# Terminology

- **Pyroprocessing:**

***Pyro*metallurgical and electrochemical *processing***

- **Key Step: *Electrorefining***

***Electrotransport in a molten salt (LiCl-KCl) electrolyte***

- **Electrorefining:**

***Metal is electronically dissolved at an anode made of impure metal and re deposited at a cathode in a condition of greater purity***

***Anode: $M \rightarrow M^{+3} + 3e^-$***

***Cathode: $M^{+3} + 3e^- \rightarrow M$***

# Chemical Basis of Pyroprocessing

- **Separations based on the relative ease of oxidation into a molten salt**

*-Free energy of formation of metal chloride is primary determinant of ease of oxidation*

- **Some Separations are Chemically Complete**

*-Halides remain in salt as anions*
*-Alkali metal and alkaline earth metals (plus Sm and Eu) are completely oxidized and remain in salt*
*-Noble metals not oxidized; remain as metals*

**• Actinide and Rare Earth Metals Partition Between Salt and Metal Phases**

*-Can be transferred to salt by oxidation, or to metal by reduction*

# Pyroprocess Chemistry

**• Treat as a Series of Equilibrium Reactions**

$$M + M'Cl_3 \text{ <---> } M' + MCl_3$$

**• $\Delta G$ = Free Energy Change**

$$\Delta G = \Delta G_f^0(MCl_3) - \Delta G_f^0(M'Cl_3)$$

**•** $$K_{eq} = \exp\left(\frac{-\Delta G}{RT}\right) = \frac{\left(a_{M'} a_{MCl_3}\right)}{\left(a_M a_{M'Cl_3}\right)}$$

**Process is Controlled by Adjusting Redox State of Electrorefining Cell**

# Free Energies of Formation

| $-\Delta G_f^0$ in kcal/g-mole equiv. Cl @ 500°C | | |
|---|---|---|
| ***Elements that remain in salt (very stable chlorides)*** | ***Materials that can be electrotransported efficiently*** | ***Elements that remain in Cd pool as metals (less stable chlorides)*** |
| $BaCl_2$ 87.9 | $CmCl_3$ 64.0 | $CdCl_2$ 32.2 |
| $CsCl$ 87.8 | $PuCl_3$ 62.4 | $FeCl_2$ 29.2 |
| $RbCl$ 87.0 | $AmCl_3$ 62.1 | $NbCl_5$ 26.7 |
| $KCl$ 86.7 | $NpCl_3$ 58.1 | $MoCl_4$ 16.8 |
| $SrCl_2$ 84.7 | $UCl_3$ 55.2 | $TcCl_4$ 11.0 |
| $LiCl$ 82.5 | $ZrCl_2$ 46.6 | $RhCl_3$ 10.0 |
| $NaCl$ 81.2 | | $PdCl_2$ 9.0 |
| $CaCl_2$ 80.7 | | $RuCl_4$ 6.0 |
| $LaCl_3$ 70.2 | | |
| $PrCl_3$ 69.0 | | |
| $CeCl_3$ 68.6 | | |
| $NdCl_3$ 67.9 | | |
| $YCl_3$ 65.1 | | |

# Plutonium Recovery

- **Chemical Reaction at Solid Cathode**

  *-$UCl_3$ + Pu (s) <-----> $PuCl_3$ + U (s)*

  *-$PuCl_3$ is more stable than $UCl_3$*

  *- Deposition of Pu is favored if*

$$\frac{[PuCl_3]}{[UCl_3]} > 10^5$$ *(not practical)*

- **In the Presence of Cd, the Pu Chemical Activity is Greatly Lowered and It Behaves as though Its Chloride were Only Very Slightly More Stable Than $UCl_3$**

- **Chemical Reaction-Liquid Cd Cathode**

  *-$UCl_3$ + Pu (Cd) <---> $PuCl_3$ + U (Cd)*

  *- Deposition of Pu is favored only if*

$$\frac{[PuCl_3]}{[UCl_3]} > 2$$

  *- Deposition of TRU elements occurs as the intermetallic compound; e.g., $PuCd_6$*

  *- U also deposits in a quantity roughly equal to the TRU elements*