The Ohio State University

Calculations of distribution factors of Fission Products between KCl-LiCl and Liquid Metals (Bi and Cd)

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Molten Salt Lab at The Ohio State University

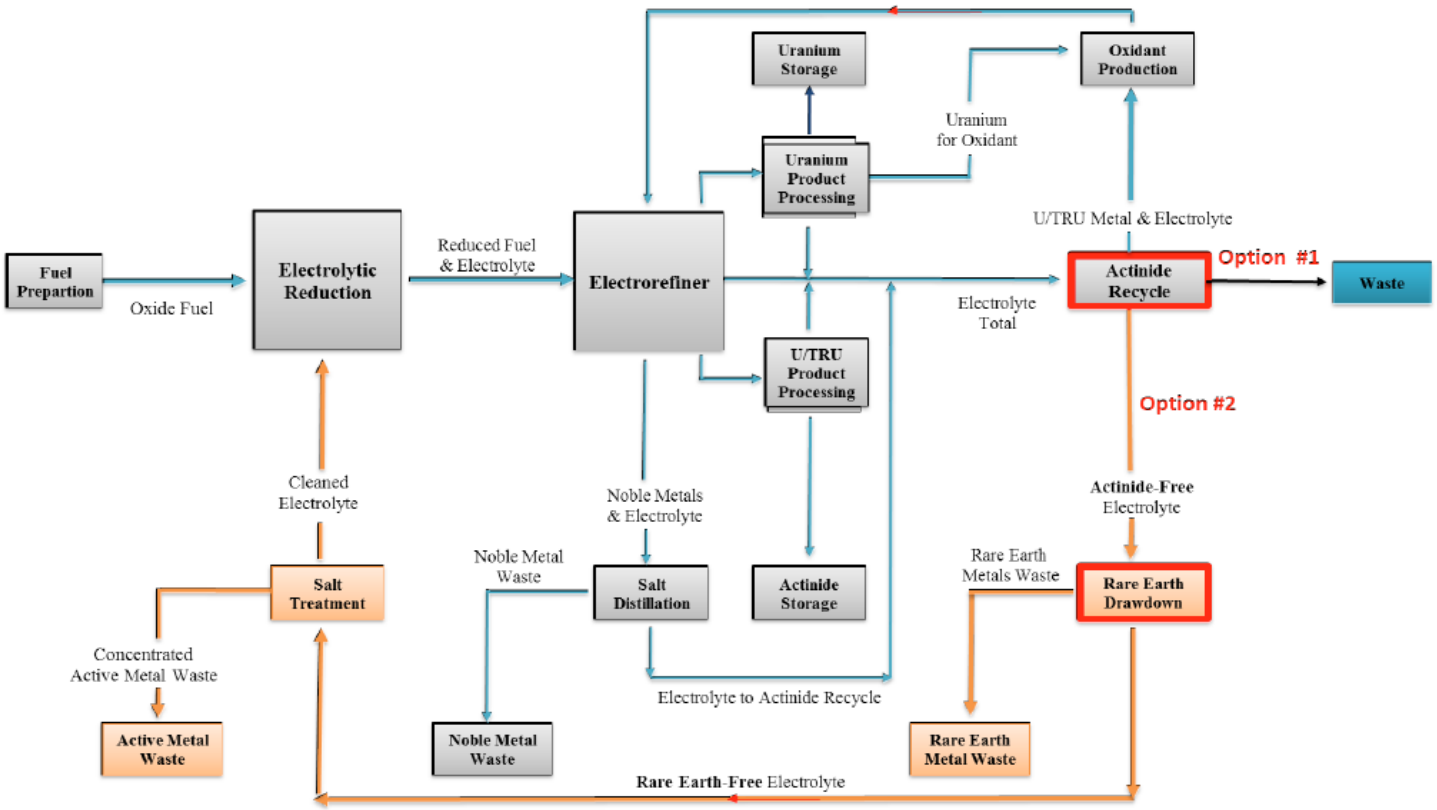
- **Pyroprocess-Safeguarding, electrorefining, and molten salt recycle**
- **Electrochemical Separation-Fundamental data of rare earth metals and actinides in complex molten KCl-LiCl**
- **Fluoride salt cooled high temperature reactor (FHR)- Materials cleanup system design and development**
- **Material Corrosion in molten salt- for both FHR and Pyroprocessing**

Highlights

- Fundamental data of Fission products and actinides in Liquid metals (Bi and Cd)
- Fundamental data of fission products and actinides in KCl-LiCl.
- Equilibrium distribution factor calculations
- Effects by initial condition on the distribution factors

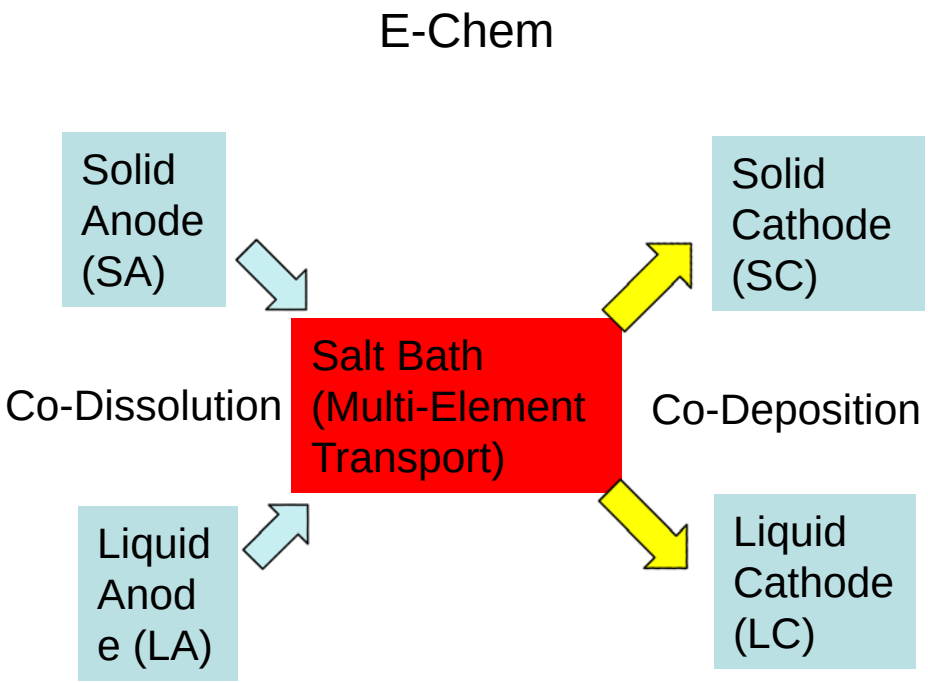
Liquid Metal (Cd, Bi) Applications in Pyroprocessing

- As liquid electrode (Cd) in ER
- As extractor (Bi) in the molten salt recycle



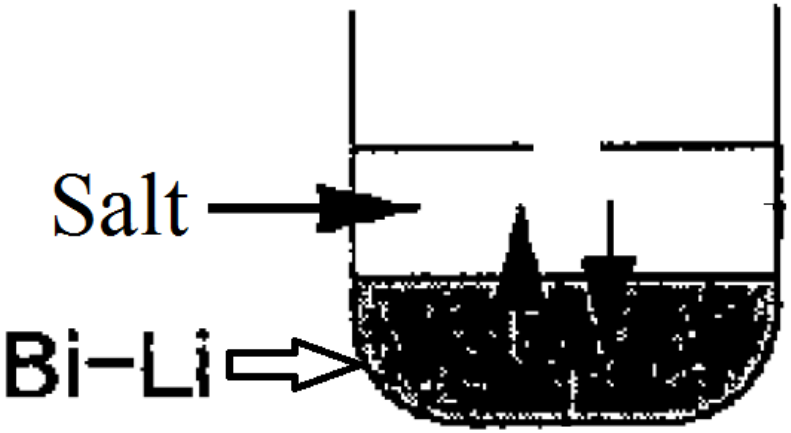
ANL PYRO Flowsheet

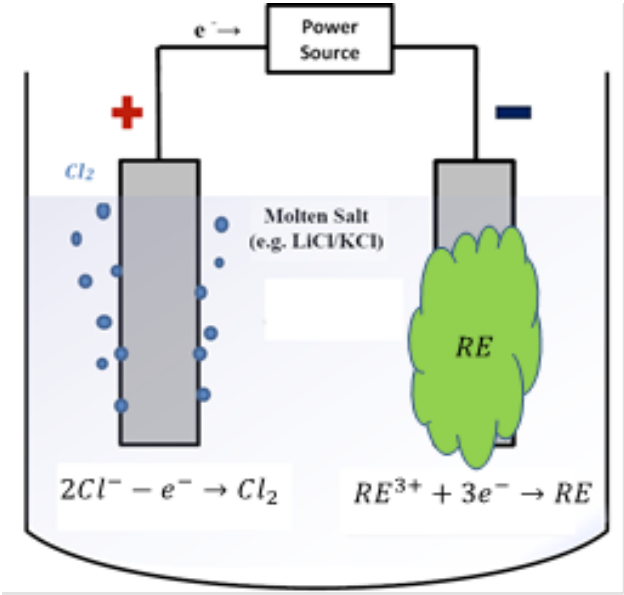
A simplified Electrorefiner (ER)



Rare Earth Drawdown Processes

- Using Active Li-Bi
- Using Electrolysis





Thermodynamic Fundamentals

- **The exchange Reaction:**

$$M\ (Cd/\boldsymbol{Bi}) + M'Cl_n \rightleftharpoons MCl_n + M'(Cd/\boldsymbol{Bi})$$

- **Dissolution Reaction of a metal into a liquid metal:**

$$M\ (s) \leftrightharpoons M(soln)$$

$$RTlna_{M,s} = RTln\gamma_{M,s}X_{M,s} = 0$$

$$X_{M,s} = \frac{1}{\gamma_{M,s}}$$

Thermodynamic Fundamentals

- **Dissolution Reaction of a metal compounds into a liquid metal:**

$$MN_m\ (s) \leftrightharpoons M(soln) + mN\ (soln)$$

$$RTln\gamma_{M,s}X_{M,s} + mRTlna_N - \ \Delta G_{NM_m} = 0$$

- **Fundamental Correlations:**

$$lnX_{M,s} = A_{M,s} + \frac{B_{M,S}}{T}$$

$$ln\gamma_M = A_{M,\gamma} + \frac{B_{M,\gamma}}{T}$$

Thermodynamic Fundamentals

- **Concentration dependent properties**

$$ln\gamma_{Pu} = \left[(A_1 + A_2 X_{Pu}) + \frac{B_2 + B_2 X_{Pu}}{T}\right](1 - X_{Pu})^2$$

Infinite Dilution

$$ln\gamma_{Pu} = A_1 + \frac{B_1}{T}$$

Thermodynamic Properties of Actinides and Fission Products in Liquid Cd

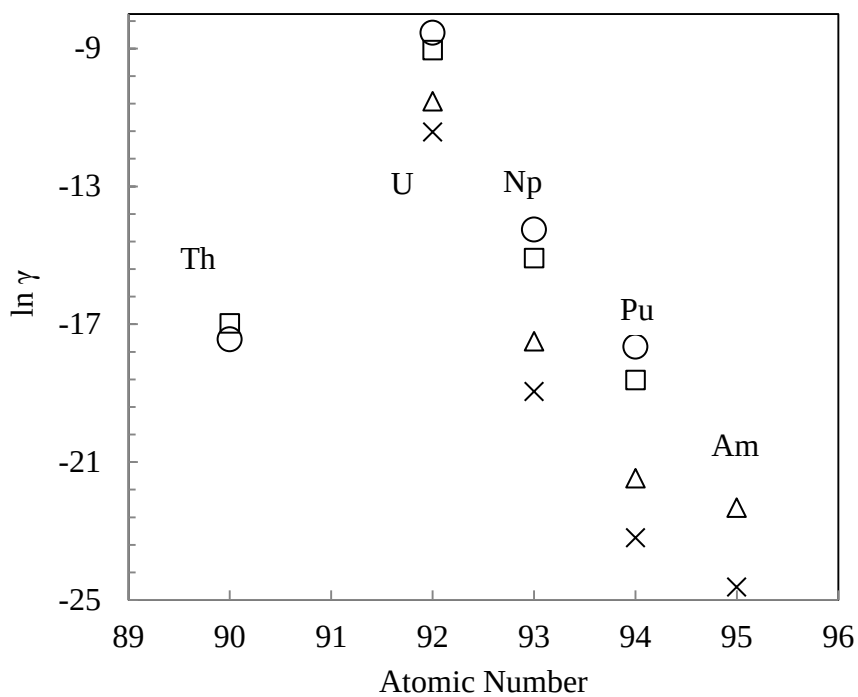
Element	(at%)					
	At 673K	At 773K	At 673K	At 773K	At 673K	At 773K
Y	0.556	1.791			0.843	1.03
La	0.022	0.322			1.14	1.12
Ce	0.044	0.600			1.19	1.13
Pr	0.084	0.921			0.990	0.981
Nd	0.146	1.46			0.994	1.03
Sm	0.665	2.591	-		-	0.967
Gd	0.481	1.38			1.20	1.17
Er	0.566	1.68			0.807	0.722
U	0.163	1.12	50.0	89.0	1.03	-
Np	0.368	2.20		0.0187	0.996	0.968
Pu	0.725	1.86			0.975	0.960

Thermodynamic Properties of Actinides and Fission Products in Liquid Bi

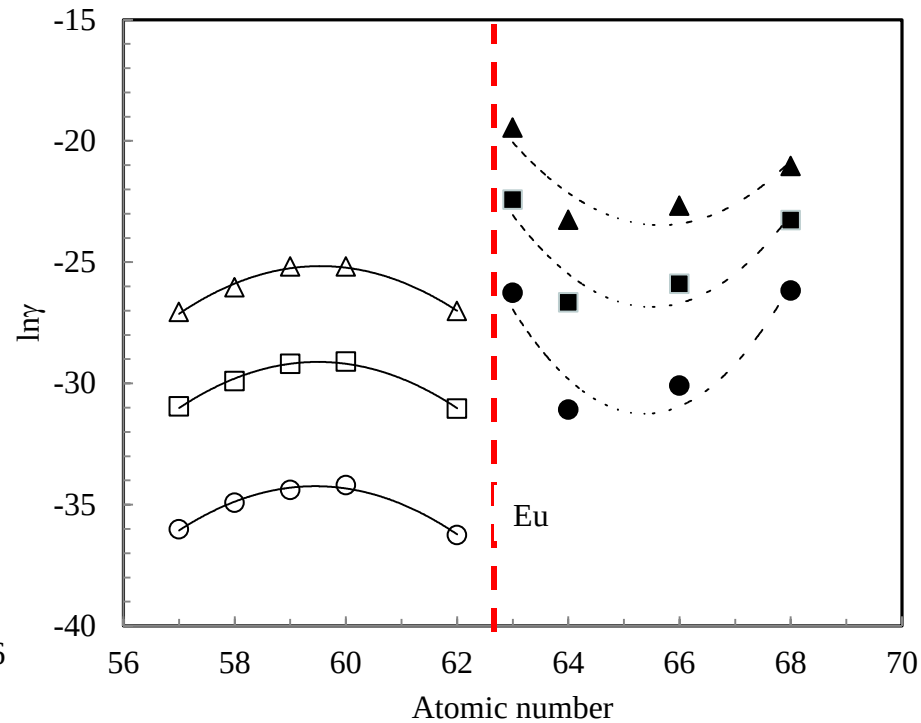
Metals	A	B	Temperature range (K) (Tmin, Tmax)
Y	-2.1049	16502	673-773
	0.8291	20063	773-1023
La	1.9437	25494	673-953
	3.8249	-26750	653-823
	3.2836	-26437	673-773
	3.3810	-26646	850-1100
	3.1083	-26332	653-1100
Ce	4.6751	-26254	773-923
	2.8145	-25235	673-773
	3.7046	-26089	653-823
	5.5280	-27155	
	2.3606	-25612	735-937
	3.8165	-26067	653-937
Pr	6.2425	-27315	673-823
	2.8386	-24994	673-773
	6.6995	-27496	
	7.6137	-28554	
	5.8486	-27090	673-823
Nd	5.1335	-26470	
Sm	4.0293	-27111	
Eu	3.4520	-20002	
Gd	3.1689	-23060	775-1055
	4.4311	-24326	850-1100
	3.7226	-24163	
	2.8386	-22697	
	1.2268	-20724	673-773
	3.0776	-22994	673-1100
Tb	4.6295	-24035	850-1100
Dy	3.3305	-23310	850-1100
	2.3099	-21811	850-1101
Er	3.9391	-21946	850-1100
	-3.7677	-15082	773-973

Rare earth metals	Solid in Equilibrium with the liquid	A	B	Temperature range (K) (Tmin, Tmax)
Y	YBi	0.8549	6195	588-1000
	YBi	-2.8783	5941	648-948
La	$LaBi_2$	2.1359	5366	548-933
	$LaBi_2$	5.8391	8044	648-948
	$LaBi_2$	3.9875	6705	548-948
Ce	$CeBi_2$	2.4958	5804	573-723
	$CeBi_2$	4.4073	6978	
	$CeBi_2$	2.9748	6289	648-948
	$CeBi_2$	2.7353	6046	573-948
Pr	$PrBi_2$	0.4704	4502	548-623
	$PrBi_2$	3.3100	6287	623-723
Nd	$NdBi_2$	2.2366	5873	573-773
	$NdBi_2$	3.3813	6287	573-923
Sm	$SmBi_2$	5.6721	7492	573-773
Eu	$EuBi_2$	6.0346	6847	598-823
Ho	HoBi	-0.65	1818	673-873
Er	ErBi	2.7927	7054	775-975
	ErBi	1.0378	5509	890-1090
	ErBi	1.9153	6281	775-1090
Yb	$YbBi_2$	4.6154	5527	553-673
Lu	Unknown	0.9790	6587	623-773

Activity Coefficient in Bi

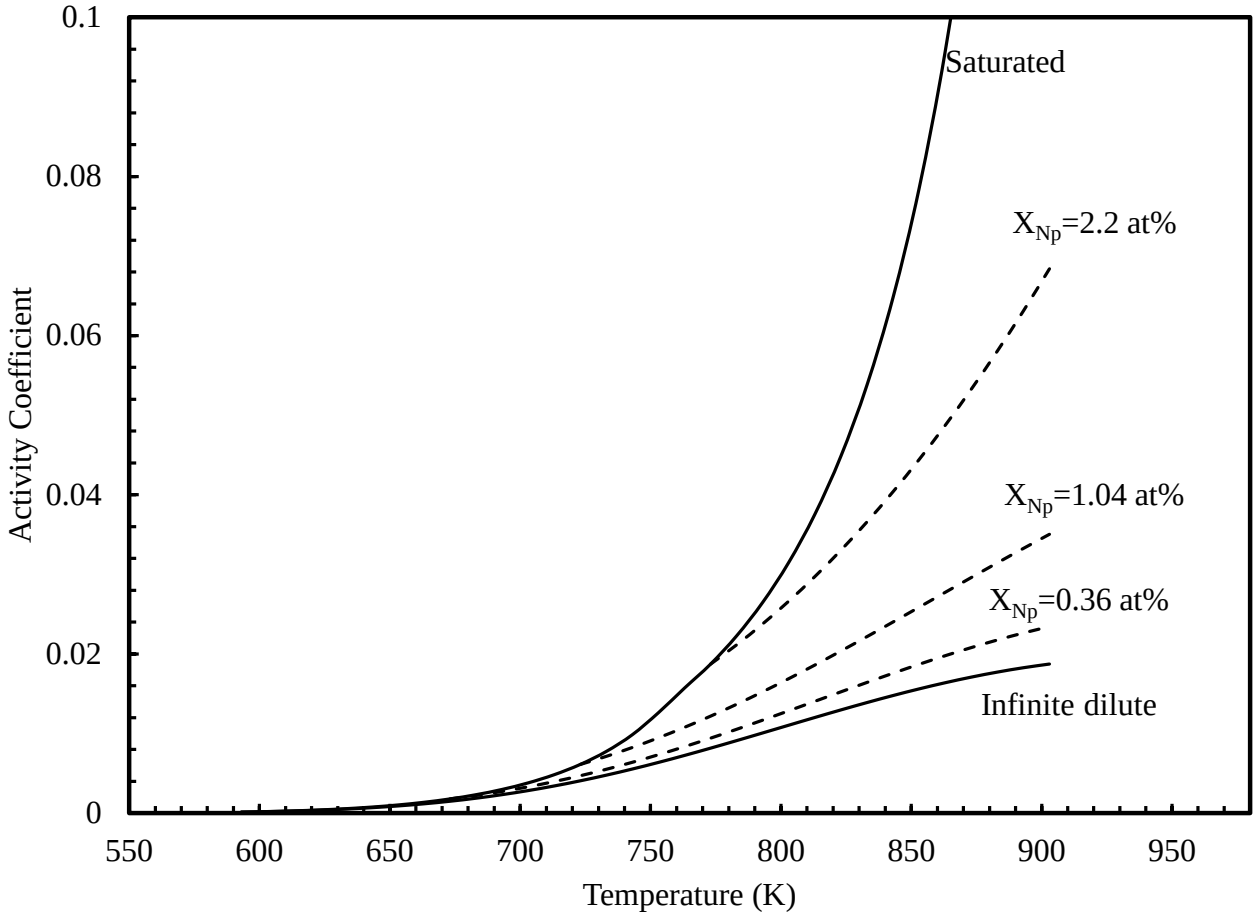


Activity coefficients of actinides against atomic number, (Circle: 913K, Square: 873K, Triangle: 773K, Crossing: 723 K)



Activity coefficients of lanthanides in liquid Bi against element atom number (circle: 673K, square: 773 K, triangle: 873 K)

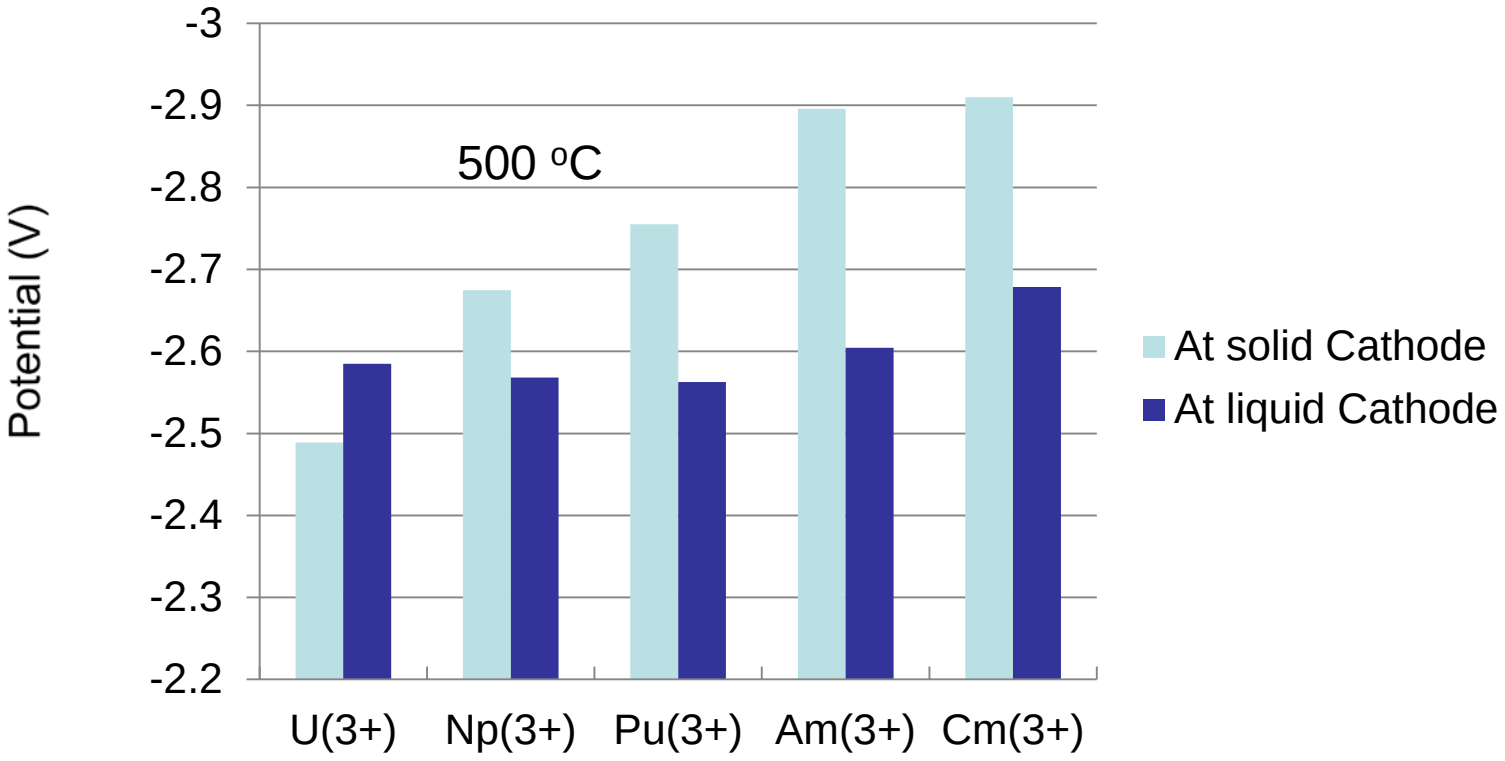
Concentration-dependent



Apparent potential in liquid LiCl-KCl E=H1+H2*T

Reduction reaction	H_1 (V)	H_2*10^4 (V/K)	E (V) @723K	Temperature range (K)
Th^{4+}/Th^0	-2.9845	5.5589	-2.5825	693-823
Pa^{4+}/Pa^0	-2.7538	6.0	-2.32	673-773
U^{3+}/U^0	-2.9429	5.8724	-2.5183	673-823
U^{4+}/U^{3+}	-1.669	2.1	-1.5171	723-823
U^{4+}/U^0	-2.6244	4.9	-2.2701	723-823
Np^{3+}/Np^0	-3.2304	7.1892	-2.7106	673-823
Np^{4+}/Np^{3+}	-1.25	6.637	-0.7701	673-823
Np^{4+}/Np^0	-2.7353	7.0512	-2.2254	673-823
Pu^{3+}/Pu^0	-3.3374	7.5364	-2.7925	673-823
Am^{3+}/Am^{2+}	-3.2083	6.959	-2.7051	733-823
Am^{2+}/Am^0	-2.9615	1.0914	-2.8825	673-823
Am^{3+}/Am^0	-3.0437	3.0473	-2.8233	733-823
Cm^{3+}/Cm^0	-3.285	5.48	-2.8888	723-923
Y^{3+}/Y^0	-3.603	6.88	-3.1056	673-823
Zr^{2+}/Zr^0	-2.2978	4.12	-1.9999	723-823
La^{3+}/La^0	-3.575	6.064	-3.1365	650-870
Ce^{3+}/Ce^0	-3.5338	5.923	-3.1056	673--973
Pr^{3+}/Pr^0	-3.5412	6.2971	-3.0859	673-823
Nd^{3+}/Nd^0	-3.5672	6.28	-3.1132	673-823
Sm^{3+}/Sm^{2+}	-2.6176	7.7763	-2.0554	673-873
Eu^{3+}/Eu^{2+}	-1.421	7.8	-0.8571	698-723
Gd^{3+}/Gd^0	-3.5136	7.32	-2.9844	722-873

Potential comparisons at solid and liquid Cd electrode



Distribution Factor Calcuation

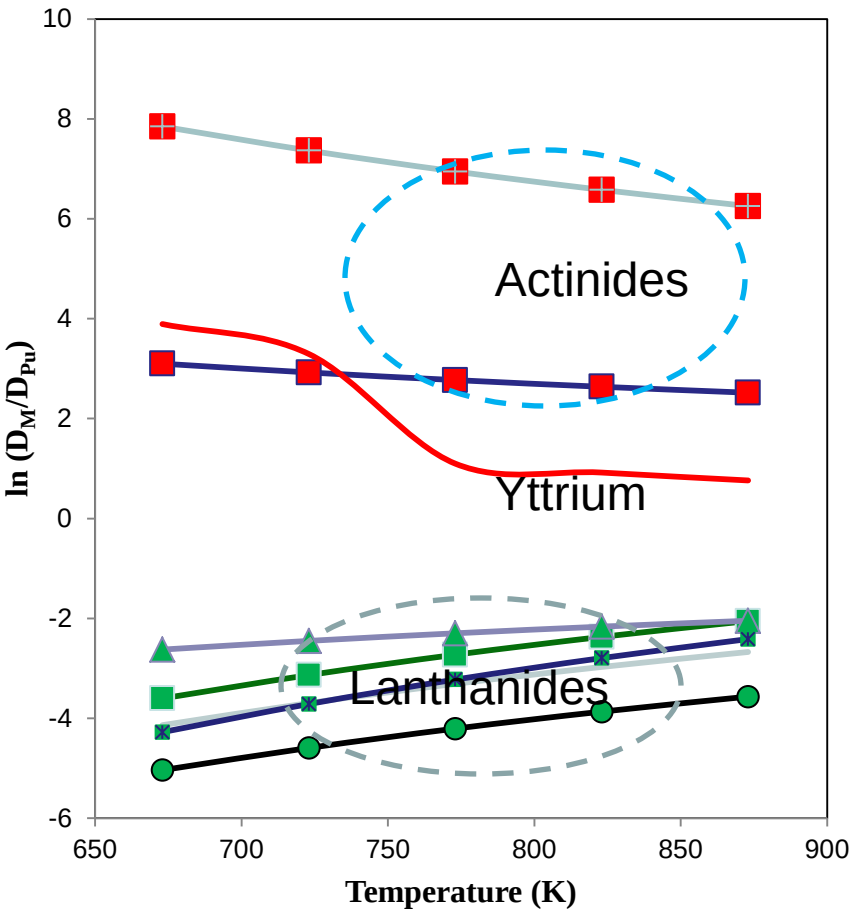
$$M^{n+}(MS) + ne \leftrightarrow M(EL)$$

$$E_L = E^{ap}_{M^{n+}} + \frac{RT}{nF}\ln\left(\frac{X_{M^{n+}}}{\gamma_M X_M}\right)$$

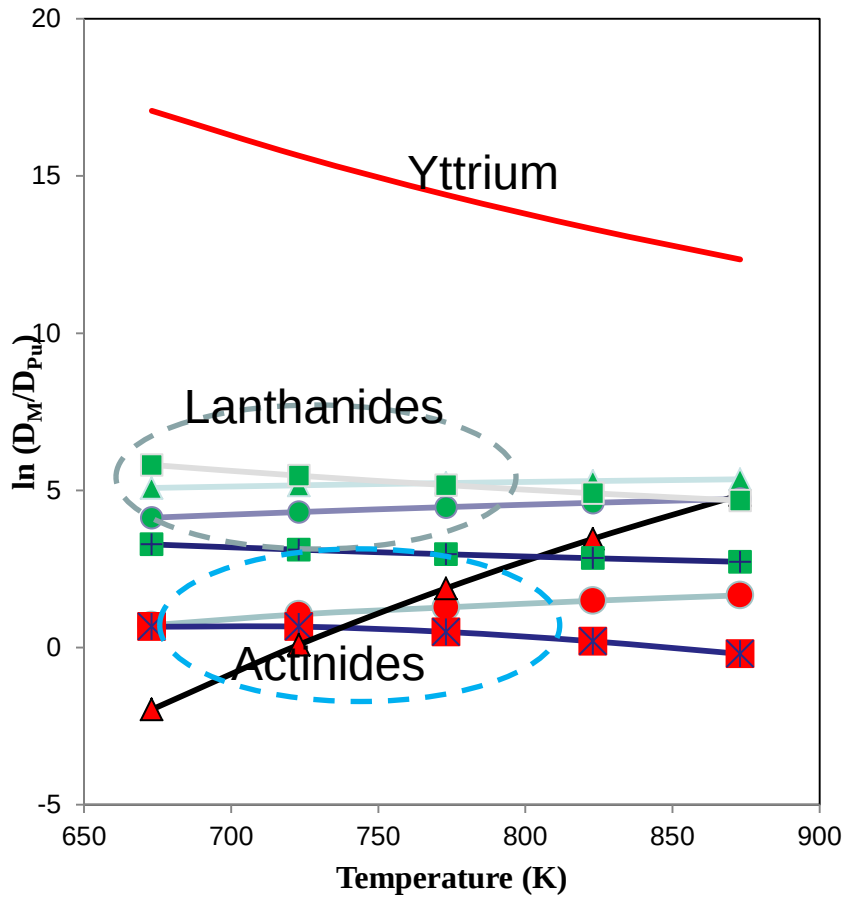
$$D_M = \frac{X_{M^{n+}}}{X_M} = \gamma_M \exp\left(\frac{nF}{RT}\left(E_L - E^{ap}_{M^{n+}}\right)\right)$$

$$SF_{M_i} = \frac{D_{M_i}}{D_{Li}} = \frac{\gamma_{M_i}}{\gamma_{Li}^{n_i}} D_{Li}^{n_i-1} \exp\left(\frac{n_i F}{RT}\left(E^{ap}_{Li} - E^{ap}_{M_i^{n_i+}}\right)\right)$$

Separation Factor at Liquid Metal

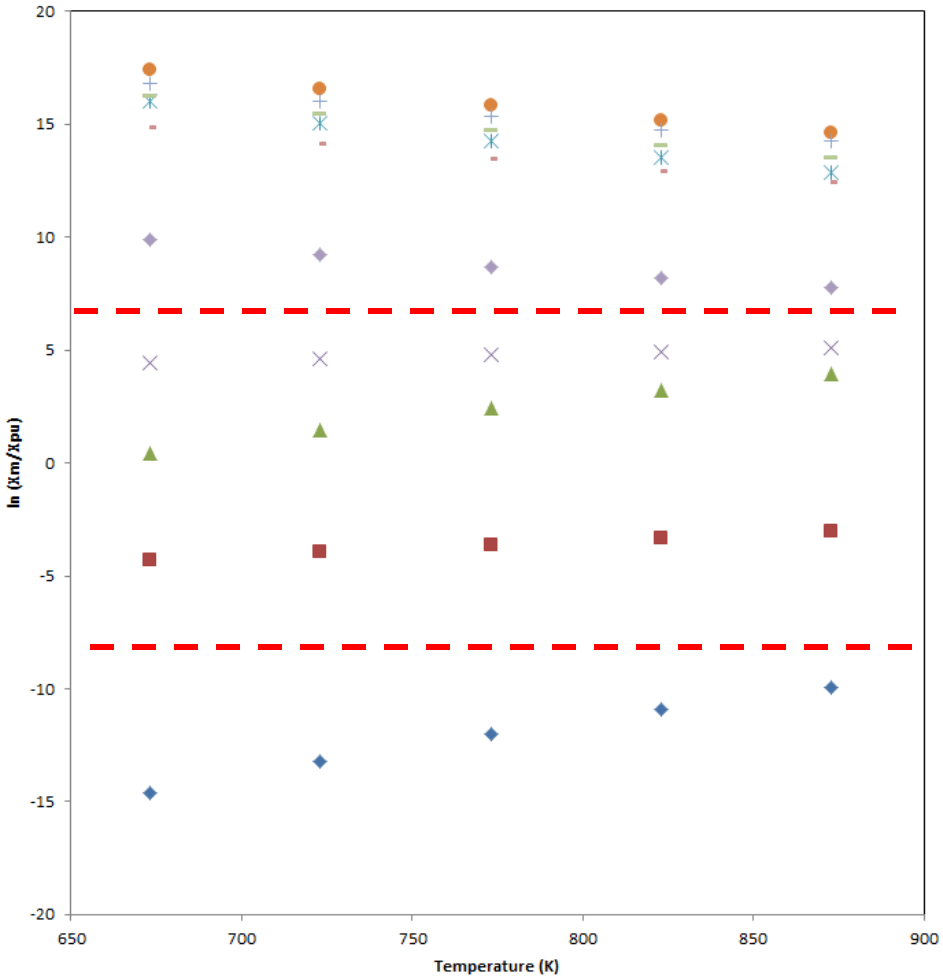


Liquid Bi



Liquid Cd

At inert solid electrode

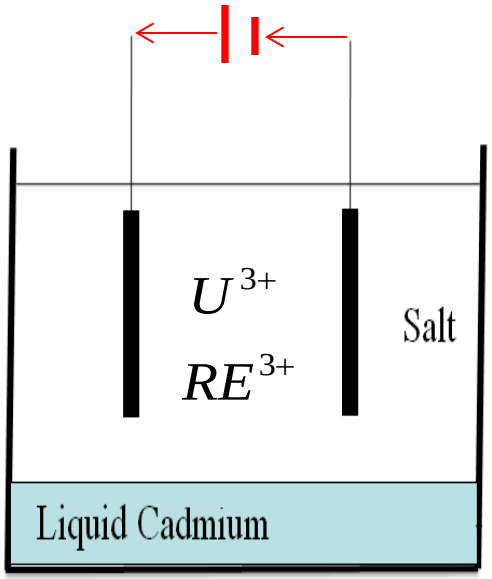


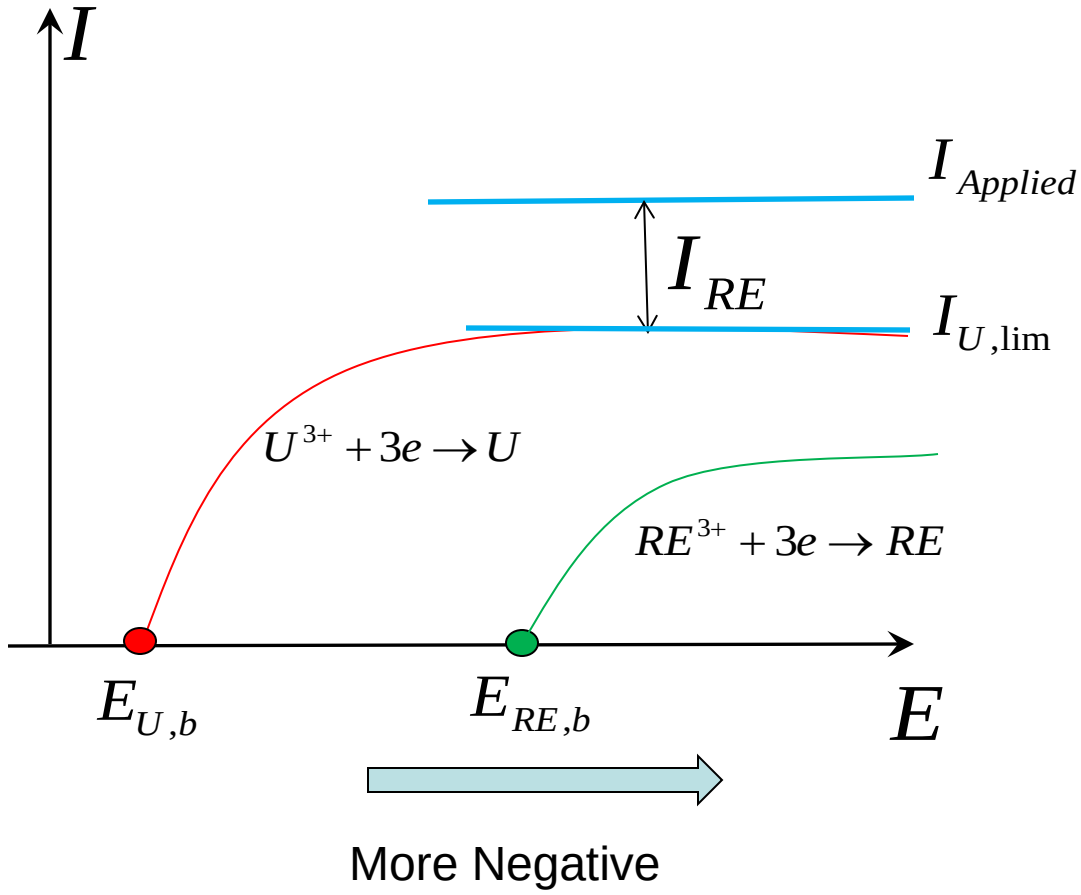
Rare earth Metals

Minor Actinides

Uranium

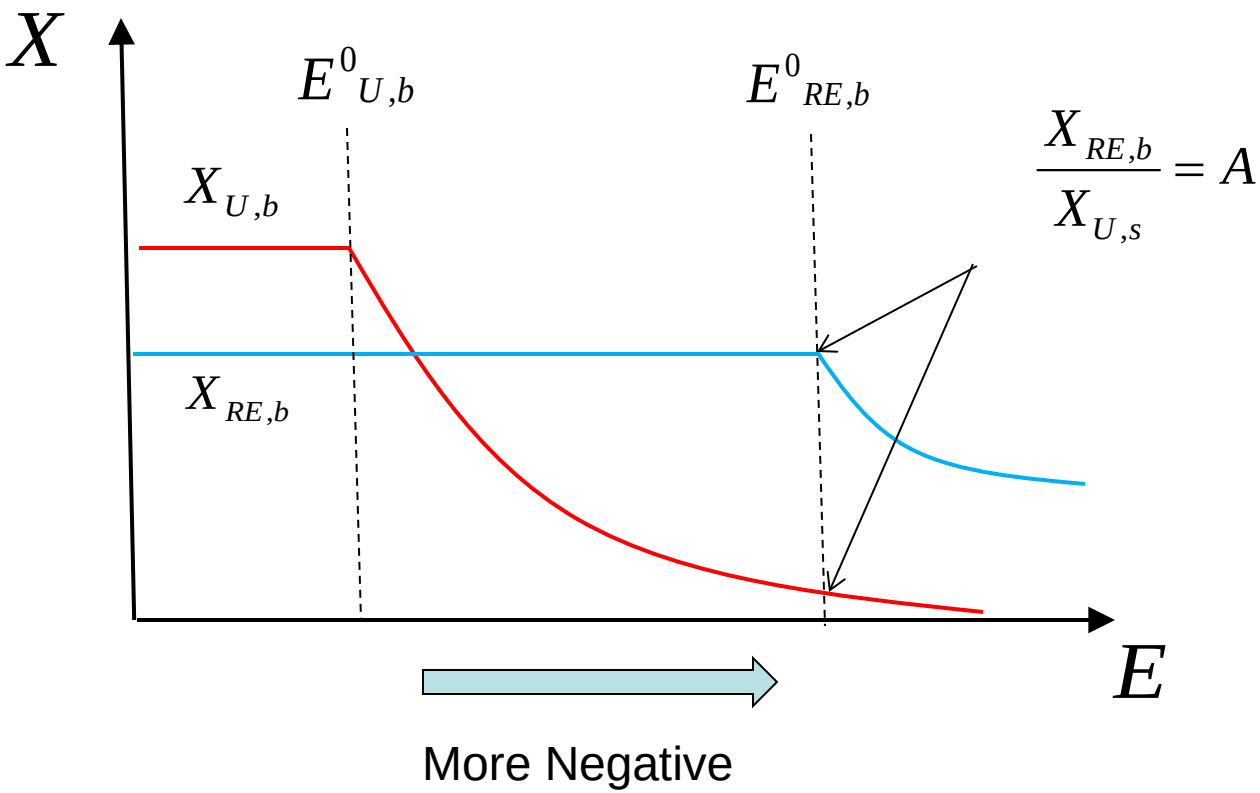
Possibility of co-deposition of U and RE at a solid electrode-Applied Current





Possibility of co-deposition of U and RE at a solid electrode-Concentration Change

Concentration change



Possibility of co-deposition of U and Pu at a solid electrode-the Model Correlation for Diffusion Control

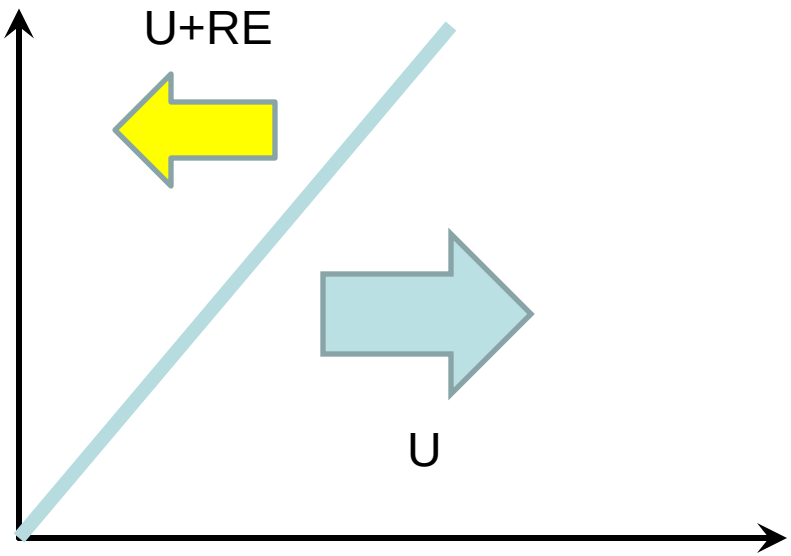
$$C_{U,b}^{ms,c} = \frac{I_{Applied}}{3FAK_U^{ms}} + C_{RE,b}^{ms} \exp\left[\frac{3F(E_{RE}^{00} - E_U^{00})}{RT}\right]$$

- **Critical value depends on:**
  - ✓ **the applied current**
  - ✓ **the surface area of electrode**
  - ✓ **the mass transfer coefficient**
  - ✓ **the Pu concentration**
  - ✓ **the temperature**

Possibility of co-deposition of U and Pu at a solid electrode-the Model Correlation for Diffusion Control

- **For avoiding the co-deposition, the applied current must follow:**

$$I_{Applied} \leq 3FAK_U^{ms}\left\{C_{U,b}^{ms,c} - C_{RE,b}^{ms}\exp\left[\frac{3F(E_{RE}^{00} - E_U^{00})}{RT}\right]\right\}$$



A New Separation Model

- **Distribution Coefficient**

$$D_{M_i} = \varphi_{M_i}(T) D_{Li}^{n_i}$$

$$\varphi_{M_i}(T) = \frac{\gamma_{M_i}}{\gamma_{Li}^{n_i}} \exp\left(\frac{n_i F}{RT}\left(E_{Li}^{ap} - E_{M_i^{n_i+}}^{ap}\right)\right)$$

- **Series of Chemical reactions**

$$M_i Cl_{n_i} + Li \leftrightharpoons n_i LiCl + M_i$$

L_m: The total Mole of Liquid Metal

S_m: The total mole of Moten Salt

Solution of Distribution Coefficient of Li

$$\sum_{i=1}^{m} \frac{n_i X^I_{M_i^{n_i+}}}{L_M + S_m \varphi_i D_{Li}^{n_i}} = \frac{X^I_{Li} D_{Li} - X^I_{Li^+}}{L_M + S_M D_{Li}}$$

$$D_{M_i} = \varphi_{M_i}(T) D_{Li}^{n_i}$$

Key Points of the Electrochemical Reactions

- **Electrochemical Reactions Mechanisms**

$$A^{n+} + ne \rightleftharpoons A$$

- **Chemical Reaction Mechanisms**

$$ACl_n + \frac{n}{m}B \leftrightharpoons \frac{n}{m}BCl_m + mA$$

- **Multi-step Electrochemical Mechanisms**

$$\underbrace{A^{(n_1+n_2)+} + n_2 e \leftrightharpoons A^{n_1+}}_{\text{Step 1}} + \overbrace{n_1 e \rightleftharpoons A}^{\text{Step 2}}$$

- **Co-Deposition/Dissolution Mechanisms**

$$E_A^{ap} + \frac{RT}{n_A F} ln\left(\frac{x_{A^{n+}}}{x_A}\right) + \eta_A = E_B^{ap} + \frac{RT}{n_B F} ln\left(\frac{x_{B^{n+}}}{x_B}\right) + \eta_B$$

Boundary Conditions of Concentration

- **Surface Concentration in Molten Salt**

$$\delta_l \frac{\partial c_{A^{n+}}}{\partial t} = R_{e,A^{n+}} + R_{c,A^{n+}} + R_{m,A^{n+}} + R_{M,A^{n+}}$$

- **Surface Concentration in Liquid Electrode**

$$\delta_l \frac{\partial c_A}{\partial t} = R_{e,A} + R_{c,A} + R_{m,A}$$

- **Surface Concentration in Solid Electrode**

$$\frac{\partial c_A}{\partial t} = R_{e,A} + R_{c,A}$$

Conclusion

- Thermodynamic data of actinides and rare earth metals in liquid Bi and Cd were critically reviewed
- Separation factors (relevance to Pu) were calculated
- Effects of Electrochmical / chemical reactions were taken into account in the model.