

DEVELOPMENT OF PYROMETALLURGICAL PARTITIONING TECHNOLOGY  
OF LONG-LIVED NUCLIDES  
- DEVELOPMENT OF SALT WASTES TREATMENT TECHNOLOGY -

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In order to stabilize chloride wastes generated by the pyrometallurgical partitioning process of TRU, a process to vitrify chlorides is being developed. In the process, chlorides are reduced to metals by molten salt electrolysis and the metals are oxidized by air and then vitrified, when lithium metal and chlorine gas are recycled. The behaviors of lithium and other elements during molten salt electrolysis were studied as a function of composition of salt and cathode materials. It was shown that every metal can be recovered into liquid lead cathode by electrolysis, and that liquid cadmium and solid cathode are suitable for recovering lithium and sodium metal, respectively. Consequently, the flow sheet for the salt wastes treatment process was demonstrated.

## INTRODUCTION

The pyrometallurgical partitioning technology to recover transuranium elements (TRU) from high level radioactive wastes (HLW) generated by PUREX reprocessing is being developed by CRIEPI<sup>(1)(2)</sup>. The flow diagram for the pyrometallurgical partitioning process is shown in Fig.1. HLW are denitrated to oxides by microwave heating and the oxides are converted to chlorides by chlorine gas and carbon. Then in a molten chlorides/liquid cadmium system noble metals, TRU and most of rare earth elements are reduced by addition of lithium metal and extracted into liquid cadmium. Alkali and alkaline earth metal chlorides such as CsCl and SrCl<sub>2</sub> remain in the molten chlorides. Finally TRU are separated from the liquid cadmium by electrorefining and/or multistage extraction in LiCl-KCl eutectic salt.

Two types of salt which should be treated for disposal are generated by the pyrometallurgical partitioning process. One is mixed chloride consisting of LiCl, NaCl, RbCl, CsCl, SrCl<sub>2</sub>, BaCl<sub>2</sub>, SmCl<sub>2</sub> and EuCl<sub>2</sub> from reductive extraction step. The other is LiCl-KCl eutectic salt containing rare earth trichlorides from electrorefining and/or multistage extraction step.

Since chlorides are easily soluble in water, they must be converted to stable waste form suitable for geologic disposal. So a vitrification process for chlorides is being developed. In the process chlorides are decomposed into metals and chlorine gas by molten salt electrolysis. Then the metals are converted to oxides with air and are vitrified. It is desirable that lithium metal, chlorine gas and LiCl-KCl eutectic salt are recycled in the TRU partitioning process to reduce secondary wastes. In order to demonstrate this vitrification process, behaviors of elements during molten salt electrolysis were studied experimentally and the process flow sheet was discussed.

## EXPERIMENTAL

Experiments of molten salt electrolysis were carried out by use of various composition of salt with

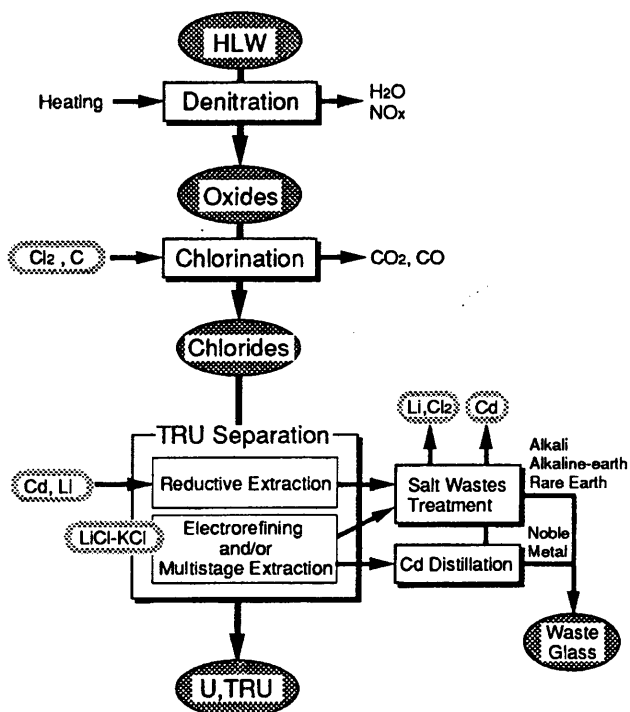


Fig. 1 Schematic flow diagram for TRU pyrometallurgical partitioning from high level wastes.

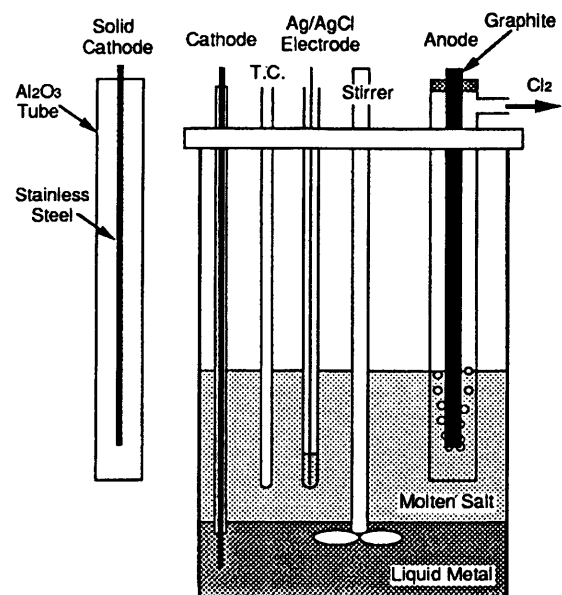


Fig. 2 Experimental cell for molten salt electrolysis.

three types of electrode which are liquid cadmium, liquid lead and solid cathode. The experimental cell is shown schematically in Fig.2. There were a graphite anode, a lead for liquid metal cathode, an Ag/AgCl reference electrode, a thermocouple and a stirrer in an alumina crucible containing molten chloride and liquid metal. Cadmium or lead was used as liquid cathode. In some experiments a solid cathode made of stainless steel was used instead of liquid metal cathode. The solid cathode was surrounded by an alumina tube to prevent metal deposit dispersing. At graphite anode chlorine gas was generated during electrolysis. The cell was located in a stainless steel thermowell attached to the floor of a glove box. The atmosphere in the glove box was high purity argon. The well was heated externally with an electric furnace. Salt and liquid metal samples were taken with pyrex glass tube and dissolved in nitric acid. The content of each element in the solutions was determined by ICP-AES or atomic absorption spectrometry.

## RESULTS

A typical result for a electrolysis with liquid metal cathode is shown in Fig.3. Initial salt consisted of 68mol% of LiCl, 29mol% of NaCl, and small amount of CsCl, BaCl<sub>2</sub> and SmCl<sub>3</sub>. As electrolysis proceeded, concentrations of all elements except cesium in liquid lead increased and samarium concentration in the salt decreased. Concentrations of lithium and sodium in liquid lead were high because of those in salt were high. To evaluate which element can be reduced easily, distribution coefficients were calculated. Distribution coefficient  $D$  is defined by equation [1].

$$D_M = X_{M \text{ in liquid metal}} / X_{M \text{ in salt}} \quad \dots [1]$$

where  $X_{M \text{ in liquid metal}}$  is mol% of metal in liquid metal and  $X_{M \text{ in salt}}$  is mol% of metal chloride in salt. The relationship between logarithm of distribution coefficients of elements and that of lithium is shown in Fig.4. The straight lines were fitted by the least squares method. The slopes

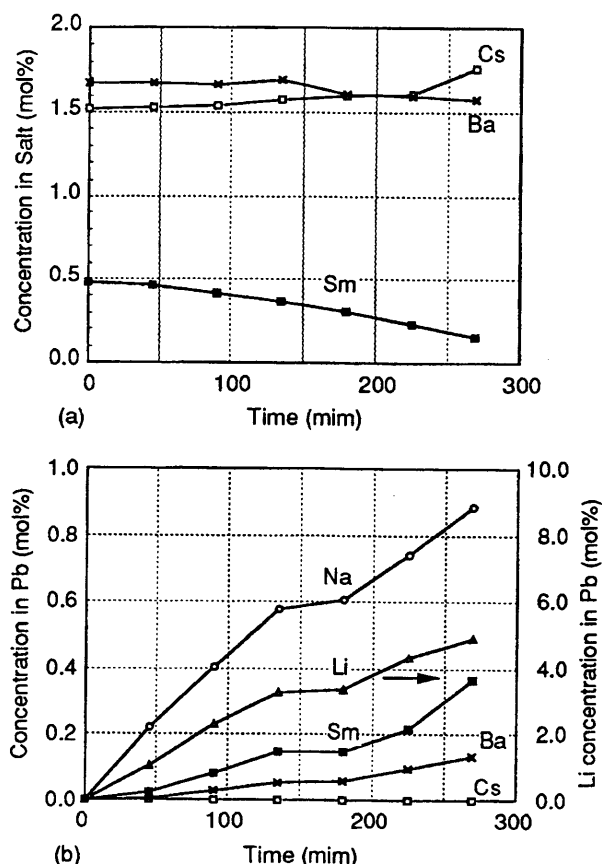


Fig.3 Concentration of elements in molten salt phase (a) and liquid lead phase (b) during constant current electrolysis. Conditions of the electrolysis were as follows: temperature =600°C ; current =3A weight of lead =1030g ; initial weight of salt =353g ; initial composition of salt (mol%) LiCl:NaCl:CsCl:BaCl<sub>2</sub>:SmCl<sub>3</sub> =67.6:28.7:1.5:1.7:0.5

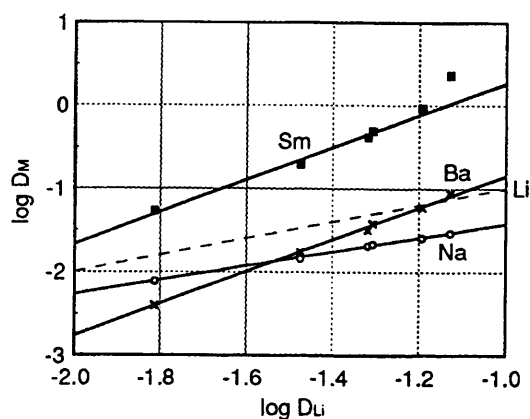


Fig.4 Distribution coefficient of metals against that of lithium during electrolysis. Distribution coefficient,  $D_M = (X_{M \text{ in liquid metal}}) / (X_{M \text{ in salt}})$ .

of the lines for samarium, barium and sodium were 1.97, 1.93 and 0.85, respectively. It is explained that as samarium and barium form dichloride in salt, their slopes are near two. As sodium form monochloride, its slope is near one ( At equilibrium there is a thermodynamic relationship that  $\log D_M = n_M \log D_L + const.$ , where  $n_M$  is the oxidation state of the element in salt). It is indicated that samarium is more easily reduced than lithium and that lithium is more easily reduced than sodium. Where  $\log D_L$  is more than 1.17, barium is more easily reduced than lithium.

Separation factor  $SF$  of a element against lithium is defined by equation [2].

$$SF = D_M / D_L \quad \dots [2]$$

Separation factors obtained by four electrolysis experiments and one equilibrium experiment <sup>(3)</sup> are shown in Table 1. These SFs were calculated by extrapolation of the lines to  $\log D_L = 0$ , which obtained by the least squares method with the slopes of the fitted lines regarded as  $n_M$ . The results in Table 1 indicates that (1)trivalent rare earth elements such as yttrium and cerium can be reduced into liquid metal very easily, (2)divalent rare earth elements such as samarium and europium can be reduced into liquid metal easily, (3)alkaline earth elements such as strontium and barium are more easily reduced than lithium where concentration of lithium in liquid metal is higher, (4)sodium is not so much as reduced than lithium, (5)cesium cannot be reduced into liquid metal cathode until concentration of cesium in salt becomes higher, (6)cadmium cathode is more suitable to separate lithium from sodium than lead cathode, and that (7)lead cathode is more suitable to separate lithium from alkaline earth elements than cadmium cathode.

Table 1 Separation factors (SF) in molten chlorides / liquid metal systems, where  $(X_{Li} \text{ in metal}) / (X_{Li} \text{ in salt}) = 1$

Element	Separation Factor ( SF )				
	During Electrolysis				Equilibrium
	Li-NaCl/Pb (Li:Na=7:3) 600°C	CsCl/Pb (Cs:96mol%) 700°C	Li-NaCl/Cd (Li:Na=7:3) 600°C	Li-Na-CsCl/Cd (Li:Na:Cs=38:16:45) 600°C	LiCl-KCl/Cd * (Li:K=59:41) 500°C
Li (basis)	1	1	1	1	1
Na	0.42	2.1	0.078	0.26	0.19
K	-	0.25	-	-	$2.7 \times 10^{-4}$
Cs	ND	0.11	ND	ND	ND
Sr	-	13	-	-	3.7
Ba	15	58	3.0	16	6.7
Y	-	-	10000	-	$2.2 \times 10^8$
Ce	-	-	10000	-	$2.1 \times 10^{10}$
Sm	200	-	100	-	680
Eu	-	100	-	-	150

ND : not detected in the liquid metal

\* M.Kurata et al. (3)

The result of electrolysis experiment using solid cathode is shown in Table 2. The electrolysis was carried out in molten salt consisting of LiCl, NaCl, CsCl, BaCl<sub>2</sub> and SmCl<sub>2</sub>. During electrolysis the deposit of metal floated at the surface of salt surrounded by alumina shroud, as the density of the metal was less than that of molten salt. Finally 4.4g of the deposit of metal was recovered and it was determined that more than 99% of the metal was sodium. It was demonstrated that sodium metal without lithium is

recovered by electrolysis by using solid cathode.

Table 2 Compositions of initial salt phase and metal deposit for the electrolysis with a solid cathode (stainless steel rod). The conditions of the electrolysis were as follows: temperature =500°C; weight of salt =690g; current =0.7A; time for electrolysis =380min; weight of the deposit of metal recovered =4.4g

Element	Composition (mol%)	
	Initial salt	Metal deposit
Li	43.8	< 1
Na	14.4	> 99
Cs	38.2	< 1
Ba	3.0	< 1
Sm	0.6	< 1

### FLOW SHEET FOR SALT TREATMENT PROCESS

The flow sheet of salt wastes treatment shown in Fig.5 is proposed on the basis of experimental results. There are two types of salt waste. One is LiCl-KCl eutectic salt containing rare earth trichloride from TRU/RE separation step. It is not difficult to remove rare earth from LiCl-KCl eutectic salt by molten salt electrolysis with lead cathode. Purified LiCl-KCl eutectic salt is recycled. The other is mixed chloride consisting of alkali (Li,Na,Rb,Cs), alkaline earth (Sr,Ba) and rare earth (Sm,Eu) chlorides. The latter salt is treated by the following procedure: (1) rare earth is recovered in lead cathode; (2) lithium is recovered in cadmium cathode to recycle in TRU separation process; (3) all of elements are recovered in lead cathode; (4) lead alloys containing active metals (alkali, alkaline earth and rare earth metals) are reacted with oxygen in air and active metals are converted to oxide; (5) the oxide is mixed with glass materials and vitrified. The lead metal in which active metals are removed is recycled. Chlorine gas generated at carbon anode during electrolysis is recycled in chlorination step for HLW. Sodium comes from solvent cleaning of PUREX processing. If a large amount of sodium accompanies the recycled lithium, the melting point of salt in reductive extraction step gets higher. Therefore, sodium would be removed by electrolysis with solid cathode so that more lithium metal can be recycled.

The advantage of this salt treatment process is that waste form of glass is familiar and that it is possible to reduce an amount of secondary wastes by recycling lithium metal, chlorine gas and LiCl-KCl eutectic salt.

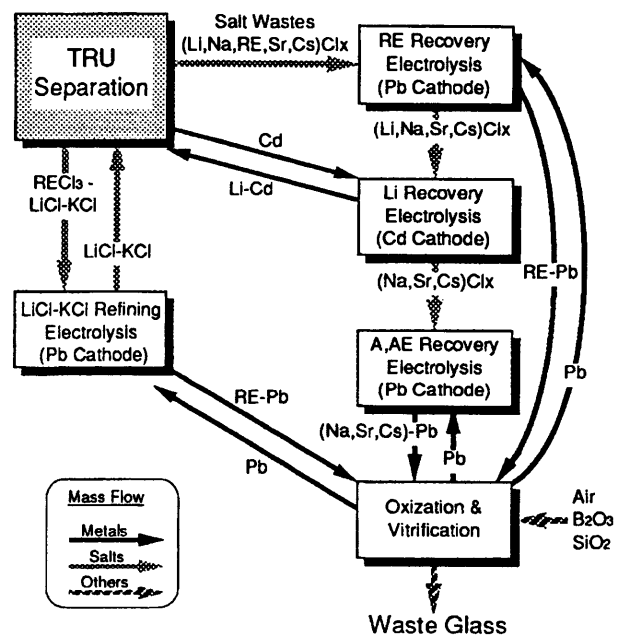


Fig. 5 Schematic flow diagram of salt wastes treatment.

## REFERENCE

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