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Distribution of actinides in molten chloride salt/cadmium metal systems

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Abstract

The equilibrium concentrations of uranium, neptunium, plutonium, americium and curium between molten chloride salts and cadmium at 773 K have been measured by several researchers who are developing fuel recovery processes for the Integral Fast Reactor. The data were statistically analyzed based on a thermodynamic relationship between the distribution coefficient of any transuranic (TRU) element and the uranium coefficient. The TRU coefficients were found to be directly proportional to the uranium coefficient over wide ranges of actinide concentrations in the salt and metal phases. For salts containing large fractions of LiCl and KCl, the proportionality factors, or separation factors relative to uranium, at 773 K were: neptunium, 2.1; plutonium, 1.9; americium, 3.1; curium, 3.5.

1. Introduction

The Integral Fast Reactor (IFR) is being developed at Argonne National Laboratory as one of the Department of Energy's advanced power reactors. This reactor has a closed fuel cycle in which processes employing liquid chloride salts and cadmium are used to recover actinides from spent fuel [1, 2]. In the course of experiments to develop these processes, a large body of data on the equilibrium concentrations of actinides in chloride salt/cadmium metal systems at about 773 K has been collected. Information on the concentrations of cerium and neodymium was also obtained, but more accurate relationships among the rare earths are being obtained by Ackerman and Settle [3].

2. Thermodynamic background

In a liquid chloride salt/cadmium metal system, equilibrium among the elements is achieved by redox reactions between cations in the salt and metal atoms in the cadmium. As discussed by Ackerman [2] and Ackerman and Settle [3], the equilibrium among several trivalent cations can be represented by a series of exchange reactions between any pair of elements, *e.g.*

$$UCl_3 + Pu = U + PuCl_3 \qquad (1)$$

The equilibrium constant K_e for this reaction is

$$K_e = \frac{[U][PuCl_3]}{[UCl_3][Pu]} = \exp\left(\frac{-[\Delta G^\circ(PuCl_3) - \Delta G^\circ(UCl_3)]}{RT}\right) \qquad (2)$$

where [U] is the activity of uranium in the cadmium phase, $[UCl_3]$ is the activity of UCl_3 in the salt phase, ΔG° is the standard free energy of formation, R is the gas constant and T is the temperature. This leads to the following expression for the separation factor:

$$SF_{Pu} = \frac{D_{Pu}}{D_U} = K_e\left(\frac{\gamma_{Pu}\gamma_{UCl_3}}{\gamma_{PuCl_3}\gamma_U}\right) \qquad (3)$$

where γ is the activity coefficient, equal to (activity)/(mole fraction metal cations or metal atoms), and D is the distribution coefficient, equal to (mol fraction in salt)/(atom fraction in metal).

The term in large parentheses on the right-hand side of eqn. (3) is a constant if the activity coefficients in the salt and metal phases are constant over the concentration ranges of interest. Similar expressions can be written between any other pair of elements that form trivalent chlorides. This results in the following equation relating distribution coefficients of trivalent elements:

$$D_U = \frac{D_{Pu}}{SF_{Pu}} = \frac{D_{Np}}{SF_{Np}} = \frac{D_{Am}}{SF_{Am}} = \frac{D_{Cm}}{SF_{Cm}}$$

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$$= \frac{D_{Ce}}{SF_{Ce}} = \frac{D_{Nd}}{SF_{Nd}} = \dots \qquad (4)$$

where the separation factors are relative to uranium. The choice of uranium as the reference element is arbitrary; any trivalent element could be used. This relationship illustrates that the distribution coefficients of all trivalent elements in a salt/metal system are determined once the distribution of one element is specified.

This approach can also be used to relate the distribution coefficient of any element that forms cations of any valence in the chloride salt to the uranium coefficient. In general,

$$3M + nUCl_3 = 3MCl_n + nU \qquad (5)$$

$$K_e = \left(\frac{[MCl_n]}{[M]}\right)^3 \left(\frac{[U]}{[UCl_3]}\right)^n \qquad (6)$$

and

$$SF_M = \frac{D_M}{D_U} = (K_e)^{1/3}(D_U)^{(n-3)/3}\left(\frac{\gamma_M}{\gamma_{MCl_n}}\right)\left(\frac{\gamma_{UCl_3}}{\gamma_U}\right)^{n/3} \qquad (7)$$

Thus, in a salt/metal system with two elements that form cations in the salt phase with different valences, a change in the distribution coefficient of one element, through oxidation or reduction, results in a change in the separation factor. Conversely, if the separation factor is independent of a change in the distribution coefficient of one element, the two cations have the same valence in the salt phase.

As indicated by eqn. (7), separation factors can be calculated from thermodynamic properties, but it is generally not possible because some of the required data are inaccurate or have not been measured. For the IFR program it has been necessary to measure the actinide and rare earth separation factors for representative salt compositions.

Standard free energies of formation for pure, subcooled liquid actinide chlorides derived from values listed by Fuger *et al.* [4] for the solids are given in Table 1. Free energies of some rare earth chlorides for the subcooled liquids derived from Pankratz [5] are also included in Table 1.

TABLE 1. Free energies of formation of subcooled liquids at 773 K

Actinide	$\Delta G°$ (kcal mol^{-1}) [4]	Rare earth	$\Delta G°$ (kcal mol^{-1}) [5]
UCl_3	−162.3	$LaCl_3$	−206.5
$NpCl_3$	−170.9	$CeCl_3$	−202.3
$PuCl_3$	−183.8	$PrCl_3$	−203.8
$AmCl_3$	−191	$NdCl_3$	−200.7
$CmCl_3$	−190		

Johnson and coworkers [6–10] measured the activities of several actinides and rare earths in cadmium-rich solution at 773 K. Activity coefficients at infinite dilution derived from their data are listed in Table 2. The standard states are the pure, solid actinide or rare earth. They found that these coefficients increased with concentration; for example, the uranium coefficient is 89 for a saturated solution (0.0112 atomic fraction of uranium) and the plutonium coefficient is 2.3×10^{-4} for a saturated solution (0.0174 atomic fraction of plutonium). With the exception of uranium, the other elements form quite stable intermetallic compounds with cadmium. At temperatures above 746 K, pure uranium metal is the solid phase in equilibrium with saturated U–Cd solutions. Values for the UCl_3 and $PuCl_3$ activity coefficients (relative to a standard of the pure, subcooled liquid chlorides) in the LiCl–KCl eutectic at 773 K are listed in Table 2; they were estimated by Johnson [11, 13] from literature data [12, 14]. The activity coefficients at 723 K of several rare earth chlorides using the same standard state reported by Miyashiro *et al.* [15] are also listed in the table.

3. Experimental methods

The actinide and rare earth distribution data were obtained from several different experiments conducted at Argonne starting in 1985. In general, the apparatus consisted of a heated steel crucible which contained the liquid salt and cadmium. Although phase equilibrium was established rapidly, the liquids were stirred for several hours to ensure equilibrium, and then stirring was stopped for at least 2 h to allow the phases to separate before sampling. Samples taken several hours apart usually had equal compositions within analytical error. Samples were obtained in tantalum tubes by drawing the liquids through a tantalum filter. Care was taken to ensure that only one liquid phase was drawn into the tube.

Most uranium and plutonium determinations were made by mass spectrometry, which had an estimated standard deviation of 0.5%. A few of the uranium and plutonium determinations and all the rare earth determinations were done by inductively coupled plasma–atomic absorption spectroscopy, which had a standard deviation of 5%–10% for samples containing more than 0.1 wt.% of the element being analyzed. Americium and curium determinations were made by γ counting with an error of less than 5% for most samples. Neptunium determinations were done by liquid scintillation α counting with a standard deviation of 5%.

TABLE 2. Activity coefficients of actinides and rare earths at infinite dilution

Element	Coefficient in liquid Cd[a]	Ref.	Chloride[b]	Coefficient in LiCl–KCl	Ref.
U	75	6	UCl_3	5.79×10^{-3}	11, 12
Np	8.2×10^{-3}	7			
Pu	1.38×10^{-4}	8	$PuCl_3$	6.62×10^{-3}	13, 14
Ce	9.76×10^{-9}	9	$CeCl_3$[c]	1.5×10^{-3}	15
La	3.58×10^{-9}	9	$LaCl_3$[c]	4.7×10^{-3}	15
Pr	1.80×10^{-8}	9	$PrCl_3$[c]	3.3×10^{-3}	15
Nd	$\approx 6\times10^{-9}$	10	$NdCl_3$[c]	1.8×10^{-2}	15
			YCl_3[c]	6.3×10^{-6}	15

[a] Standard state: pure solid metal.
[b] Standard state: pure subcooled liquid.
[c] Temperature is 723 K for these compounds; all other temperatures are 773 K.

To change the relative amounts of actinide and rare earths in each phase, thus changing their distribution coefficients, lithium or $CdCl_2$ was added. Lithium metal reacted completely with the chlorides to produce metals that dissolved in the cadmium. Cadmium chloride oxidized metallic actinides and rare earths to produce chlorides dissolved in the salt.

The initial experiments were done with a salt having the nominal composition 23wt.%LiCl–10%NaCl–32%$CaCl_2$–35%$BaCl_2$. In later experiments the salts were the LiCl–KCl eutectic (56 wt.% KCl) with up to 7% NaCl and up to a total of 5% $CaCl_2$ and $BaCl_2$. The separation factors did not vary measurably with small variations in salt composition, but there were significant differences between the separation factors measured in the alkaline-earth-rich salt and those measured in the alkali-metal-rich salt.

4. Data analysis

The data were obtained primarily as byproducts of experiments whose main objective was determining actinide behavior in electrorefining or waste treatment operations. In most cases the actinide contents of the salt and metal phases ranged from about 0.1 to 2 wt.%. The estimated standard deviations of the analytical procedures over this range were about ±5% for uranium and plutonium and ±10% for the other actinides. As a result, the estimated standard deviations of the calculated actinide distribution coefficients are less than ±10% for uranium and plutonium and about ±15% for the other actinides. There was considerable scatter in the rare earth data because most of these data were obtained under conditions where the metal phase contents were low, and consequently the analyses were relatively inaccurate. Distribution data were omitted if the content in either liquid phase was less than 5×10^{-3} wt.% for uranium, neptunium, plutonium, cerium or neodymium and less than 1×10^5 disintegrations/min (g) for americium or curium.

4.1. Alkali-metal-rich salts

Distribution coefficients (weight fraction basis) for several actinides in the alkali-metal-rich salts are plotted *vs.* the uranium coefficient in Figs. 1–4. The separation factor for an element relative to uranium can be determined from the slope of the least-squares line drawn through the data, but this technique overweights the higher values, which tend to have a larger error. Estimates of the separation factors were obtained by averaging the factors calculated for each pair of distribution coefficients. These averages, listed in Table 3, were used to draw the lines in Figs. 1–4. The linear

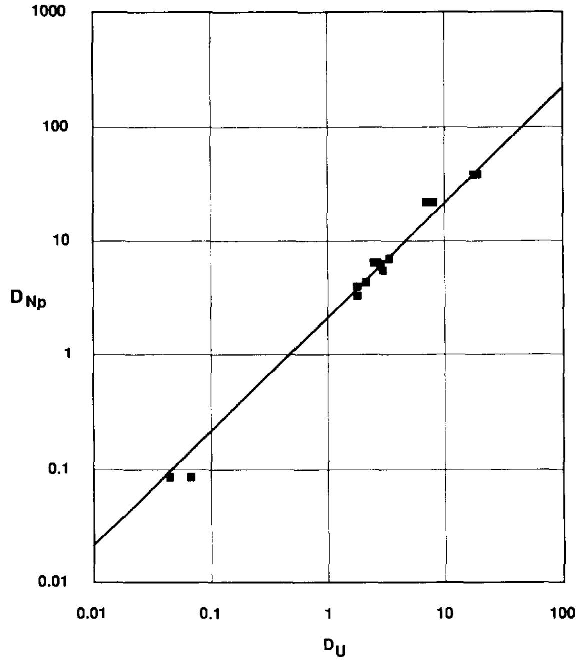

Fig. 1. Neptunium distribution coefficient in alkali-metal-rich salt/cadmium systems at 773 K (weight fraction basis).

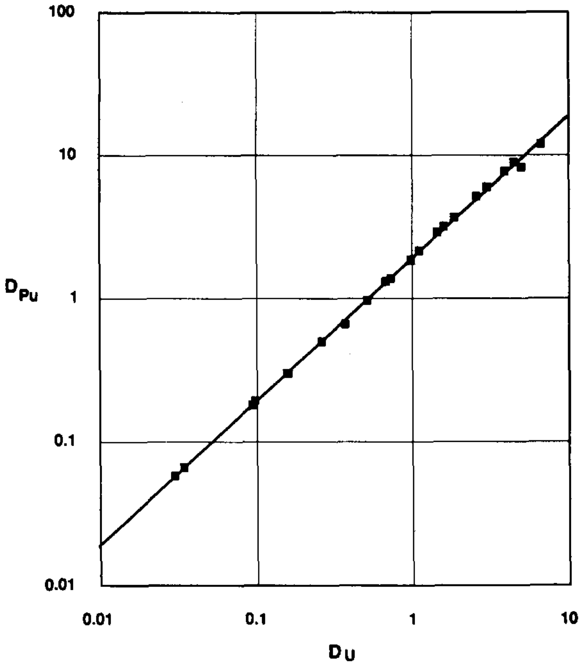

Fig. 2. Plutonium distribution coefficient in alkali-metal-rich salt/cadmium systems at 773 K (weight fraction basis).

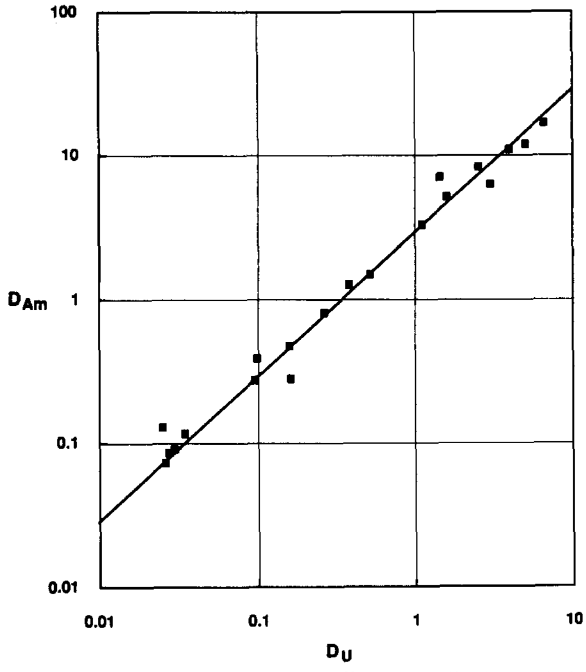

Fig. 3. Americium distribution coefficient in alkali-metal-rich salt/cadmium systems at 773 K (weight fraction basis).

relationship between the distribution coefficients, as evidenced by the fit of the distribution data by the average separation factor, suggests that these elements have the same valence in the salt and that their separation factors are independent of distribution coefficients for either element. The average separation

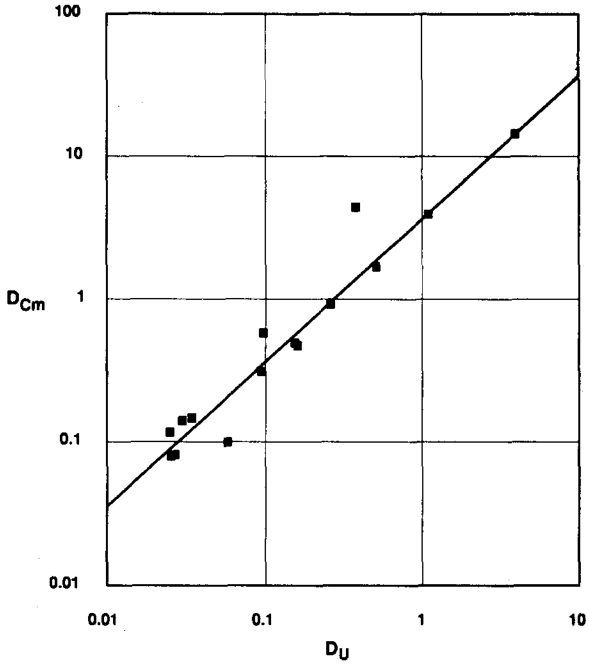

Fig. 4. Curium distribution coefficient in alkali-metal-rich salt/cadmium systems at 773 K (weight fraction basis).

TABLE 3. Average separation factors for several actinides and rare earths in alkali-metal-rich salt/cadmium systems at 773 ± 5 K

Actinide	Separation factor	Rare earth	Separation factor
U	1.00 (basis)	Ce	45 ± 6
Np	2.12 ± 0.42	Nd	39 ± 6
Pu	1.88 ± 0.09		
Am	3.08 ± 0.78		
Cm	3.52 ± 0.59		

factors for cerium and neodymium also fit the measurements within the analytical errors.

4.2. *Alkaline-earth-rich salts*

In a similar manner, distribution coefficients and separation factors were derived for the alkaline-earth-rich salt/cadmium system. Except for americium in reducing systems, the distribution coefficients of the TRU elements, cerium and neodymium were linearly related to the uranium coefficient in this salt. The average separation factors for the alkaline-earth-rich salt system are listed in Table 4. Neptunium distribution data were not obtained for this salt system. The americium factor was determined by averaging the data where the uranium distribution coefficient was greater

TABLE 4. Average separation factors for several actinides and rare earths in alkaline-earth-rich salt/cadmium systems at 773 ± 5 K

Actinide	Separation factor	Rare earth	Separation factor
U	1.00 (basis)	Ce	48 ± 13
Pu	1.32 ± 0.14	Nd	33 ± 5
Am	2.85 ± 0.98 ($D_U > 0.2$)		
Cm	2.3 ± 1.2		

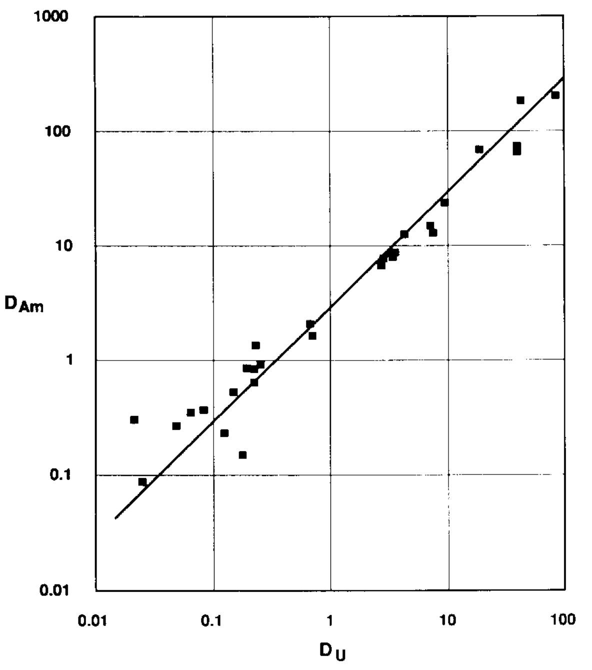

Fig. 5. Americium distribution coefficient in alkaline-earth-rich salt/cadmium systems at 773 K (weight fraction basis).

than 0.2; below 0.2 the americium–uranium separation factor appeared to increase with decreasing uranium coefficient (Fig. 5), which may be due to the formation of $AmCl_2$.

5. Discussion

5.1. Concentration dependence of separation factors

The separation factor for plutonium relative to uranium was found to be independent of the uranium and plutonium contents in the salt and metal phases. This is illustrated in Figs. 6(a) and 6(b), where the plutonium separation factors calculated for each data point in the alkali-metal-rich salt/cadmium systems are plotted against uranium and plutonium concentrations in the salt and metal phases. The dashed line in each figure is the average plutonium separation factor. The uranium contents ranged up to about 2.5 wt.% in the salt and 2% in the metal; plutonium contents ranged up to 3% in the salt and 0.8% in the metal. Similar plots can be made from the data for the other TRU elements, which show that their separation factors are also independent of concentrations, with the exception of americium in reducing systems with alkaline-earth-rich salts.

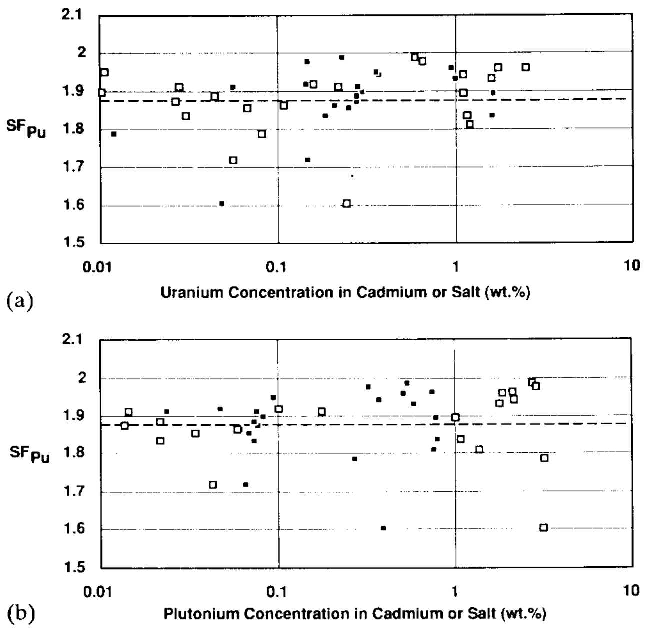

Fig. 6. Effect of (a) uranium content and (b) plutonium content in salt and metal phases on plutonium separation factor. (Open symbols are salt concentrations; filled symbols are metal concentrations.)

This finding is somewhat surprising, because the actinide activity coefficients in salt/cadmium are reported to be concentration dependent and thus the separation factors should also depend on concentrations. Another analysis of the plutonium distribution data was made to investigate concentration effects further. The results from this analysis are summarized in Fig. 7, where the measured separation factors (filled symbols) are compared with the factors (open symbols) calculated from eqn. (3) using activity coefficients obtained from the reported empirical correlations of experimental data. The line in this figure was determined from the reported activity coefficients at infinite dilution (see Table 2).

The separation factors calculated from the activity coefficients at infinite dilution agree quite well with the measured line in Fig. 7. In contrast, the separation factors calculated from activity coefficients that vary with concentrations do not agree with this curve at larger values of the distribution coefficients, where the uranium and plutonium contents of the salt are high.

5.2. Valences of actinide chlorides

The distribution data for the alkali-metal-rich salts were treated in a different manner to show that the TRU distribution coefficients are linearly related to

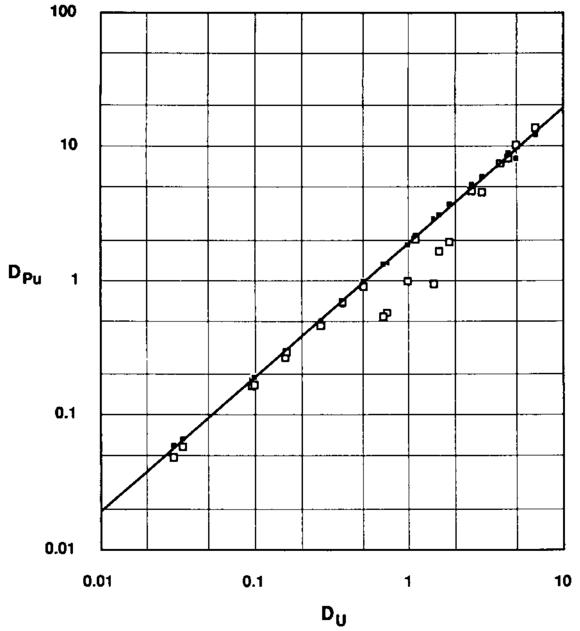

Fig. 7. Comparison of measured and calculated separation factors. (Open symbols are calculated from concentration-dependent activity coefficients; filled symbols are measurements; line is calculated from activity coefficients at infinite dilution.)

the uranium coefficient. The data were fit by least squares to a rearrangement of eqn. (7),

$$\log(D_M) = \frac{n}{3}\log(D_U) + \frac{1}{3}\log(K_e)\left(\frac{\gamma_M}{\gamma_{MCl_n}}\right)^3\left(\frac{\gamma_{UCl_3}}{\gamma_U}\right)^n \tag{8}$$

where n is the valence of the other element and the activity coefficient term is assumed to be constant. The least-squares fits for the distribution data in log–log graphs should have slopes equal to $n/3$. For alkali-metal-rich salts the slopes are: neptunium, 1.08; plutonium, 1.00; americium, 0.96; curium, 0.99; cerium, 1.01; neodymium, 0.99. These values are not statistically different from 1.0. Least-squares slopes for similar graphs for the alkaline-earth-rich salt systems are also close to 1.0, with the exception of the slope for americium.

The observation that the actinide distribution coefficients are linearly related is strong evidence that uranium, the TRU elements, cerium and neodymium form cations of the same valence in these salts. Poa *et al.* [16] have shown by chronopotentiometric measurements that uranium exists in these salt systems as the trivalent cation. Similar studies have shown that plutonium [17] and neptunium [18] are also present in the salt as trivalent cations. Thus uranium, the TRU elements and the two rare earths primarily form trivalent cations in the IFR pyroprocess salts.

5.3. Effect of salt composition

The separation factors for the TRU elements and the two rare earths are slightly different in the two salt systems (see Tables 3 and 4), and this difference must be related to activities in the salt phase, because the metal phases were similar cadmium solutions. Only the difference between the plutonium factors is sufficiently accurate to draw any inferences. Using the free energies of formation for the chlorides in Table 1 and the uranium and plutonium activity coefficients at infinite dilution in cadmium from Table 2, the ratio of salt phase activity coefficients is

$$\frac{\gamma_{PuCl_3}}{\gamma_{UCl_3}} = \frac{K_e}{SF_{Pu}}\frac{\gamma_{Pu}}{\gamma_U} \tag{9}$$

$$= 1.08 \text{ (alkali-metal-rich salts)}$$

$$= 1.54 \text{ (alkaline-earth-rich salts)}$$

These values are considerably less than the value of 3.74 for $MgCl_2$ solutions derived from experimental data [19]. Assuming that van der Waals interaction and ligand field effects are relatively small, deviations of this ratio for the actinide chlorides from ideality can be attributed to polarization of cations and thus can be related to the cation radii of the solvent salt. According to Blander [20], solvent cations with larger radii will have a larger effect on the cations in solution. This effect is illustrated in Fig. 8, where the activity coefficient ratio is shown to be a linear function of the cube of the average cation radius for some salt systems.

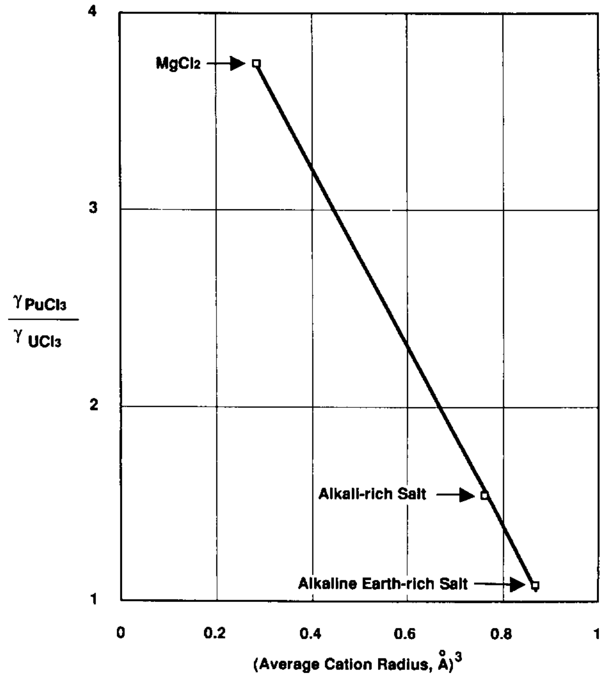

Fig. 8. Effect of average cation radius in solvent salt on activity coefficient ratio of solute plutonium and uranium cations.

(The average cation radius is $\Sigma Y_i r_i$, where Y_i is the mole fraction of cation i and r_i is the reported radius for solid chloride.) At this point there is no satisfactory theoretical basis for this relationship. According to Blander's hypothesis, this relationship suggests a greater polarization of Pu^{3+} compared to U^{3+}. However, it may be important to the IFR process to investigate the effects of fission product chlorides on TRU element behavior.

5.4. Free energy of formation of $NpCl_3$

The measured neptunium separation factor suggests that the reported [4] free energy of formation for $NpCl_3$ is in error. The following discussion is based on a more detailed analysis by Johnson [21] for the Np–U separation factor, which can be expressed as

$$SF_{Np} = \frac{K_e \gamma_{Np} \gamma_{UCl_3}}{\gamma_{NpCl_3} \gamma_U} \qquad (10)$$

where K_e is the equilibrium constant for the reaction

$$UCl_3 + Np = U + NpCl_3 \qquad (11)$$

If the salt phase activity coefficients are equal and the metal phase coefficients determined by Johnson and Feder [6] and Krumpelt *et al.* [7] (see Table 2) are used, the equilibrium constant is

$$K_e = \frac{SF_{Np} \gamma_U}{\gamma_{Np}} = \frac{2.12 \times 75}{8.2 \times 10^{-3}} = 1.94 \times 10^4$$

The standard free-energy change is

$$\Delta G^o = -RT \ln(K_e)$$
$$= \Delta G^o_{NpCl_3} - \Delta G^o_{UCl_3} = -15\,200 \text{ cal gmol}^{-1}$$

and the standard free energy of formation of subcooled liquid $NpCl_3$ at 773 K is

$$\Delta G^o_{NpCl_3} = -15.4 + (-162.3) = -177.7 \text{ kcal gmol}^{-1}$$

This value is close to a recent measurement (-183.8 kcal $gmol^{-1}$) by Krueger *et al.* [22] and is more negative than the estimate (-170.8 kcal $gmol^{-1}$) derived for the subcooled liquid chloride from Fuger *et al.* [4].

5.5. Estimated americium and curium activity coefficients

Crude estimates of the activity coefficients of americium and curium in cadmium can be derived from the separation factors. These coefficients are useful for pyroprocess design but have not been measured directly. Assuming that the UCl_3 and $AmCl_3$ activity coefficients in the LiCl–KCl-base salts are equal, eqn. (3) when applied to the U–Am pair becomes

$$SF_{Am} = \frac{K_e \gamma_{Am}}{\gamma_U} \qquad (12)$$

The equilibrium constant calculated from the free energies of formation for UCl_3 and $AmCl_3$ given in Table 1 is

$$K_e = \exp\left(-\frac{\Delta G}{RT}\right) = 1.3 \times 10^8 \qquad (13)$$

If $\gamma_U = 75$ (Table 2) and $SF_{Am} = 3.08$ (Table 3), then $\gamma_{Am} \approx 2 \times 10^{-6}$. Similarly, $\gamma_{Cm} \approx 3 \times 10^{-5}$. These values are tenuous because they depend on the accuracies of the free energies of formation for the chlorides and on the assumption that the activity coefficients of uranium, americium and curium chlorides are equal.

6. Conclusions

The measured actinide and rare earth distribution coefficients in molten chloride salt/cadmium metal systems that are reported in this and other reports support the feasibility of pyrochemical processing of spent IFR fuels. The behavior of these elements appears to be uncomplicated in multicomponent salt and metal solutions. The small differences among the actinide distribution coefficients show that uranium and the TRU elements will behave similarly in these systems, which is a distinct advantage for the IFR fuel cycle. The relatively large differences between the coefficients for actinides and rare earths indicate that practical pyrochemical processes can be designed to adequately separate rare earths from the actinides. However, these data also suggest that there are significant deficiencies in the supporting thermodynamic properties, especially the properties of neptunium, americium and curium chlorides and the activities of all actinide chlorides in molten salt solutions.

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References

1 L. Burris, R. Steunenberg and W. Miller, The application of electrorefining for recovery and purification of fuel discharged from the Integral Fast Reactor, *AIChE Symp. Ser., 254-83* (1987) 135–142.

2 J. P. Ackerman, Chemical basis for pyrochemical reprocessing of nuclear fuel, *Ind. Eng. Chem. Res., 29* (1991) 141.

3 J. P. Ackerman and J. L. Settle, Partition of lanthanum and neodymium metals and chloride salt between molten cadmium and molten LiCl–KCl eutectic, *J. Alloys Comp., 177* (1991) 129.

4 J. Fuger, V. B. Parker, W. N. Hubbard and F. L. Oetting, *The Chemical Thermodynamics of Actinide Elements and Compounds. Part 8. The Actinide Halides,* International Atomic Energy Agency, Vienna, 1983.

5 L. B. Pankratz, Thermodynamic properties of halides, *Bulletin 674,* 1984 (US Department of the Interior, Bureau of Mines).

6 I. Johnson and H. M. Feder, Thermodynamics of the uranium–cadmium system, *Trans. Metall. Soc. AIME, 224* (1962) 468.

7 M. Krumpelt, I. Johnson and J. J. Heiberger, Thermodynamics of the cadmium–neptunium system: solute–solvent interactions in liquid alloys, *Metall. Trans., 5* (1974) 65.

8 I. Johnson, M. G. Chasanov and R. M. Yonco, Pu–Cd system: thermodynamics and partial phase diagram, *Trans. Metall. Soc. AIME, 233* (1965) 1408.

9 I. Johnson and R. M. Yonco, Thermodynamics of cadmium- and zinc-rich alloys in the Cd–La, Cd–Ce, Cd–Pr, Zn–La, Zn–Ce and Zn–Pr systems, *Metall. Trans., 1* (1970) 905.

10 I. Johnson, Argonne National Laboratory, Chemical Technology Division, personal communication, December 12, 1990.

11 I. Johnson, Argonne National Laboratory, Chemical Technology Division, personal communication, June 28, 1989.

12 L. Yang, R. G. Hudson and C.-Y. Chen, in G. R. St. Pierce (ed.), *Physical Chemistry of Process Metallurgy,* Vol. 2, Interscience, New York, 1961, pp. 925–943.

13 I. Johnson, Argonne National Laboratory, Chemical Technology Division, personal communication, June 28, 1989.

14 G. M. Camball and J. A. Leary, Thermodynamic properties of plutonium compounds from EMF measurements, *Los Alamos National Laboratory Rep. LA-3399,* March 1966.

15 H. Miyashiro *et al.*, Development of pyrometallurgical partitioning, *Proc. Information Exchange Meeting on Actinide and Fission Product Separation and Transmutation, Mito City, November 6–8, 1990,* OECD Nuclear Energy Agency, Paris, 1991, p. 231.

16 D. S. Poa, Z. Tomczuk and R. K. Steunenberg, Voltammetry of uranium and plutonium in molten LiCl–NaCl–$CaCl_2$–$BaCl_2$. Reduction of U(III) to uranium metal, *J. Electrochem. Soc., 135* (1988) 1161–1166.

17 D. S. Poa, Z. Tomczuk and R. K. Steunenberg, Cyclic voltammetric study of the reduction of Pu(III) to plutonium metal in molten LiCl–NaCl–$CaCl_2$–$BaCl_2$, *Electrochemical Society Fall Meeting, October 1988,* Vol. 88-2, Electrochemical Society, Pennington, NJ, 1988, Extended Abstract 714, p. 1022.

18 L. Martinot, Kinetics of the electrochemical reduction of trivalent neptunium ion in the Li–K/Cl eutectic at 450 °C, *J. Radioanal. Nucl. Chem., Lett., 106* (1986) 135–144.

19 I. Johnson, The thermodynamics of pyrochemical process for liquid metal reactor fuel cycles, *J. Nucl. Mater., 154* (1988) 169–180.

20 M. Blander, Thermodynamic properties of molten salt solutions, in M. Blander (ed.), *Molten Salt Chemistry,* Interscience, New York, 1964, pp. 148–161.

21 I. Johnson, Argonne National Laboratory, Chemical Technology Division, personal communication, April 9, 1990.

22 C. L. Krueger *et al.*, Measurement of the standard potential of the Np(III)/Np(0) couple in LiCl–KCl eutectic, *J. Electrochem. Soc., 138* (1991) 1186.