

## Development of the Electrowinning Technology for TRU Recovery in Pyroprocessing

Do-Hee Ahn\*, Seungwoo Paek, Joon-Bo Shim, Kwang-Rag Kim, Tack-Jin Kim, Jae-Hoo Jung, Gha-Young Kim  
Nuclear Fuel Cycle Process Division, KAERI, 1045 Daedeokdaero, Yuseong, Daejeon, Korea, 305-353  
\*Corresponding author: dhahn2@kaeri.re.kr

### 1. Introduction

Electrowinning technology is implemented to recover TRU from the molten salt system, a major process in pyroprocessing technology with proliferation resistance. Electrowinning technology using an LCC was employed to recover group actinides such as uranium and TRU in the molten salt (LiCl-KCl) transferred from the electrorefining process, and it collected uranium of high purity. Cadmium distillation technology was also used to separate Cd and actinides from actinide/Cd products recovered by LCC electrowinning, while residual actinide recovery was incorporated for the treatment of spent salt with low concentrations of actinides. Development of the electrowinning system at KAERI is presented.

### 2. Methods and Results

#### 2.1 LCC electrowinning technology

Electrolysis experiments were carried out to observe the TRU recovery characteristics using uranium and simulated TRU elements with a various concentration ratios of U/TRU and current densities. The order of metal deposition on Cd from molten salt was following U, Nd, Cd, La, and Y. It was confirmed that the difference of standard formal potential of RE (Nd, Cd) between solid and liquid electrode was due to the formation of intermetallic compound between RE and Cd.

Lab-scale LCC electrolytic system was designed and prepared to develop a LCC assembly which can be easily disassembled from the system. Molten salt of 2.5 kg was contained in an electrolytic bath (ID = 15 cm) and U-loaded anode basket and LCC (liquid Cd cathode) crucible (ID = 5 cm) were setup in the bath. In order to prevent the growth of U dendrite effectively, automatically operated mesh-type LCC assembly was developed. It enabled to sink the U deposits into the bulk of liquid Cd directly by its vertical movement as well as by rotation, thus no U dendrite formed on the Cd surface. Using the developed mesh-type LCC assembly, the electrolysis experiments were conducted. The maximum amount of U deposition was obtained to be 10 wt% U/Cd without the growth of U dendrite out of the alumina crucible as shown in Fig. 1. This outstanding result of U recovery can be compared with 8 wt% U/Cd in Japan[1] and 9 wt% HM/Cd in US[2].

The inert anode material used in the LCC electrolytic system was selected as a pyrographite in terms of the electrical and mechanical stabilities. More detail, tube-

type of pyrographite was loaded in a porous SiC basket to increase the surface area of anode. The SiC basket was embedded in a SUS tube to prevent the loss of anode materials. Also, the developed anode structure consisted to SUS tube and SiC basket where tube-type graphite was loaded has a vent system which allows to collect and emit the  $\text{Cl}_2$  gas generated during the operation of the LCC electrolytic process effectively.

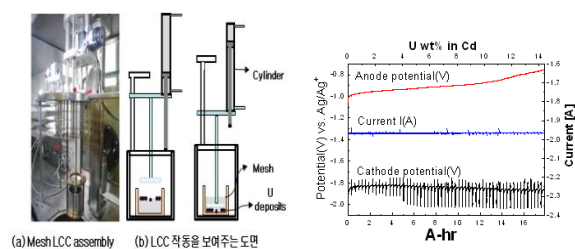


Fig. 1. Automatically operated mesh-type LCC assembly and its performance test results

#### 2.2 Distillation technology of TRU deposits on LCC

The cadmium evaporation rate-temperature-vacuum pressure relations for the design and operation mode decision of a cadmium distiller were examined. An attempt was made to control vacuum pressure by using a throttle valve, a pressure sensor and a controller. The vacuum pressure can be controlled very precisely. Therefore, the apparent evaporation rate of cadmium can be measured at a constant vacuum pressure.

The apparent evaporation rate of cadmium increased with an increasing temperature, whereas the apparent evaporation rate decreased with an increasing vacuum pressure. The evaporation rate of cadmium varied within  $9.7 \sim 40 \text{ g/cm}^2/\text{h}$  in the temperature range of  $500 \sim 650 \text{ }^\circ\text{C}$  and pressure range of  $0.5 \sim 10 \text{ Torr}$  as shown in Fig. 2.

The distillation experiments with pure Cd metal were conducted in 100 g scale. Cadmium was heated and evaporated in vacuum at various temperature gradient conditions. In the distillation at a temperature profile range of  $500 \sim 900 \text{ }^\circ\text{C}$  with a water cooling condition at the bottom flange,  $\sim 99\%$  of the initial Cd amount evaporated was collected in the condensing crucible. A Ce-Cd alloy was prepared and the distillation behavior of the alloy was investigated. Cadmium was effectively distilled and separated from cerium. The evaporation rate of cadmium in the alloy was lower than that of cadmium metal. In addition, a Cd-Salt(LiCl-KCl) mixture was also effectively evaporated and collected

up to 98% of the initial amount at the temperature profile range of 600 ~ 900 °C.

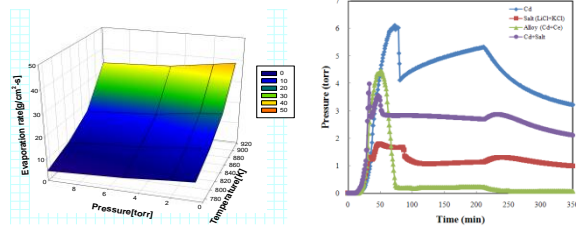


Fig. 2. Cd evaporation rate as functions of temperature and pressure and optimum operating condition of the Cd distiller

### 2.3 Residual actinides recovery technology

KAERI has developed a hybrid residual actinides recovery(RAR) method which has new concept combining LCC electrolysis and oxidation using CdCl<sub>2</sub> oxidant. Also, a lab-scale RAR equipment that has functions to test an LCC electrolysis and an oxidation of RE metals in series was manufactured according to a RAR process concept. The equipment was consist of a reaction vessel which has a capacity of processing 2 kg salt in one batch operation and an LCC assembly to be inserted into or removed from the salt.

In order to evaluate recovery characteristics of LCC electrolysis and oxidation methods a series of experiments was carried out using U, La, Nd, Ce, Gd, Y elements. A RAR process was established based on the evaluation results such as selectivity, target residual actinide concentration(0.01 wt%), on-line monitoring by CV measurement for a diagnosis of process, equipment construction and operation method. A target residual actinide concentration, 0.01 wt%(100 ppm) in the waste salt can be achieved in an LCC electrolysis step at a condition of 50 rpm stirring, current density 30 mA/cm<sup>2</sup>, using glassy carbon anode. If the amount of CdCl<sub>2</sub> oxidant added into a salt can be controlled at a condition of oxidizing about 75 % of RE metals codeposited with An in an LCC the residual concentration of U can be maintained at less than 100 ppm in a oxidation step as shown Fig. 3..

A RAR operation method applying an LCC electrolysis for recovering An metals and CdCl<sub>2</sub> oxidant addition for oxidizing RE metals co-deposited in LCC was established. Same electrowinning equipment using an LCC for a recovery of the fuel material such as uranium and transuranic elements can be used for a RAR operation. The RAR process has promising merits such as compact equipment and a simple operation compared to the multi staged counter-current reductive extraction process which is under development at CRIEPI in Japan[3]. These features are very good benefits considering a special situation that a RAR equipment will be used by remote devices in a hot cell.

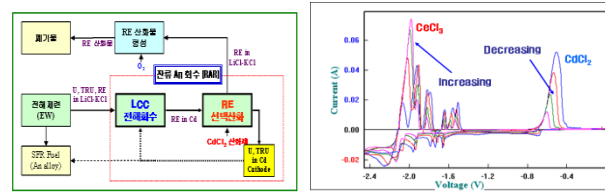


Fig. 3. RAR concept and CV results during oxidation step by CdCl<sub>2</sub> addition

### 2.4 Design & Construction of PRIDE Electrowinning System

The engineering scale electrowinning system (PRIDE) was designed and constructed based on the operation experiences of lab-scale LCC electrowinner, Cd distiller and RAR equipment. The remote operation tests at the mock-up facility were successfully completed. An engineering-scale LCC electrowinner which can recover 1 kg HM/batch was designed and constructed based on not only the operation experiences of lab-scale LCC electrowinner but also the computational simulation results of heat transfer and current distribution depending on the electrode positions in a electrolytic salt. It has a dimension of electrolytic cell of 40 cm (ID) where 20 kg of Cd and 50 kg of salt was used.

### 3. Conclusions

Laboratory-scale electrowinning process equipment including LCC electrowinner, residual actinide recovery equipment and Cd distiller were developed. The engineering scale electrowinning system (PRIDE) was designed and constructed based on the operation experiences of lab-scale electrowinning process equipment, which should contribute to KAPF (Korea Advanced Pyroprocessing Facility) by 2025 which is a major milestone of national R&D program approved by AEC on Dec. 22, 2008..

### REFERENCES

- [1] T. Koyama, M. Iizuka, N. Kondo, R. Fujita, H. Tanaka, Electrodeposition of Uranium in Stirred Liquid Cadmium Cathode, Journal of Nuclear Materials, vol. 247, p. 227, 1997
- [2] D. Vaden, S.X. Li, B.R. Westphal, K.B. Davis, T.A. Johnson, D.M. PACE, Engineering-scale Liquid Cadmium Cathode Experiments, Nuclear Technology, vol. 162, p. 124, 2008
- [3] K. Kinoshita, T. Inoue, S.P. Fusselman, D.L. Grimmitt, J.J. Roy, R.L. Gay, C.L. Krueger, C.R. Nabelek, T.S. Storvick, Separation of Uranium and Transuranic Elements from Rare Earth Elements by Means of Multistage Extraction in LiCl-KCl/Bi System, Journal of Nuclear Science and Technology., vol. 36, p. 189, 1999.