Development of a Simple Reprocessing Process Using Selective Precipitant for Uranyl Ions
- Fundamental studies for evaluating the precipitant performance -

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UO$_2^{2+}$ + FP in HNO$_3$ → **Precipitation**

Rapidly

**Filtration**

Washing

**Filterability**: Good

U-NCP precipitate: UO$_2$(NO$_3$)$_2$(NCP)$_2$

**Calcination**

$800 \, ^\circ C$ for 2h

NCP consists of C, H, O, N.

**Fully combustible**

N-Cyclohexyl-2-Pyrrolidone

N-Cyclohexyl-2-Pyrrolidone (NCP) consists of C, H, O, N.

Fully combustible
Flow Diagram of the Simple Reprocessing Process for FBR Spent Nuclear Fuels Using NCP.

Pu and U are precipitated together. Whole process can be carried out in HNO₃ solution. NCP consists of C, H, O, N (Fully combustible).

- High nuclear proliferation resistance
- Simple and economical
- Reduce the amounts of HLLW
Objectives

1. Investigation of selective precipitation by NCP

   *Precipitation test of U and Pu by NCP*
   Does NCP precipitate U(VI) and Pu(VI) in high yields?

   *Decontamination factors in this process*
   Does NCP precipitate fission products?

   *Examination of resistance to $\gamma$-ray radiation*
   Does NCP have sufficient resistance for precipitation?

2. Development of high-performance precipitants

   *Evaluation of the performances*
   Precipitation ability
   Decontamination factors
   Resistance to $\gamma$-ray radiation ($N$-$n$-butyl-2-pyridone)
Precipitation Ratios of Uranyl Ion by NCP

1M $\text{UO}_2^{2+}$ in 3 M HNO$_3$ at 25 ºC

Precipitation ratios can be controlled by the amounts of NCP.

Pu contents can be readily adjusted.

Pu content ~ 10 %

Blanket fuel

Pu content ~ 30 %

Pu/U NCP precipitate

MOX fuel
Precipitation test of Pu(VI) by NCP

$[\text{PuO}_2^{2+}] = 40 \text{ mM in 1.5 M HNO}_3$

at room temperature

Added 0.40M NCP

After centrifuge

Plausible structural formula
$\text{PuO}_2(\text{NO}_3)_2(\text{NCP})_2$

Precipitation ratio of Pu(VI) = 83 %
Decontamination factors in the Reprocessing Process by Using NCP

<table>
<thead>
<tr>
<th>Dissolvent in 3M HNO₃</th>
<th>1st</th>
<th>2nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>[UO₂²⁺] ≈ 1M NCP</td>
<td>U-NCP ppt</td>
<td>[\text{FP, TRU}]</td>
</tr>
<tr>
<td>[UO₂²⁺] ≈ 0.3M NCP</td>
<td>U(Pu)-NCP ppt</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>DF (1M UO₂²⁺)</th>
<th>Ba²⁺</th>
<th>RuNO₃⁺</th>
<th>Ce³⁺</th>
<th>Nd³⁺</th>
<th>ZrO₂⁺</th>
<th>MoO₂²⁺</th>
<th>ReO₄⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;100</td>
<td>&gt;100</td>
<td>22</td>
<td>20</td>
<td>6</td>
<td>27</td>
<td>20</td>
<td></td>
</tr>
</tbody>
</table>

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<tr>
<th>DF (0.3M UO₂²⁺)</th>
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</thead>
<tbody>
<tr>
<td>&gt;100</td>
<td>&gt;100</td>
<td>&gt;100</td>
<td>100</td>
<td>46</td>
<td>≈100</td>
<td>≈100</td>
<td></td>
</tr>
</tbody>
</table>

ReO₄⁻ was used as a simulated ion of TcO₄⁻.

1st treatment (1M UO₂²⁺): DFs of Ba²⁺ and RuNO₃⁺ are more than 100.
2nd treatment (0.3M UO₂²⁺): DFs of most of FPs (except ZrO₂⁺) can be achieved >100.

DF = \(\frac{\left[\text{FP}\right]_S}{\left[\text{UO}_2^{2+}\right]_S} / \frac{\left[\text{FP}\right]_P}{\left[\text{UO}_2^{2+}\right]_P}\) | \(\frac{\left[\text{FP}\right]_S}{\left[\text{UO}_2^{2+}\right]_S} / \frac{\left[\text{FP}\right]_P}{\left[\text{UO}_2^{2+}\right]_P}\)

[FP]ₜ, [UO₂²⁺]ₜ: Concentrations of FP and UO₂²⁺ in treated solution
[FP]ₚ, [UO₂²⁺]ₚ: Concentrations of FP and UO₂²⁺ in precipitate
SEM images of U-NCP precipitate (× 1000)

<table>
<thead>
<tr>
<th></th>
<th>Ba$^{2+}$</th>
<th>RuNO$^{3+}$</th>
<th>Ce$^{3+}$</th>
<th>Nd$^{3+}$</th>
<th>ZrO$^{2+}$</th>
<th>MoO$_2^{2+}$</th>
<th>ReO$_4^-$</th>
</tr>
</thead>
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<tr>
<td>DF (1M UO$_2^{2+}$)</td>
<td>&gt;100</td>
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<td>6</td>
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</table>

Rough surface condition

Efficient washing of precipitate

Higher DFs
## Evaluation of Precipitants Capability
(Precipitation ability for UO$_2^{2+}$)

<table>
<thead>
<tr>
<th></th>
<th>NProP</th>
<th>NBP</th>
<th>NCP</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="NProP" /></td>
<td><img src="image" alt="NBP" /></td>
<td><img src="image" alt="NCP" /></td>
<td></td>
</tr>
<tr>
<td>log $P$</td>
<td>0.88</td>
<td>1.37</td>
<td>2.16</td>
</tr>
<tr>
<td>Precipitation ratio of UO$_2^{2+}$ ion</td>
<td>58%</td>
<td>67%</td>
<td>73%</td>
</tr>
</tbody>
</table>

*a Hydrophobicity ($P$ = octanol/water partition coefficient of precipitant).

*b Condition: [precipitant]/[UO$_2^{2+}$] = 1.5 in 3M HNO$_3$ at 25 ºC.

The precipitation abilities are high enough to adjust Pu contents.

Decontamination factors?
## Comparison of decontamination factors

<table>
<thead>
<tr>
<th>Precipitant</th>
<th>NProP $P_{cal}$</th>
<th>NBP $P_{cal}$</th>
<th>NCP $P_{cal}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{log } P_{cal}$</td>
<td>0.88</td>
<td>1.37</td>
<td>2.16</td>
</tr>
<tr>
<td>$\text{Ba}^{2+}$</td>
<td>$&gt; 100$</td>
<td>$&gt; 100$</td>
<td>$&gt; 100$</td>
</tr>
<tr>
<td>$\text{Ce}^{3+}$</td>
<td>$&gt; 100$</td>
<td>$&gt; 100$</td>
<td>22</td>
</tr>
<tr>
<td>$\text{Nd}^{3+}$</td>
<td>$&gt; 100$</td>
<td>$&gt; 100$</td>
<td>20</td>
</tr>
<tr>
<td>$\text{RuNO}^{3+}$</td>
<td>$&gt; 100$</td>
<td>$&gt; 100$</td>
<td>$&gt; 100$</td>
</tr>
<tr>
<td>$\text{ZrO}^{2+}$</td>
<td>$\approx 100$</td>
<td>91</td>
<td>6</td>
</tr>
<tr>
<td>$\text{MoO}_2^{2+}$</td>
<td>$&gt; 100$</td>
<td>$\approx 100$</td>
<td>27</td>
</tr>
<tr>
<td>$\text{ReO}_4^{-}$</td>
<td>$&gt; 100$</td>
<td>16</td>
<td>20</td>
</tr>
</tbody>
</table>

**SEM image**

*($\times 1000$)*

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**Images:**
- [SEM image 1](image1.png)
- [SEM image 2](image2.png)
- [SEM image 3](image3.png)
**Resistance of NCP to γ-ray Radiation**

NCP in 3M HNO₃ → \(^{60}\text{Co}\) γ-ray → UO\(_2^{2+}\) → U-NCP precipitate

\([\text{NCP}]/[\text{UO}_2^{2+}] = 3\)

<table>
<thead>
<tr>
<th>Irradiated dose</th>
<th>0 Gy</th>
<th>100 kGy</th>
<th>200 kGy</th>
<th>1 MGy</th>
<th>3 MGy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance of NCP</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
</tr>
<tr>
<td>Appearance of ppt</td>
<td><img src="image6.png" alt="Image" /></td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
</tr>
<tr>
<td>Precipitation ratio*</td>
<td>99.9%</td>
<td>99.9%</td>
<td>44.3%</td>
<td>22.1%</td>
<td>10.9%</td>
</tr>
</tbody>
</table>

NCP has sufficient resistance to γ-ray (>>3.3 kGy).

γ-ray radiation order in NCP precipitation

\(~ 3.3\) kGy (6.5 kGy/h × 30 min)
Decomposition of NCP by $\gamma$-ray radiation

Pyridone derivatives would have higher resistance to $\gamma$-ray radiation.
Conclusion

It was confirmed that NCP is applicable to our proposed reprocessing process for FBR spent fuels.

Fundamental studies → Engineering studies

The performances of alternative precipitants were examined.

Lower hydrophobic precipitants such as NProP and NBP give higher DFs.

NBPyr has higher resistance to $\gamma$-ray radiation, which could reduce the cost for reprocessing.

Our reprocessing process is flexible.
Precipitation test of Pu(IV) with U(VI) by NCP

U : 0.67 M
Pu: 0.06 M
in 2 M HNO₃

NCP
(1.4 mol/mol U)

Pu(IV) ratio (%) vs Stirred time (min)

in Liquid

in Solid

Rinsed with 2 M HNO₃ solution
Possible Mechanism of NCP Decomposition

**1H NMR spectra**
- Peaks became broadening.
- Peaks appeared in lower fields

**IR Spectra**
The peak at 1727 cm\(^{-1}\) could be assigned to carboxyl group.
Solubility of uranyl precipitant in nitric acid solution

A precipitant with higher precipitation ability (lower solubility) and higher decontamination ability would solve the problems.
Resistance of NCP to Radiation

NCP $\alpha$- and $\gamma$-rays radiation $\rightarrow$ Decompose?

Spent Nuclear Fuel of FBR
$\gamma$-ray radiation dose $\sim$ 6.5 kGy/h

Retention time for precipitation ($\sim$30 min)

$\gamma$-ray radiation order in NCP precipitation $\sim$ 3.3 kGy

Does NCP have enough Resistance under $\gamma$-ray radiation? ($>3.3$ kGy)
Precipitation Ratios of Uranyl Ion by NCP in nitric acid (3M)

<table>
<thead>
<tr>
<th>[UO$_2^{2+}$] (M)</th>
<th>$T$ (°C)</th>
<th>[NCP]/[UO$_2^{2+}$]</th>
<th>Precipitation ratios (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>25</td>
<td>2.1</td>
<td>96.0</td>
</tr>
<tr>
<td>0.3</td>
<td>25</td>
<td>3.1</td>
<td>99.3</td>
</tr>
<tr>
<td>0.3</td>
<td>25</td>
<td>4.2</td>
<td>99.8</td>
</tr>
<tr>
<td>0.3</td>
<td>50</td>
<td>2.1</td>
<td>89.9</td>
</tr>
<tr>
<td>0.3</td>
<td>50</td>
<td>3.1</td>
<td>98.6</td>
</tr>
<tr>
<td>0.3</td>
<td>50</td>
<td>4.2</td>
<td>99.5</td>
</tr>
</tbody>
</table>

U(VI) can be recovered by NCP with high yield.
<table>
<thead>
<tr>
<th>[UO$_2^{2+}$] (M)</th>
<th>[NCP]/[UO$_2^{2+}$]</th>
<th>Precipitation ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>1.5</td>
<td>66.0</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
<td>80.7</td>
</tr>
<tr>
<td></td>
<td>2.2</td>
<td>98.8</td>
</tr>
<tr>
<td></td>
<td>3.2</td>
<td>99.9</td>
</tr>
<tr>
<td>0.3</td>
<td>2.1</td>
<td>96.3</td>
</tr>
<tr>
<td></td>
<td>3.1</td>
<td>99.4</td>
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<td></td>
<td>4.2</td>
<td>99.8</td>
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<tr>
<td></td>
<td>5.2</td>
<td>99.8</td>
</tr>
<tr>
<td>0.1</td>
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<td>3.8</td>
<td>99.2</td>
</tr>
</tbody>
</table>
A Simple Reprocessing Process for Spent FBR Fuels Using NCP

Direct recovery of U and Pu mixture to satisfy a high Pu content in MOX fuel from nitric acid solution of spent nuclear fuels

Pu and U are precipitated together. → High nuclear proliferation resistance
Whole process is in HNO₃ solution. → Simple and economical
NCP consists of C, H, O, N. → Fully combustible