New Approach to Collecting Transuranic Elements in the Electrorefiner

2014 International Pyroprocessing Research Conference
October 21, 2014, Idaho Falls

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Liquid Cd Cathode in Electrorefining Process

Liquid Cd cathode (LCC)

- ✓Pu and MAs (minor actinides) are collected together with U.
- ✓LCC is mainly composed of a ceramic crucible and a moving device to help the deposited actinides settle in the liquid Cd.

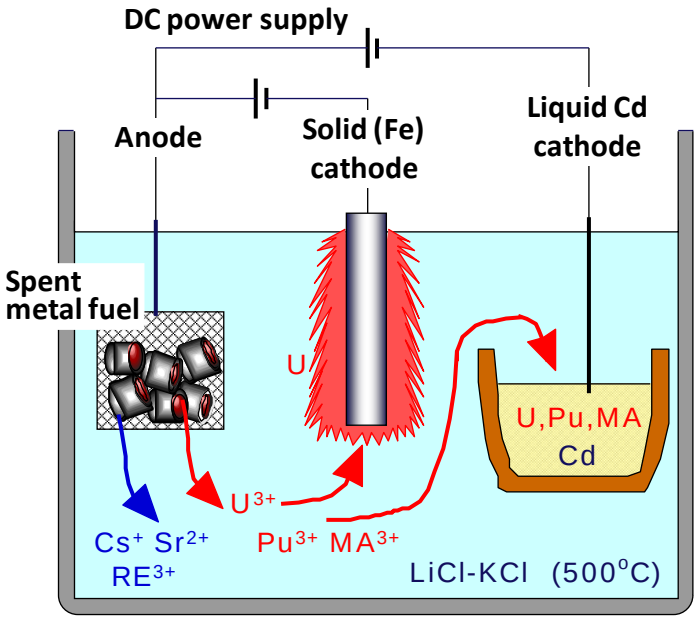

Fig. Electrorefining process

Major achievements

- ✓Kato et al. (CRIEPI)
  - 120 g of Cd / AlN crucible (42 mm i.d.) / paddle stirrer
  - 10.4 wt% of U and Pu was collected at 101 mA/cm^2.
- ✓Paek et al. (KAERI)
  - 400 g of Cd / Al_2O_3 crucible (50 mm i.d.) / mesh pounder
  - 5 wt% of U was collected at 100 mA/cm^2.
- ✓Vaden et al. (INL)
  - 26 kg of Cd / BeO crucible / paddle pounder
  - 6.3 wt% of U and Pu was collected from the EBRII spent fuel.

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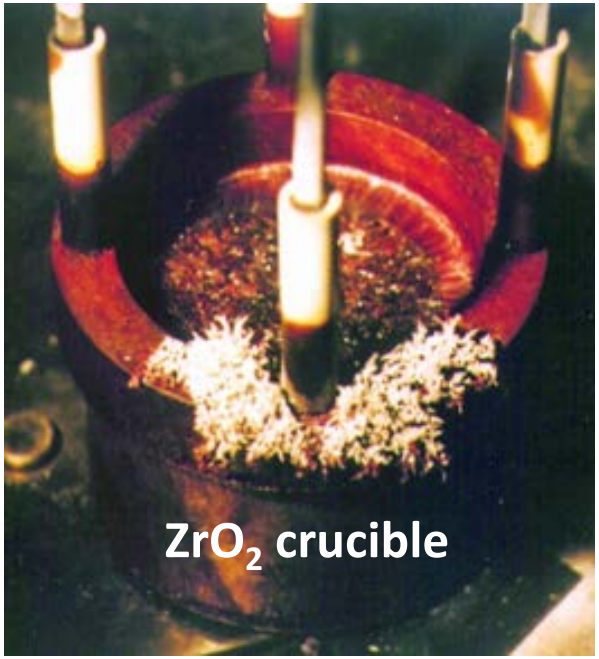
Liquid Cd Cathode

Weaknesses of the Liquid Cd cathode (LCC)

✓ **The crucible must be made of ceramics** (Al_2O_3, AlN, ZrO_2, BeO, etc.) to prevent the U metal from being deposited on the outer wall of the crucible.

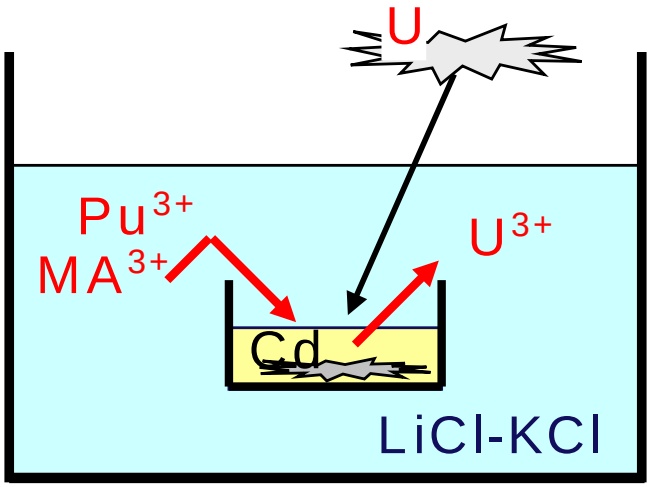
- The multiple reuse of ceramic crucibles was difficult in the previous LCC tests.
- Ceramic crucibles have an inherent risk of cracking due to thermal and mechanical shocks.

✓ A high current density at LCC often causes **the formation of dendrites of U metal** that grow rapidly outward from the Cd.

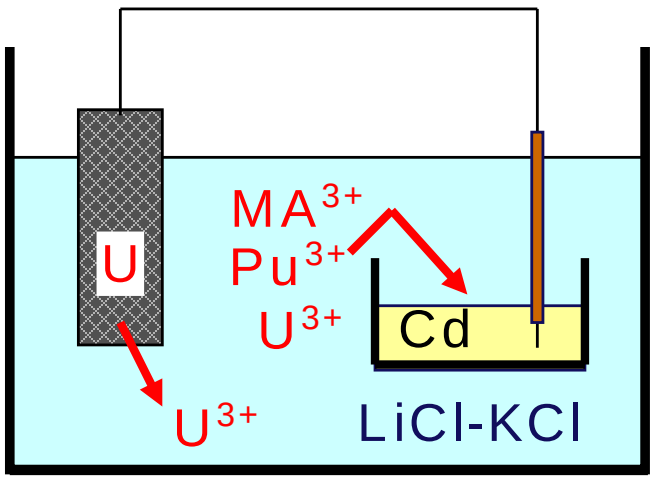


Typical dendritic U metal growing from the Cd outward

New Approach to Collecting Pu and MAs



Direct extraction (DE) method



Electrochemical extraction (EE) method

Fig. A new approach to collecting Pu and MAs using U metal as a reductant.

Advantages

- ✓The formation of dendritic U metal outside the liquid Cd will not occur.
- ✓Steel crucibles can be used as containers for the liquid Cd.
- ✓U metal can be obtained from the solid cathode.
- ✓It is considered that the liquid Cd-actinides alloy can be pumped out of the crucible as the product.
- ✓The operation is simple and stable.

A concern is that the extraction of Pu and MAs may proceed slowly.

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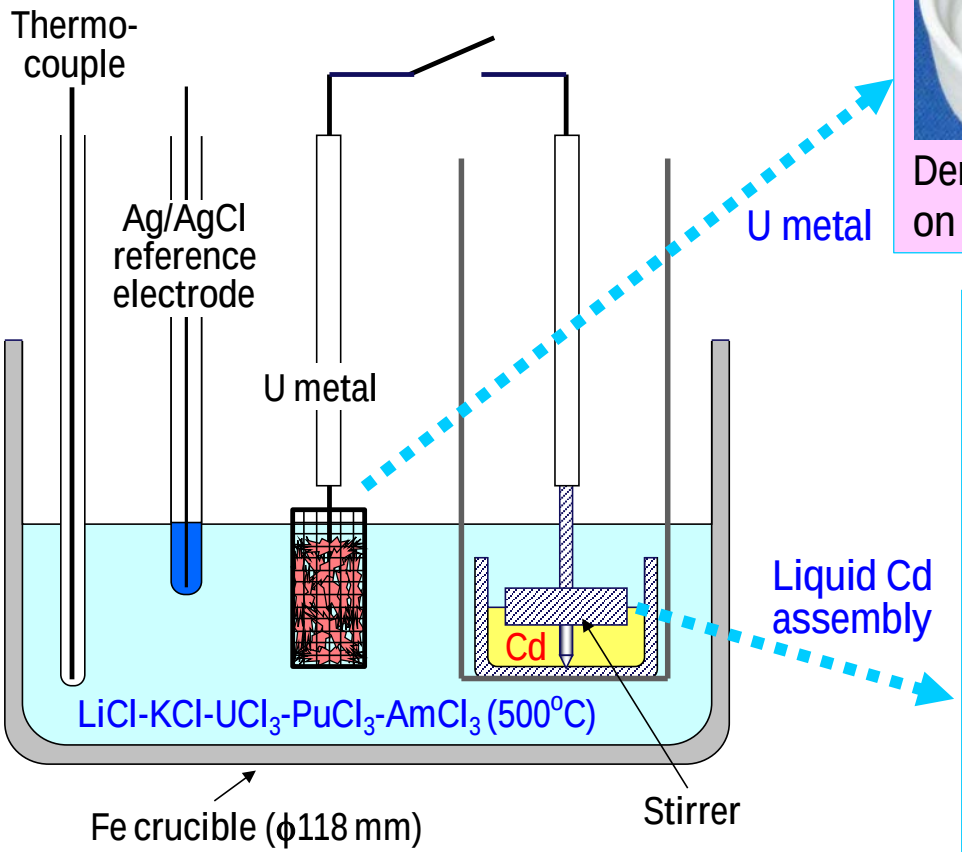
Objectives

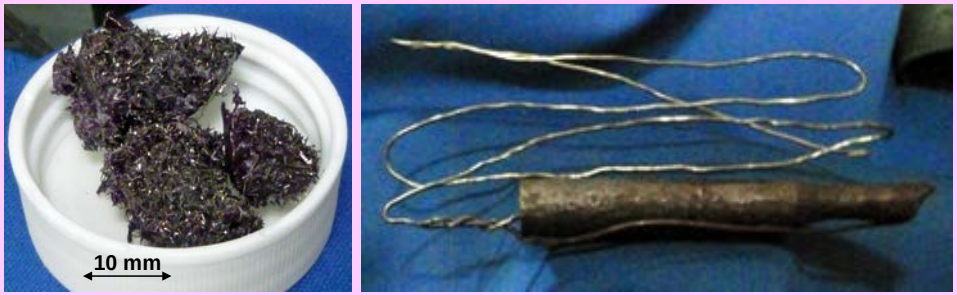
✓ To experimentally demonstrate the direct exraction (DE) and electrochemical extraction (EE) methods

- Can Pu and Am be collected in Cd?
- Can a steel crucible be used as a container for Cd?
- Pu/Am/U ratio in Cd?
- The extraction rate of Pu?

✓ To evaluate the usefulness of the DE and EE methods, a concept TRU extractor was designed on the basis of the experimental results.

Experimental Apparatus

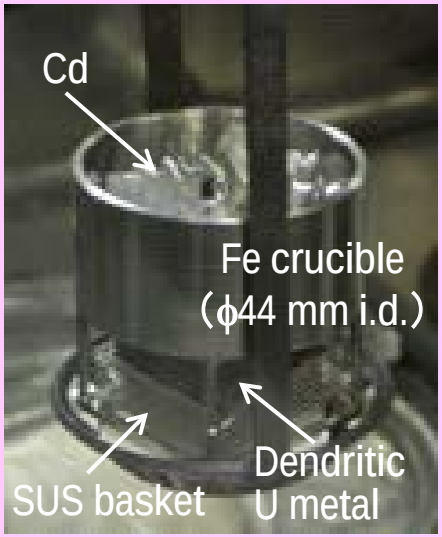




Dendritic U metal collected on the solid cathode

U metal tube with Ta wire lead

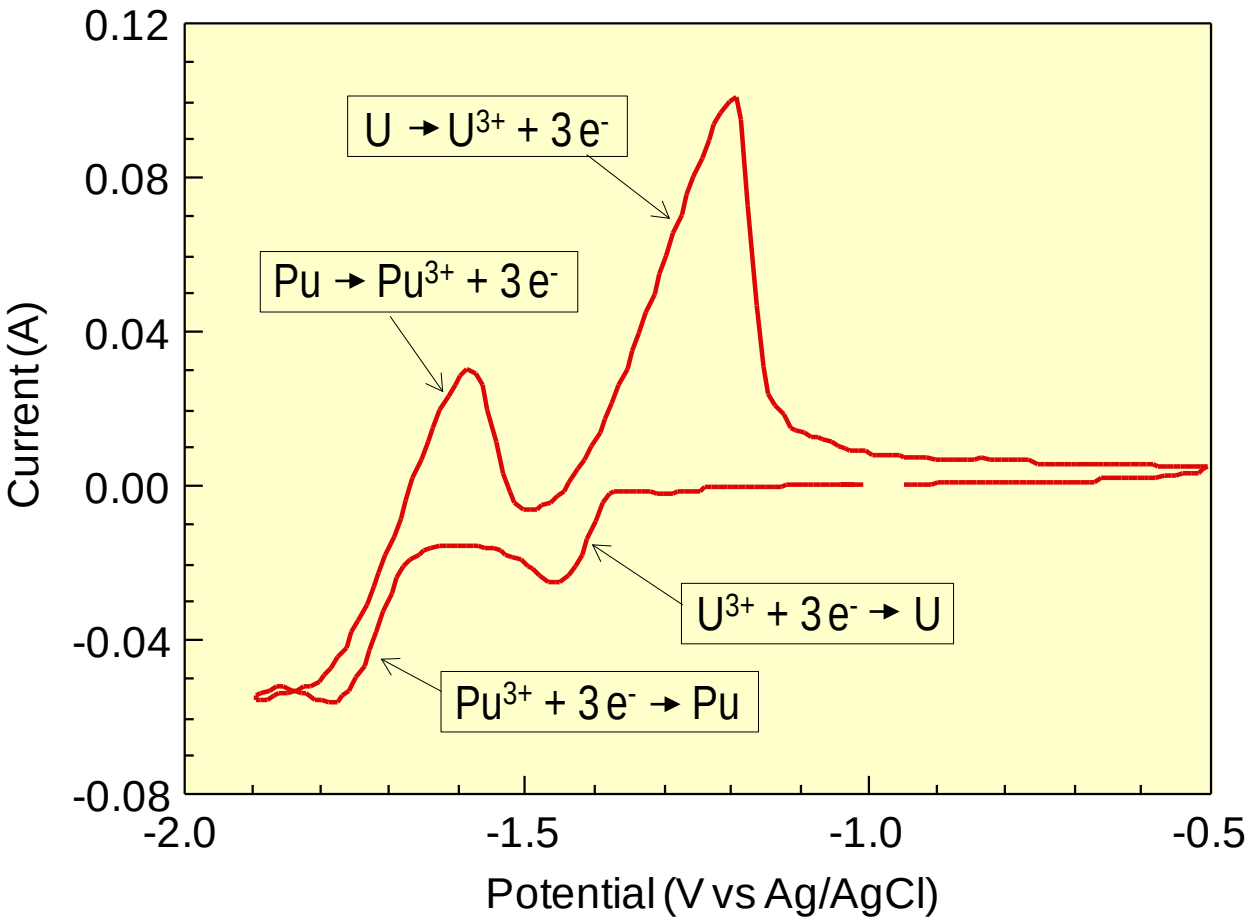
Tests 1 to 4



Test 5
(Integrated-type extractor)

Fig. Experimental apparatus for EE tests.

Experimental Conditions: Concentration in Salt



Concentration in salt

U^{3+} : 1.9-2.4 wt%

Pu^{3+} : 2.9-3.6 wt%

Am^{3+}: ~ 3% of Pu

Method of analysis

- **ICP-AES: U and Pu**
- **γ counting: Am**

Fig. Typical cyclic voltammogram of W electrode with scan rate of 0.1 V/s in LiCl-KCl-UCl_3-$PuCl_3$-$AmCl_3$ at 500 °C. The U^{3+}, Pu^{3+} and Am^{3+} concentrations were 2.2, 3.6, and 0.11 wt%, respectively.

Experimental Conditions

Test No.	Extraction method	Salt	Crucible for Cd		Cd loaded		U metal added		Stirring
		Conc. (wt%)	Material	I.D. (mm)	Amount (g)	Depth (mm)	Configuration	Amount (g)	
1	DE	U: 2.2 Pu: 3.6	Al_2O_3	40	172	17	Dendrite [a)]	8.0	Yes
2	DE	U: 1.9 Pu: 3.2	Fe	40	180	18	Dendrite [a)]	4.3 + 2.9 = 7.2	Yes
3	EE	U: 2.2 Pu: 3.6	Al_2O_3	40	167	17	Tube	144.3	Yes
4	EE	U: 2.0 Pu: 3.4	Fe	40	180	18	Tube	141.1	Yes
5	EE (integr-ated type)	U: 1.9 Pu: 3.1	Fe	44	100	8	Dendrite [a)]	7.8	No
6-1	EE	U: 2.4 Pu: 2.9	Al_2O_3	25	40	10	Dendrite [a)]	14.4	Yes
6-2					39	10			No
6-3					59	15			Yes
6-4					78	20		15.9	Yes

a) The amount of U metal was estimated assuming 100% current efficiency.

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Direct Extraction (DE) Method

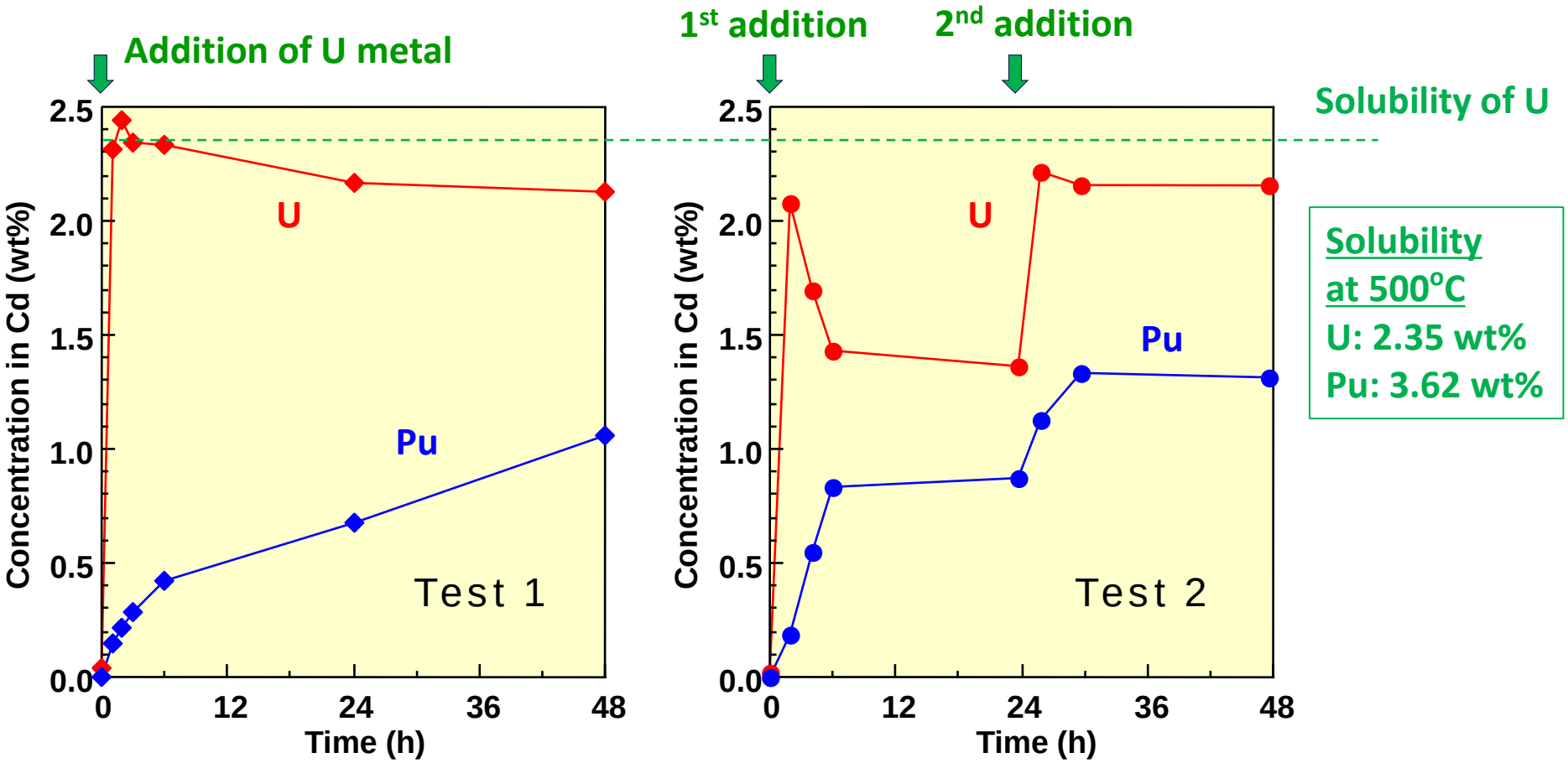

Fig. Change in concentrations of U and Pu in Cd after addition of U metal.

- ✓ Dendritic U metal collected on the solid cathode readily dissolved in Cd and then Pu was gradually extracted: $U(Cd) + Pu^{3+} \rightarrow Pu(Cd) + U^{3+}$.
- ✓ To enhance the extraction of Pu, U metal should be added in two or three batches so that excess undissolved U metal does not remain in the Cd.

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Electrochemical Extraction (EE) Method

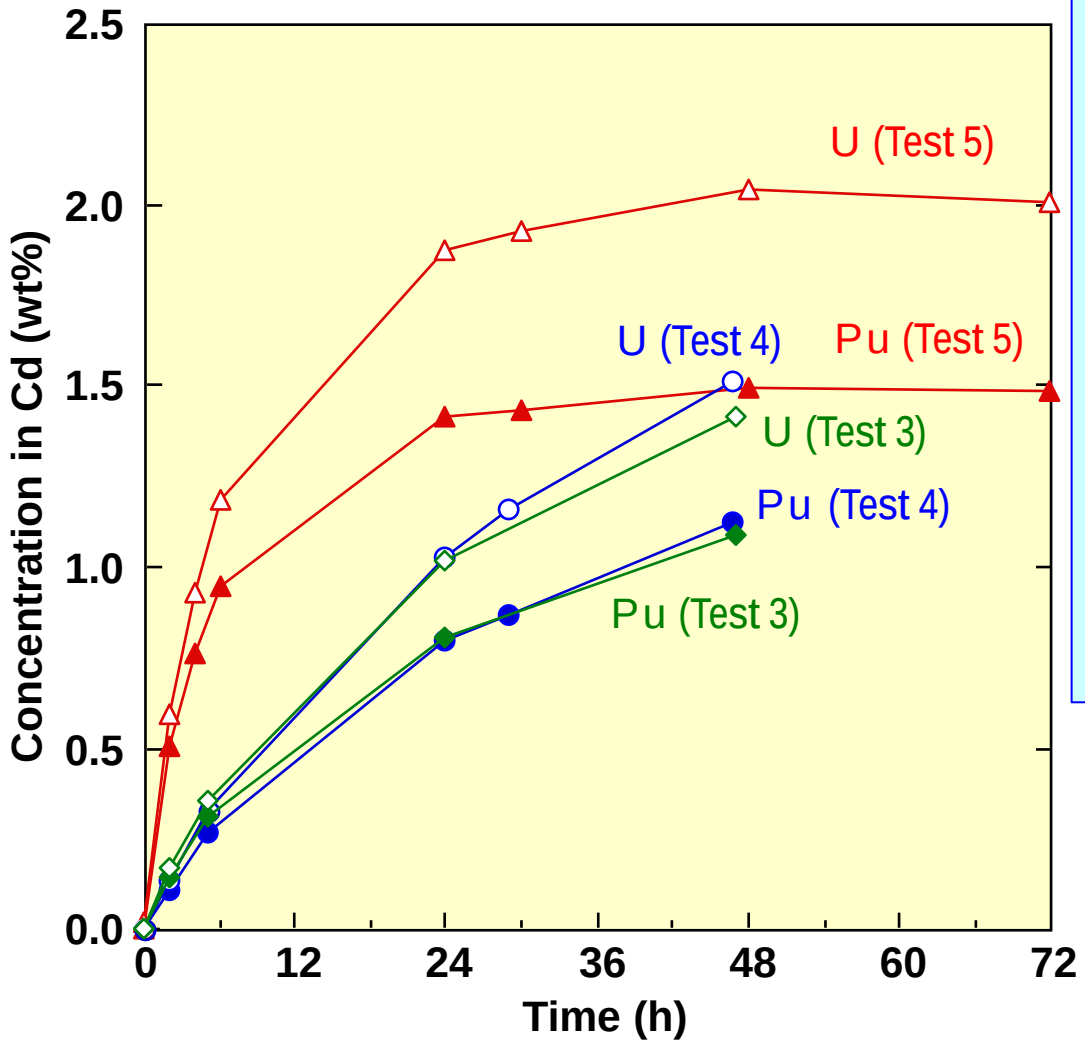


Fig. Change in concentrations of U and Pu in Cd after electrical short circuit was induced (Test 3 to 5).

- ✓ U and Pu could be collected in Cd.
- ✓ The crucible material (Al_2O_3 or Fe) did not affect the results.
- ✓ No corrosion or deposit on the walls of the crucibles was observed.
- ✓ It was verified that Fe crucibles can be used as containers for Cd.
- ✓ The dendritic U metal is preferable because of its large surface area.
- ✓ $SF_{U/Pu}$ was always in good agreement with the value at equilibrium (~1.9).

Separation factor of U vs Pu:

$$SF_{U/Pu} = \frac{(C_{U\ in\ Cd}) / (C_{U\ in\ Salt})}{(C_{Pu\ in\ Cd}) / (C_{Pu\ in\ Salt})}$$

Visual Examination of Cd Containers

Remaining Cd at the bottom

Inside

Outside

(a) Fe crucible used in Test 2 (DE method)

Salt/Cd interface

Top view

Bottom view

(b) Integrated-type extractor used in Test 5 (EE method)

Fig. Photographs of Cd containers after salt and Cd were poured out at the end of the tests.

Electrochemical Extraction (EE) Method

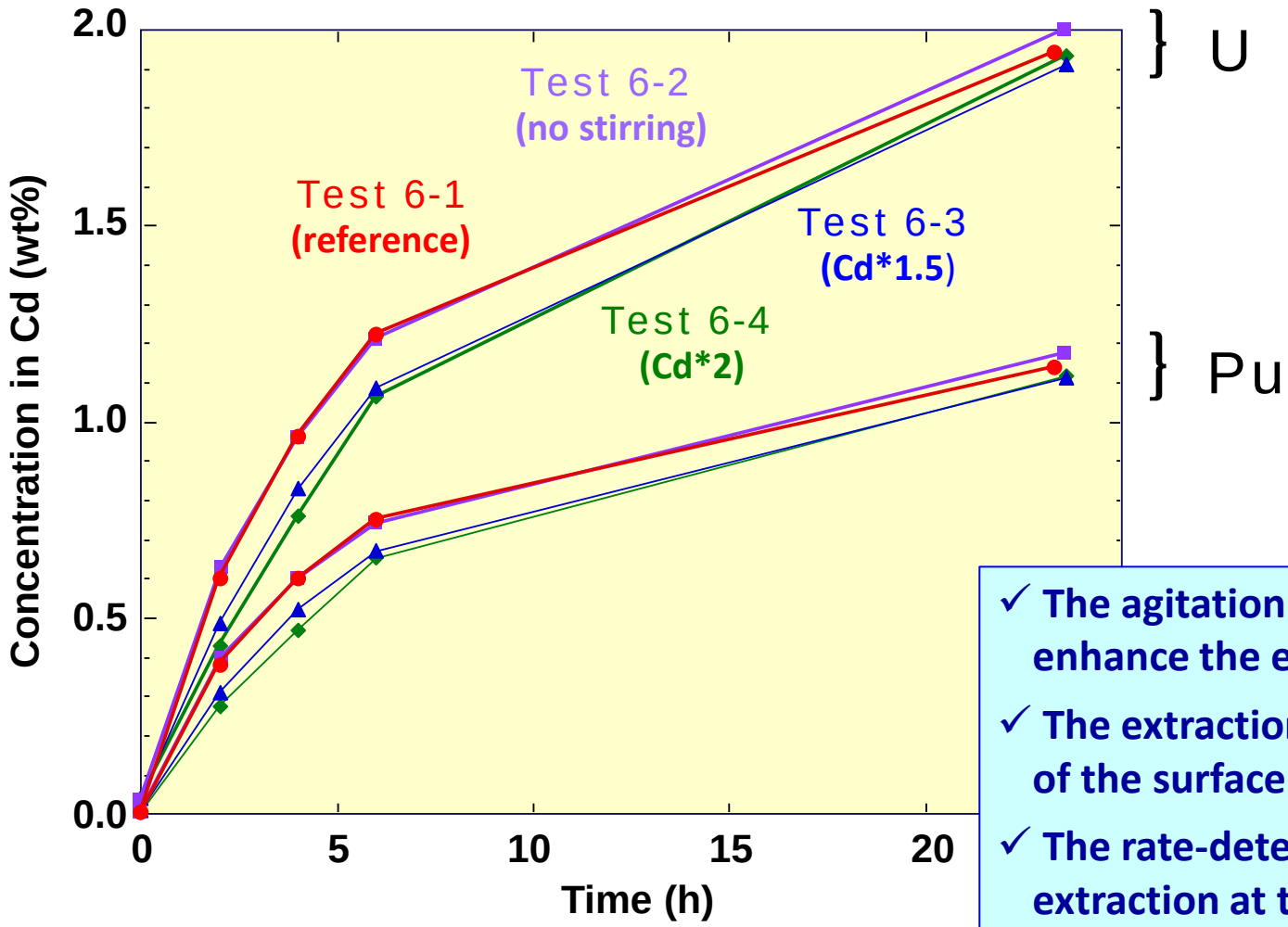


Fig. Change in concentrations of U and Pu in Cd after electrical short circuit was induced.

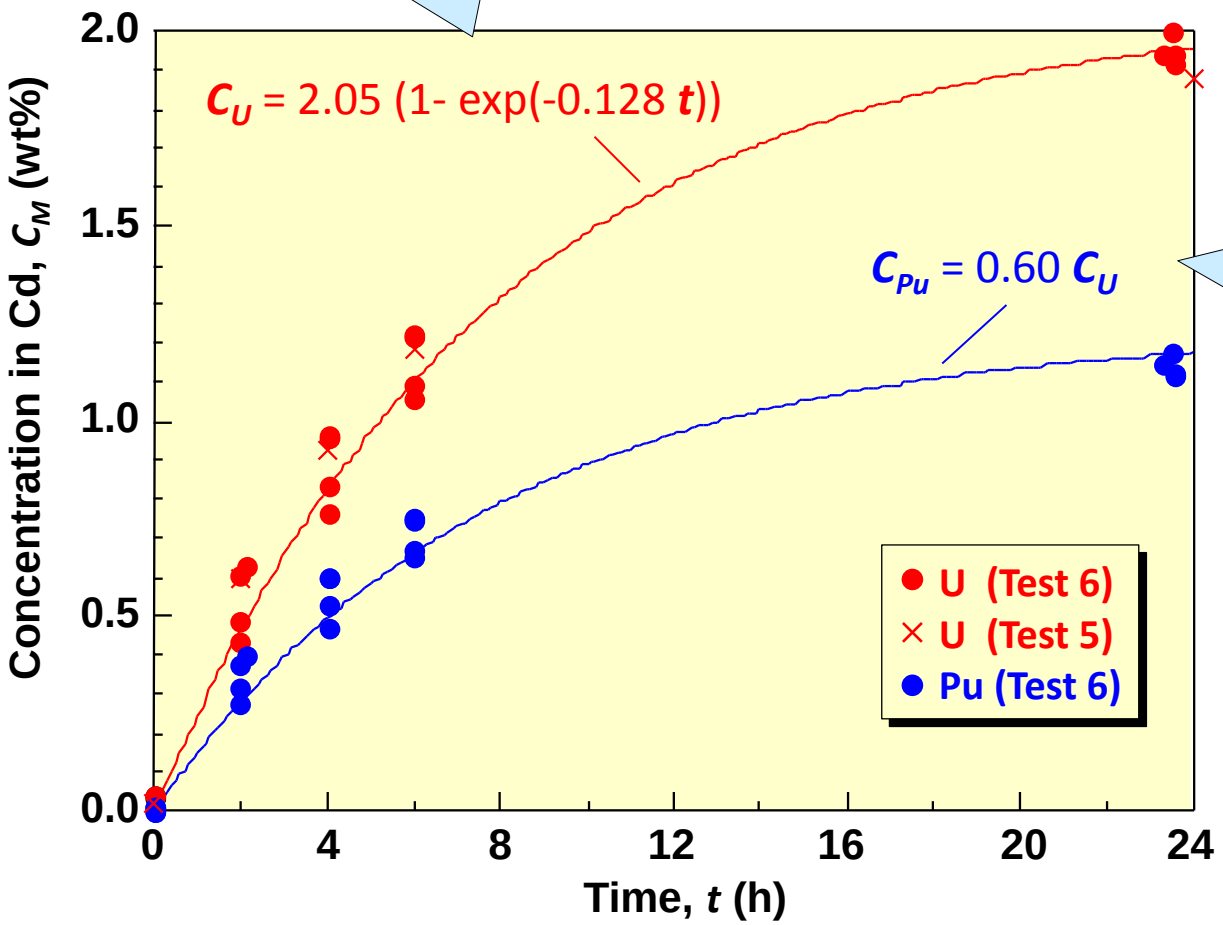
- ✓ **The agitation of Cd and salt did not enhance the extraction rate.**
- ✓ **The extraction rate was independent of the surface area/volume ratio of Cd.**
- ✓ **The rate-determining step for the extraction at the Cd electrode is not the mass transfer in the Cd or salt phase but the electron transfer at the Cd/salt interface.**

Electrochemical Extraction (EE) Method

$$\frac{dC_U}{dt} = A\,(S_U - C_U)$$

S_U = 2.05 wt%

It is assumed that the rate of increase of the U concentration in Cd (C_U) is proportional to the difference between the solubility of U (S_U) and C_U.



Calculated using $SF_{U/Pu}$~1.9 and concentration ratio of U^{3+}/Pu^{3+} in salt.

Fig. Experimental results for U and Pu concentrations in Cd and fitted curves.

Behavior of Am

Table Final concentrations of U, Pu and Am in the salt and Cd phases.

Test No.	Method	Concentration in salt (wt%)			Concentration in Cd (wt%)			$SF_{U/Pu}$	$SF_{Am/Pu}$
		U	Pu	Am	U	Pu	Am		
1	DE	2.40	3.49	N/A	2.13	1.06	0.024	2.94	0.75 [a)]
2	DE	2.28	3.11	0.096	2.16	1.32	0.026	2.23	0.63
3	EE	2.27	3.28	0.100	1.41	1.09	0.024	1.88	0.72
4	EE	2.17	3.14	0.086	1.51	1.12	0.024	1.95	0.79
5	EE	2.03	2.99	N/A	2.00	1.48	N/A	1.99	N/A
6-1	EE	2.50	2.89	N/A	1.94	1.14	N/A	1.96	N/A
6-2		2.52	2.88	N/A	2.00	1.18	N/A	1.94	N/A
6-3		2.60	2.93	N/A	1.91	1.11	N/A	1.94	N/A
6-4		2.68	2.98	N/A	1.94	1.12	N/A	1.92	N/A

a) Calculated assuming the concentration ratio of Am/Pu in salt was 3.0%.

- ✓Am can be extracted in Cd along with Pu.
- ✓$SF_{Am/Pu}$ were in the range of 0.63-0.79, which agree with the equilibrium values of 0.61, 0.65 and 0.56 reported by Koyama, Ackerman and Sakamura, respectively.

Design of Concept TRU Extractor

EE method

- ✓ The Pu/MAs/U ratio of the product is always equal to the thermodynamically determined equilibrium value.
- ✓ There is no upper limit to the amount of U metal that should be loaded in the container.

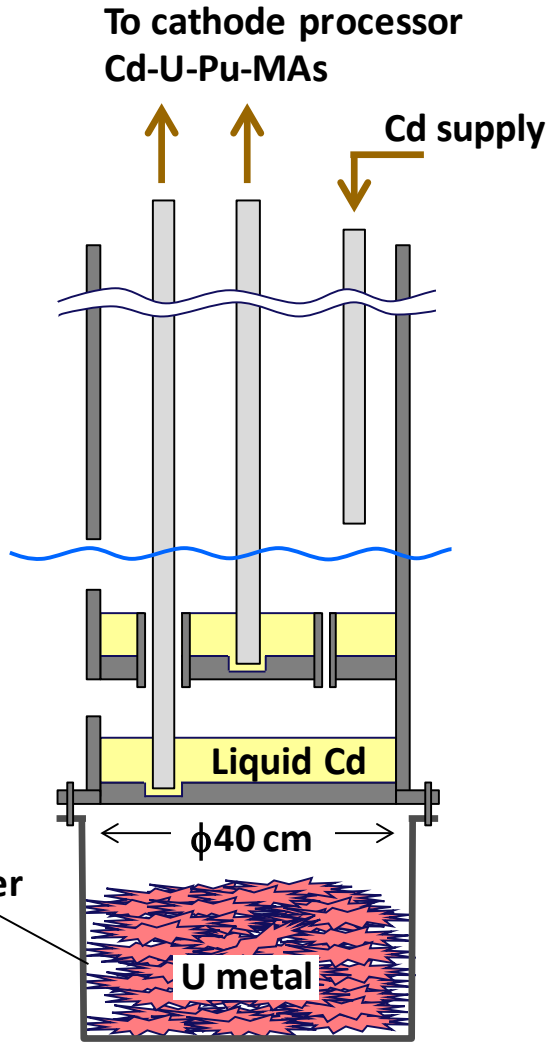
DE method

- ✓ No container loaded with U metal is required, which can increase the space in the electrorefiner.
- ✓ The rates of Pu extraction in the DE and EE methods appear to be roughly equal.

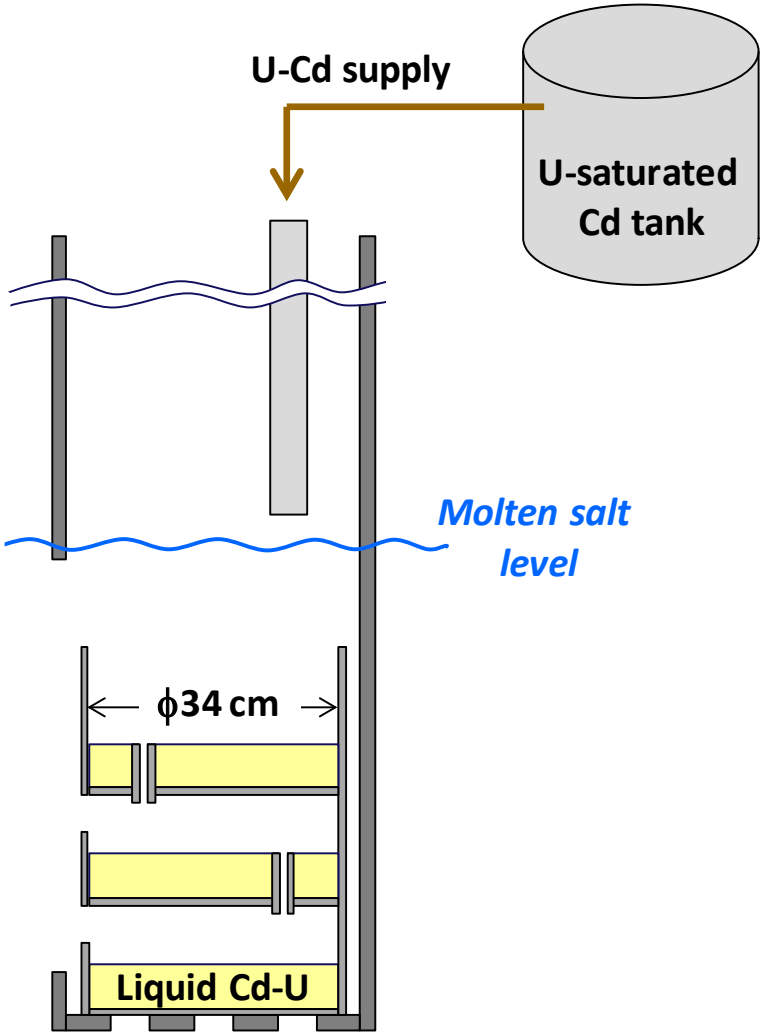
Design of Concept TRU Extractor

An electrorefiner whose throughput is 40 kg-HM of spent metallic fuel per day needs one EE or DE module designed in this study.

U metal collected by the anode-solid cathode module



(a) EE module



(b) DE module

3.1 kg of HM can be collected in 10 h.

Summary

A new approach to collecting Pu and MAs into liquid Cd using U metal as a reductant was investigated for the electrorefining process.

- Totally ~3 wt% of U, Pu and Am in the Cd could be extracted in 10 h using both the DE and EE methods.
- Crucibles made of steel could be used as containers for the Cd.
- In the DE tests, U metal had to be added in two or three batches so that excess undissolved U metal did not remain in the Cd to enhance the extraction of Pu.
- In the EE tests, $SF_{U/Pu}$ always agreed with the value at equilibrium, which is a favorable feature from the viewpoint of quality control.
- The rate-determining step for the extraction was not the mass transfer in the Cd or salt phase but the electron transfer at the Cd/salt interface.
- Concept TRU extractors of the EE and DE methods were preliminarily designed to process 40 kg-HM of spent metallic fuel per day.
- In the next stage, the extraction rate of Pu should be investigated under the conditions of a high Pu/U concentration ratio in the salt and a high volume/ surface area ratio of Cd.