Separation of Rare Metal Fission Products in Radioactive Wastes in New Directions of Their Utilization

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JAPAN
Separation, Transmutation and Utilization

Radioactive Waste

Separation

Isotope Spth
Environment
Non Proliferation

Green Chemistry
Salt-Free
Radio Activity

Transmutation
Nano-tech
Functional Material

Utilization

Russia extracted Re (ReS₂?) from Volcano gas of Kudryavy at Etorohu Island. Annually 500 kg (possible max. 20 ton) of Re will be produced; News, 11 Sep., 2003.
### RMFP in SNF-1

#### Spent Nuclear Fuel, As an Artificial Ore

<table>
<thead>
<tr>
<th>Rare metal</th>
<th>Ru</th>
<th>Rh</th>
<th>Pd</th>
<th>Tc</th>
<th>Te</th>
<th>Se</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount (kg/HMt)</td>
<td>12.5</td>
<td>3.6</td>
<td>11.1</td>
<td>3.3</td>
<td>2.7</td>
<td>0.2</td>
<td>FBR-SF; 150,000MWd/t, Cooled 4 years.</td>
</tr>
</tbody>
</table>

![Graph showing concentration factors of 5th and 4th series elements in the FBR-S.F. and Earth Crust](image)

- ∞: Elements in the FBR-S.F. (g/t)
- ∅: Elements in the Earth Crust (g/t)
Fig. Specific Radio Toxicity (Hazard Index) of RMFP in FR Spent Fuel after 4 years cooling.

Fig. Time Dependency of Specific Activities of RMFP Separated from the FBR Spent Fuels cooled for 4 years

“Clearance levels” are proposed by IAEA”TECDOC-855” from $10^{-3}$ to $10^{3}$ Bq/g, for instance,
0.1 $\bullet$ Ru-106 $<$10, 100 $\square$ Tc-99$<$1000 (as for reference, 74 Bq/g, Japan domestic legal index).
Fig. Catalytic Electrolytic Extraction of RMFP from Simulated HLLW

Galvanostatic Electrolysis: 500 mA/cm² (Cathode), Room temp. Cathode; Pt-Ti, 20 cm², S/V: 1/15 cm⁻¹, Pd²⁺ Addition; Continuously (2.53 g Pd²⁺/hr), Pd_{added}/Ru=3.6, Pd_{added}/Rh=16.0, Pd_{added}/Re=9.1
**Effect of CEE (II) ; Tc**

![Graph showing electro-deposition of Tc and Ru](graph.png)

**Electro-deposition of Tc and Ru, x10^{-6}g/l**

- 0.1 g/l Tc, pH=4 (1st run)
- 0.1 g/l Tc, 0.5 M HNO₃ (2nd run)
- 0.1 g/l Tc, 2.0 M HNO₃, 0.5 g/l Pd (3rd run)
- 0.25g/lRu, 2.5M HNO₃

**Fig. Acceleration of Electro-deposition of TcO₄⁻ by Addition of Pd^{2+}**

Data obtained by KRI through JNC-KRI Collaboration 2003
**Deposition of Tc or Re with Pd**

- Interaction between TcO$_4^-$ or ReO$_4^-$ and Pd$^{2+}$ in the bulk solution
- Deposition of ReO$_3$ and Pd on the cathode
- No change of the deposition potential for Re from the mono ionic solution of Re

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**Deposition of Ru with Pd**

- No interaction between RuNO$_3^+$ and Pd$^{2+}$ in the bulk solution
- Deposition of Ru-Pd alloy on the cathode
- Decrease of the deposition potential for Ru comparing to that in the mono ionic solution of Ru

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**Structural Parameters from EXAFS Curve Fitting**

<table>
<thead>
<tr>
<th></th>
<th>$r$ (Å)</th>
<th>Coordination No.</th>
<th>Calculation with metallic bonding radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd - Pd</td>
<td>2.77</td>
<td>7</td>
<td>2.76</td>
</tr>
<tr>
<td>Pd - Ru</td>
<td>2.74</td>
<td>5</td>
<td>2.71</td>
</tr>
<tr>
<td>Ru - Pd</td>
<td>2.69</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Ru - Ru</td>
<td>2.69</td>
<td>2</td>
<td>2.66</td>
</tr>
</tbody>
</table>

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**Model of Catalytic Electrolytic Extraction**

- **“Island state”**
  - Interaction between TcO$_4^-$ or ReO$_4^-$ and Pd$^{2+}$
  - Deposition of ReO$_3$ and Pd on the cathode
  - No change of the deposition potential for Re from the mono ionic solution of Re

- **“Solid solution”**
  - No interaction between RuNO$_3^+$ and Pd$^{2+}$ in the bulk solution
  - Deposition of Ru-Pd alloy on the cathode
  - Decrease of the deposition potential for Ru comparing to that in the mono ionic solution of Ru

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Sptn. of RMFP-4
Utilization -1

Fig. Experimental Cell
# Table  Reduction Ratios by Catalytic Electrolytic Extraction

<table>
<thead>
<tr>
<th>System</th>
<th>Reduction ratio / %</th>
<th>Composition on electrode Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pd</td>
<td>Ru</td>
</tr>
<tr>
<td>Pd</td>
<td>&gt;99</td>
<td>-</td>
</tr>
<tr>
<td>Ru</td>
<td>-</td>
<td>14</td>
</tr>
<tr>
<td>Rh</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Re</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tc</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pd-Ru</td>
<td>99.3</td>
<td>60.9</td>
</tr>
<tr>
<td>Pd-Rh</td>
<td>99.0</td>
<td>-</td>
</tr>
<tr>
<td>Pd-Re</td>
<td>99.4</td>
<td>-</td>
</tr>
<tr>
<td>Ru-Rh</td>
<td>-</td>
<td>58.2</td>
</tr>
<tr>
<td>Ru-Re</td>
<td>-</td>
<td>14.5</td>
</tr>
<tr>
<td>Rh-Re</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pd-Ru-Rh-Re(1:1:1:1)</td>
<td>95.7</td>
<td>46.0</td>
</tr>
<tr>
<td>Pd-Ru-Rh-Re(3.5:4:1:1)*</td>
<td>99.0</td>
<td>11.8</td>
</tr>
<tr>
<td>Pd-Ru-Rh-Re(3.5:4:1:1)*</td>
<td>94.7</td>
<td>16.5</td>
</tr>
</tbody>
</table>

*1: Pd block addition  
*2: Pd 5 divided additon
Fig. EDS(EPMA) of the deposits on the Pt Electrode from Nitric Acid Solution; Soln. Composition: Pd-Ru-Rh-Re(3.5:4:1:1), Divided Addition of Pd²⁺

Average diameter of individual particle \( \approx 1000 \text{nm} \)

Utilization -3
Fig. The Cathodic Polarization Curves of Pd, Ru, Rh, Re and Tc deposit Pt Electrodes and Pt Electrode (left), and Pd-Ru-Rh-Re deposit Pt Electrode* (right) *Soln. Composition: 3.5:4:1:1, Pd²⁺ Divided Addition
Fig. Relation between Cathodic Current Corresponds to Hydrogen Evolution at -1.25V and Initial Hydrogen Evolution Potential (f_{Hinit.}) on each Deposit Electrode in 1M NaOH.

Deposits from the quaternary ionic solution; *1, Pd:Ru:Rh:Re=1:1:1:1, *2, Pd:Ru:Rh:Re=3.5:4:1:1(Pd^{2+} bloc addition), *3, Pd:Ru:Rh:Re= 3.5:4:1:1(Pd^{2+} divided addition)
Fig. Energy Consumption for Electrolysis of 1M NaOH, in the case of RMFP deposit Ti Electrodes
Fig. Total Separation Flow Diagram to Recover RMFP, Pu+U+Np, Cm and Am Products by IX with CEE Method
### SF Dissolver Solution

**0.5M HCl**

<table>
<thead>
<tr>
<th>Element</th>
<th>Bq</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Am 241</td>
<td>9.88E+4</td>
<td>100</td>
</tr>
<tr>
<td>Eu 155</td>
<td>6.10E+4</td>
<td>100</td>
</tr>
<tr>
<td>Ce 144</td>
<td>1.24E+5</td>
<td>100</td>
</tr>
<tr>
<td>Sb 125</td>
<td>1.07E+4</td>
<td>100</td>
</tr>
<tr>
<td>Ru 106</td>
<td>2.76E+4</td>
<td>100</td>
</tr>
<tr>
<td>Cs 137</td>
<td>7.18E+5</td>
<td>100</td>
</tr>
</tbody>
</table>

### Pre-Filtration

**Gelated Tertiary Pyridine Resin**

<table>
<thead>
<tr>
<th>Element</th>
<th>Bq</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Am 241</td>
<td>4.77E+1</td>
<td>0.05</td>
</tr>
<tr>
<td>Eu 155</td>
<td>2.59E-1</td>
<td>0.00</td>
</tr>
<tr>
<td>Ce 144</td>
<td>-</td>
<td>0.00</td>
</tr>
<tr>
<td>Sb 125</td>
<td>4.26E-2</td>
<td>0.00</td>
</tr>
<tr>
<td>Ru 106</td>
<td>-</td>
<td>0.00</td>
</tr>
<tr>
<td>Cs 137</td>
<td>3.27E+2</td>
<td>0.05</td>
</tr>
</tbody>
</table>

### H₂O Rinsing

**Resin**

### 1M NaOH Rinsing

**Alkaline soln.- rinsed Resin**

<table>
<thead>
<tr>
<th>Element</th>
<th>Bq</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Am 241</td>
<td>7.16E+0</td>
<td>0.01</td>
</tr>
<tr>
<td>Eu 155</td>
<td>3.28E+0</td>
<td>0.01</td>
</tr>
<tr>
<td>Ce 144</td>
<td>1.70E+1</td>
<td>0.01</td>
</tr>
<tr>
<td>Sb 125</td>
<td>1.17E+3</td>
<td>10.9</td>
</tr>
<tr>
<td>Ru 106</td>
<td>5.51E+2</td>
<td>2.00</td>
</tr>
<tr>
<td>Cs 137</td>
<td>1.19E+1</td>
<td>0.00</td>
</tr>
</tbody>
</table>

### Ru106- free Feed D.S. *

<table>
<thead>
<tr>
<th>Element</th>
<th>Bq</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Am 241</td>
<td>7.28E+2</td>
<td>0.74</td>
</tr>
<tr>
<td>Eu 155</td>
<td>3.16E+4</td>
<td>&gt; 51.8</td>
</tr>
<tr>
<td>Ce 144</td>
<td>5.36E+4</td>
<td>&gt; 43.2</td>
</tr>
<tr>
<td>Sb 125</td>
<td>3.57E+2</td>
<td>&gt; 3.34</td>
</tr>
<tr>
<td>Ru 106</td>
<td>0.00</td>
<td>-</td>
</tr>
<tr>
<td>Cs 137</td>
<td>5.01E+5</td>
<td>&gt; 69.8</td>
</tr>
</tbody>
</table>

* * Oyo Mox SF (143.8 GWe/t, 2.23x10²³(n/cm²)(E 0.1MeV)) : 1.27g/30ml

* * FP, Pu fractions, excluding MA fraction

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Am 241 4.77E+1 0.05
Eu 155 2.59E-1 0.00
Ce 144  -  0.00
Sb 125 4.26E-2 0.00
Ru 106  -  0.00
Cs 137 3.27E+2 0.05

Am 241 7.16E+0 0.01
Eu 155 3.28E+0 0.01
Ce 144 1.70E+1 0.01
Sb 125 1.17E+3 10.9
Ru 106 5.51E+2 2.00
Cs 137 1.19E+1 0.00

Am 241 7.28E+2 0.74
Eu 155 3.16E+4 > 51.8
Ce 144 5.36E+4 > 43.2
Sb 125 3.57E+2 > 3.34
Ru 106 - 0.00
Cs 137 5.01E+5 > 69.8

* * FP, Pu fractions, excluding MA fraction
Fig. New Back-End Concept; *Fission-Energy Cycle and Fission-Product Cycle*
Spent Fuel (Dissolver solution, HLLW)

**TcO₄⁻, RuNO₃⁺, Rh₃⁺, Pd²⁺, Ag⁺, Te⁴⁺, Se⁴⁺**

Separation by Catalytic Electrolytic Extraction

**Ru⁺⁺, Rh⁺⁺, Te**

*With cooling > several decades*

**Tc, Pd, Se**

*With light shielding*

**Principles of Salt-Free Concept**

**RF** and **H₂ Energy Systems**

- Catalyst for Fuel Cell
- Catalyst for Hydrogen Generation & Purification
- Catalyst for Solar Energy
- Hydrogen Generation

**Industrial Utilization**

- Chemical Industry
- Nuclear Medicine

**Primary Electricity**

**FBR System**

**Rare Metal Fission Products**

**Fig. Symbiotic Energy System by Hydrogen and Nuclear, Bridging by RMFP**
Conclusions

- **Separation and Fabrication**
  - Abundance of RMFP (Ru, Rh, Pd, Tc, Se, Te) in Spent Fuel
  - Applicable of Catalytic Electrolytic Extraction (CEE) Method

- **Utilization**
  - RMFP as Catalysts of $\text{H}_2$ Production and Fuel Cell
  - Excellent Ability of Quaternary, Pd-Ru-Rh-Re deposit Pt or Ti electrodes for Electrolysis of either Alkaline or Sea Water
  - Expectation of $^{99}\text{Tc}$ and Re in this direction of Utilization

- **Strategic View**
  - Symbiotic Energy System by hydrogen and Nuclear, bridging by RMFP
  - New Distribution of Precious Rare Metal
    - Natural RM → “Noble” Use, RMFP → Industrial Use
  - New Back-End Fuel Cycle
    - *Fission-Energy cycle and Fission-Product cycle*
Fig. Elemental Composition of High Level Liquid Waste (HLLW)

*(H+ : mol/l)*
Utilization -5

*1 Pd-Ru-Rh-Re=1-1-1-1  *2 Pd-Ru-Rh-Re=3-4-1-1  ;Pd(Ru+Rh+Re)=1.6 Bloc Addition of Pd2+

*3 Pd-Ru-Rh-Re=3-4-1-1  ;Pd(Ru+Rh+Re)=1.6 Continuous Addition of Pd2+

Fig. The Initial Hydrogen Evolution Potentials on Various RMFP-deposited Pt Electrodes
Fig. Cathodic Currents for Hydrogen Evolution of RMFP deposit Pt Electrodes at $\bar{V}$ -1.25V ($\bar{V}$ vs.Ag/AgCl)) in 1M NaOH and in Artificial Sea Water