Processing of Spent TRISO-Coated GEN IV Reactor Fuels

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Eighth Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation
November 9—11, 2004
Las Vegas, Nevada

Session II. Partitioning Technology
Tuesday November 9, 2004

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Configuration of HTGR/AHTR Fuels
—General Description—

- Fuel begins with small kernels
- Coatings applied for fission product containment
- Coated particles are mixed with a carbon-based mastic
  - Formed as "rods" (compacts) or "pebbles"
- Compacts are loaded into machined graphite, prismatic fuel elements
- Large amount of carbon associated with a small amount of fuel
  - Unique challenges to processing
## HTGR/AHTR Fuels

### Composition and Material Balances

<table>
<thead>
<tr>
<th>Component</th>
<th>Complete Element</th>
<th>Compacts†</th>
<th>Particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>90.00</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Filler C</td>
<td>12.14</td>
<td>12.14</td>
<td>0</td>
</tr>
<tr>
<td>Pyro C</td>
<td>6.89</td>
<td>6.89</td>
<td>6.89</td>
</tr>
<tr>
<td>Porous C</td>
<td>1.72</td>
<td>1.72</td>
<td>1.72</td>
</tr>
<tr>
<td>SiC</td>
<td>4.63</td>
<td>4.63</td>
<td>4.63</td>
</tr>
<tr>
<td>Fuel + FPs</td>
<td>5.68+1.25</td>
<td>5.68+1.25</td>
<td>5.68+1.25</td>
</tr>
<tr>
<td>TOTAL</td>
<td>122.31†</td>
<td>32.31</td>
<td>20.17</td>
</tr>
</tbody>
</table>

*Assume: 20% initial enrichment; after burn ~18% fission product by weight and 2.5% enriched in $^{235}\text{U}$.  

†Mass of C in the compacts alone is 20.75 kg.
Summary of Recent Evaluations of Processing GENIV Fuels

- Methods developed in the 1960s and 1970s
  - Generally the entire fuel element was processed
  - Crush-Burn-(Crush-Burn)-Leach
    - Seemed to have the fewest processing problems
    - Large quantities of CO₂ (atmospheric disposal now questionable)
    - Large off-gas processing equipment needed
    - Capture greatly increases mass and volume (e.g. CaCO₃) compared to the elemental C
  - Grind-Leach
    - Grinding to sufficiently small particle size was problematic
    - Thorough wetting and solid-liquid separations difficult
    - Troublesome soluble organic species produced in leaching step

- Fuel and process changes alleviates several difficulties
  - Fuel is UCO (UO₂—UC₂ mix) instead of all UC₂
    - Organics arise from metal carbide—nitric acid reactions
  - Mechanical head-end may be used to remove the compacts from the prismatic block
    - Graphite—nitric acid reactions also responsible for soluble organics
    - Decreased volume and mass of carbon per unit of fuel

- Two promising alternatives to crush-burn-leach identified
  - Grind-leach (modified/improved)
  - Carbochlorination
  - Both methods minimize combining C with other elements
  - Both support a robust carbon-based waste form

- Aqueous grind-leach selected for further study
Aqueous Treatment Process—Concept Selected for Further Study—

- Harvest fuel compacts
- Process to recover fuel
  - Crushing and grinding
  - Optional solid-solid separation
  - Leaching with nitric acid
    - Adaptation of commercial graphite purification process
    - May require steps to destroy carboxylic acids
    - Solution routed to standard aqueous process
    - Residual C processed into waste form
- Methods result in smallest volume of carbon waste
Focus of Initial Research —UCO Fuel Processing—

- Dissolution of UCO fuel
  - Some organic acids may form
    - Occurs with mono- or di-carbide fuels
    - Buffer C may contribute less
  - Evaluate extent of problem
- Evaluate separation of carbon
- Address soluble organics problems
  - Interference with solvent extraction
    - Foaming w/solution cross-contamination
    - Emulsions
    - Reduced distribution ratios
  - An ozonation, or similar, step could destroy the mellitic acid
Summary of Experiments

• Crushed TRISO fuel surrogates were primarily used due to unavailability of actual materials
  – Substitutes were made as follows

<table>
<thead>
<tr>
<th>Substitute</th>
<th>For:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon black</td>
<td>Buffer C</td>
</tr>
<tr>
<td>Activated Carbon</td>
<td>Pyrolytic C</td>
</tr>
<tr>
<td>Carbon black</td>
<td>Filler carbon</td>
</tr>
</tbody>
</table>

  – Substitutes not needed for UO$_2$/UC$_2$ or SiC

• A small quantity of TRISO-coated zirconia was available
  – Provided prototypical carbon layers for testing
  – UO$_2$ powder added to make system more realistic
Summary of Experiments —continued—

- Test ID and Materials tested
  - A: UO$_2$ (as a standard)
  - B: UO$_2$ (as a standard)
  - C: UO$_2$ with stand-in carbon components
  - D: UO$_2$ with stand-in carbon components
  - E: UO$_2$-15%UC$_2$ (e.g. UCO)
  - F: UO$_2$-15%UC$_2$ with stand-in carbon components
  - G: Stand-in carbon components alone
  - H: Graphite
  - I: Crushed TRISO-coated ZrO$_2$ with UO$_2$ powder
  - J: Crushed BISO-coated$^a$ ZrO$_2$ with UO$_2$ powder
  - K: UO$_2$-30%UC$_2$
  - L: UO$_2$-30%UC$_2$ with stand-in carbon components

$^a$ Same as the TRISO but without the SiC layer
Crushed TRISO-Coated Zirconia

- Initial particle size
  - Total: 850 µm dia
  - Kernel: 500 µm dia
  - Buffer C: 100 µm thickness
  - IPyC: 40 µm thickness
  - SiC: 35 µm thickness

- For scale, yellow wire is 1448 µm dia

- Crushing method—pounding with steel bar
  - No unbroken shells
  - Note many kernels not broken
Qualitative Results

- Filtration was difficult with the very finely divided carbon black used for surrogates
  - Industry has solved the problem
  - For the experiments, separated via centrifugation and decantation
    - carry-over is thus atypical of a filtration process

- Color of leachate
  - Generally the yellow of uranyl nitrate solution
  - With TRISO-coated zirconia, solution was greenish
    - Y is used to stabilize Zr, and could have altered the color (it is usually red-brown alone)

- The leachate did not foam upon shaking
  - Indicates low amounts of organic acids
Analysis for Mellitic Acid

- Fourier Transform Infra-Red (FTIR) analysis was tested with standards
  - Carboxylic acid O-H stretch appeared to work
    - Sensitivity was too low
  - Mellitic acid was added to NaNO₃ solutions in varying concentrations
    - Similar to solution from which U is quantitatively precipitated
    - Uncorrelated interferences appeared to exist

- Actual results with leachate solutions were inconclusive
  - Even at pH around 7.5, some U remains in solution
  - Higher pH values can precipitate the mellitic acid
  - Possibly other species are keeping some U in solution
Solvent Extraction Tests

- Inferred from the literature that organic acids, mellitic acid in particular, would affect distribution ratios.

- Leachate was equilibrated with UREX solvent in a 1:1 aq:org ratio:
  - No foaming noted during mixing
  - Phases readily separated upon standing
  - No emulsions were observed

- Distribution ratios were calculated from analysis of the aqueous phase before and after contact with the UREX solvent.
## Solvent Extraction Tests—continued—

<table>
<thead>
<tr>
<th>Test</th>
<th>Experimental D</th>
<th>Calculated D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>low</td>
<td>high</td>
</tr>
<tr>
<td>A</td>
<td>5.30</td>
<td>8.42</td>
</tr>
<tr>
<td>B</td>
<td>6.10</td>
<td>9.61</td>
</tr>
<tr>
<td>C</td>
<td>28.95</td>
<td>43.74</td>
</tr>
<tr>
<td>D</td>
<td>16.82</td>
<td>25.62</td>
</tr>
<tr>
<td>E</td>
<td>10.89</td>
<td>16.75</td>
</tr>
<tr>
<td>F</td>
<td>8.50</td>
<td>13.19</td>
</tr>
<tr>
<td>G</td>
<td>33.07</td>
<td>49.89</td>
</tr>
</tbody>
</table>

Blanks indicate no uranium in test material or D not measured
Solvent Extraction Tests —continued—

• The measured distribution ratios are slightly larger than predicted by either SEPHIS or AMUSE codes.

• Experimental data on U concentration were estimated to be in error by as much as 10%:
  – High and low distribution ratios were calculated based on this band.
  – The lower experimental values are barely above predictions.

• Systematically high measured values can indicate:
  – Systematic error in methodology.
  – Problems with models at high nitric acidity (> 7 M).
  – Organic acids in the organic phase enhanced U extraction.

• But the control sample with only UO₂ also had high D.
Summary

- Traditional processing of HTGR fuel reviewed
- Waste reduction goals favor retaining elemental carbon
- Two flow sheets were identified for further development
  - Carbochlorination as a precursor to pyro-processing
  - Modernized crush-leach for aqueous based processing
    - Relies on industrial carbon-processing technology
    - Was selected for evaluation
- No problems with solution foaming was observed
- Ultra-milling is problematic in conventional filtering
  - Adaptation of filtering methods from the graphite & carbon black production industries is potential solution
  - Careful control of particle size provides more options
Summary —continued—

- **Solvent extraction**
  - No mechanical problems (e.g. foaming, emulsion or phase separation problems not observed)
  - Distribution ratios slightly larger than predicted by accepted models (e.g. AMUSE and SEPHIS)
  - Large Ds possibly (but not likely) due to an organic acid

- **Potential organic acid problem**
  - Needs to be further investigated (real or not)
  - Need to know if it accumulates in the organic phase and interferes with stripping of product
  - Could be addressed with an organic destruction step between leaching and solvent extraction (e.g. ozonation)