ESTIMATION OF MATERIAL BALANCE IN PYROMETALLURGICAL PARTITIONING PROCESS FOR TRUs FROM HLLW

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Abstract

A pyrometallurgical partitioning process has been proposed and studied by CRIEPI. In this process, more than 98% of alkali metals were separated in a denitration step. Almost all of the another elements were converted to chlorides from oxides in a chlorination step. Separation experiments by means of multiple batch extraction was also carried out in the LiCl-KCl/Bi system, and more than 99% of each TRU was recovered. The material balance of solutes and solvents in the partitioning process was estimated from the experimental results of each step in the process. The refining salt, Cd, Bi, and Pb as solvent, Li as reductant, and generated chlorine gas can be recycled to the process. This process is, therefore, expected to generate less secondary radioactive waste in comparison with an aqueous process and should require relatively compact facilities.

Introduction

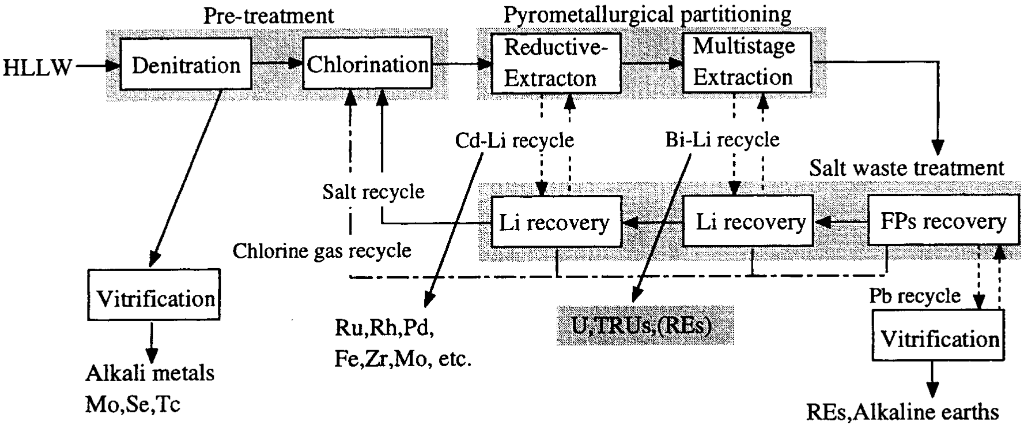
High level liquid waste (HLLW) from a reprocessing of light water reactor spent fuels contains a small amount of long-lived nuclides consisting mainly of transuranic elements (TRUs), such as Np, Pu, Am, and Cm. A pyrometallurgical partitioning process for TRUs from HLLW is expected to generate less amount of secondary radioactive waste in comparison with conventional aqueous process, and should require relatively compact facilities [1]. U and TRUs recovered from the HLLW will be blended in metallic fuels and transmuted in a fast breeder reactor.

Table 1 **Composition of elements in the HLLW calculated by ORIGEN-II code with burn-up of 48 CWd/t-U in PWR and cooling time of 4 years (99.5% of U an dPu are recovered by reprocessing)**

element		mol	wt.(g)	wt.%		mol	wt.(g)	wt.%		mol	wt.(g)	wt.%
uranium	U	19.73	4694	7.44								
TRUs	Np	3.02	715.5	1.13	Am	2.41	583.6	0.93				
	Pu	0.22	52.10	0.08	Cm	0.41	100.1	0.16				
fission products (FP)	Rb	5.48	473.7	0.75	Nd	39.81	5770	9.15	Ru	32.78	3346	5.31
	Cs	27.01	3646	5.78	Pm	0.32	46.27	0.07	Rh	5.59	575.3	0.91
	Sr	12.56	1119	1.77	Sm	7.78	1163	1.84	Pd	22.45	2376	3.77
	Ba	17.25	2370	3.76	Eu	1.51	231.0	0.37	Ag	1.08	117.5	0.19
	Y	6.94	617.7	0.98	Gd	1.57	244.5	0.39	Cd	1.82	202.9	0.32
	La	12.49	1736	2.75	Zr	53.34	4976	7.89	Sn	1.13	137.0	0.22
	Ce	24.08	3393	5.38	Mo	49.13	4795	7.60	Se	0.98	78.88	0.13
	Pr	11.20	1579	2.50	Tc	10.61	1050	1.67	Te	5.53	715.8	1.14
corrosion product	Fe	62.67	3500	5.55								
solvent cleaning	Na	550.24	12650	20.06								

The composition of the HLLW shown in Table 1 were based on ORIGEN-II calculations with burn up of 48 GWd/t-U in PWR and cooling of 4 years [2]. Because of the chemical similarity to TRUs and rare earth elements (REs), the separation of TRUs from REs is considered to be difficult. The target of the pyrometallurgical partitioning process is to recover more than 99% of each actinide contained in HLLW in a product where the weight ratio of TRUs to REs is more than one [1]. The flow diagram of the pyrometallurgical partitioning process is illustrated in Figure 1. It consists of denitration, chlorination, reductive-extraction, countercurrent extraction, and salt waste treatment process.

Figure 1. **Pyrometallurgical partitioning process**



The objective of this paper is to propose the pyrometallurgical partitioning process with estimated material balance of solutes and solvents. The material balance is estimated by use of the distribution coefficient of each element measured in the LiCl-KCl/Cd, Bi, and Pb system [3,4,5,6] and the amount of solvents in each process decided by the previous experiments.

Concept and experimental results for the partitioning process

Denitration process

The elements except for alkali metals in the HLLW are converted from nitrates to oxides with generating H_2O and NO_x gas at 773K at the denitration process. The experimental result for denitration used non-radioactive elements is shown in Figure 2 [7]. More than 98% of each alkali metal were separated by water rinse method because alkali nitrates which were soluble in water did not convert to oxides at 773K. Rb and Cs are FPs, and Na is originated from solvent cleaning materials. About 3% of Sr and 1% of Ba also remained as nitrates and were separated in this process. More than 60% of Mo, 80% of Se, and 98% of Re which substituted for Tc, were converted water-soluble complex oxide with alkali metals and were also separated from other oxide elements in this process.

Figure 2. **Mass balance in denitration**

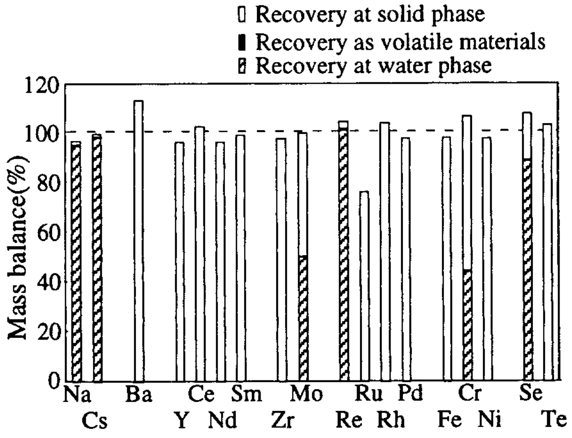
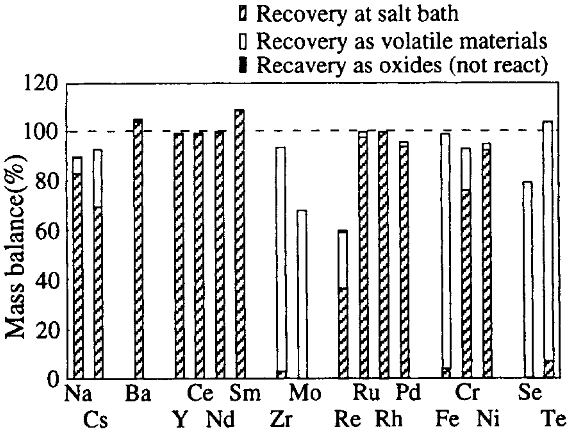


Figure 3. **Mass balance in chlorination**



Chlorination process

The oxides generated at the denitration process are mixed into LiCl-KCl salt and are converted to chlorides under Cl_2 gas flow at 973K at the chlorination step. The experimental result for chlorination used non-radioactive elements is shown in Figure 3 [8]. More than 99% of REs, alkaline earths, and Rh, and 97% of Ru and Pd were converted to chloride at this process. More than 95% of Fe, Zr, Mo, Te, and Se, however, evaporated at this process. They were captured into a LiCl-KCl molten salt bath maintained the temperature at 700K. The experimental result for Fe, Zr, and Mo is presented in Table 2 [9]. The salt bath with captured chlorides will be returned to the reductive-extraction process.

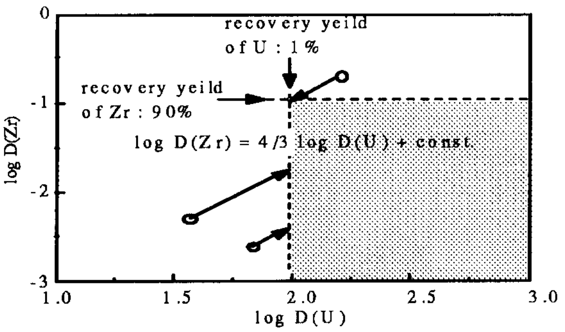
Table 2. **Recovery yield of volatile chloride at molten salt trap**

	MoC15	ZrC14	FeC13
Initial amount (mg): A	195	198	206
Amount remained as oxide (mg): B	67	192	142
Recovery at molten salt trap (mg): C	133	50	53
Recovery behind molten salt trap (mg): D	0.6	0.1	0.3
Recovery yield (%): C/(C+D)	99.6	99.8	99.5
Mass balance (%): (B+C+D)/A	103	123	95

Reductive-extraction process

The FPs which are more noble than U are extracted into Cd phase by use of Li as reductant in LiCl-KCl/Cd system at 773K to 823K [10]. The purpose of this process is to remove as much of these FPs as possible from the salt while carrying less than 0.1% of each TRU into the Cd. Fe, a corrosion product, is also extracted into Cd. These elements are expected to separate from U easily from the estimation by use of free energies of formation in LiCl-KCl. Some part of U was, nevertheless, extracted into Cd when some part of Zr and Fe still remains in the salt phase in previous tests [10]. It assumed that the solubility of U in Cd decreased and U formed intermetallic compound in Cd with Fe and Zr. Figure 4 shows the experimental results of distribution of U and Zr between LiCl-KCl and Cd. This figure shows more than 90% of Zr and less than 1% of U can be extracted into Cd on the assumption that Zr is tetravalent and U is trivalent chloride in the salt.

Figure 4. **Relationship between distribution coefficients of U and those of Zr at reductive-extraction process (O : experimental data in LiCl-K Cl/Cd at 723 K)**

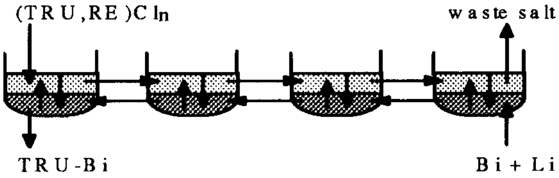


The elements extracted into the Cd are recovered as metal form waste by means of a distillation of the Cd. The Cd is collected and reused in this process. The salt phase which includes U, TRUs, REs, alkaline earth elements, and some part of Zr are processed in the countercurrent extraction process.

Countercurrent extraction process

U and TRUs are extracted into Bi phase and are separated from FPs by the difference between the distribution coefficients of actinides and that of FPs in molten LiCl-KCl and liquid Bi system at 773 K. For greater than 99% of TRUs to be recovered in a single step reductive-extraction, most of the REs would accompany the TRUs. This separation criteria, therefore, are expected to be achieved by means of a countercurrent extraction. The concept of a countercurrent extraction process shows in Figure 5. The salt contained TRUs and REs is put into the first stage as salt phase. Liquid Bi-Li alloy is put into the last stage as metal phase. The salt phase and the metal phase are transferred to the next stage after equilibrium condition attained.

Figure 5. **Concept of counter current extraction system**



It is assumed for this estimation that each element can be treated as the dilute solution in salt phases and doesn't form intermetallic compounds in Bi phases. The separation factor (SF) measured between LiCl-KCl eutectic salt and liquid Bi at dilute concentration can be used for the simulation study under the above condition. SF of metal "M" is defined as follows:

$$SF_M = D_M / D_{Nd} = [X(M) / Y(M)]/[X(Nd) / Y(Nd)] \quad (1)$$

In this equation, D_M means distribution coefficient of M, and X(M) and Y(M) mean mole fraction of MCl_n in the salt and that of M in Bi phase, respectively. The separation factors are shown in Table 3 [3, 4]. Figure 6(a) and Figure 6(b) shows the calculated recovery yield of U and TRUs and that of REs, respectively, in case that 99% of Am were recovered in 2 to 5 stages countercurrent extraction. Figure 7 shows the weight ratio of recovered TRUs to REs calculated in case that 99.9% of Am was recovered is 3.08, which fully satisfied the requirement for the fabrication of metallic fuel.

Table 3. **Separation factor of U TRUs, and REs to Nd measured in LiCl-KCl/Bi system at 773 K**

	ref.(4)	ref.(3)
U	0.00065	0.0011
Np	0.0051	0.012
Pu	0.0076	-
Am	0.015	-
Nd	1.0	1.0
Pr	-	0.99
Ce	-	0.89
La	-	2.7
Gd	-	11
Y	-	630

The recovered TRUs are separated from Bi and will be transmuted in a metallic fuelled FBR. Bi is reused in this process and the salt contained REs and alkaline earth elements are processed in a salt waste treatment process.

Figure 6. **Recovery of (a) U and TRUs (b) REscalculated in case of 99.9% of Am recovered using counter current extraction in LiCl-KCl/Bi system at 723 K**

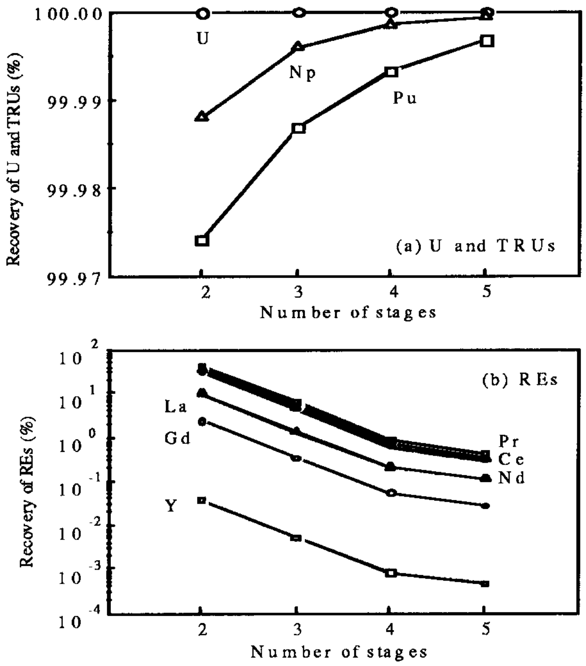
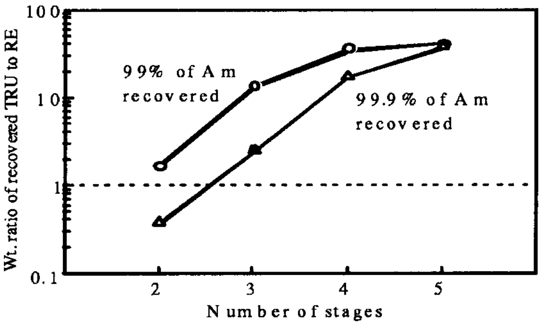


Figure 7. **TRUs/REs wt. ratio calculated in case of 99% or 99.9% of Am recovered using counter current extraction in LiCl-KCl/Bi system at 723 K**



Salt waste treatment process

The salt with FPs is treated at salt waste treatment process to minimise the amount of disposal LiCl-KCl solvent as waste. REs, alkaline earths and alkali elements included in the salt from the countercurrent extraction process are extracted into Pb anode by electrolysis in this process. The separation between Li and FPs is considered difficult, because the free energy of formation of Li chloride is close to that of alkali and alkaline earth FPs. Separation factors of FPs to Li in LiCl-KCl/Pb system at 723K are shown in Table 4 [5]. The amount of Li accompanied FPs increases with an increase in the amount of FPs recovered into Pb anode. Some part of alkali and alkaline earth FPs are, therefore, expected to recycle with LiCl-KCl in order to minimise the amount of disposal Li as waste. The metals recovered into Pb anode are converted to oxides at 1073 K with B_2O_3 under air flow condition and then are vitrified. Pb metal does not convert to oxides in this treatment [11] and is reused in this process.

Table 4. **Relationship between distribution coefficient of alkali metals and divalent elements and that of Li measured in LiCl-KCl/Cd, Bi, or Pb system**

log D(M) = a log D(Li) + b

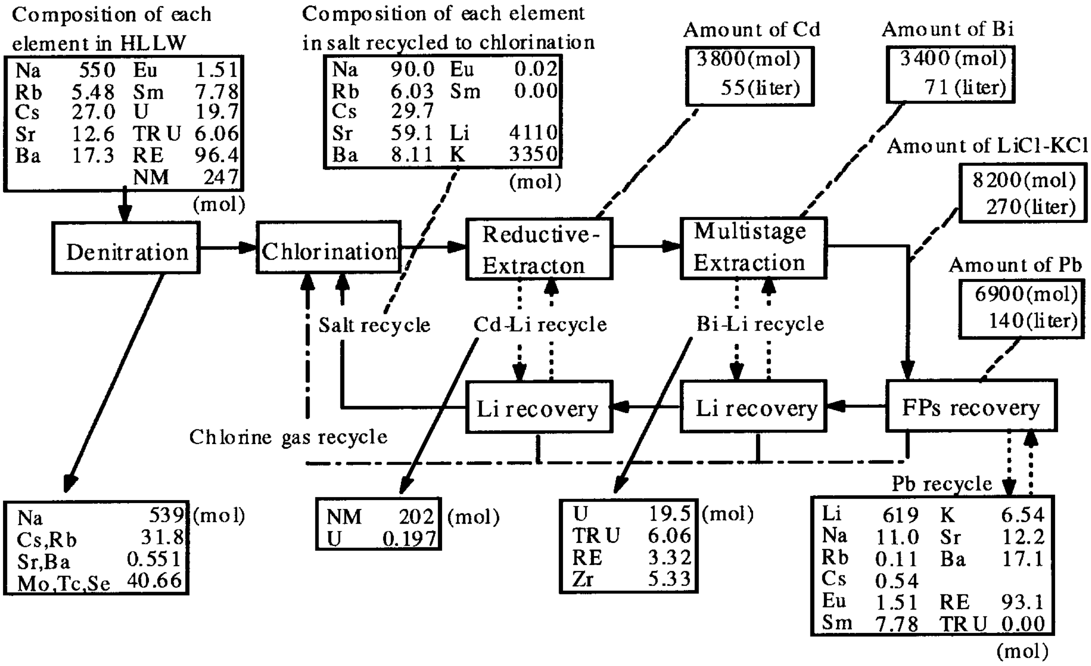
	LiCl-KCl/Cd (773K)			LiCl-KCl/Bi (773K)			LiCl-KCl/Pb (723K)		
	b	a	ref.	b	a	ref.	b	a	ref.
Sm	-2.57	1.88	(3)	-3.60	1.96	(3)	-3.14	2	(5)
Eu	-2.16	1.99	(3)	-2.76	1.96	(3)	-2.48	2	(5)
Ba	-0.93	2.07	(3)	-2.28	1.91	(3)	-1.74	2	(5)
Sr	-0.45	1.93	(3)	-1.07	1.87	(3)	-0.90	2	(5)
Na	0.72	1	(11)	-	-		0.10	1	(5)
K	3.57	1	(11)	0.80	1	(11)	1.88	1	(5)
Cs	-	-		-	-		0.91	1	(5)

Reductant Li for the reductive-extraction process and for the countercurrent extraction process is also recovered by electrolysis into Cd anode and Bi anode, respectively. Alkali and alkaline earth FPs also recovered into Cd or Bi with Li in accordance with their separation factor shown in Table 4. Chlorine gas and LiCl-KCl refined with small part of alkali and alkaline earth elements generated in this process are recycled to the chlorination process.

Estimation of material balance

The process flow with material balance is shown in Figure 8. The values of amount for each element in this figure are estimated in case that about 500 litre of the HLLW generated from PUREX process for 1 ton-U of PWR fuel is treated as 1 batch in the pyrometallurgical partitioning process which is reached the steady condition.

Figure 8. **Material balance in pyrometallurgical partitioning process**



Material balance of products and wastes

The product is recovered at countercurrent extraction process and the wastes are generated from denitration, reductive-extraction, and salt waste treatment process. The recovery yield of each element in each step is shown in Table 5. It is assumed that all of oxides are converted chlorides at the chlorination process and vaporised chlorides are recovered completely and transferred to the reductive-extraction process.

Table 5. **Experimental recovery yield of each element at each process in pyrometalurgical partitioning**

	Ru, Rh, Pd	Mo	Se	Re (Tc)	Fe	Zr	Te	Cd	U	TRU	RE	Ba, Sr	Na, Rb, Cs
Separation at denitration		60	85	98								<3	>98
Volatile at chlorination	(2)	(40)	(15)		(95)	(97)	(100)	(40)				(<1)	(<1)
Separation at reductive-extraction	100	40	15	2	100	>90	100	100	<1				
Recovery from multistage extraction						<10			>99	>99	<10		
Separation at salt waste treatment										<1	>90	>97	<2

It is expected that more than 99.9% of U and TRUs are separated from FPs by 3 stages' countercurrent extraction. The weight ratio of recovered TRUs to REs is 3.08 in case that 99.9% of Am was recovered, which fully satisfied the requirement for the fabrication of metallic fuel. It was assumed that 10% of Zr remained in salt phase in the reductive-extraction process and it is recovered into Bi with U and TRUs.

The waste from denitration process contains alkali nitrates, complex oxides of Tc, Mo, Se with alkali metals, and small part of alkaline earth nitrates, which are vitrified after oxidation. The waste from reductive-extraction process consists of 1% of U, 90% of Zr and the all of metals more noble than Zr, which are disposed of as metallic form waste, or are oxidised and vitrified. The another waste with REs, alkaline earths, and alkali metals in Pb alloy from salt waste treatment process are oxidised, separated from Pb, and vitrified.

Amount of salt and metal solvents

Amount of LiCl-KCl in the pyrometallurgical partitioning is estimated about 450 kg, 270 litre in order that the total concentration of U, TRUs, and REs is less than 1.5 mol% in the salt phase of the 1st stage in the countercurrent extraction process. In this condition, the concentration of each element of U, TRUs, and REs is less than 0.5 mol%, which is similar condition of previous separation test [4] and is low concentration enough for the simulation by use of the distribution coefficients measured in dilute system [12]. The total concentration of all solutes is about 7.1 mol% in the salt phase after the chlorination in this case. The concentration of the solutes affects the volume of the salt phase and the size of the facility. For the operation at higher concentration of the solutes, melting point and viscosity of the salt and distribution coefficients of each element in the system have to be obtained.

Amount of Pb in the salt treatment process is estimated about 1 400 kg, 140 liter in order that the concentration of REs and alkaline earth metals extracted into Pb by electrolysis is less than 10 mol% which is attained in previous study [11]. To decrease the amount of Pb causes to make the facility compact, but requires to extract REs and other FPs into Pb with higher concentration by electrolysis. It is assumed that 100% of Pb can be reused in this process after removal of FPs in this estimation.

Amount of Cd in the reductive-extraction process is estimated about 430 kg, 55 liter in order that the concentration of noble FPs, such as noble metals, Mo, Fe, Zr and so on, extracted into Cd is less than 5 mol%. The concentration of FPs in the reductive-extraction process affects that of reductant extracted into Cd by electrolysis. The concentration of the reductant in Cd is about 14.6 mol% in the case of the concentration of FPs is 5 mol% in Cd. This is expected to obtain because Cd-Li alloy including 20 mol% of Li could be made in previous study [13]. It is assumed that 100% of Cd can be reused in this process after distillation in this estimation.

Amount of Bi in the countercurrent extraction process is estimated about 710 kg, 71 liter in order that the concentration of U, TRUs, and REs in Bi is less than 1 mol%. It is expected that no intermetallic compounds are found in Bi phase for steady operation of the countercurrent extraction process. The solubility of REs in Bi at the multi-elements system become significantly smaller than those in the binary system [12]. When the total concentration of them is less than 1 mol%, intermetallic compounds seemed not to be formed [12]. The concentration of reductant extracted into Bi by electrolysis is less than 3 mol% in this case. It is assumed that 100% of Bi can be reused in this process after separation of U and TRUs in this estimation.

Amount of chlorine gas generated from three different electrolysis in salt waste treatment process is estimated about 12.8 m^3 which is reused in chlorination process.

Amount of FPs in the recycled salt

The salt solvent is recycled in the pyrometallurgical partitioning process to reduce the secondary waste. The concentration of each alkali and alkaline earth FP in the recycled salt decreases with an increase in the amount of Li extracted into Pb with FPs, but the excess amount of Li to be fed vitrification becomes the secondary waste. Some part of alkali and alkaline earth FPs is, therefore, remained in the recycled salt to minimise the amount of disposal LiCl-KCl solvent as waste. A typical vitrified product of HLLW contains 3 wt.% of Li_2O and 10 wt.% of FPs oxides [14]. It can be considered that no Li is generated from the partitioning process as a secondary waste, in the case that the amount of Li extracted into Pb is less than 3/10 by weight of amount of FPs. In this estimation, 12.8% of Li is extracted into Pb with other FPs and same amount of Li is added as LiCl.

Summary

The material balance in pyrometallurgical partitioning of TRUs from HLLW was estimated by use of distribution coefficients measured in LiCl-KCl/ Cd, Bi or Pb. When 99.9% of Am was recovered, the weight ratio of recovered TRUs to REs was estimated 3.08 at 3 stages' countercurrent extraction between LiCl-KCl and Bi, which was enough for metallic fuel fabrication. The waste generated as three different forms. There were alkali nitrate and complex oxide of Tc, Mo, and Se with alkali from denitration process, noble metals from reductive-extraction process, and REs and alkaline earth as Pb alloy from countercurrent extraction process.

Amount of solvents were estimated by using previous experimental conditions. 270 liter of LiCl-KCl eutectic salt, 55 liter of Cd, 71 liter of Bi, and 140 liter of Pb are used in the pyrometallurgical partitioning process. It was found that almost all of them including chlorine gas and reductant could be recycled , and Li disposed at salt treatment process becomes one of the matrix composition of glass form. Less secondary waste, therefore, will be generated in comparison with aqueous process and should require relatively compact facilities.

REFERENCES

[1] T. Inoue, M. Sakata, Y. Sakamura, T. Hijikata, and K. Kinoshita, IAEA-TECDOC-783 (1995)117.

[2] T. Inoue, M. Sakata, H. Miyashiro, M. Matsumoto, A. Sasahara, and N. Yoshiki, *Nucl. Technol.* 93(1991)206.

[3] M. Kurata, Y. Sakamura, T. Hijikata, and K. Kinoshita, *J. Nucl. Mater.* 227(1995)110.

[4] K. Kinoshita, T. Inoue, S.P. Fusselman, R.L. Gay, C.L. Krueger, T.S. Storvick, and N. Takahashi, *Proc. of Global '97 vol. 2* (Yokohama, Japan, 1997) p.820.

[5] K. Kinoshita and T. Inoue, *CRIEPI Report T97015*, Central Research Institute of Electric Power Industry (1998) [in Japanese].

[6] Y. Sakamura, T. Inoue, T.S. Storvick, and L.F. Grantham, Proc. of the Twenty-sixth Symposium on Molten Salt Chemistry (Sapporo, Japan, 1994) p.101 [in Japanese].

[7] M. Kurata, CRIEPI Report T98002, Central Research Institute of Electric Power Industry (1998) [in Japanese].

[8] H. Konagaya, M. Kurata, T. Hijikata, and K. Nakamura, CRIEPI Report T97076, Central Research Institute of Electric Power Industry (1998) [in Japanese].

[9] T. Hijikata, K. Nakamura, M. Kurata, and H. Konagaya, CRIEPI Report T96068, Central Research Institute of Electric Power Industry (1997) [in Japanese].

[10] S.P. Fusselman, R.L. Gay, D.L. Grimmett, J.J. Roy, C.L. Krueger, C.R. Nabelek, T.S. Storvick, T. Inoue, K. Kinoshita, and N. Takahashi, *Proc. of Global '97 vol. 2* (Yokohama, Japan, 1997) p.816.

[11] Y. Sakamura, T. Inoue, T. Shimizu, and K. Kobayashi, *Proc. of Global '97 vol. 2* (Yokohama, Japan, 1997) p.1222.

[12] M. Kurata, Y. Sakamura, T. Hijikata, K. Kinoshita, and T. Inoue, CRIEPI Report ET96001, Central Research Institute of Electric Power Industry (1997).

[13] T. Kato, Y. Sakamura, and T. Inoue, *Proc. of Global '97 vol. 2* (Yokohama, Japan, 1997) p.806.

[14] H. Igarashi,H, *NEW GLASS* 11[3](1996)11 [in Japanese].