Study on the Feed Form Fabrication for Oxide Reduction Process

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5. Summary
Introduction (I)

- Benefits of pretreatment (fission products removal)
  - Pt anode protection in OR process
  - Extension of salt replacement cycle due to very low Cs buildup rate in OR process
  - Salt purification by layer crystallization method and salt recycling in OR process

- Removal rate of fission products
  - Increase in diffusivity of fission products in hyperstoichiometric UO$_{2+x}$

- Review on the appropriate methods to fabricate feed forms using U$_3$O$_8$ powder
  - Mixing methods of excessive binder and lubricant for forming of U$_3$O$_8$ powder were excluded due to the bad effect on off-gas treatment during pretreatment
  - Selected techniques: (1) thermal granulation, (2) cold pressing and sintering, and (3) hot pressing
Introduction (II)

[Flow sheet of feed form fabrication process]

(1) Granule Fabrication

- Disassembly/Cutting
- Oxidative decladding
- Rod-cut

\[\text{U}_3\text{O}_8\text{ powder}\]

- Thermal granulation
- Sieving
- Electrolytic reduction

Recycle: particle $\leq 1 \text{ mm}$

(2) Porous Pellet Fabrication

- Pretreatment of oxide material
- Compaction
- Sintering

\[\text{UO}_{2+x}\text{ pellet}\]

- Electrolytic reduction

(3) Porous Plate Fabrication

- High temp. voloxidation
- Hot pressing

\[\text{UO}_{2+x}\text{ plate}\]

- Electrolytic reduction
Reduction Behavior of $\text{U}_3\text{O}_8$

Reduction Behavior of $\text{U}_3\text{O}_8$ into $\text{UO}_{2+x}$ during Pretreatment

- Analysis using TGA
- Flowing gas
  - Ar : 99.999% (0.001% $\text{H}_2\text{O}$)
  - Ar flow rate : 0.1 L/min
- Reduction behavior (TG analysis)
  - Initiation of thermal decomposition : 600°C
  - Rapid decomposition : 1250°C
  - $\text{U}_3\text{O}_8$ phase converted into $\text{UO}_{2+x}$ phase : after 5 h above 1300°C
Design of Granule Fabrication

- $\text{UO}_{2+x}$ granule fabrication from $\text{U}_3\text{O}_8$ powder by thermal granulation in Ar using rotary voloxidizer (cylindrical chamber without baffles)
- Particle $\leq 1$ mm is recycled for thermal granulation
Granule Fabrication (II)

- Granule (Particle Size > 1mm) Fabrication Using SIMFUEL (No rotation)
  - Agglomeration of U₃O₈ powder by sintering during pretreatment at high temperature
  - Weak bonding of agglomerate finement fine powder production during sieving: affected by sieving condition rather than pretreatment time
  - Granule fabrication in Rotating mode was carried out

<table>
<thead>
<tr>
<th>SIMFUEL</th>
<th>Sintering conditions</th>
<th>Sieving</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO₂</td>
<td>1200 °C. 10 hrs,</td>
<td>15 min</td>
</tr>
<tr>
<td></td>
<td>(Ar)</td>
<td>(Retsch AS200)</td>
</tr>
<tr>
<td>30,000 MWd/tU</td>
<td>1200 °C. 3 hrs,</td>
<td>5 min</td>
</tr>
<tr>
<td></td>
<td>(Ar)</td>
<td></td>
</tr>
<tr>
<td>60,000 MWd/tU</td>
<td>1200 °C. 3 hrs,</td>
<td>5 min</td>
</tr>
<tr>
<td></td>
<td>(Ar)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Particle size</th>
<th>Cumulative Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO₂ 30,000 MWd/tU</td>
<td>30,000 60,000</td>
</tr>
<tr>
<td>&gt; 4 mm</td>
<td>18 0 0</td>
</tr>
<tr>
<td>&gt; 2 mm</td>
<td>20 26 24</td>
</tr>
<tr>
<td>&gt; 1 mm</td>
<td>21 35 27</td>
</tr>
<tr>
<td>&gt; 75 μm</td>
<td>27 50 43</td>
</tr>
<tr>
<td>&gt; 45 μm</td>
<td>39 66 56</td>
</tr>
<tr>
<td>&lt; 45 μm</td>
<td>61 34 44</td>
</tr>
</tbody>
</table>
Granule Fabrication (III)

- Fabrication parameters
  - Initial particle bed motion of U₃O₈: slumping, rolling
  - Pretreatment temperature: 1150-1200°C, Time: 5-15 h
  - Rotation speed: slumping, 1-3 rpm

- Fabrication conditions considering properties and recovery rate of granule
  - 1200°C/10 h, 2 rpm (slumping)

<table>
<thead>
<tr>
<th>Density (g/cm³)</th>
<th>Porosity (%)</th>
<th>Recovery rate of granule (%)</th>
<th>Crushed strength(N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.38</td>
<td>55.3</td>
<td>~ 85 %</td>
<td>17</td>
</tr>
</tbody>
</table>

<Particle Bed Motion>

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Granule Fabrication

- Strong and weak point of granule
  • Process simplicity, highly porous
  • Weak mechanical stability ➔ fine powder production during handling
- Granule properties were significantly effected by temperature ➔ related to rotary cylinder chamber material
- Requirement of chamber material(alloy) with resistance to high temperature corrosion for density enhancement

<table>
<thead>
<tr>
<th>Temp.(°C)/10 hrs</th>
<th>Density (g/cm³)</th>
<th>Crushed strength (N)</th>
<th>Recovery rate of granule (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1150</td>
<td>3.16</td>
<td>5</td>
<td>78</td>
</tr>
<tr>
<td>1200</td>
<td>4.38</td>
<td>17</td>
<td>85</td>
</tr>
<tr>
<td>Increasing rate</td>
<td>39%</td>
<td>340%</td>
<td>9%</td>
</tr>
</tbody>
</table>
Granulation Fabrication (V)

UO₂ Granule Fabrication

- Fabrication conditions
  - (200g U₃O₈ powder) Thermal granulation(1200 °C/10 hrs/2 rpm in Ar) Sieving (Granule) Reduction treatment of UO₂₄.₉₉ granule(1000 °C/5 h in 4%H₂-Ar) (UO₂ Granule )

- Porosity and grain size by reduction treatment of UO₂₄.₉₉ into UO₂ : hardly effected
- Mechanical stability by reduction treatment : hardly increased

< UO₂ Granule >

<table>
<thead>
<tr>
<th>Granule size (mm)</th>
<th>Density [% TD]</th>
<th>Crushed strength (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1~5</td>
<td>40</td>
<td>17</td>
</tr>
</tbody>
</table>

<GS of UO₂₄.₉₉ : 2~10 μm>  <GS of UO₂ : 2~10 μm>
Porous Pellet Fabrication (I)

- Design of Porous Pellet Fabrication
  - To enhance mechanical stability of feed form
  - Porous $\text{UO}_{2+x}$ pellet fabrication from $\text{U}_3\text{O}_8$ powder by compaction and sintering in $\text{Ar}$ and 4% $\text{H}_2$-$\text{Ar}$ using ceramic chamber furnace and TMA
  - Compaction without milling and lubricant mixing step

[U$_3$O$_8$ powder]  [Properties of U$_3$O$_8$ powder]

<table>
<thead>
<tr>
<th>Powder</th>
<th>Average Particle Size(μm)</th>
<th>Specific surface area(m$^2$/g)</th>
<th>Bulk density (g/cm$^3$)</th>
<th>Tap density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U$_3$O$_8$</td>
<td>10</td>
<td>0.65</td>
<td>1.80</td>
<td>2.99</td>
</tr>
</tbody>
</table>
Porous Pellet Fabrication

- Density control parameters
  - Compaction pressure of U₃O₈ powder: 100-300 MPa,
  - Pretreatment temp. of U₃O₈ green pellets: 1200-1500°C
- Time and atmospheric gas for pretreatment (sintering):
  - 10 h/Ar
  * Longer pretreatment time: Cs removal
- Conditions for reduction treatment of UO₂⁺ₓ to UO₂:
  - 1200-1500°C, 2 h, 4%H₂-Ar
- Porous pellets were obtained

Compaction Pressure Effect

- Pretreatment temperature: 1400 & 1500°C
- Green densities of U₃O₈ pellets: 57.8 – 65.4 % TD (U₃O₈)
- Sintered densities of UO₂ pellets: 61.3 – 67.5 % TD (UO₂)
Porous Pellet Fabrication (III)

- Pretreatment Temperature Effect
  - Sintered densities: 65.7-67.5 % TD(UO₂)
  - SEM microstructure:
    - Grain growth: from 7.5 to 12.5 μm
    - Pore: growth and round shape

![SEM microstructure](image-url)

![Sintered density with temperature](image-url)
Porous Pellet Fabrication (IV)

- **Densification Behavior of U₃O₈ Green Pellet**
  - Analysis using TMA (Thermo Mechanical analyzer)
  - Length change at isothermal condition:
    - Low temperature: continuously increase with time
    - High temperature: very slightly increase with time
  - Reduction treatment: no effect of densification

- **Pretreatment Conditions for Porous Pellet Fabrication**
  - Sintered densities of porous pellets: very small difference with temperature
  - Removal conditions of fission products: determine the pretreatment conditions
  - Reduction treatment temperature: drop
Porous Plate Fabrication (I)

- Design of Porous Plate Fabrication
  - To enhance the compactibility and sinterability of the thermally aggregated UO$_{2+x}$ particles produced by high temperature voloxidation (pretreatment)
  - Green pellet from the thermally aggregated UO$_{2+x}$ particles could not be obtained by cold pressing without a mixing of lubricant or binder
  - Low specific surface area : 0.13 m$^2$/g
  - Hot pressing method : introduction to improve the compactibility and sinterability

[Particles produced by pretreatment :
1200°C for 10 h in Ar]
Porous Plate Fabrication

- Weight of UO$_{2.49}$ loaded in a graphite mold of 50-mm diameter : 50 g
- Density control
  - Hot pressing pressure : 20 MPa,
  - Hot pressing temp. & time : 1200°C/2h
- Atmospheric gas for sintering : Ar
- Porous plate was obtained

Porous Plate

- Sintered density : 69% TD

Requirements for Porous Plate Fabrication

- Sieving and grinding process with an increase in pretreatment temperature
- Special mold and punch for remote operation
- Press of high throughput due to batch-wise operation
Feed Form Characteristics

<table>
<thead>
<tr>
<th>Feed form</th>
<th>Density control</th>
<th>Size control</th>
<th>Packing density</th>
<th>Feed handling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granule</td>
<td>limited</td>
<td>limited</td>
<td>Poor</td>
<td>- Fine particle production</td>
</tr>
<tr>
<td>Pellet</td>
<td>easy</td>
<td>easy</td>
<td>Medium</td>
<td>- Preservation of form</td>
</tr>
<tr>
<td>Plate</td>
<td>easy</td>
<td>easy</td>
<td>1)</td>
<td>- Preservation of form</td>
</tr>
</tbody>
</table>

Oxide Reduction Characteristics (Test Results of OR Team)

<table>
<thead>
<tr>
<th>Feed form</th>
<th>Feed form</th>
<th>Oxide reduction rate</th>
<th>Processing capacity</th>
<th>Salt carryover</th>
<th>Form stability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Density (%TD)</td>
<td>Size (mm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Granule</td>
<td>40</td>
<td>1-5</td>
<td>Fast</td>
<td>Poor</td>
<td>High</td>
</tr>
<tr>
<td>Pellet</td>
<td>55-80</td>
<td>φ8x7H-φ9x8H</td>
<td>Medium</td>
<td>Excellent</td>
<td>Low</td>
</tr>
<tr>
<td>Plate</td>
<td>69</td>
<td>crushed</td>
<td>Medium</td>
<td>1)</td>
<td>NA</td>
</tr>
</tbody>
</table>

1) The processing capacity of the plate can be affected by its configuration in the basket and the shape of its pieces because the plate is horizontally large, flat and thin.
Thank you for your attention

Clean Energy! Clean Korea!