THERMODYNAMIC PROPERTIES OF ACTINIDES AND RARE EARTHS IN MOLTEN SALT AND CADMIUM, AND PREDICTION OF SEPARATION EFFICIENCY

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1. Introduction

The pyrometallurgical process is being developed to recover transuranium elements(TRUs) from PUREX wastes. This process consists of(1) microwave denigration and solidification to convert aqueous wastes to dry oxides, (2) chlorination to convert oxides to chlorides, (3) reductive extraction to partition TRUS into liquid cadmium from molten chlorides and (4) electrorefining to purify TRUS recovered(Fig. 1). It is expected that TRUs obtained by electrorefining contain some amount of rare earths (REs), because of the chemical similarity to TRUS and the existence by 10 times as much as TRUs in purex wastes(Fig.2). Thermodynamic properties of TRUS and REs in molten salt / liquid cadmium have been measured to evaluate the separation efficiency of TRUs in the design study of pyrometallurgical process.

2. Thermodynamic properties

The standard potentials of M(III) / M(0) (M:U,TRU,RE) in LiCl-KCl eutectic salt were measured and are ordered as follows(Fig.3);

U>Np>Pu>Am>Gd>Nd,Pr>Ce>Y>La(>Li>Eu,Sm)

It is expected that americium is the most difficult element to separate from REs. Activity coefficients of REs in liquid cadmium measured electrochemically are too small, whereas those of TRUS are relatively large(Fig.4,Table1). This indicates that electrorefining with <u>solid cathode</u> is effective to separate TRUS from REs.

3. Prediction of separation efficiency

(1) Reductive extraction process

Distribution coefficients of REs and TRUS between molten salt and liquid cadmium are calculated by using measured thermodynamic properties. The calculation explains satisfactorily the distribution coefficients of the elements obtained experimentally (Fig.5).

(2) Electrorefining process

As preliminary study, the purity of TRUS recovered by electrorefining was predicted by the calculation which indicates that it is feasible to separate more than 99% of each elements of TRUS by accompany with the same amount of REs in the product(Fig.6).

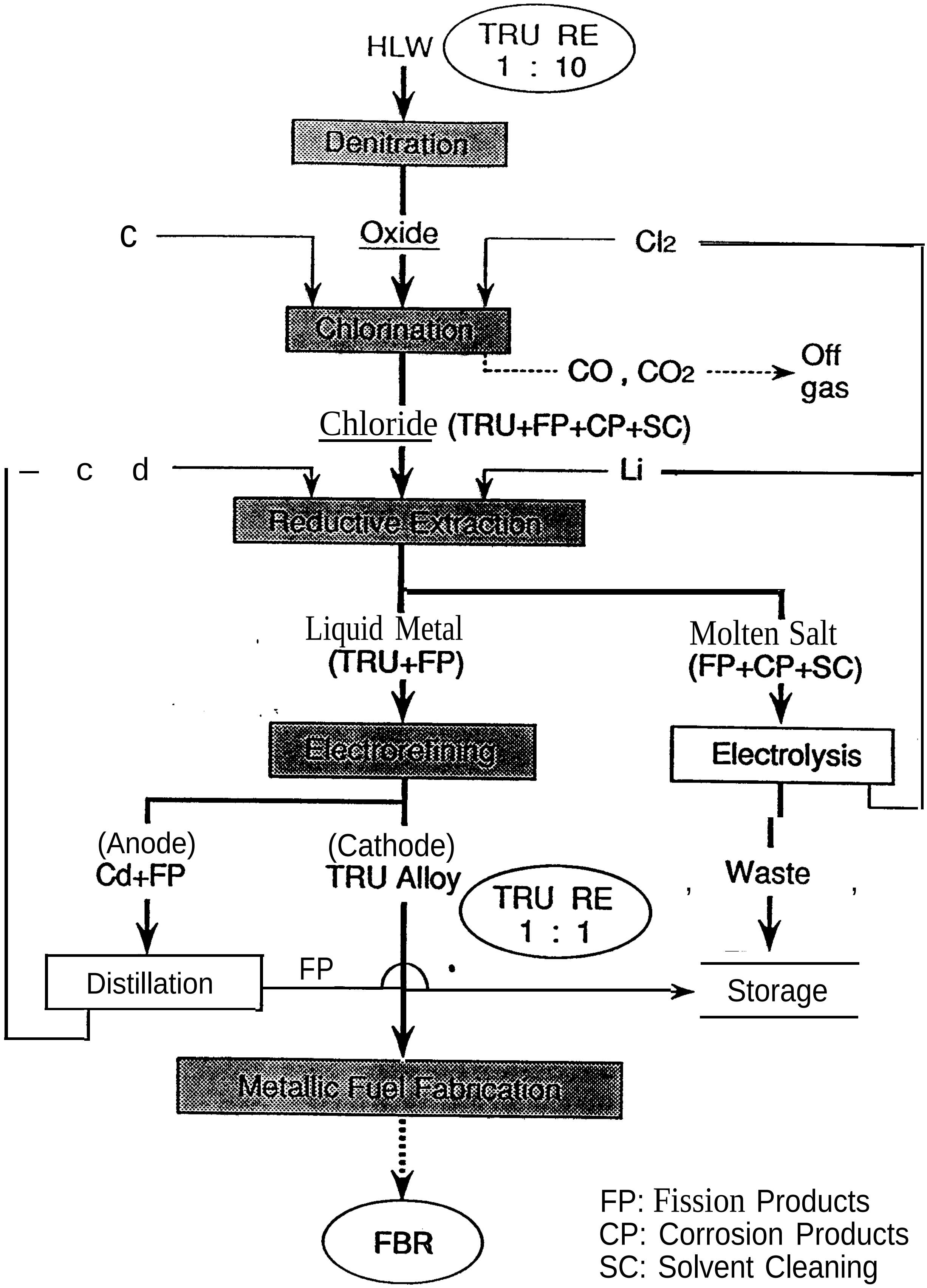

Fig. 1 Flow Diagram of Pyrometallurgical Process for Partitioning of TRUS

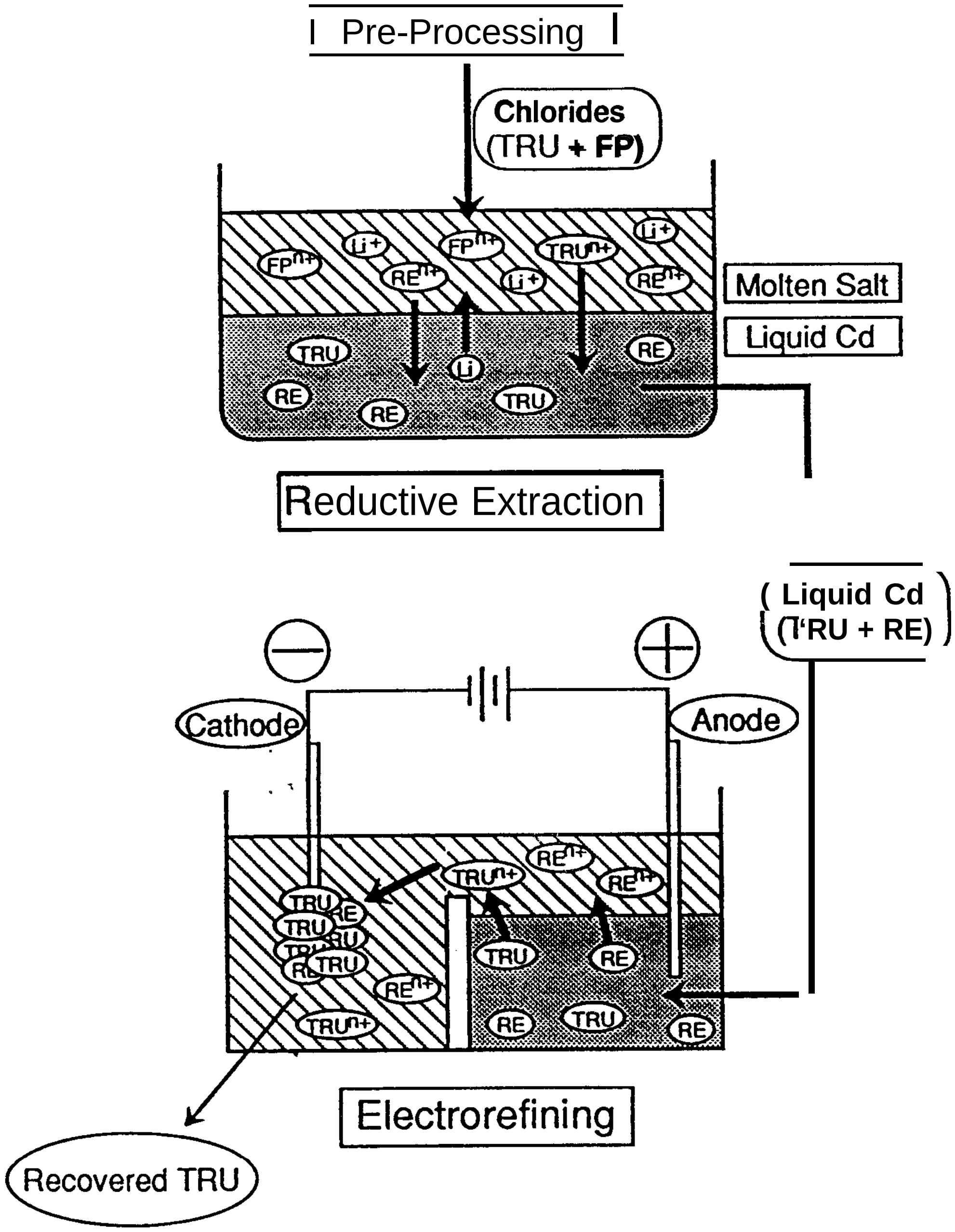

Fig.2 Schematic Illustration of Pyrometallurgical Partitioning Process

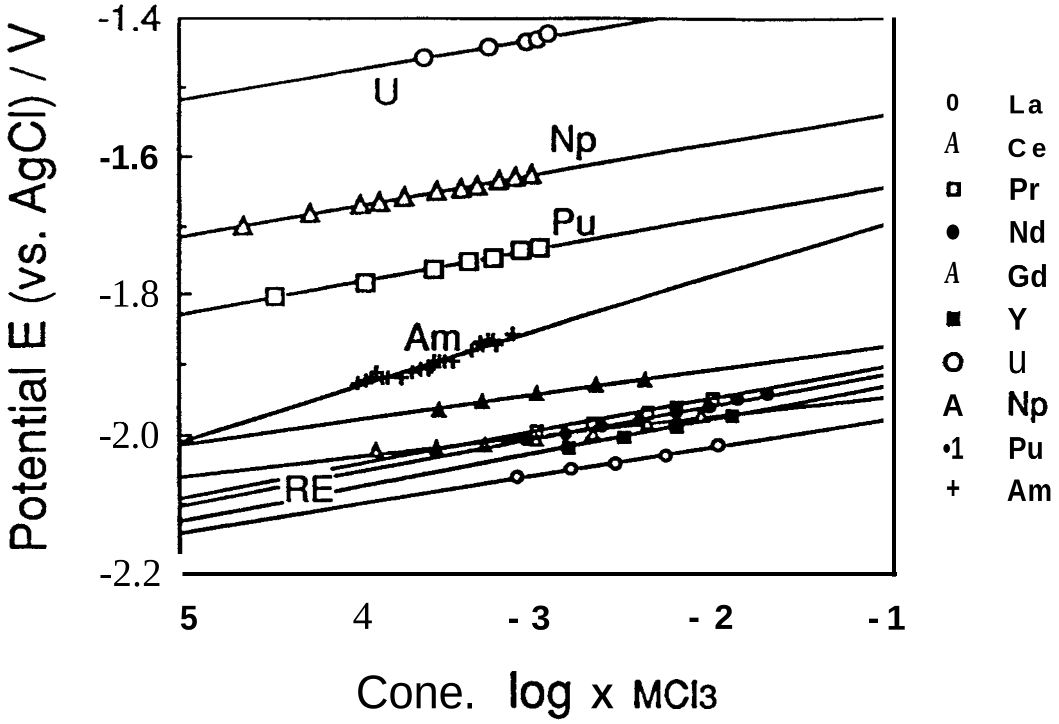

Fig.3 Potential of Metal Electrode as a Function of Mole Fraction of MC13 in LiCl-KCl Eutectic at 450"C.

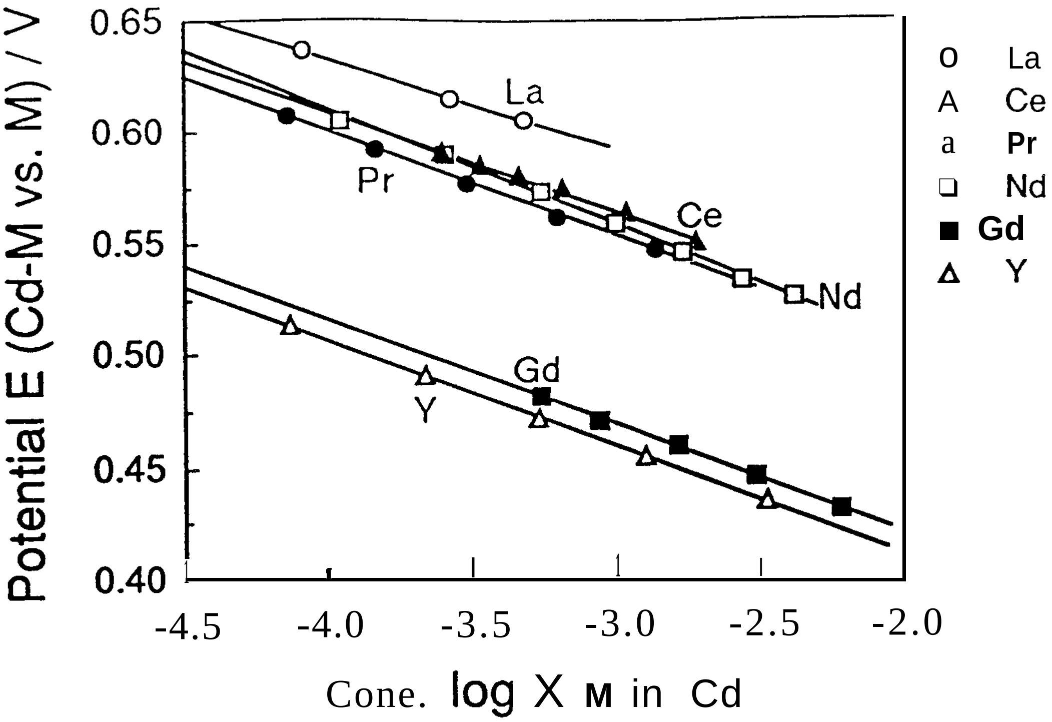

Fig.4 Potential of Cd-RE Alloy Electrode as a function of Mole Fraction of RE in Cd at 450℃

Table 1 Activity Coefficient of RE and An in Cd At 450℃

Date source	Activity Coefficient: log γ								
	La	Ce	Pr	Nd	Gd	Y	U	Np	Pu
This Experiment	-9.3	-8.8	-8.6	-8.7	-6.8	-6.6	1.9	-	-
I. Johnson et al.	-9.3	-8.8	-8.6	-	-	-	1.9	-2.2	-4.2

*) I.Johnson and R.M.Yonco, Metallug.Trans., 1, 905 (1970)
I.Johnson and H. M. Feder, Trans. Metallurg.Soc.AIME, 224, 468(1962)
M. Krumpelt, I. Lohnson and J.J.Heiberger, Metallug.Trans., 5, 65 (1974)
I. Johnson, M. G. Chasanov and R. M. Yonco, Trans. Metallurg.Soc.AIME, 233, 1408 (1965)

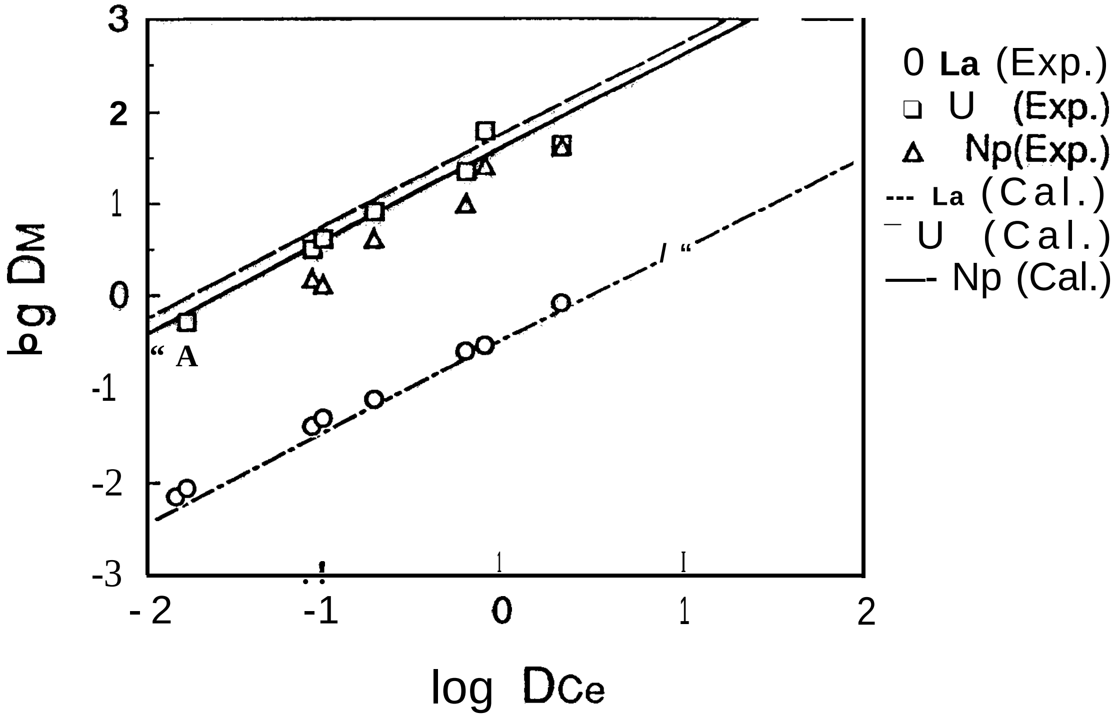

Fig.5 Distribution of Some Actinides and Rare Earths between Salt and Cadmium at 450℃.

$$D_M = \frac{X_{M \text{ in Cd}}}{X_{M \text{ in salt}}} \qquad X: \text{mole fraction}$$

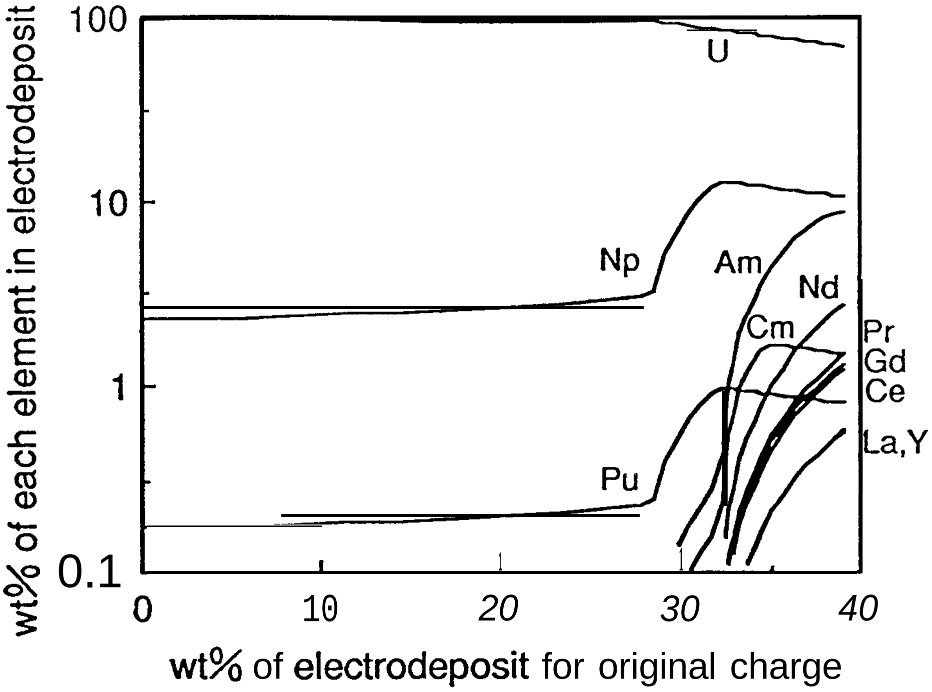

Fig.6 Calculated Composition of The Electrodeposit Using an Inert Anode.