

# Scoping Experiments on Processing of Spent TRISO- Coated GEN IV Reactor Fuels

Barry B. Spencer, Catherine H. Mattus, Guillermo D. Del Cul,  
Rodney D. Hunt, and Emory D. Collins

Oak Ridge National Laboratory

P.O. Box 2008; Oak Ridge, TN 37831-6223

Tel: (865) 574-7143; E-mail: [spencerbb@ornl.gov](mailto:spencerbb@ornl.gov)

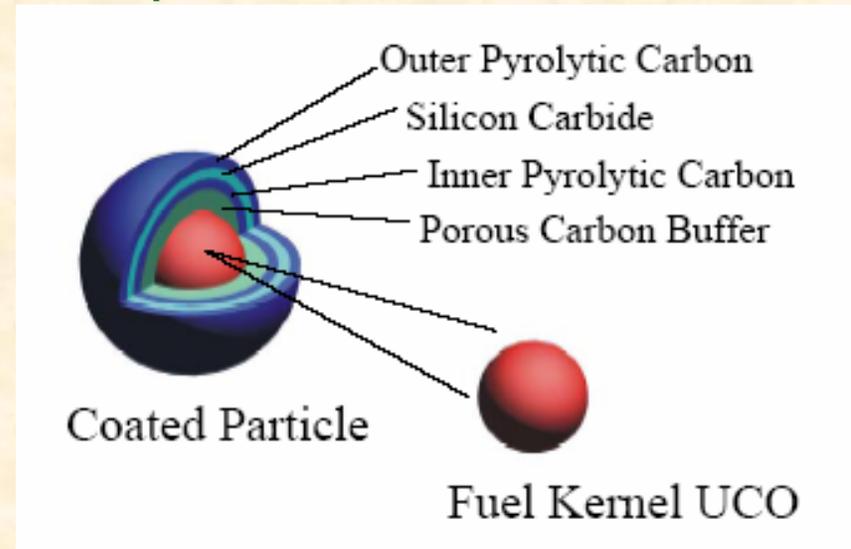
2004 ANS Winter Meeting  
November 14—18, 2004  
Washington, DC

Session: Spent-Fuel Disassembly and Head-End Treatment Developments II  
Tuesday November 16, 2004

The submitted manuscript has been authored by a contractor of the U.S. Government under contract DE-AC05-00OR22725. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes. File name: TRISO\_Fuel\_Processing\_ANS\_Winter\_Nov2004.ppt

# 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



Particles



Compacts



Fuel Elements

# HTGR/AHTR Fuels

## —Composition and Material Balances—

Component	Mass in one fuel element (kg)*		
	Complete Element	Compacts <sup>†</sup>	Particles
Graphite	90.00	0	0
Filler C	12.14	12.14	0
Pyro C	6.89	6.89	6.89
Porous C	1.72	1.72	1.72
SiC	4.63	4.63	4.63
Fuel + FPs	5.68+1.25	5.68+1.25	5.68+1.25
<b>TOTAL</b>	<b>122.31<sup>†</sup></b>	<b>32.31</b>	<b>20.17</b>

\*Assume: 20% initial enrichment; after burn ~18% fission product by weight and 2.5% enriched in <sup>235</sup>U.



<sup>†</sup>Mass of C in the compacts alone is 20.75 kg.

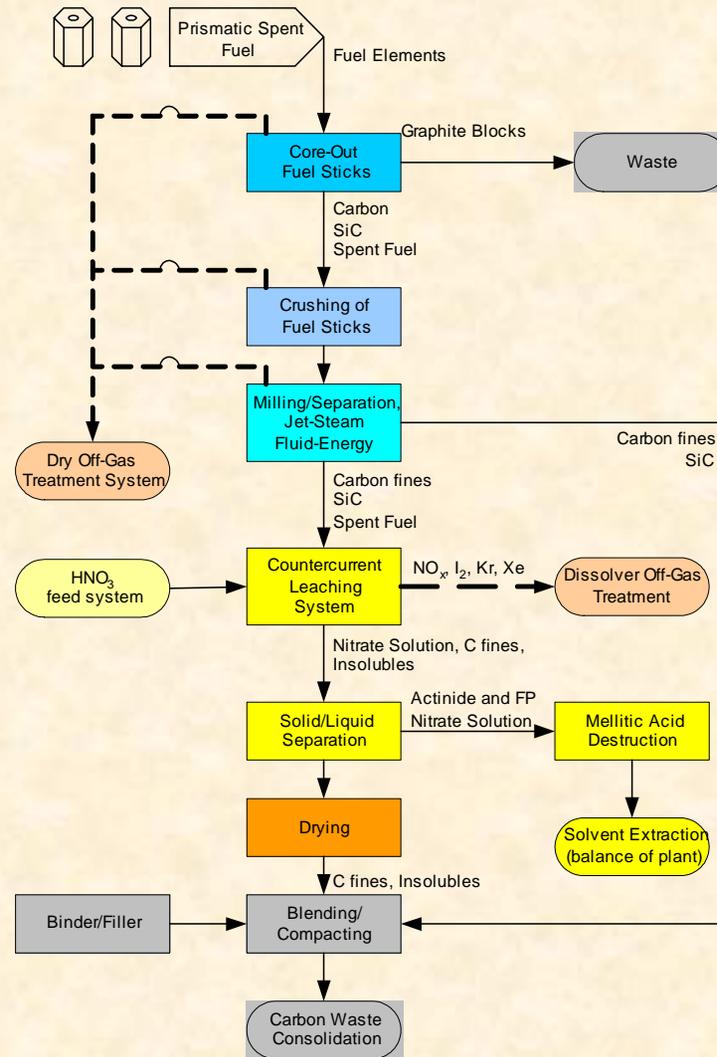
# Summary of Recent Evaluations of Processing GENIV Fuels

- **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 CO<sub>2</sub> (atmospheric disposal now questionable)
    - Large off-gas processing equipment needed
    - Capture greatly increases mass and volume (e.g. CaCO<sub>3</sub>) 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 (UO<sub>2</sub>—UC<sub>2</sub> mix) instead of all UC<sub>2</sub>
    - 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**

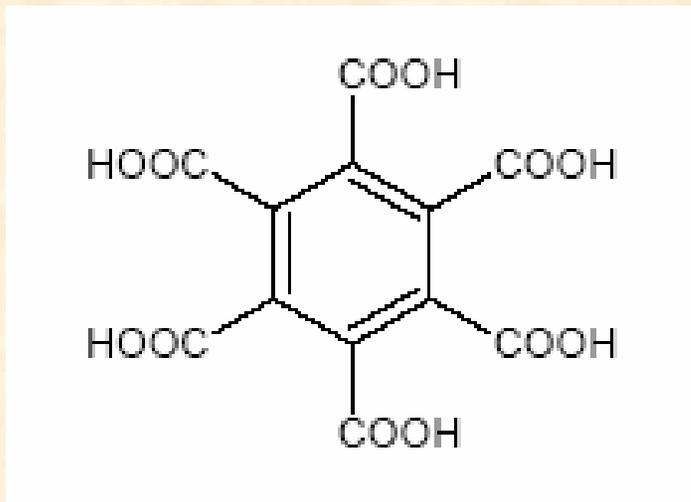
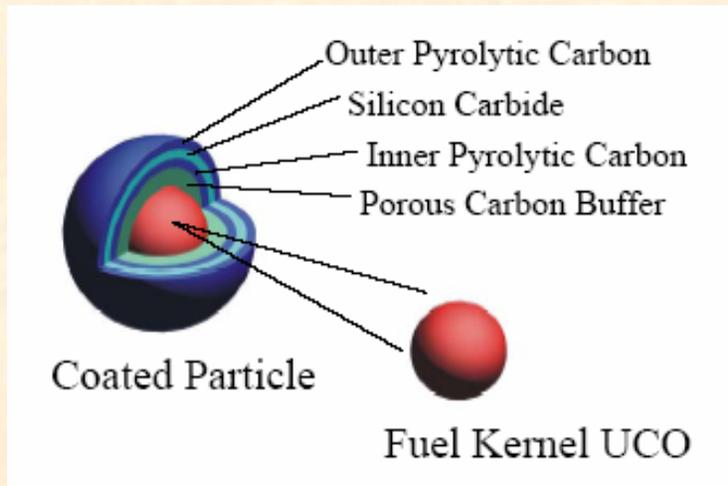
# Aqueous Treatment Process

## —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**

<b>Substitute:</b>	<b>For:</b>
<b>Carbon black</b>	<b>Buffer C</b>
<b>Activated Carbon</b>	<b>Pyrolytic C</b>
<b>Carbon black</b>	<b>Filler carbon</b>

- **Substitutes not needed for  $\text{UO}_2/\text{UC}_2$  or SiC**
- **A small quantity of TRISO-coated zirconia was available**
  - **Provided prototypical carbon layers for testing**
  - **$\text{UO}_2$  powder added to make system more realistic**

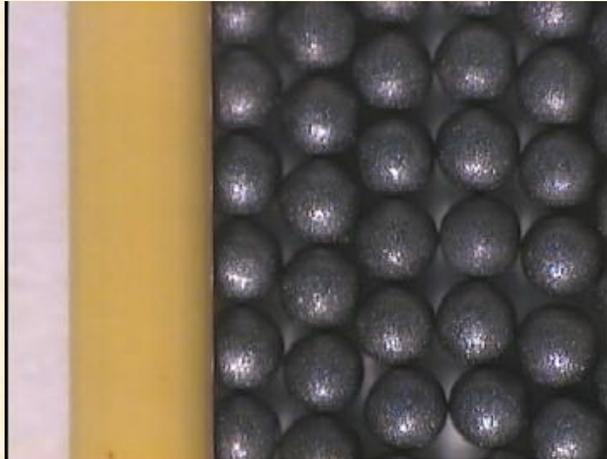
# Summary of Experiments —continued—

- **Test ID and Materials tested**

- **A:  $\text{UO}_2$  (as a standard)**
- **B:  $\text{UO}_2$  (as a standard)**
- **C:  $\text{UO}_2$  with stand-in carbon components**
- **D:  $\text{UO}_2$  with stand-in carbon components**
- **E:  $\text{UO}_2$ -15% $\text{UC}_2$  (e.g. UCO)**
- **F:  $\text{UO}_2$ -15% $\text{UC}_2$  with stand-in carbon components**
- **G: Stand-in carbon components alone**
- **H: Graphite**
- **I: Crushed TRISO-coated  $\text{ZrO}_2$  with  $\text{UO}_2$  powder**
- **J: Crushed BISO-coated<sup>a</sup>  $\text{ZrO}_2$  with  $\text{UO}_2$  powder**
- **K:  $\text{UO}_2$ -30% $\text{UC}_2$**
- **L:  $\text{UO}_2$ -30% $\text{UC}_2$  with stand-in carbon components**

<sup>a</sup> Same as the TRISO but without the SiC layer

# Crushed TRISO-Coated Zirconia



- **Initial particle size**
  - Total: 850  $\mu\text{m}$  dia
  - Kernel: 500  $\mu\text{m}$  dia
  - Buffer C: 100  $\mu\text{m}$  thickness
  - IPyC: 40  $\mu\text{m}$  thickness
  - SiC: 35  $\mu\text{m}$  thickness
- **For scale, yellow wire is 1448  $\mu\text{m}$  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  $\text{NaNO}_3$  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—

Test	Experimental D			Calculated D	
	low	high	nominal	AMUSE 3.02e	SEPHIS Mod 4
A					
B	5.30	8.42	6.70	5.69	5.38
C					
D	27.97	42.28	34.41	26.9	27.35
E	6.10	9.61	7.68	5.45	4.93
F	28.95	43.74	35.60	26.3	25.38
G					
H					
I	16.82	25.62	20.78	12.1	11.31
J	10.89	16.75	13.53	10.0	9.55
K	8.50	13.19	10.61	6.23	5.94
L	33.07	49.89	40.64	27.9	29.69

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  $UO_2$  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  $D_s$  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)