salts, for example, by measuring and comparing the diffusion coefficients of solute elements in both salts.

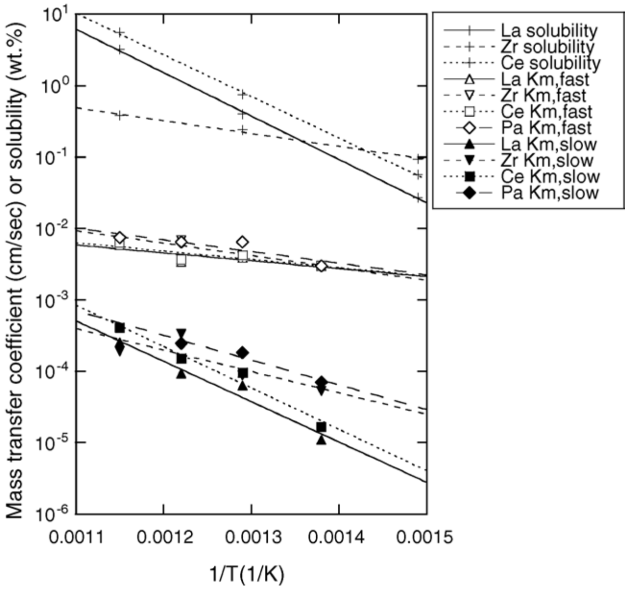

Fig. 3. Arrhenius plots of mass transfer coefficients and solubility data [8] in liquid Cd phase. Lines denote the best fits of the experimental data to Arrhenius type equations.

Fig. 3 shows the mass transfer coefficients of the two components of rapid and slow mass transfers in the Cd phase, together with the solubility data [8]. It may be found that the mass transfer coefficients of rapid components are much faster than those of slow components. In the case of rapid components, the temperature dependence seems to be described well by eq. (6), similarly to the case of the salt-side mass transfer coefficients. Thus, no effect of any intermetallic compounds is considered in this case. In the case of slow components, on the other hand, the temperature dependence may be compared with that of the solubility data as shown in Fig. 3. Very similar temperature dependences are observed between the mass transfer coefficients and the solubility data, suggesting the effect of the formation of some intermetallic compounds. It is, thus, important to study and reduce this effect for further development of the extraction system.

4. Conclusions

The rate of reductive extraction of actinide and lanthanide elements was measured in a two-phase system of molten LiCl–KCl eutectic salt and liquid cadmium at 723–873 K. The mass transfer coefficient of the solute elements which was evaluated by applying a film theory were found to be as high as expected in the present system. In some cases, however, it was found that the rate of reductive extraction was affected possibly by such low soluble solute elements as zirconium in the metal phase. Further studies are needed to understand the effect of low soluble elements and to improve the mass balance.

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