A Study on Innovative Method for Selective Recovering All Actinides in LiCl-KCl Mixture Discharging from Pyroprocess System

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Introduction

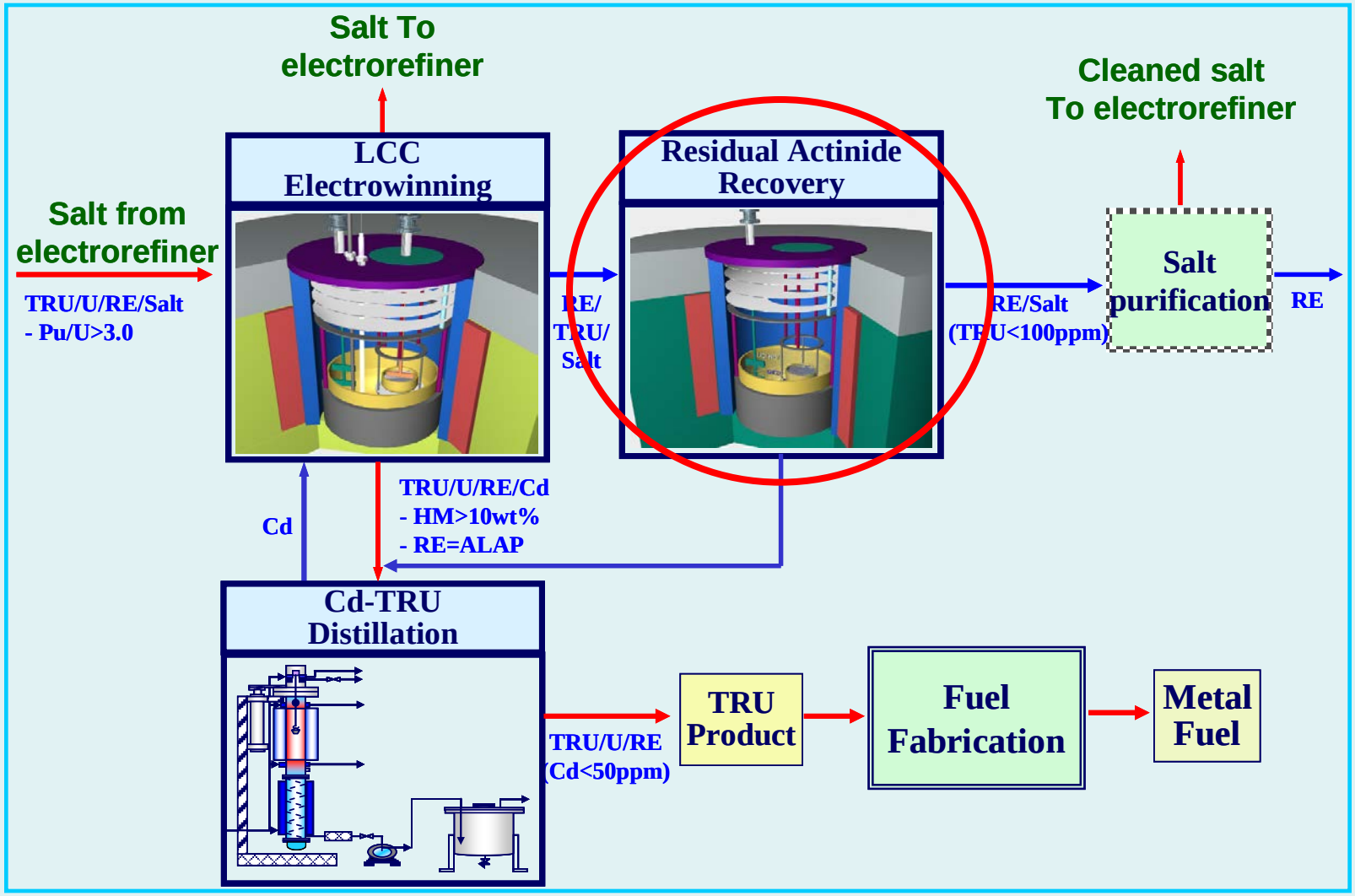
- It is necessary to establish an effective recovery method of residual actinides for minimizing the amount of waste generated from the pyroprocessing system and the content of actinides to be disposed of.

- KAERI has developed a "Residual Actinides Recovery (RAR) technology" by combining electrolysis using an LCC and an oxidation of the rare earths by $CdCl_2$ to collect most of the residual actinides in spent salt.

- Recently, the KAERI is developing a new recovery method (Adv-RAR) of the actinide elements by introducing the rare earth metals as a reducing agent of the actinide metal chlorides.

- In this presentation, some of the theoretical study and experimental results upon the new recovery method will be discussed including the equilibrium reactions of the actinide and lanthanide metal chlorides using the HSC program, the concept and features of the new recovery method, and actinide recovery test results .

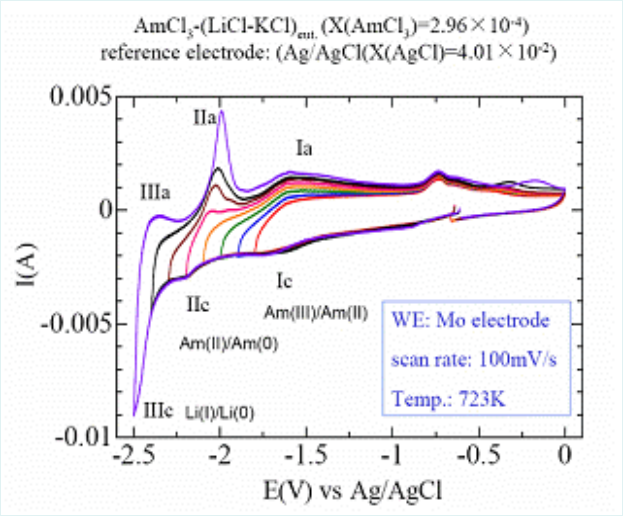
KAERI's Electrowinning System for TRU Recovery



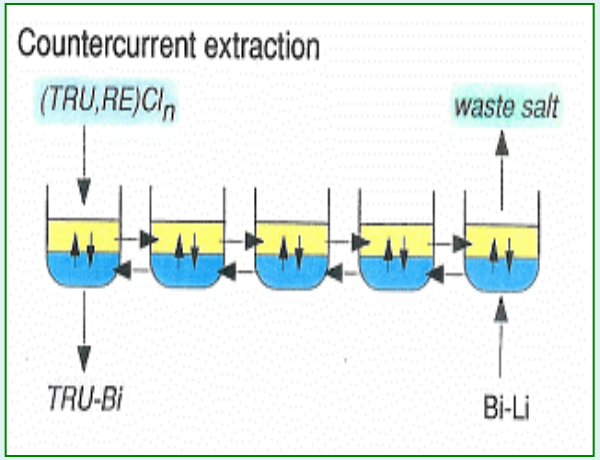
State of the Art on Drawdown of Actinides

- United States
  - ANL, electrolysis using solid cathode and Li-Cd anode in 1994
  - Low recovery yields of Am due to disproportion reaction of Am
  - INL, drawdown of actinides by adding Li metal into a salt in 2011
- Japan (CRIEPI)
  - Electrolysis using solid cathode and Li-Sb anode in 2003
  - Counter-current multi-staged reductive extraction from 2005
- Europe (EU)
  - Electrolysis using Al cathode and selective oxidation from 2007

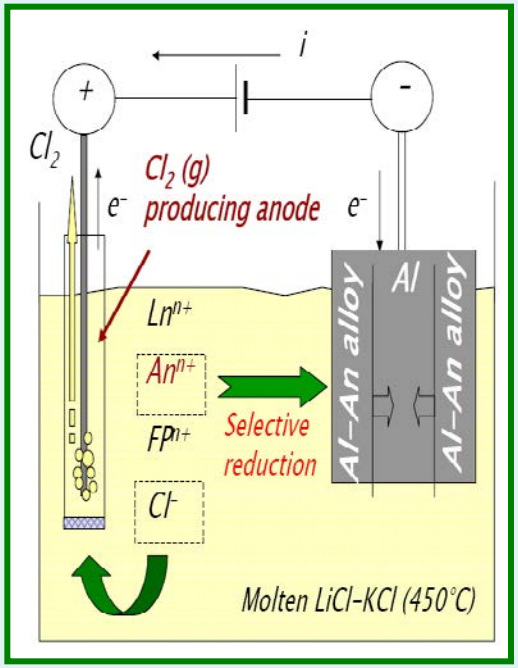
Target: Effective Recovery of Actinides (Low Concentration) in a Spent Molten Salt



Disproportion reaction of Am (Solid Cathode)



Counter-current reductive extraction (Japan)

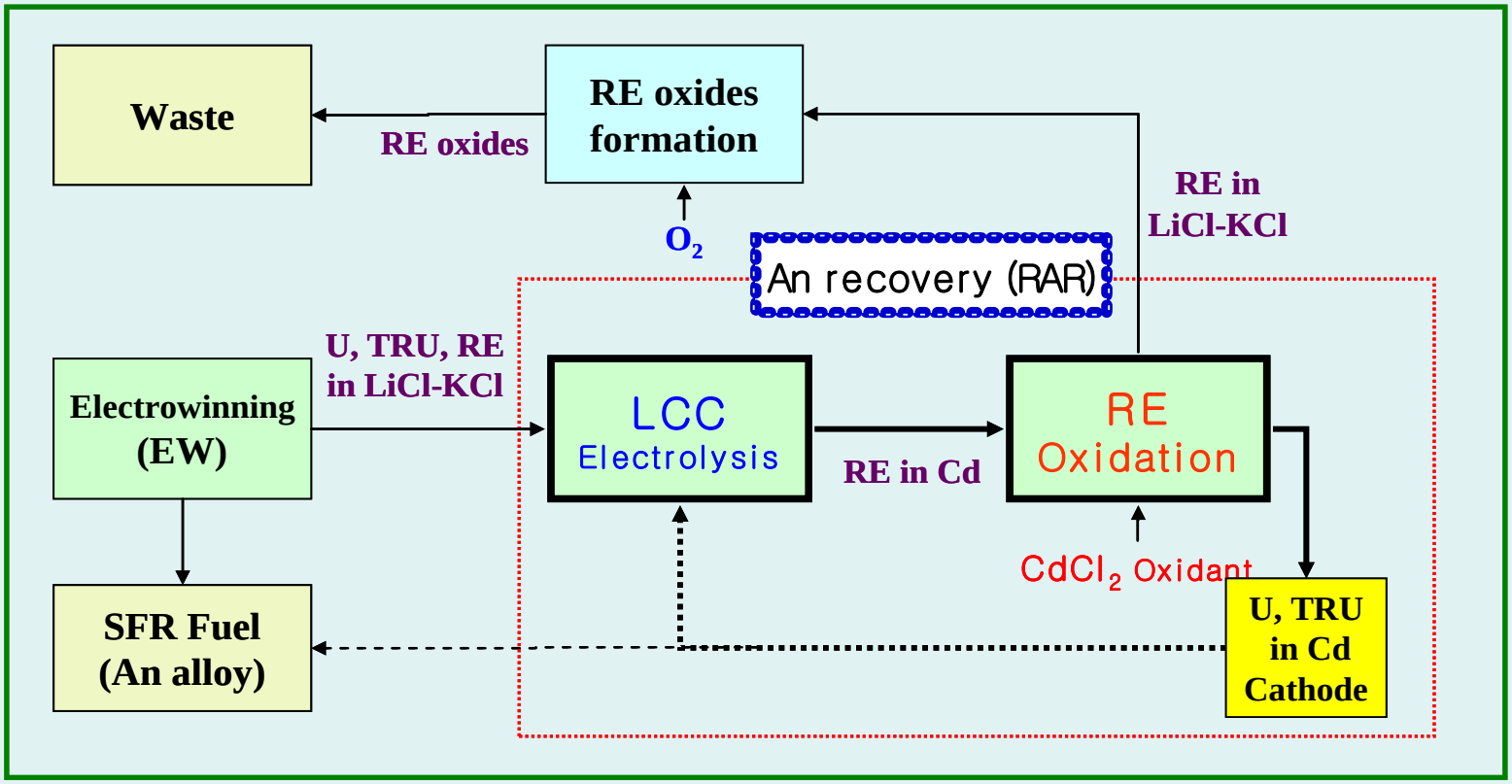


Electrolysis and selective oxidation (Europe)

State of the Art on Drawdown of Actinides

❖ Residual Actinides Recovery (RAR) Method at KAERI

(1) Recovery of An by LCC electrolysis ⇨ (2) Oxidation of RE metals using $CdCl_2$

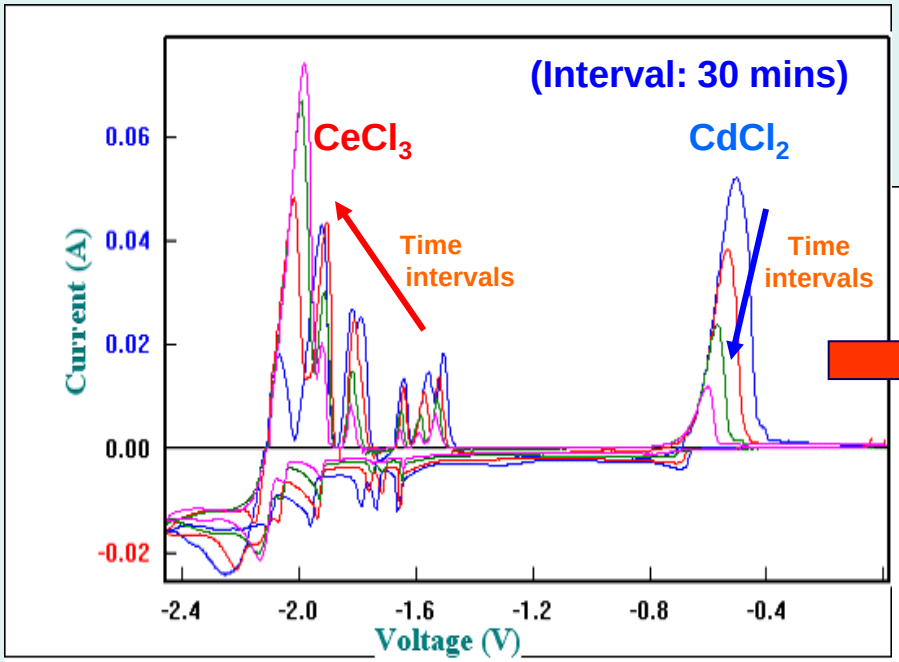


Residual actinides concentration in a LiCl-KCl salt: < 0.01 wt% (100 ppm)

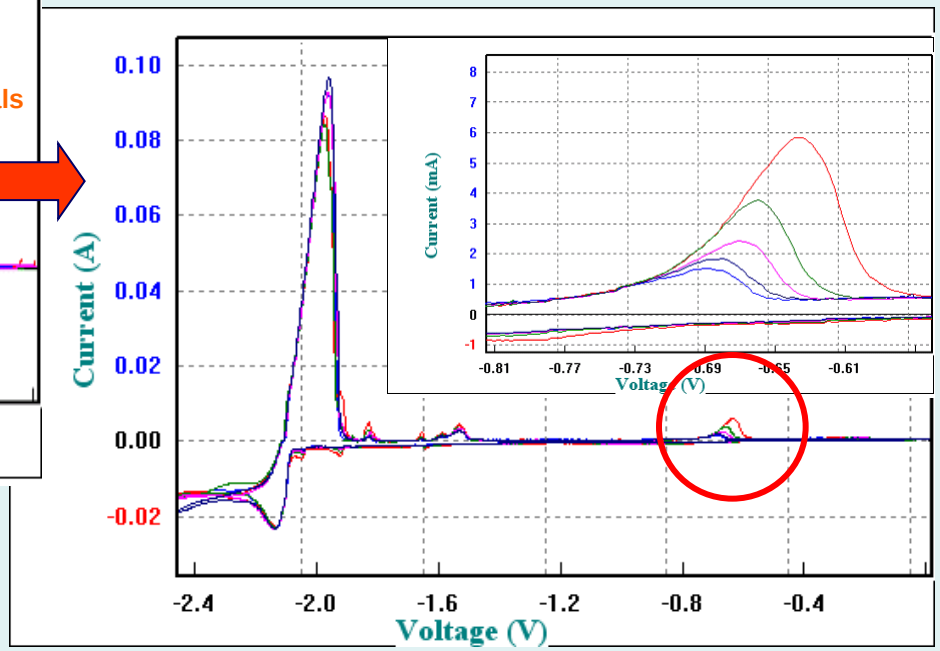
State of the Art on Drawdown of Actinides

❖ Oxidation of RE-U-Cd Alloy (2nd Step of a RAR Process)

$$2Ce(\text{-}U\text{-}Cd) + 3CdCl_2 \rightarrow 2CeCl_3 + 3Cd + 2(\text{-}U\text{-}Cd)$$



To resolve: - Cl_2 gas evolution
- Process: complex in two steps
- Throughput: more than 10 hrs



$LiCl\text{-}KCl+CdCl_2+CeCl_3$

[$CdCl_2$ addition: Ce, 50→ 75→ 95%]

Advanced RAR under Development in KAERI

❖ Need for New Method for Future Practical Application:

- **High selective recovery ratio of actinides**
- **Prominent overall processing efficiency**

  - Simplicity of the process

  - High throughput process
- **Compactness of the equipment**
- **High economical efficiency**

- **New Recovery Method: "Advanced RAR"**

  → Use RE metals for reduction of An ions

Thermodynamics of an Adv-RAR Process

Table 1. Gibbs free energy for metal chloride; (a) Literature, (b) HSC 6.0 code

Formation reaction of chlorides at 500 ℃	(a)	(b)
	$-\Delta G_f^o$ (kJ/g-equiv.-Cl)	
$La + 1.5Cl_2(g) = LaCl_3$	293.62	293.62
$Ce + 1.5Cl_2(g) = CeCl_3$	287.37	287.828
$Nd + 1.5Cl_2(g) = NdCl_3$	281.45	284.232
$Gd + 1.5Cl_2(g) = GdCl_3$	273.02	271.725
$Y + 1.5Cl_2(g) = YCl_3$	272.50	272.385
$Am + 1.5Cl_2(g) = AmCl_3$	266.38	265.094
$Cm + 1.5Cl_2(g) = CmCl_3$	264.99	255.676
$Pu + 1.5Cl_2(g) = PuCl_3$	261.41	262.561
$Np + 1.5Cl_2(g) = NpCl_3$	242.91	241.729
$U + 1.5Cl_2(g) = UCl_3$	232.35	231.267

Advanced RAR under Development in KAERI

$$RE1(s) + AnCl_3 + RE2Cl_3 \rightarrow RE1Cl_3 + RE2Cl_3 + An(s)$$

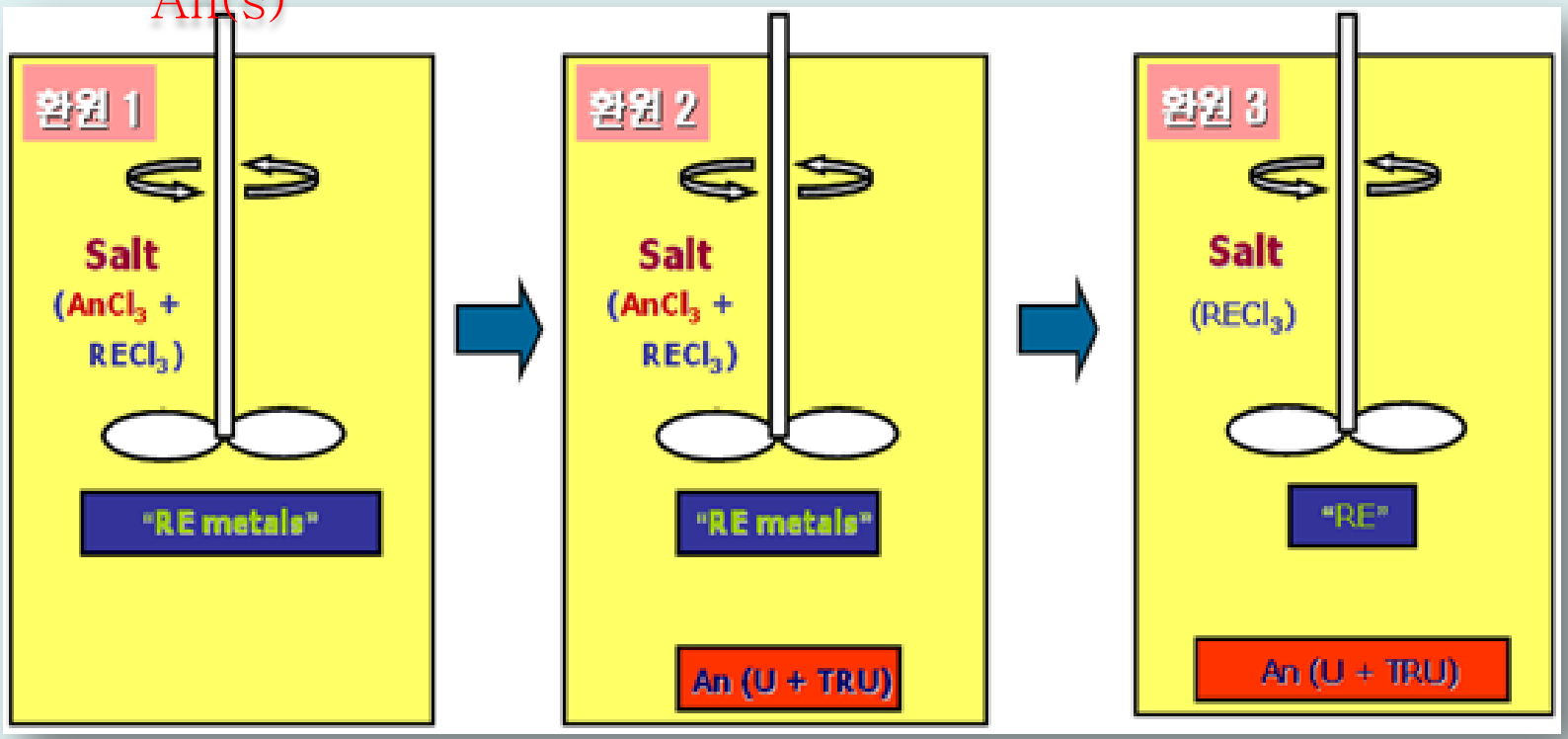
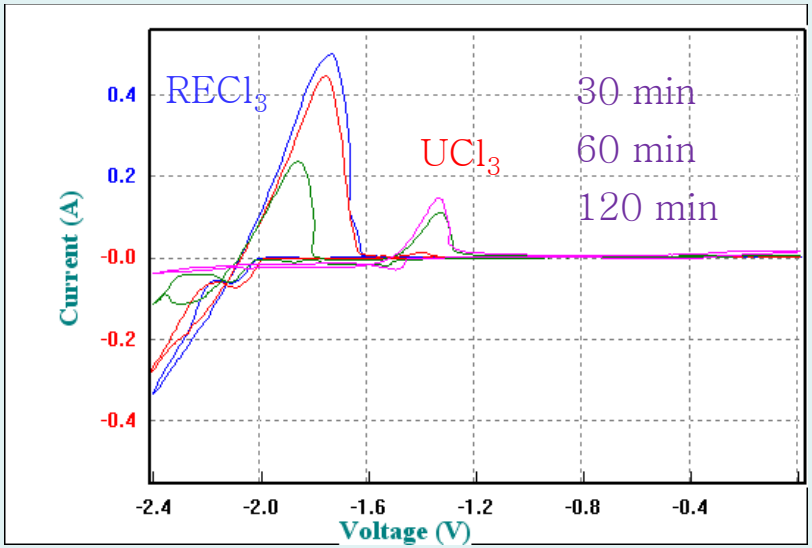


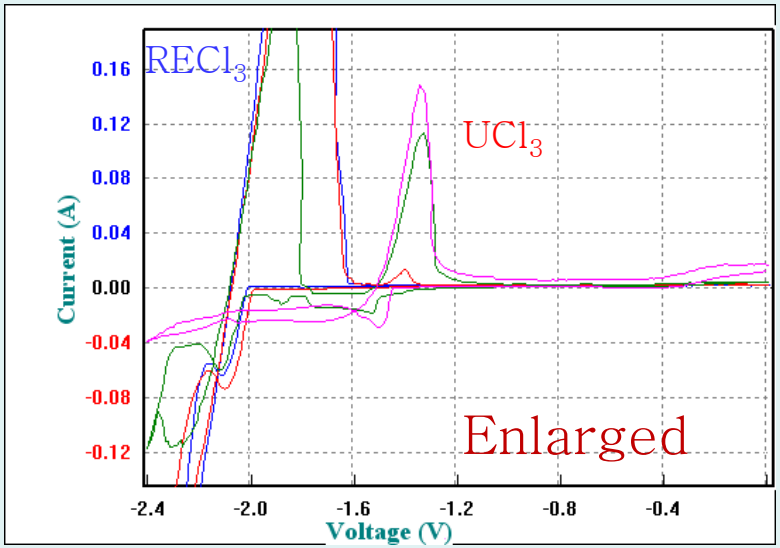
Fig. 1. Schematic for recovery of actinides by introducing RE metal into a salt

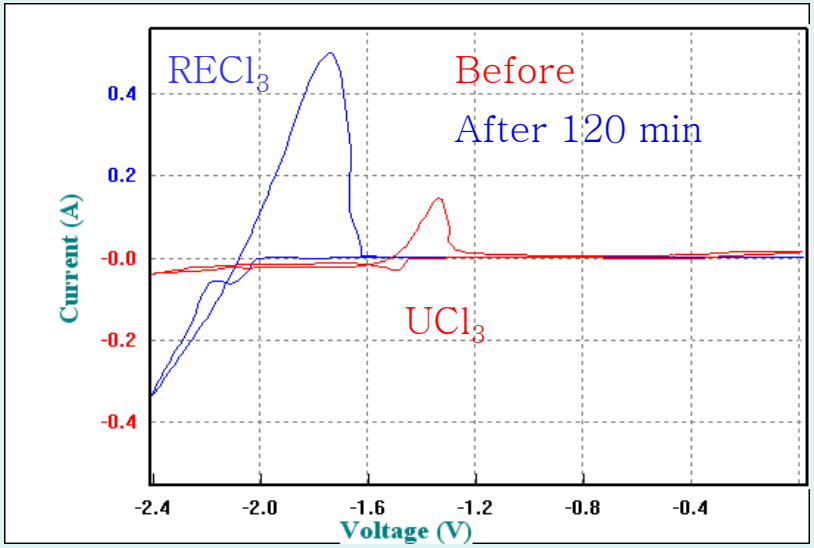
Experimental Apparatus for Adv-RAR Method

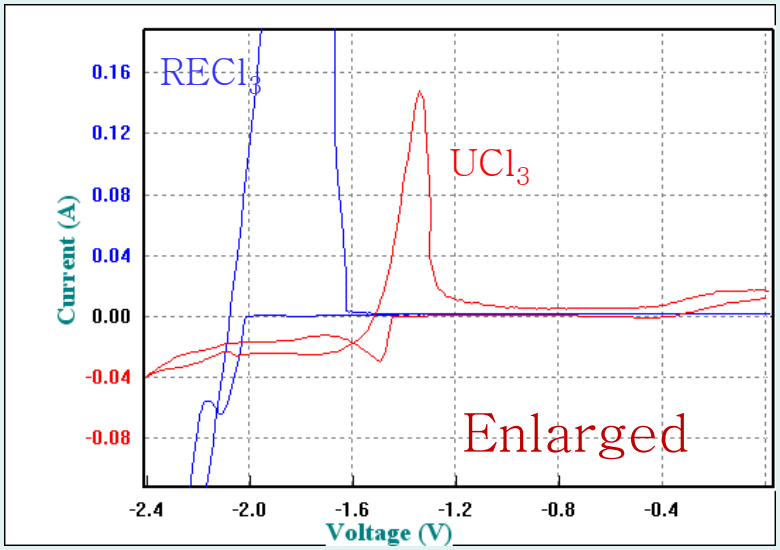
Sample for SEM/EDS

Experimental Results Using RE Metal Reducing Agent

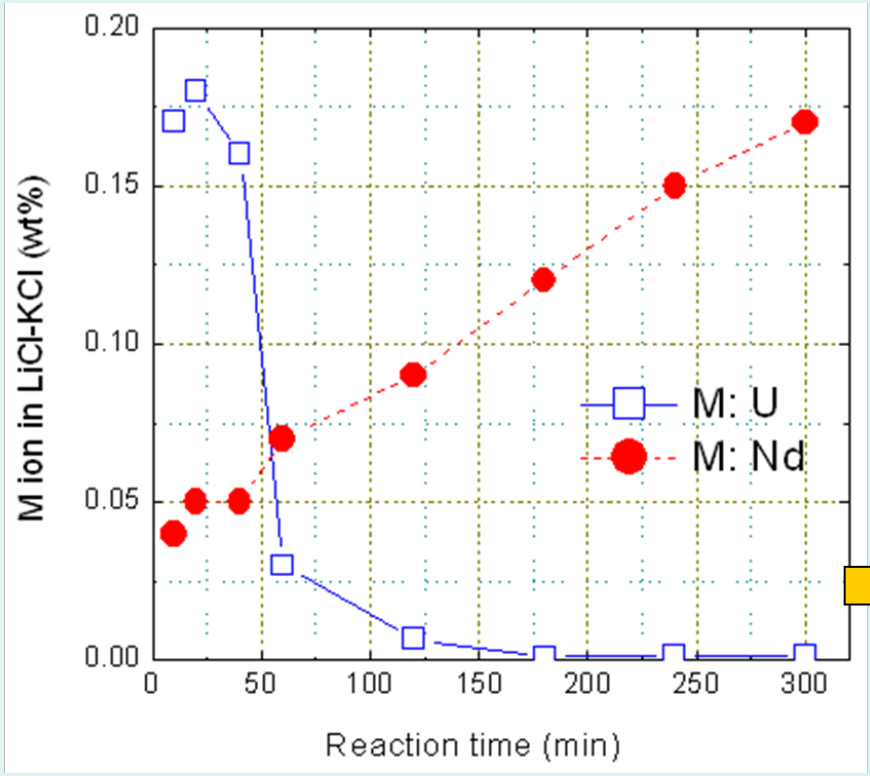








Experimental Results Using Nd Metal



U concentration:
< 10 ppm
after 3 hrs

Fig. Change of U and Nd concentrations in an LiCl-KCl salt

❖ U concentration was decreased stiffly with increasing Nd concentration.

Experimental Results Using Nd Metal

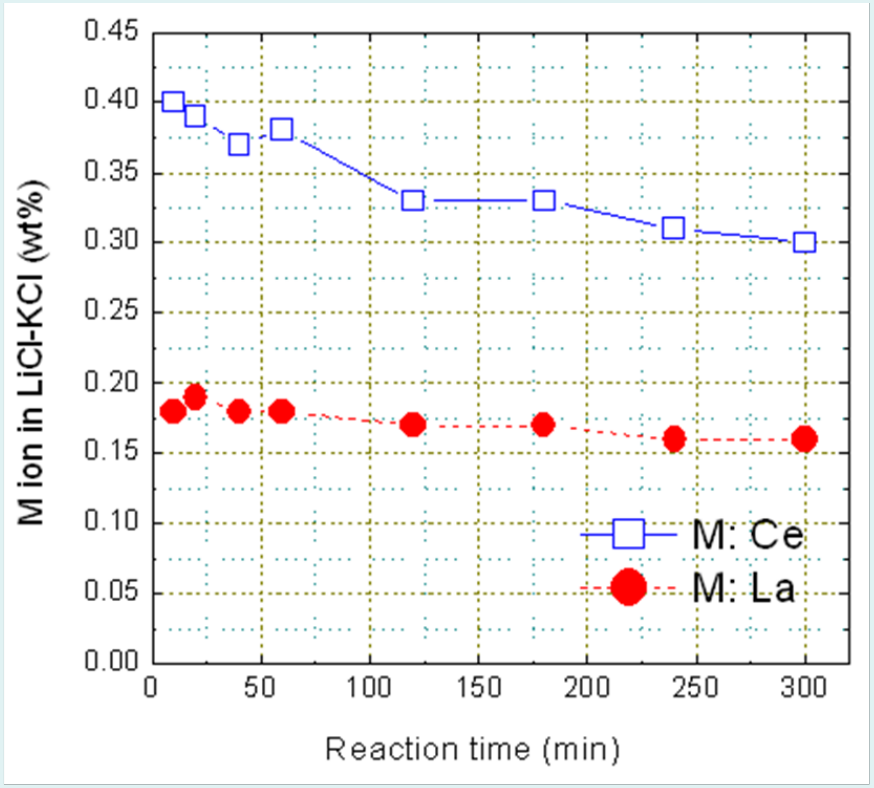
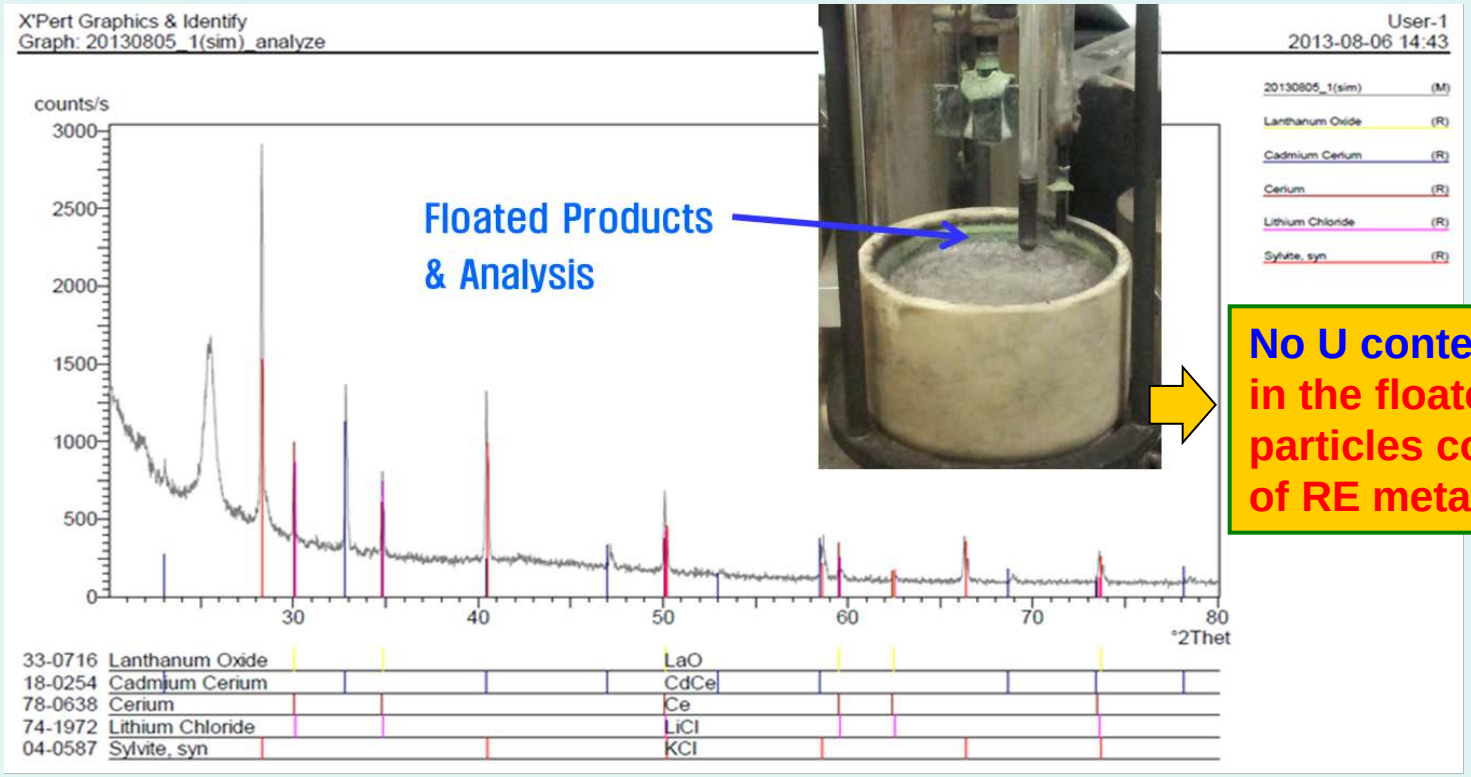


Fig. Change of Ce and La concentrations in an LiCl-KCl salt

❖ Concentration of Ce and La decreased slowly during the reaction of U with Nd.

Characterization on the Reaction Products



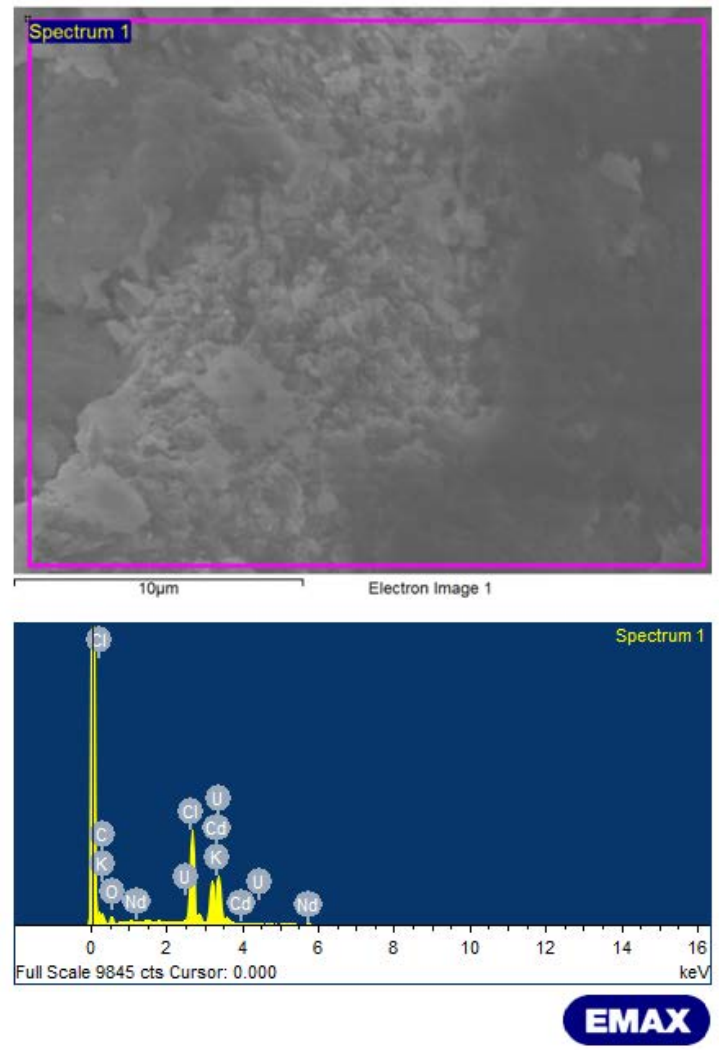
No U content:
in the floated particles composed of RE metals

Fig. XRD result of the particles floated on the surface of an LiCl-KCl salt

❖ Parts of reaction products (rare earth metal particles) were floated on the surface of a molten salt.

Characterization on the Reaction Products

❖ SEM and EDS analysis of precipitated products:



Comment:

Element	Weight%	Atomic%		
C K	11.71	34.85		
O K	9.71	21.70		
Cl K	23.79	23.99		
K K	9.35	8.55		
Cd L	23.96	7.62		
Nd L	0.79	0.19		
U M	20.68	3.11		
Totals	100.00			

Small RE content: in the precipitated particles composed of U metals

Simulated Salt Mixture for HSC Code Calculation

	M.W	Weight (kg)	wt %
La	138.906	18.44	0.574812968
Ce	140.12	33.37	1.04021197
Nd	144.24	54.44	1.697007481
Y	88.906	7.278	0.226870324
U	238.029	6.983	0.217674564
Pu	244	30.04	0.936408978
Np	237.048	2.021	0.062998753
Am	243	3.082	0.096072319

HSC Simulation for Using Nd Metal

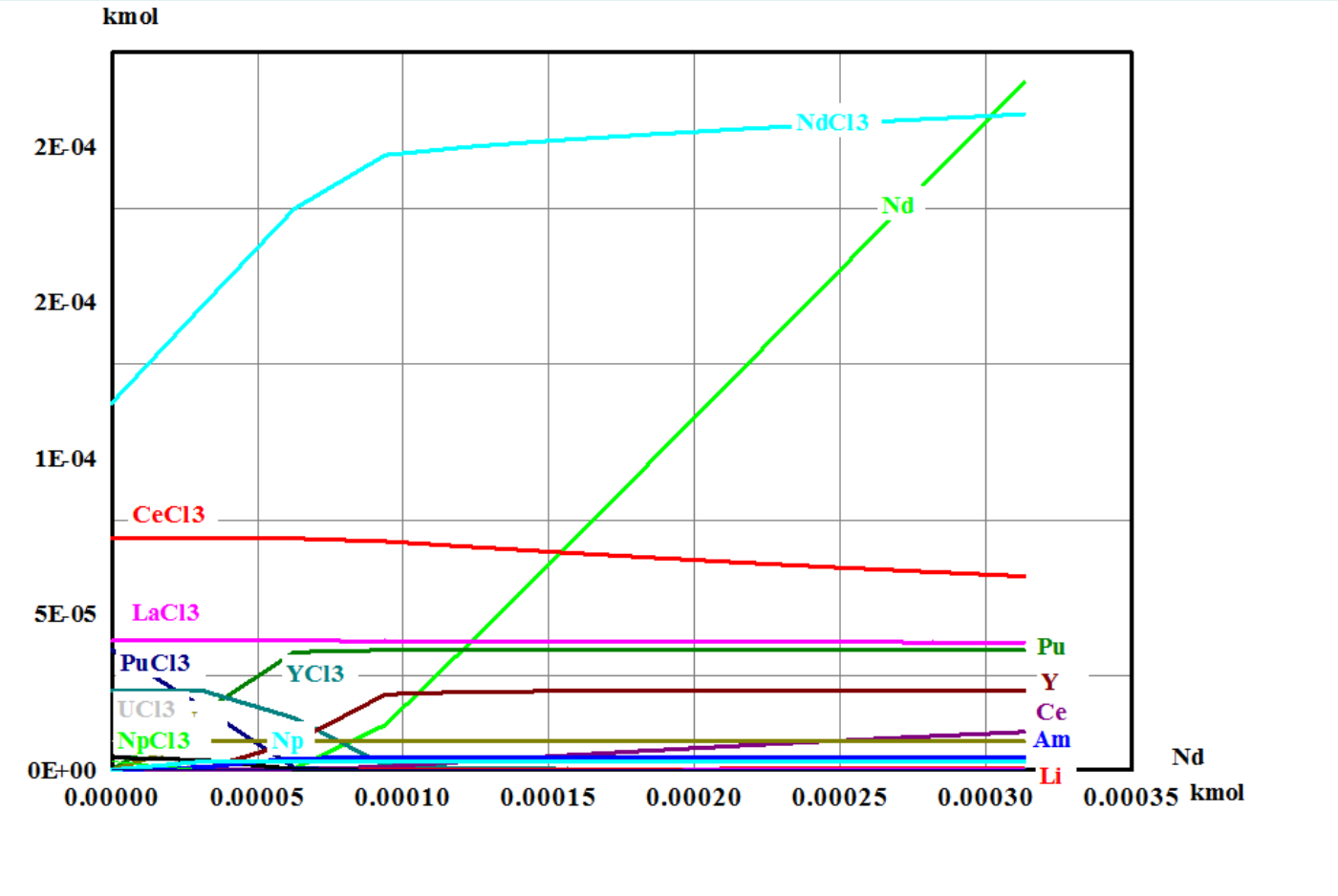


Fig. Distribution diagram for an equilibrium reactions of $AnCl_3$ with Nd metal using the HSC code

HSC Simulation for Using Nd Metal

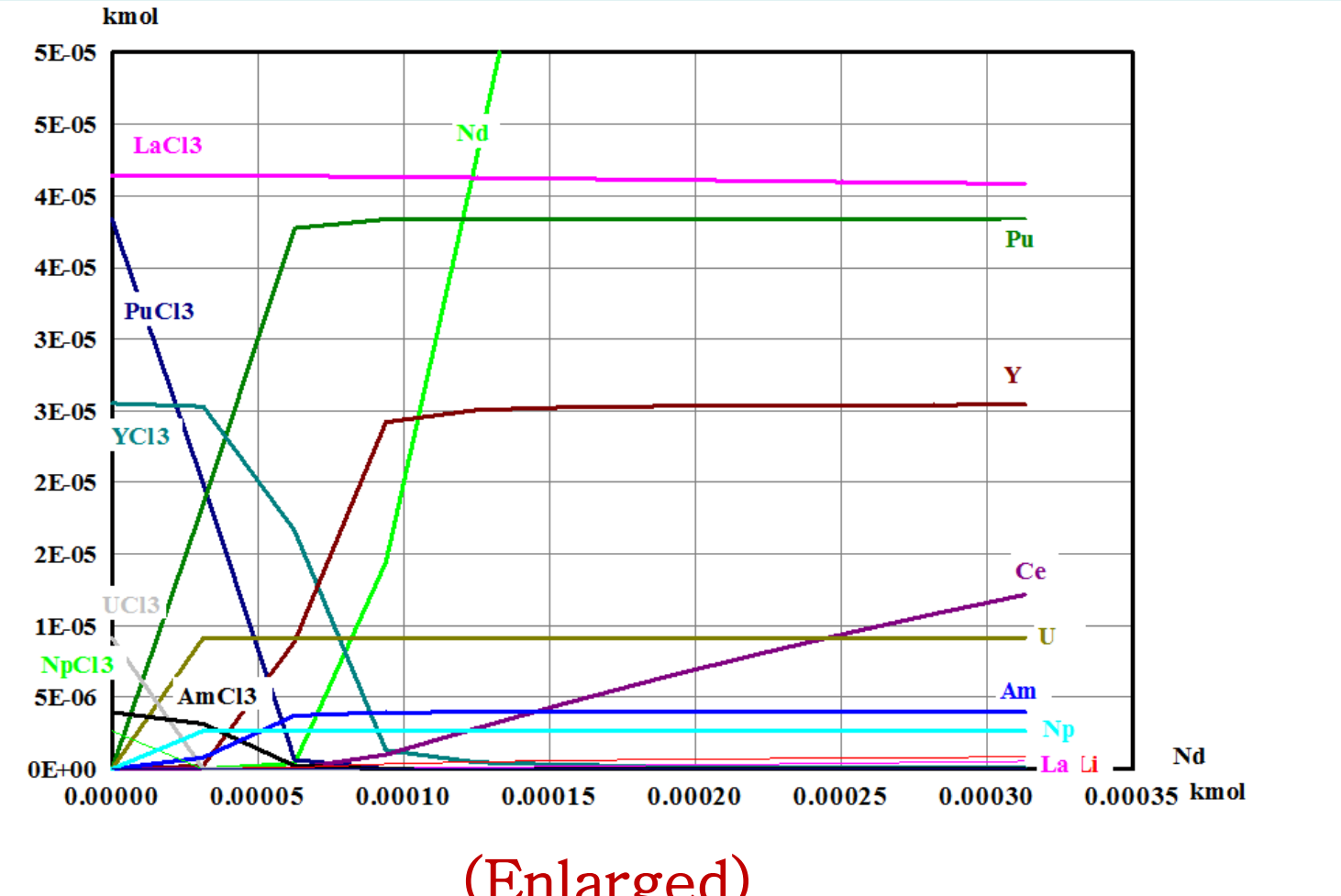


Fig. Distribution diagram for an equilibrium reactions of $AnCl_3$ with Nd metal using the HSC code

HSC Simulation for Using Nd Metal

Table 4. Analysis on recovery of the actinides using a Nd metal

Metal	Cont., ppm	DF	R-ratio, %	EW DF/ RR, %
U	3.82E-08	5.70E+10	100	
Pu	0.32	2.92E+04	99.99658	
Np	1.46E-06	4.32E+08	99.99999	
Am	0.1212	7.94E+03	99.9874	
Total	0.441	29,900	99.997	124,000/
				99.999

- Cont.: Effluent concentration, ppm
- R-ratio, RR: Recovery Ratio, %
- DF: Decontamination Factor
- EW: Electrowinning

Extent of Reduction of Metal Chlorides

* Nd Reductant

AnCl3	C/Co	RECl3	C/Co
UCl3	1.8E-11	NdCl3	1.78632
PuCl3	3.4E-05	YCl3	0.00377
NpCl3	2.3E-09	CeCl3	0.83627
AmCl3	0.00013	LaCl3	0.98705

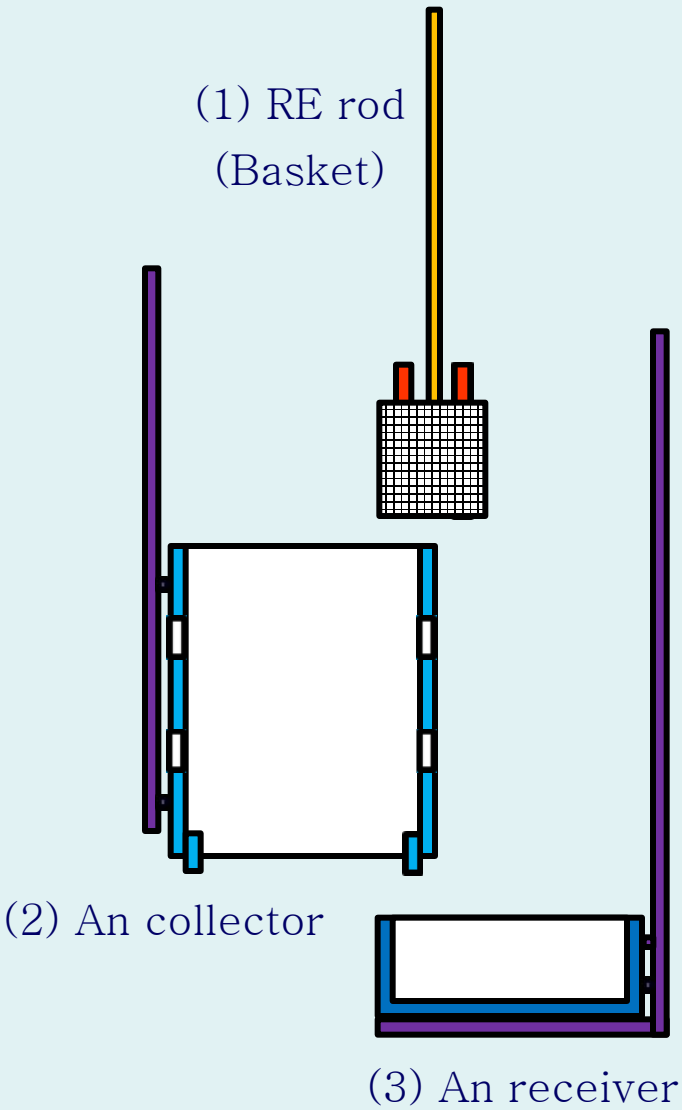
❖ Conversion of metal chlorides to the metal particles depend on the sort of rare earth metal reducing agent. Extent of the rare earth chlorides reduction increased with a series of Nd> Y> Gd.

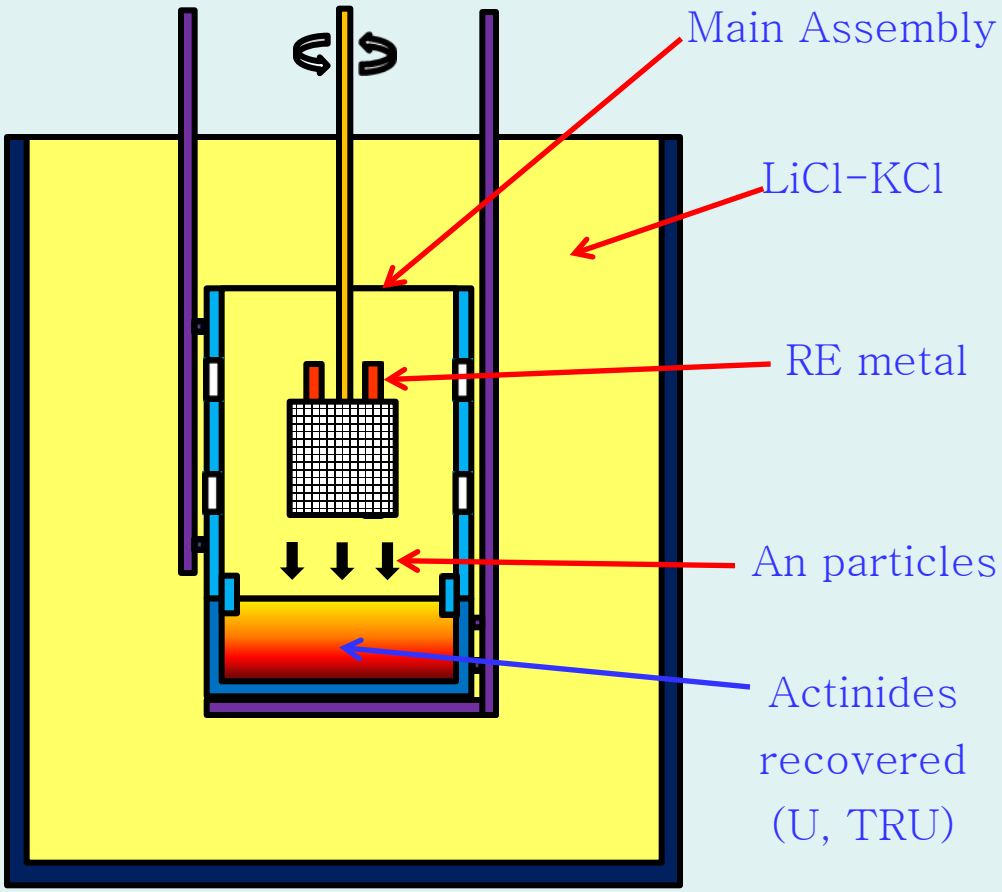
Features of Advanced RAR Method

New Recovery Method :"Advanced RAR"

- Prospective: easy remote operation in a hot cell
- Spontaneous reactions: use difference of Gibbs energy
- Process: simple, short processing time (< 5hrs)
- Equipment: compact, convenient optn. (RE metal)
- Throughput: excellent (Packed bed mesh basket)
- Selectivity: high-expected (An precipitate, RE float)
- No evolution of chlorine gas
- No need: oxidant($CdCl_2$), Cd distillation, materials,,,
- On-line monitoring: no need for adding chemicals

Features of Advanced RAR Method





❖ $RE(S) + AnCl_3(L) \rightarrow RECl_3(L) + An(S)$

Features of Advanced RAR Method

Summary

- The experimental results show a promising feasibility of a new recovery method. The residual concentration of U was reduced to 10 ppm level within 3 hrs. The reduced uranium particles were precipitated, but the rare earth particles were floated on the surface of a salt.

- One of the viewpoints for establishing an effective recovery method is a selective recovery ratio of the actinides and the other of those is an overall efficiency of processing a recovery method including simplicity of process and compactness of the equipment.

- New recovery method is called an “advanced RAR process”, which shows a powerful feasibility to replace previous KAERI’s RAR process from the viewpoint of above mentioned selection parameters, such as selectivity, simplicity, process efficiency, equipment compactness and economy.

Thank you

for your attention !

Innovation for Next Generations

- Transparent, Innovative, and Environmentally Friendly -