2012 International Pyroprocessing Research Conference

Development of Pyro-processing Fuel Cycle Technology at CRIEPI

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Central Research Institute of Electric Power Industry (CRIEPI)

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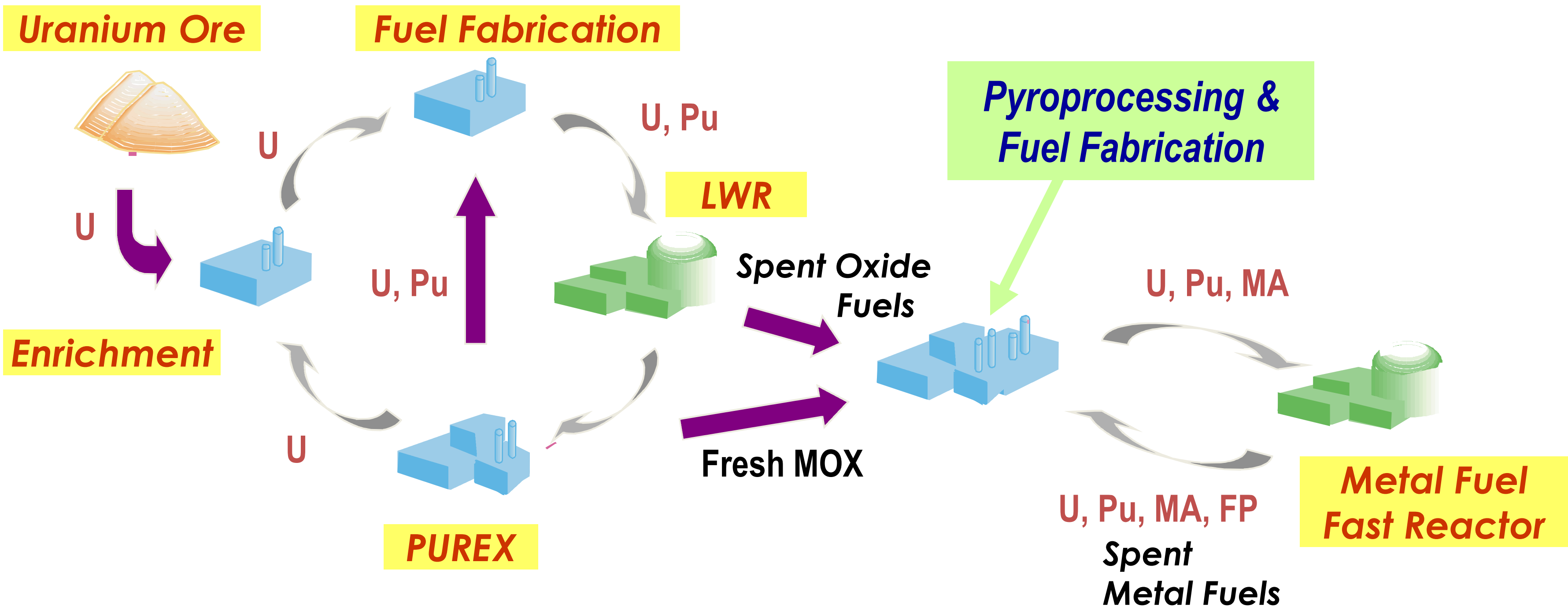
Concept of Metal Fuel Fast Reactor Cycle



Metal fuel FR cycle has high potential in

- *Proliferation resistance*
- *Transmutation of minor actinides*
- *High breeding ratio*
- *Substantial reduction of fuel cycle cost*

CRIEPI has been studying pyroprocessing since 1986

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CRIEPI's R&D Program on Pyroprocessing

Process Development

-Basic data assessment (electrochemistry, thermodynamics, etc.)
-Process test with unirradiated U, Pu, MA or irradiated materials
-Process flowsheet
-Process simulation codes

Technology Development

- Engineering-scale test with simulants and/or U
- Process equipments for ~10 ton-HM/y throughput
- Auxiliary technologies

System Development

- Nuclear materials accounting & safety Issues
- Facility design & cost estimate

Feasibility with reliable technical database !

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R & D of Advanced Fuel Cycle in Japan before March 11, 2011

FaCT (Fast Reactor Cycle Technology Development) Project has been conducted since 2006 to establish the FR cycle technological scheme at 2015 for its commercial deployment in around 2050.

Japanese main-concept:	Oxide fuel + aqueous process
sub-concept:	Metal fuel + pyroprocess

CRIEPI's Recent Activities on Pyroprocessing

Contents

- Process development using unirradiated U and Pu
- Process development using irradiated materials (HLLW, MOX fuel and metal fuel)
- Integrated fuel cycle tests using U with engineering-scale equipments
- Salt waste treatment
- Others
  - Measurement of basic data
  - Facility design & cost estimate
  - Application of pyroprocessing technology to damaged LWR fuel debris

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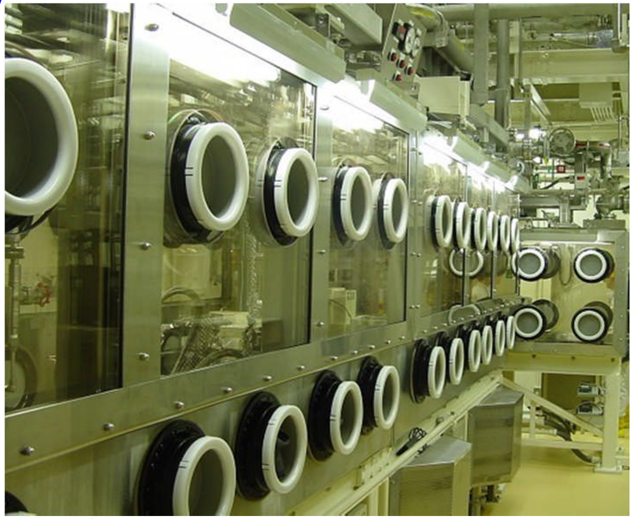
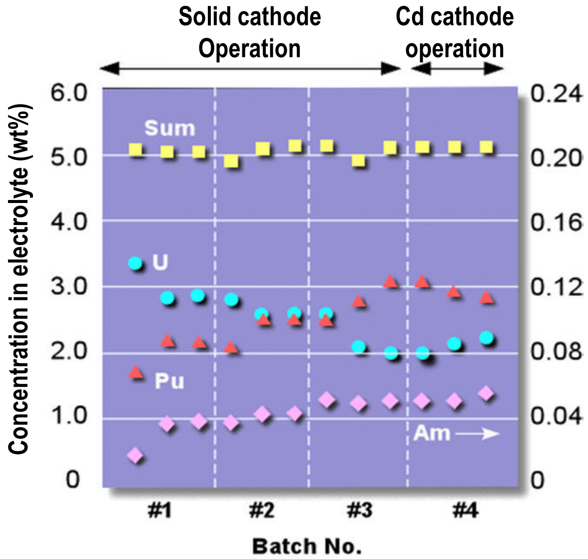
Process Development Using Unirradiated Fuels

(CRIEPI /JAEA joint program)

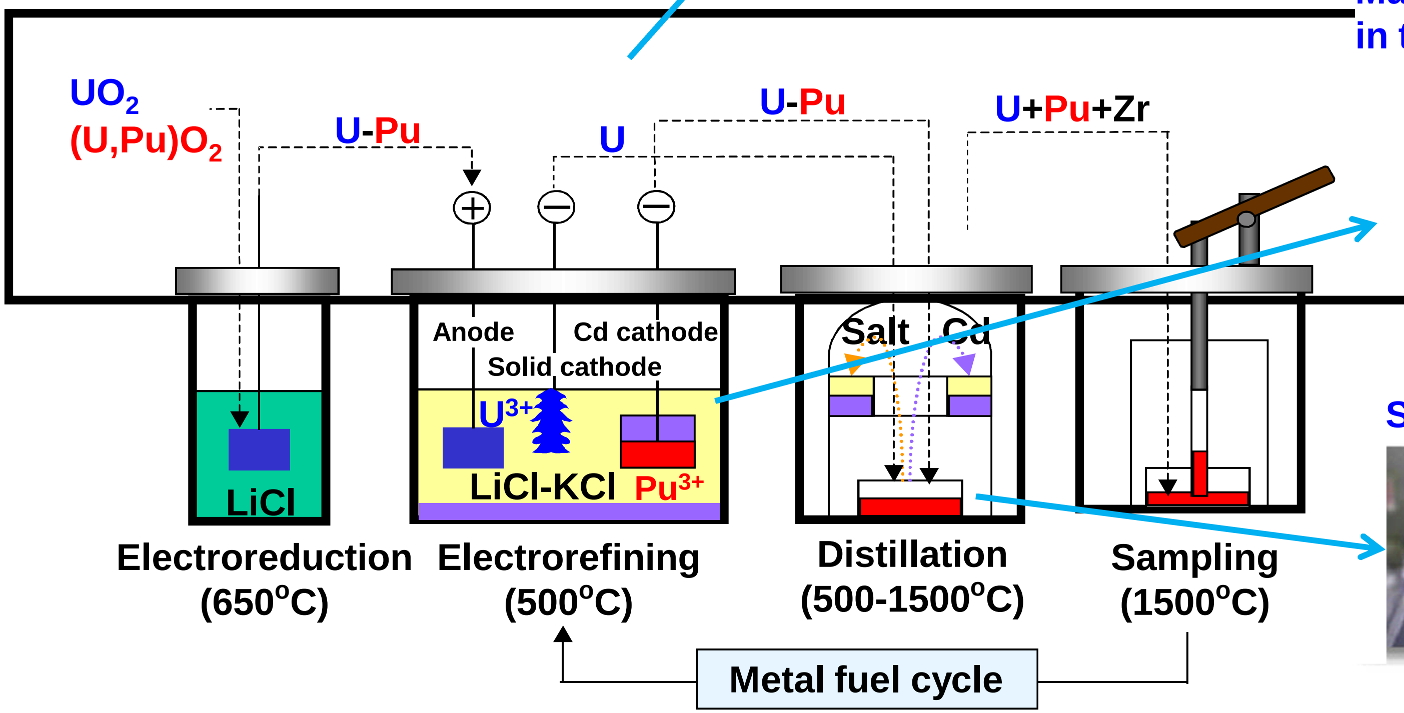
Several 10 g-Pu/batch scale tests for process optimization



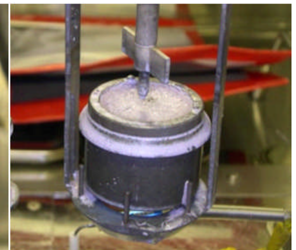
Ar atmosphere glove box



Mass balance of U, Pu and Am in the electrorefiner



Solid cathode



Cd cathode

U-Pu ingot

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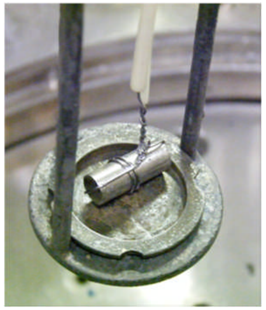
Process Development Using Unirradiated Fuels

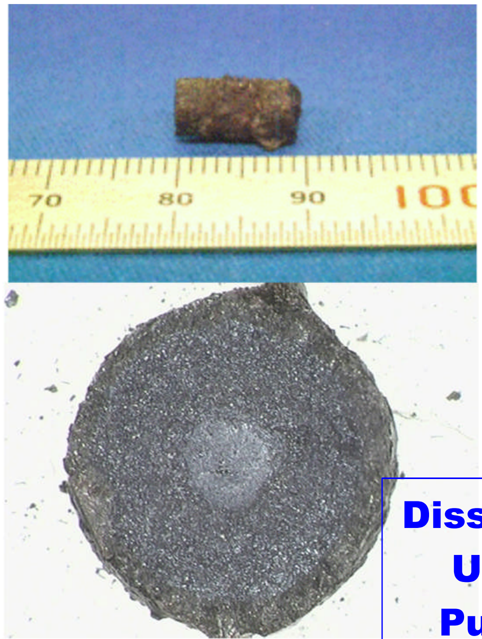
✓Anodic Dissolution of U-Pu-Zr Fuel

(CRIEPI /JAEA joint program)



U-Pu-Zr anode

Electrorefining
without Zr dissolution
(anode potential: -1.0 V)



Dissolution ratio
U : 99.6%
Pu : 99.9%

Porous Zr metal remained at anode

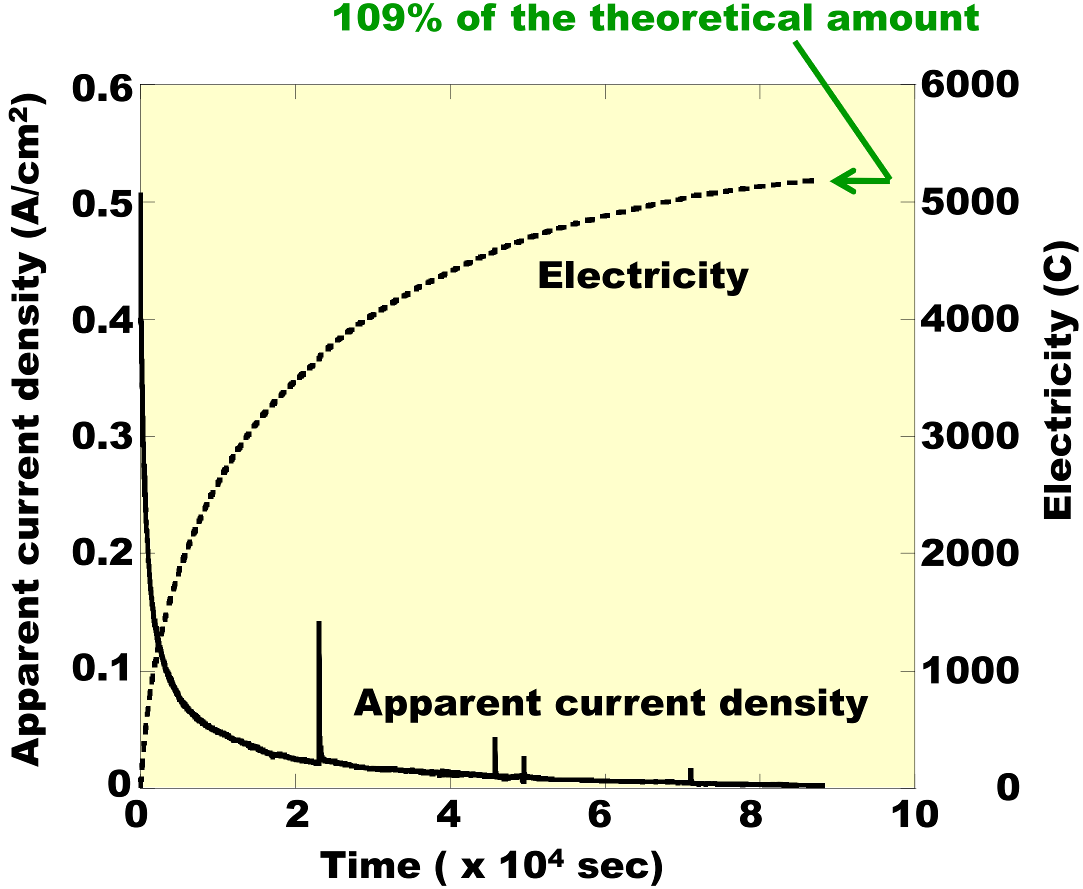


Fig. Anodic dissolution of U-Pu-Zr fuel by potentiostatic electrolysis at -1.0 V (vs Ag/AgCl).

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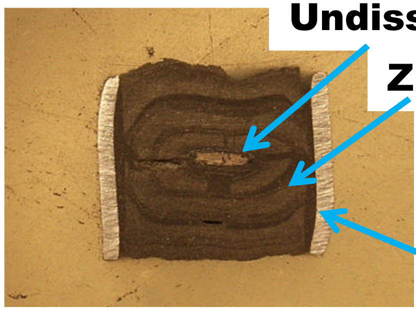
Process Development Using Unirradiated Fuels

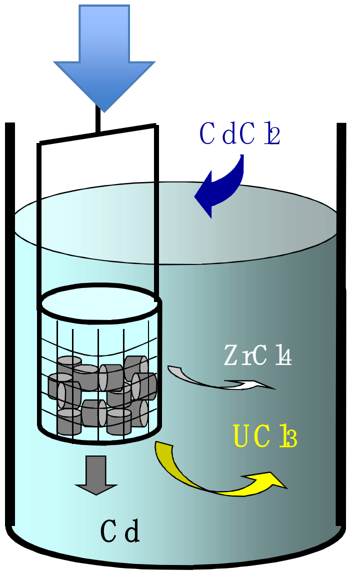
✓Anode Processing

(Research project of MEXT entrusted to CRIEPI)

To satisfy both high throughput of electrorefiner and high recovery ratio of actinides.



Anode residue obtained by electrorefining of U-Zr fuel



Anode processing: oxidation of U using $CdCl_2$ in LiCl-KCl

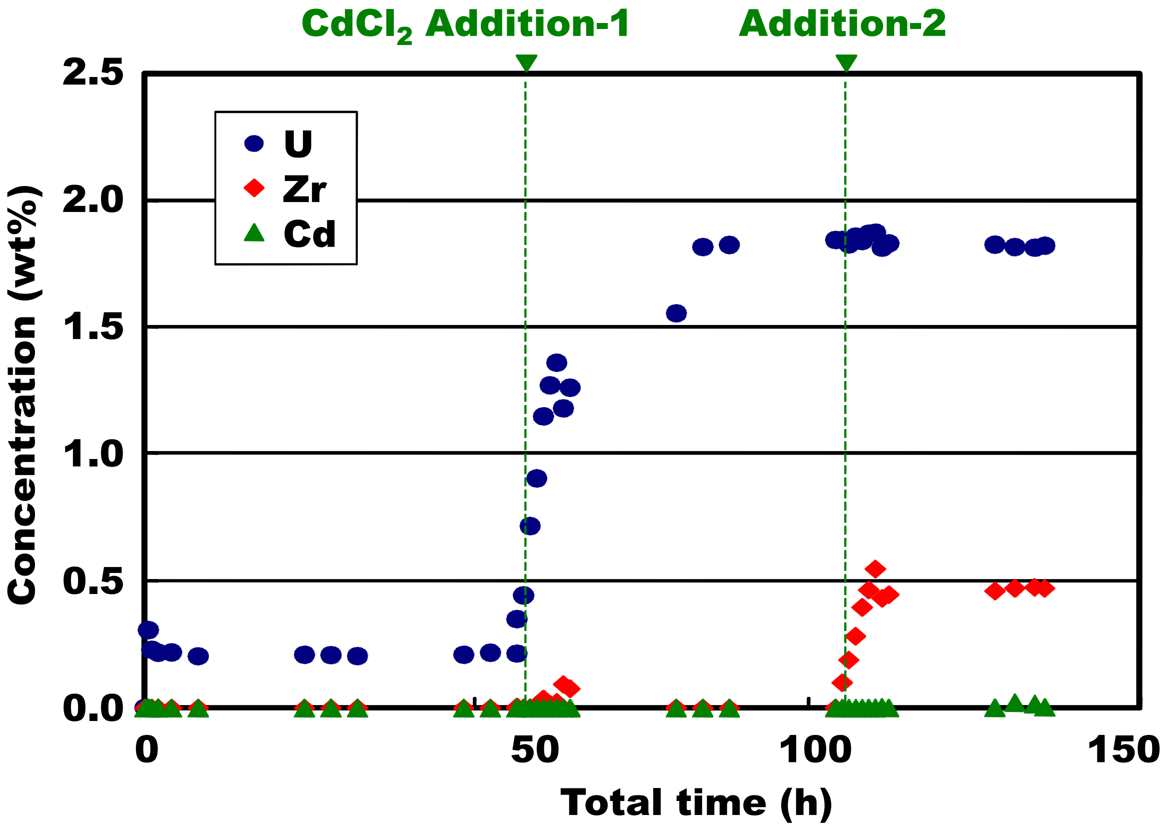


Fig. Change in U, Zr and Cd concentrations in the salt.

The remaining ratio of U after the anode processing was evaluated to be 0.04 ~ 0.20%.

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Process Development Using Unirradiated Fuels

(CRIEPI /JAEA joint program)

✓Dross Processing

Chlorination of actinides using $ZrCl_4$:

$$4\ MO_2 + 3\ ZrCl_4 + Zr \rightarrow 4\ MCl_3 + 4\ ZrO_2$$

$$4\ M + 3\ ZrCl_4 \rightarrow 4\ MCl_3 + 3\ Zr$$

✓ **Dross from U-Pu-Zr fuel fabrication test**
✓ **Partly reduced MOX**
(Estimated content: U= 25.4 g, Pu= 10.0 g)

↓

Salt: LiCl-KCl-UCl_3-$PuCl_3$-$ZrCl_4$ (~1 kg)

		72 hr
U	2.62 wt% (26.6 g) →	4.13 wt% (44.2 g)
Pu	0.40 wt% (4.1 g) →	1.33 wt% (14.2 g)
Zr	1.42 wt% (14.4 g) →	0.26 wt% (2.7 g)

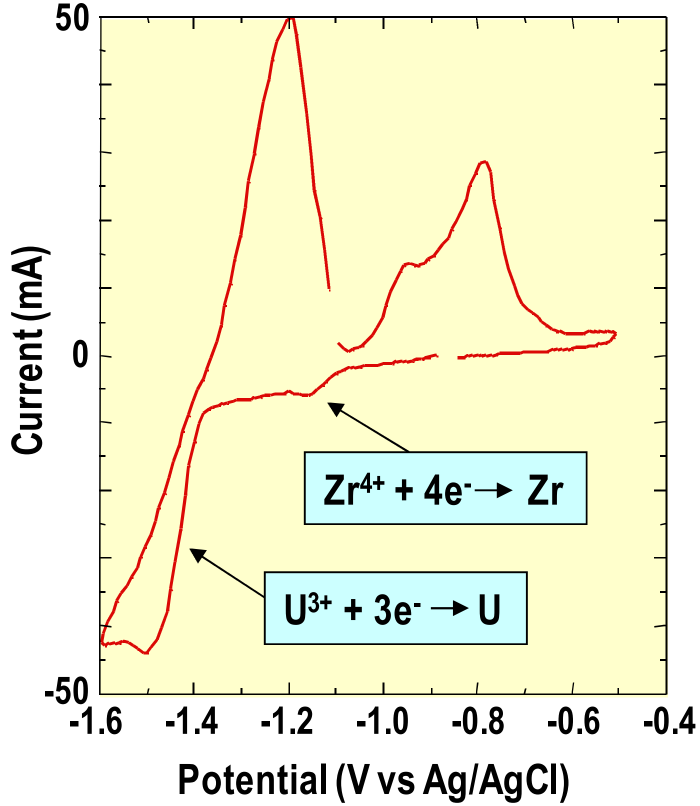

Fig. CV of tungsten electrode in LiCl-KCl-UCl_3-$PuCl_3$-$ZrCl_4$.

- Almost all of Pu was dissolved in the salt.
- Part of U had not yet been dissolved.
- "$PuO_2 + UCl_3 \rightarrow PuCl_3 + UO_2$" might help Pu dissolution.

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Process Flowsheet for Anode Residue and Dross Treatments

- *Electrorefining with most of Zr undissolved*
- *Target recovery ratio of U > 99.5%*

Anode residue

Oxydant ($CdCl_2$, etc.)

Anode residue → **Anode processing** → Metal → **Metal waste consolidation**

Anode processing ↓ Salt ($LiCl\text{-}KCl\text{-}MCl_3\text{-}ZrCl_4$)

Dross → **Dross processing**

Dross processing ↓ Salt ($LiCl\text{-}KCl\text{-}MCl_3$)

Electrorefiner

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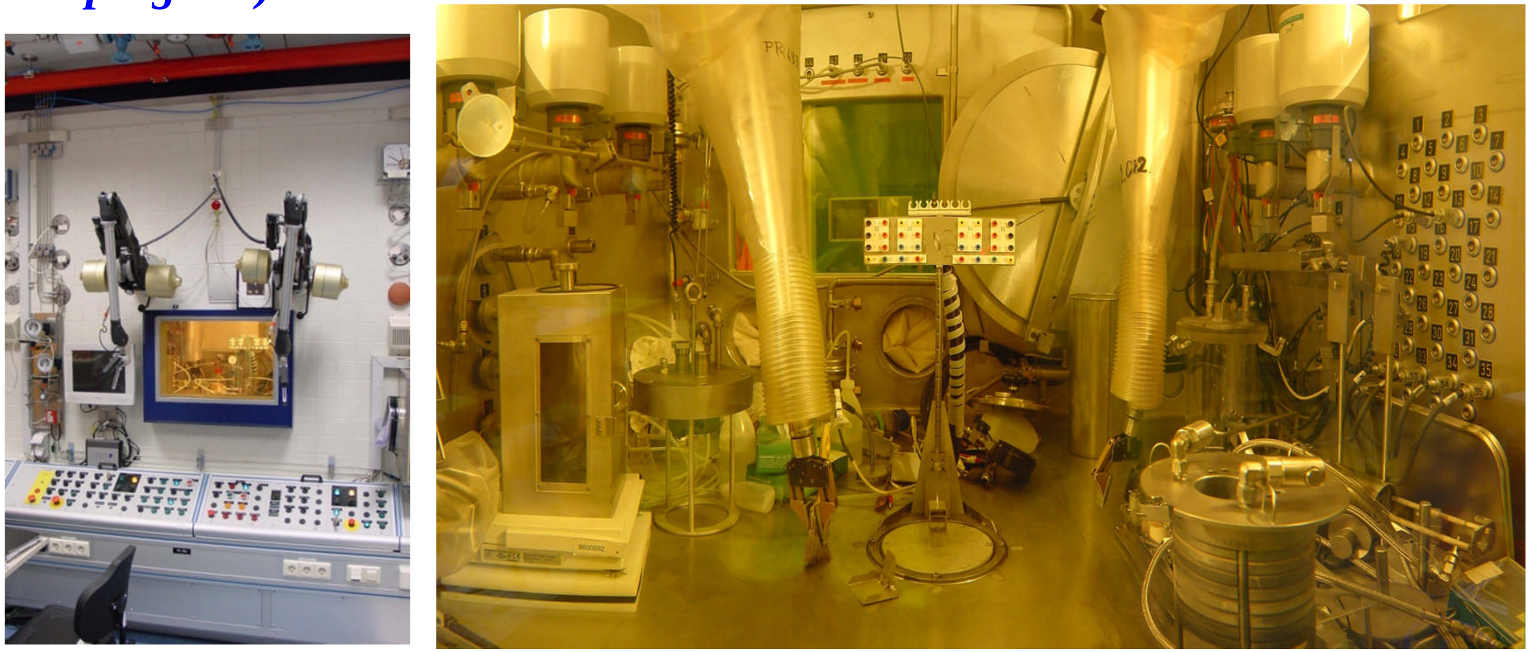
Process Development Using Irradiated Materials

(CRIEPI /ITU joint program)



Ar atmosphere hot cell dedicated for pyro-processing (JRC-ITU)

- ✓ **Partitioning of TRUs from real HLLW**
- ✓ **Electroreduction of irradiated MOX fuel**
- ✓ **Electrorefining of metal fuel irradiated at Phenix**

→ **Chemical and electrochemical reaction rate**
Effect of high radiation environment
Material balance of actinides and FPs

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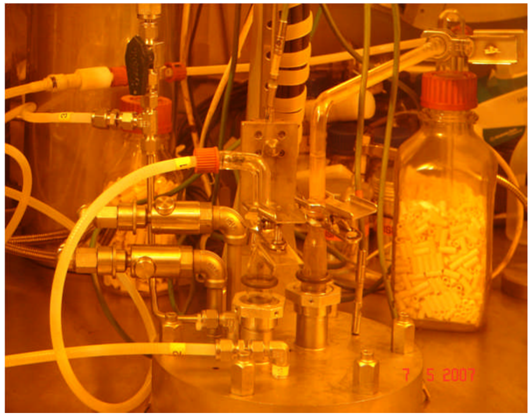
Process Development Using Irradiated Materials

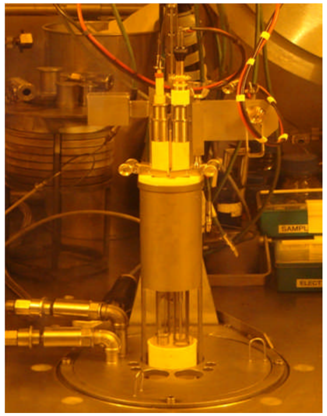
✓ *Partitioning of TRUs from real HLLW*

(CRIEPI /ITU joint program)

Denitration of HLLW (concentration & calcination)



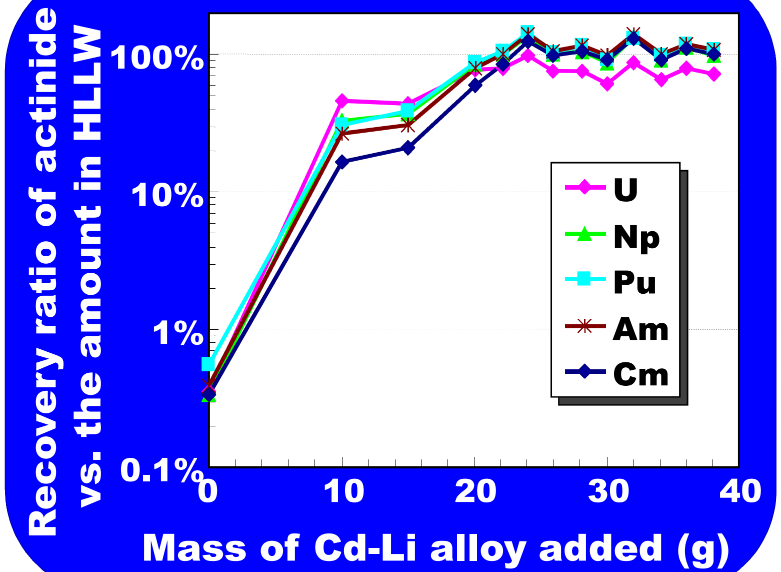
Chrorination using Cl_2 in LiCl-KCl salt at 650°C



Extraction of TRUs into Cd at 500°C

Calcined material

Chlorination product



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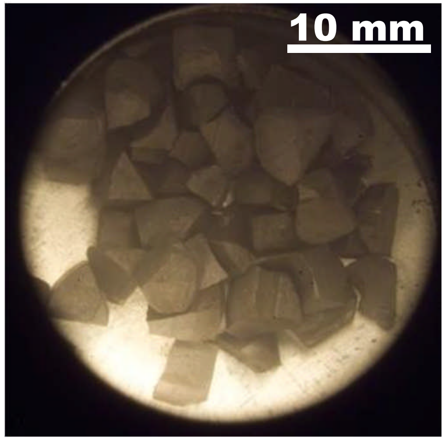
Process Development Using Irradiated Materials

✓Electroreduction of irradiated MOX fuel

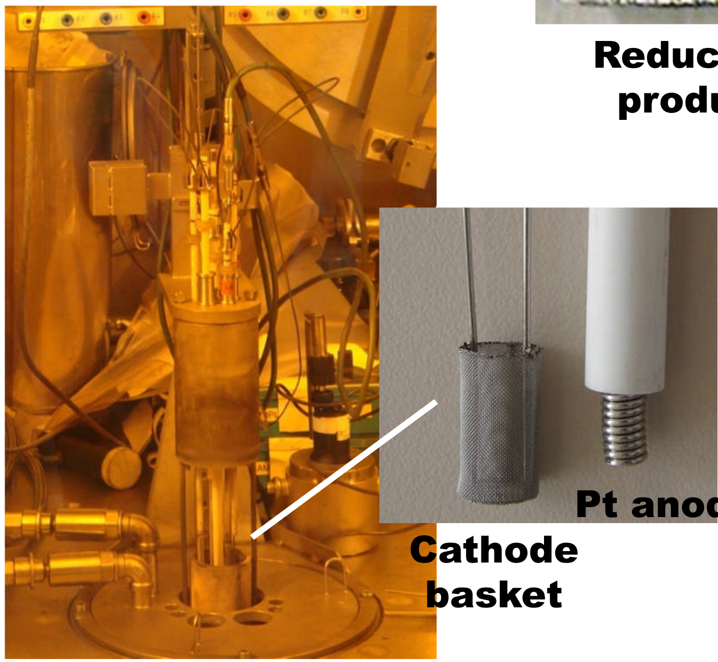
(CRIEPI /ITU joint program)



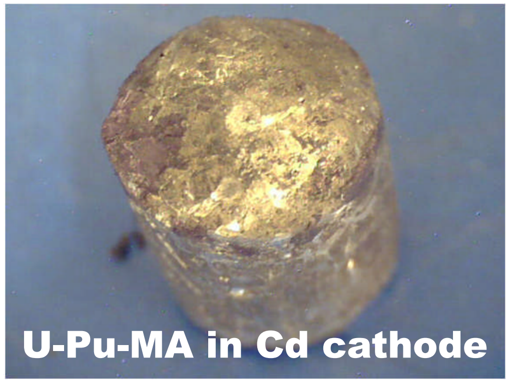
Irradiated MOX fuel

Electroreduction in LiCl-Li_2O at 650°C

Reduction product



Electrorefining in LiCl-KCl at 500°C



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Process Development Using Irradiated Materials

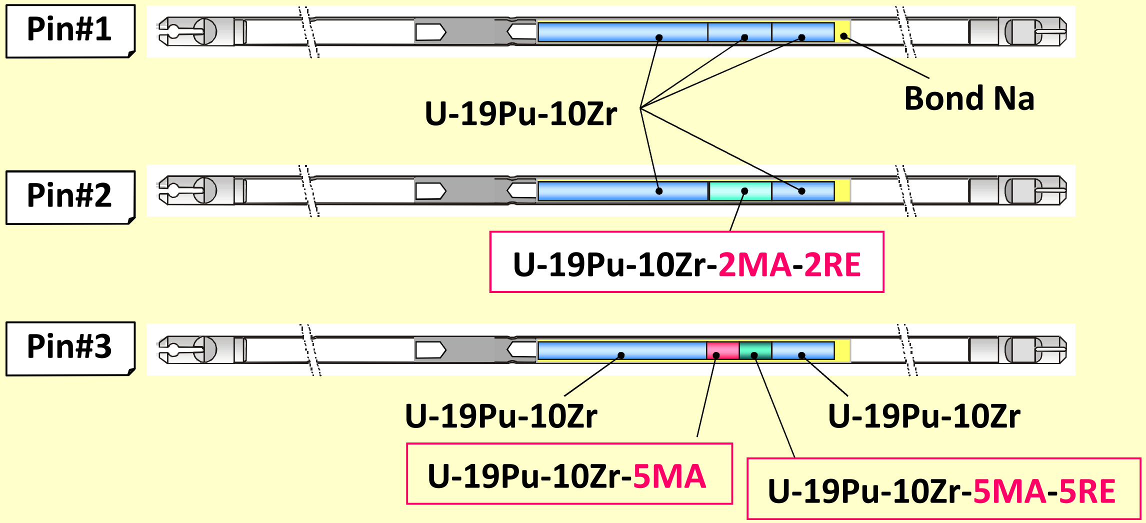
✓ *Electrorefining of irradiated metal fuel*

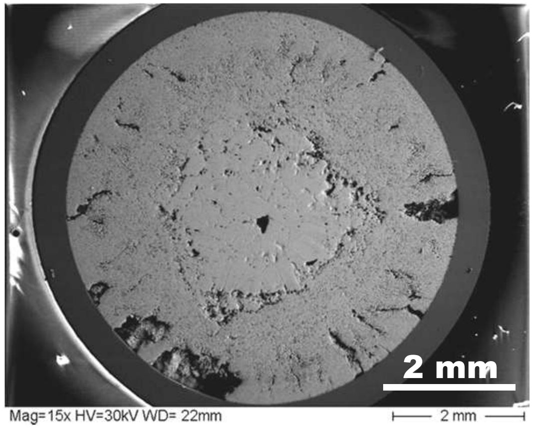
(CRIEPI /ITU joint program)

Metaphix fuel

MA-containing metal fuels irradiated at Phenix reactor (Burn-up: 2.5, 7 and 11 at%)

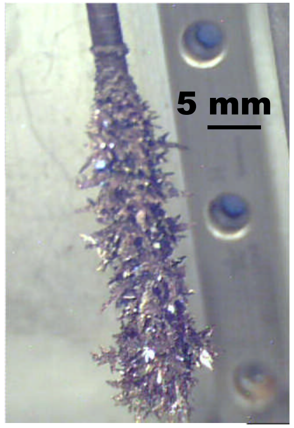
MA: Np, Am, Cm
RE: Ce, Nd, Y, Gd



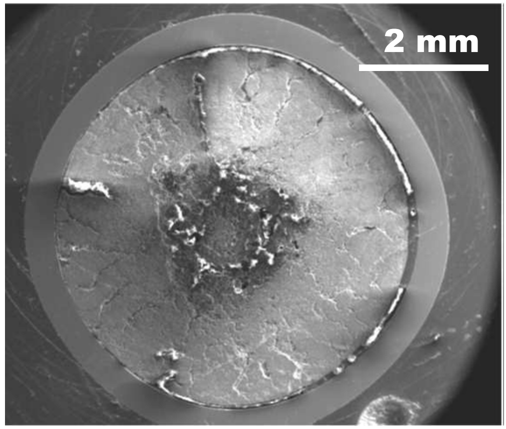


Cross-sectional Metaphix-1-1 fuel (U-Pu-Zr, 2.5 at% BU)

Electrorefining in LiCl-KCl-UCl_3 at 500°C



U deposit on solid cathode



Cross section after electrorefining

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Fuel Cycle Tests of U with Engineering-scale Equipments

To commercialize pyroprocessing technology, demonstration at ~ 10 ton-HM/year is the critical step.

- ✓ *Sequential batch processing.*
- ✓ *Cost reduction by module effect.*
- ✓ *Easy to increase throughput by multiplying the equipments according to the demand.*
- ✓ *Flexibility to employ new technologies for replacing equipments.*

Process equipments of 5~10 kg-U/batch have been developed

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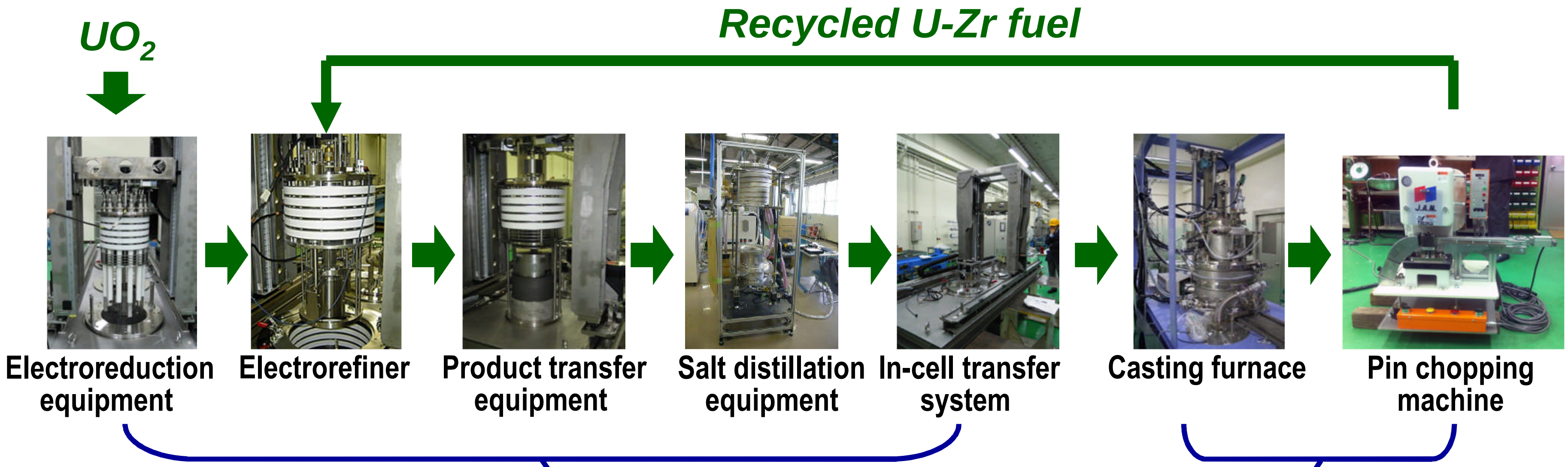
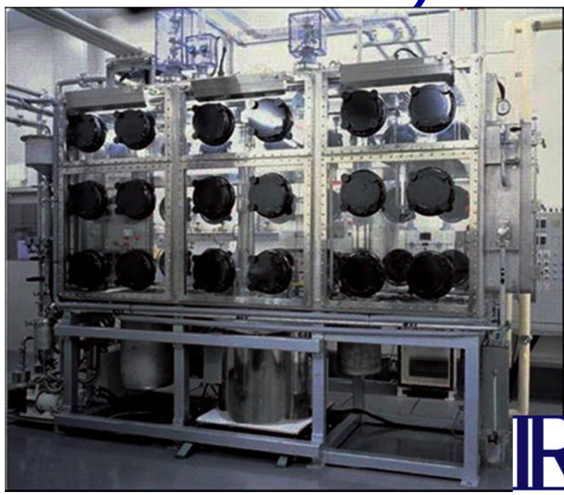
Fuel Cycle Tests of U with Engineering-scale Equipments

(Research project of MEXT entrusted to CRIEPI)

New equipments of ~5 kg-U/batch were designed for remote operation and material transfer system.





Two Ar atmosphere glove boxes were used for this project.

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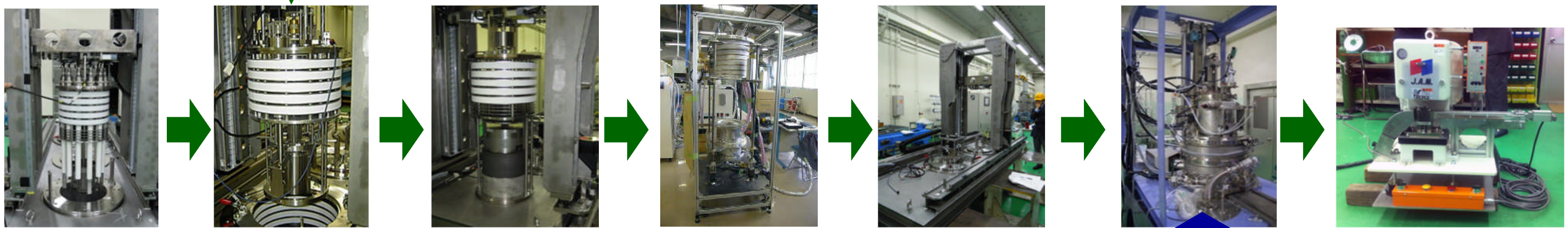
Fuel Cycle Tests of U with Engineering-scale Equipments

(Research project of MEXT entrusted to CRIEPI)

UO_2 pellets before and after reduction

The difference in total U mass between before and after the sequential operations (electrorefining, product transfer, salt distillation and injection casting) was 0.86%.

UO_2



Electroreduction equipment | Electrorefiner | Product transfer equipment | Salt distillation equipme | In-cell transfer system | Cast ace | Pin chopping

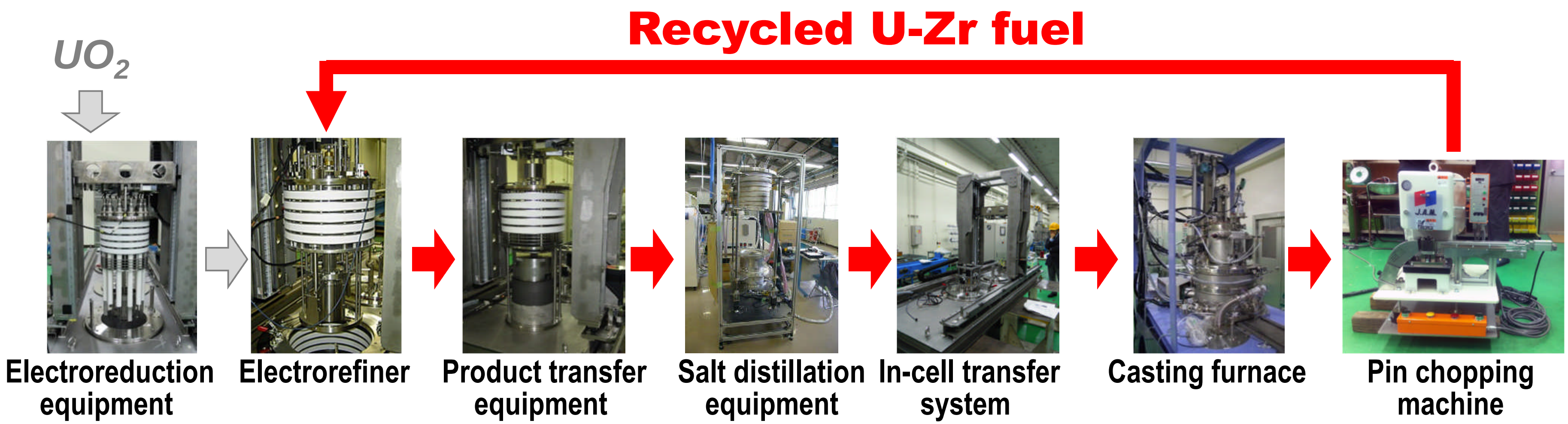
Electrorefining product of U metal

Separation of U metal from salt

Casted U-Zr fuel rods

Fuel Cycle Tests of U with Engineering-scale Equipments

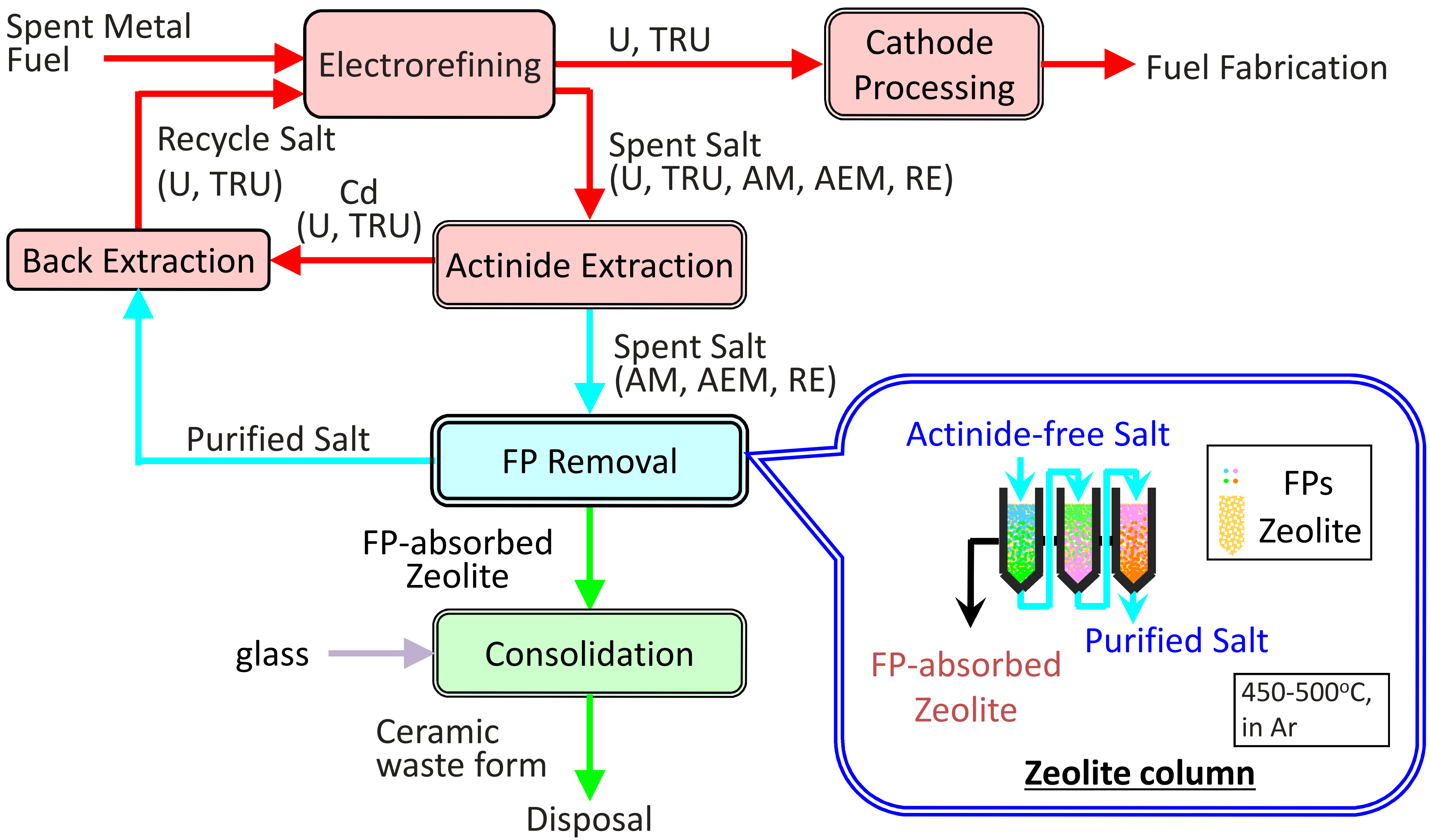
(Research project of MEXT entrusted to CRIEPI)



- ✓ *The U-Zr fuel slugs were inserted in claddings and then chopped into pieces for electrorefining.*
- ✓ *The fuel cycle operations were repeated again.*

- *The simulated metal fuel cycle was successfully demonstrated.*
- *The performance of process equipments was evaluated and the design data were accumulated to improve the equipments.*

Process Flowsheet for Salt Waste Treatment



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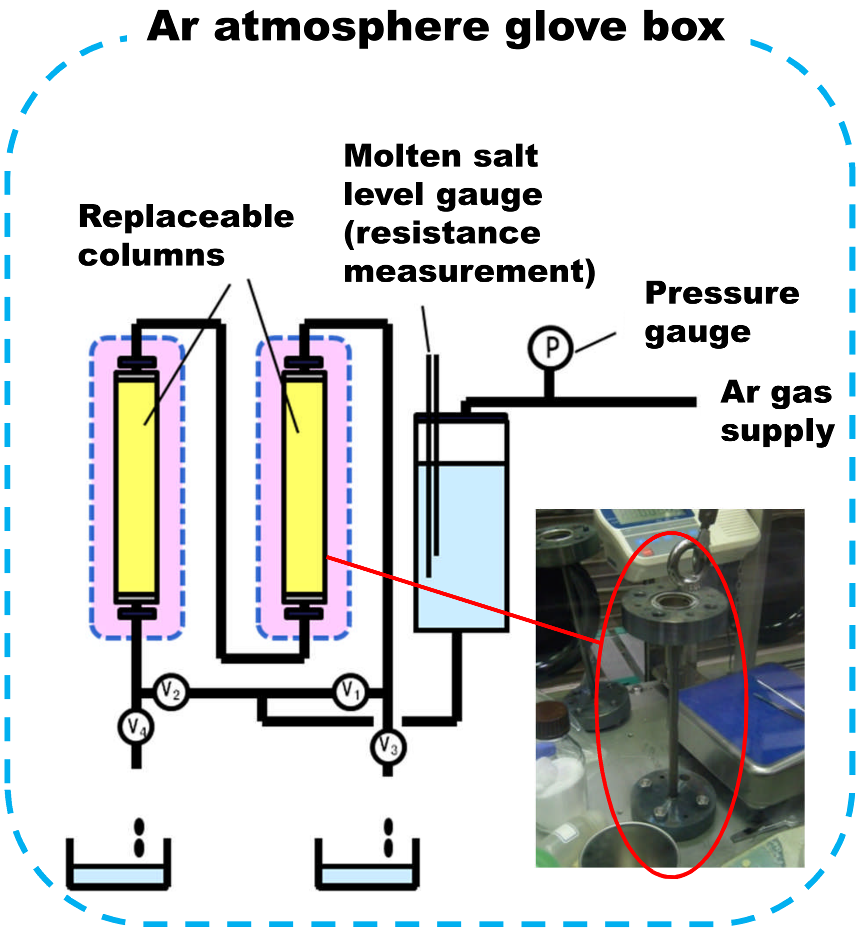
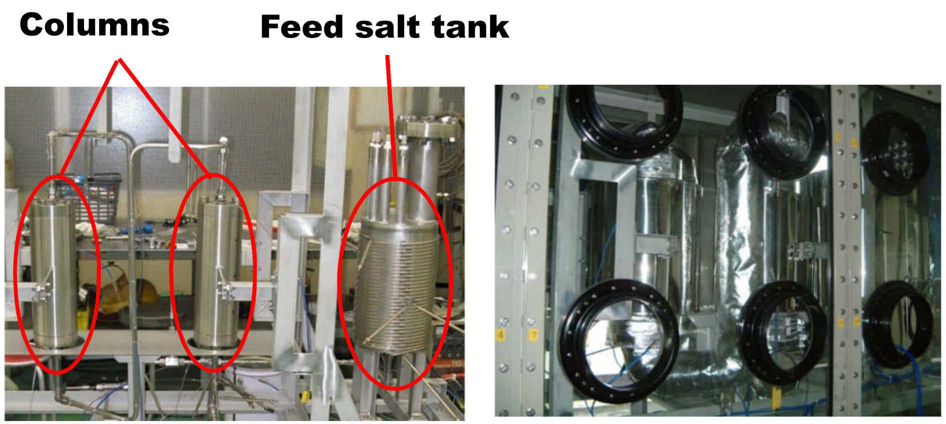
Development of Engineering-scale Zeolite Column

- *Engineering-scale zeolite column apparatus was installed in Ar atmosphere glove box.*
- *Flow rate of salt increased approximately linearly with driving pressure.*





Apparatus before and after installation in glove box

- Column length：300 mm
- Column ID：10-35 mm
- Zeolite：up to 450 g
- 2 columns in series
- Salt tank：up to 11 kg

Measurement of Diffusion Coefficient in Liquid Cd

(CRIEPI /JAEA joint program)

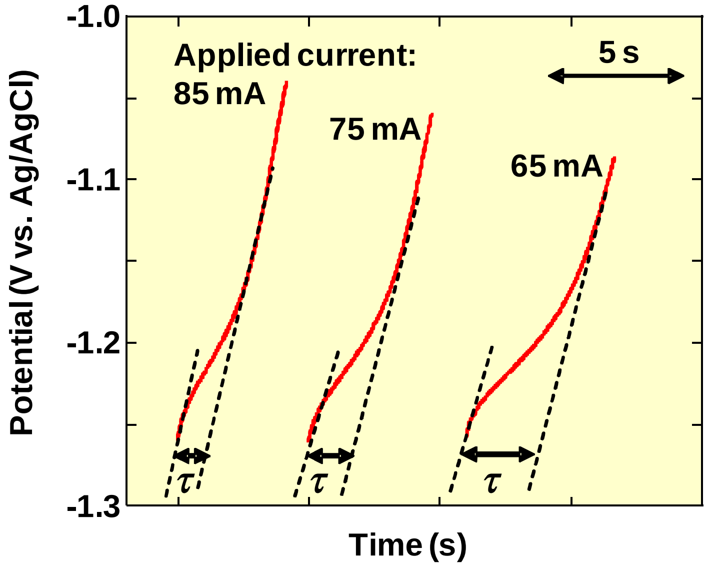


Fig. Typical chronopotentiograms of liquid Cd-U electrode in LiCl-KCl-1.6 wt%UCl_3 melt at 773 K.

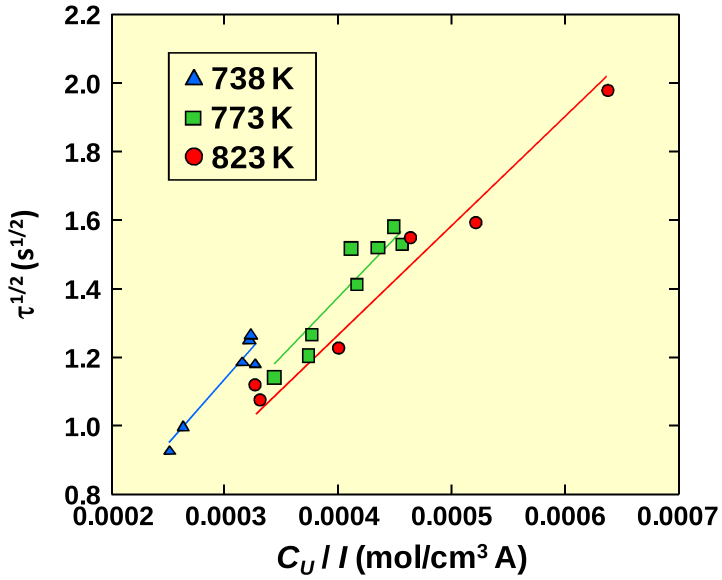


Fig. Plots of $\tau^{1/2}$ against C_U / I.

M (in Cd) → M^{3+} + $3e^-$

Sand equation:

$$\tau^{1/2} = 3/2\, \pi^{1/2} F A D_M^{1/2} (C_M / I)$$

τ : Transition time	D_M: Diffusion coefficient
F: Faraday constant	C_M: Concentration in Cd
A: Surface area	I : Applied current

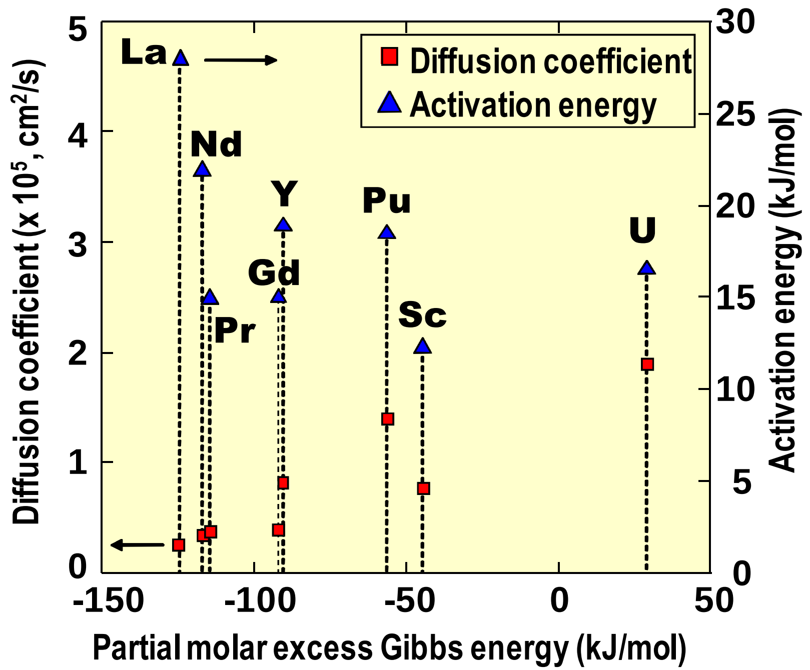


Fig. Plots of diffusion coefficient and activation energy against partial molar excess Gibbs energy at 773 K.

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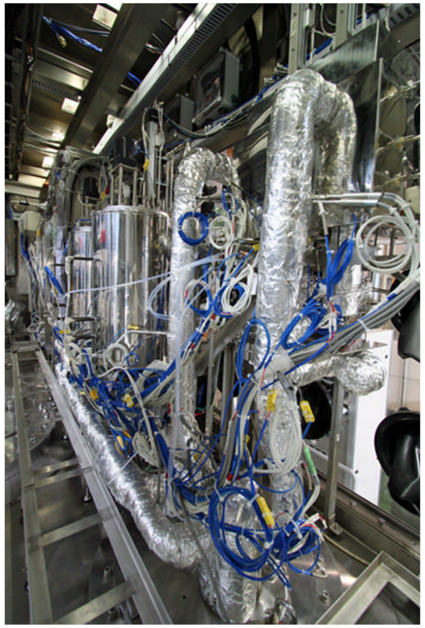
Industrial-scale Tests with Molten Salt and Liquid Cd

(Research project of MEXT entrusted to CRIEPI)

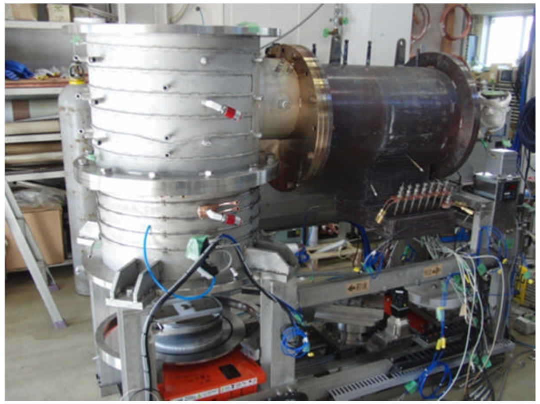
- *The electrorefiner, 6 stage contactor and Cd distillator were installed in the large Ar atmosphere glove box of cold area.*
- *Integrated tests using simulants (rare-earth elements) are underway.*

Ar atmosphere glove box

Electrorefiner



6 stage counter current contactor



Cd distillator

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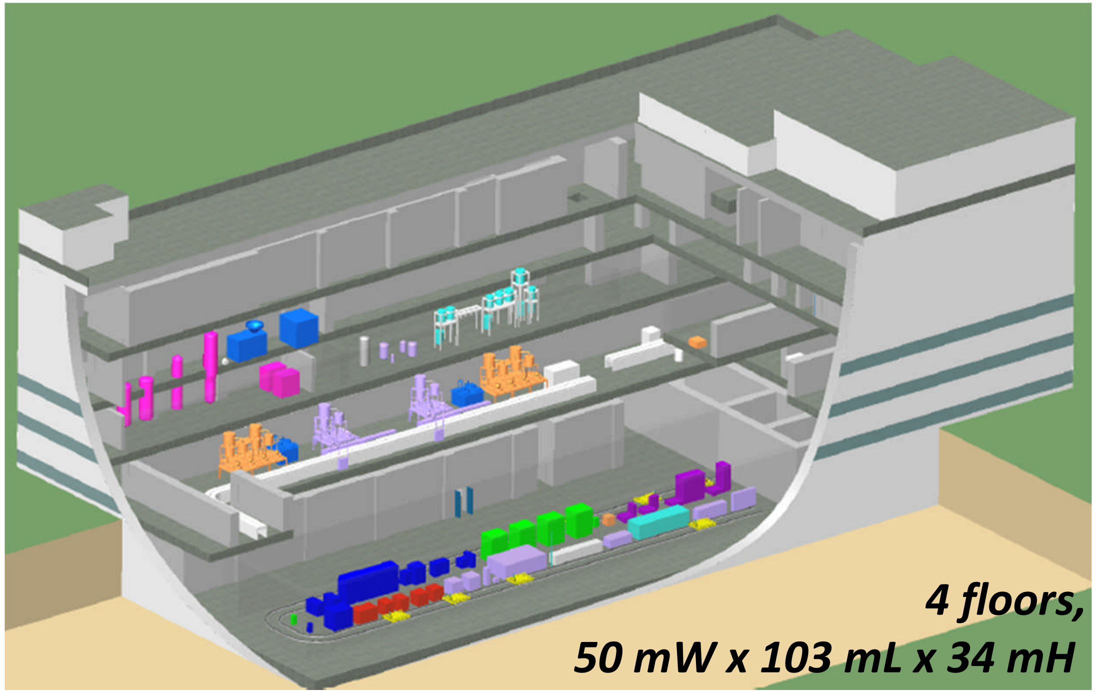
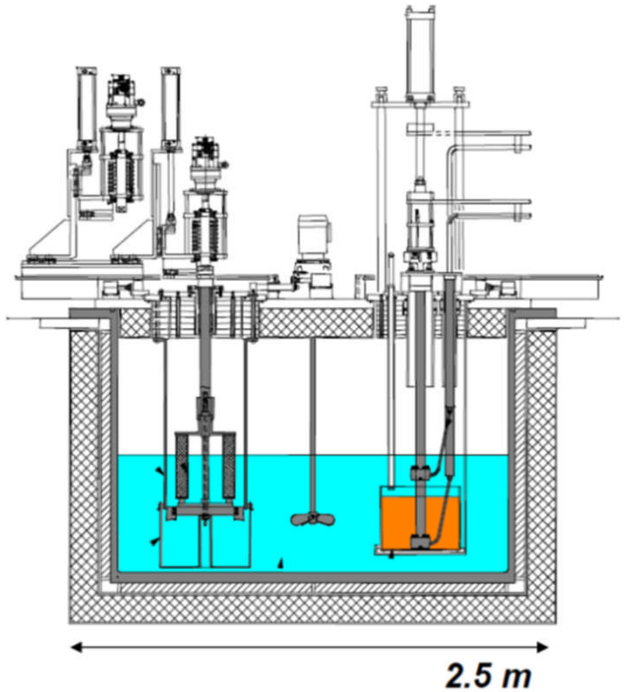
Design Study of Pyroprocessing Facility of 40 tHM/y

Conceptual design study was carried out for the equipments and the facility for 40 tHM/y throughput of spent metal fuels.

Based on this design, capital cost of the facility was roughly estimated, and relatively low fuel cycle cost was expected.



Fuel Cycle Facility of 40 tHM/y



Electrorefiner of 20 tHM/y

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Application of Pyroprocessing to Damaged LWR Fuel Debris

(CRIEPI /JAEA joint program)

- ***"Debris" mainly consists of (U,Zr)O_2.***
- ***Behaviors of ZrO_2 and (U,Zr)O_2 in LiCl-Li_2O melt have been investigated.***

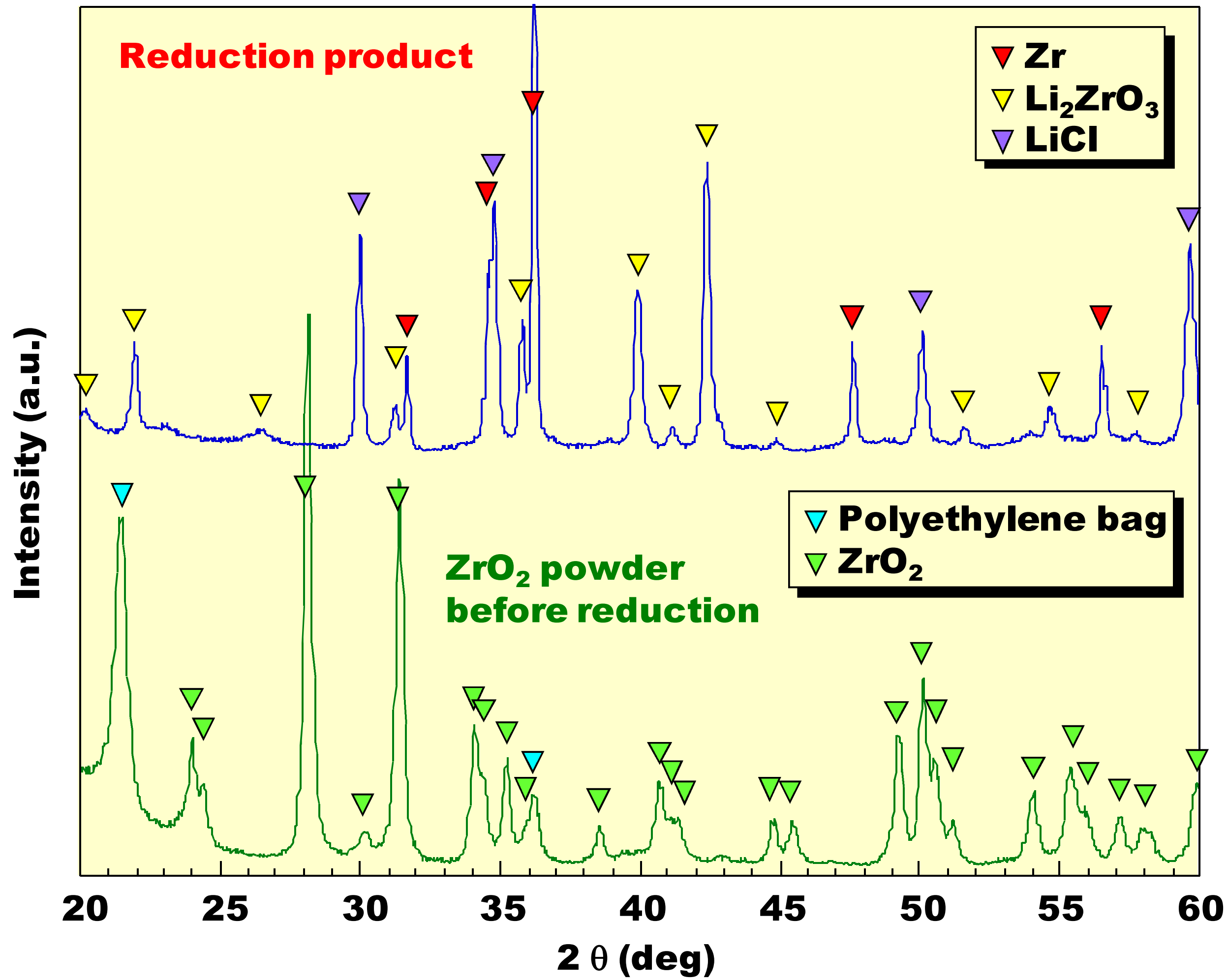

Fig. XRD patterns of ZrO_2 before and after electrolytic reduction in LiCl-Li_2O at 923 K.

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Summary & Conclusions

Recent Progress of CRIEPI's R&D on pyroprocessing is summarized.

- *Successful results were obtained for both the small-scale tests with irradiated materials and the engineering-scale tests with uranium.*
- *The process flowsheet has been continuously modified.*
- *Conceptual design study of a fuel cycle facility of 40 tHM/y capacity showed feasibility to meet process and safety requirements with lower fuel cycle cost.*
- *Any technological problems impossible to be overcome have not yet been found. Consequently, necessary data for the next step, engineering-scale experiments with irradiated materials, have been almost assessed.*
- *After Fukushima-daiichi reactor accident, different role is come to be expected for pyrochemical technology. A study on the applicability to damaged fuel debris is underway.*

Acknowledgement

Thank you for kind attention!

This presentation contains the results of the following research projects entrusted to CRIEPI by ***Ministry of Education, Culture, Sports, Science and Technology (MEXT****) :*

- *Development and improvement of pyrometallurgical process*
- *Development of technologies for processing of anode residue and cathode product from electrorefining of metallic nuclear fuel*
- *Development of metal fuel cycle technology for closing FBR fuel cycle*
- *Development of engineering technology basis for pyrometallurgical process equipment*

The authors would like to acknowledge that this presentation refers the results of joint studies with ***JRC-ITU*** *and* ***JAEA****.*

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