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

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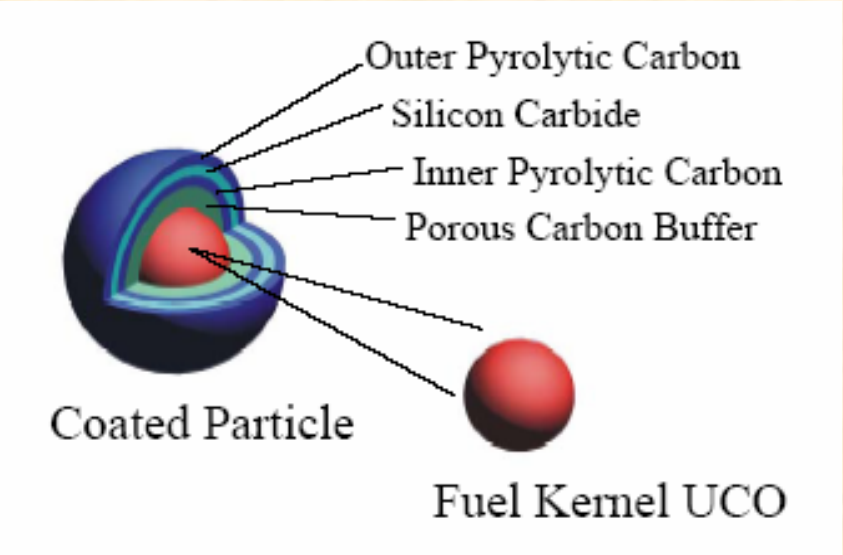
Configuration of HTGR/AHTR Fuels
—General Description—

- 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



Particles

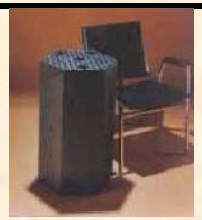
Compacts

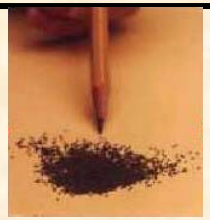
Fuel Elements

HTGR/AHTR Fuels
—Composition and Material Balances—

	Mass in one fuel element (kg)*		
Component	Complete Element	Compacts†	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
TOTAL	122.31†	32.31	20.17

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





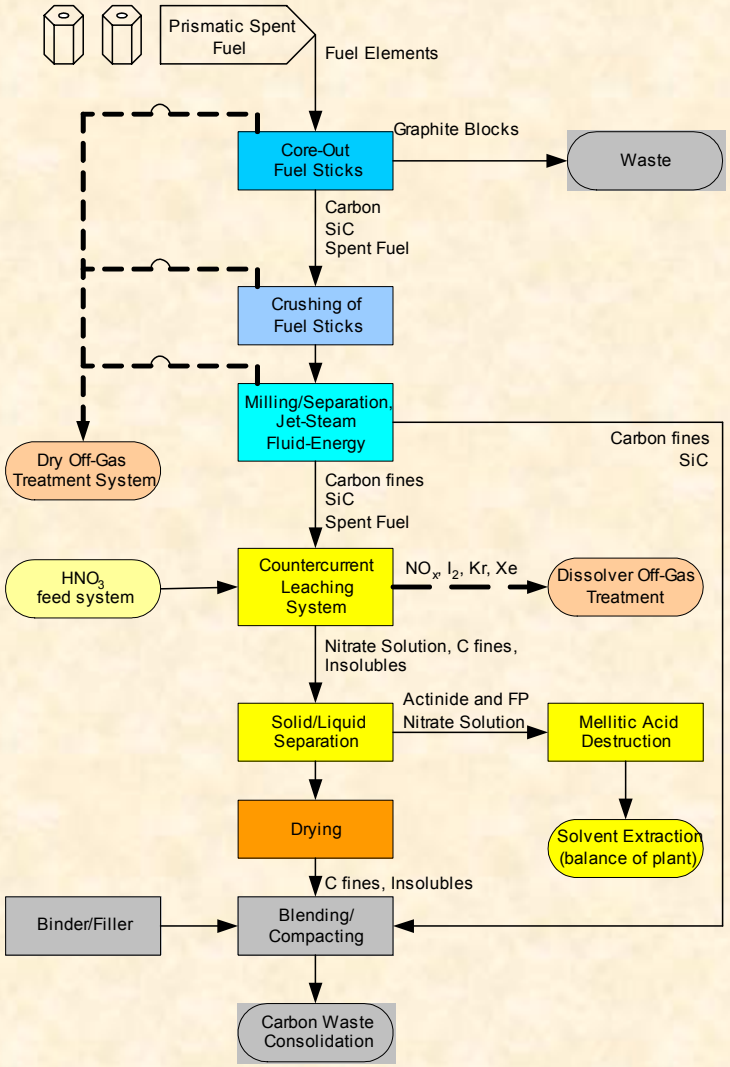
†Mass of C in the compacts alone is 20.75 kg.

Summary of Recent Evaluations of Processing GENIV Fuels

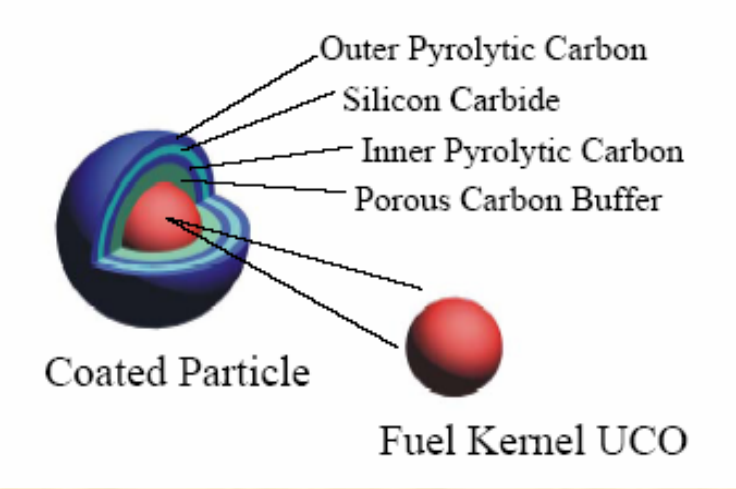
- Methods developed in the 1960s and 1970s
  - Generally the entire fuel element was processed
  - Crush-Burn-(Crush-Burn)-Leach
    - Seemed to have the fewest processing problems
    - Large quantities of CO_2 (atmospheric disposal now questionable)
    - Large off-gas processing equipment needed
    - Capture greatly increases mass and volume (e.g. $CaCO_3$) 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_2—UC_2 mix) instead of all UC_2
    - 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

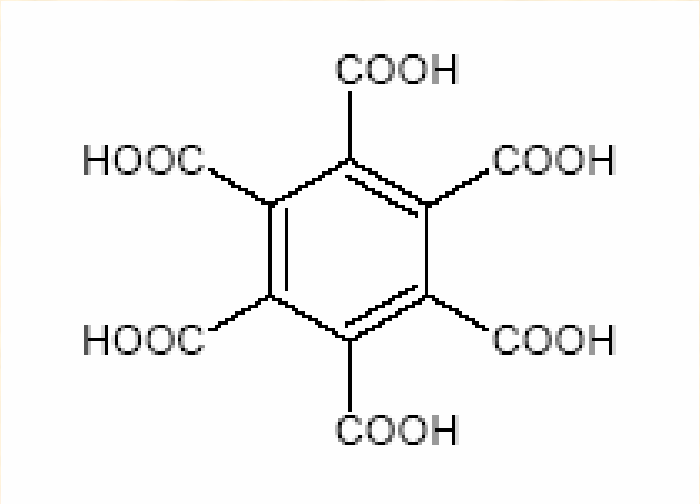
Aqueous Treatment Process
—Concept Selected for Further Study—

- 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

Substitute:	For:
Carbon black	Buffer C
Activated Carbon	Pyrolytic C
Carbon black	Filler carbon

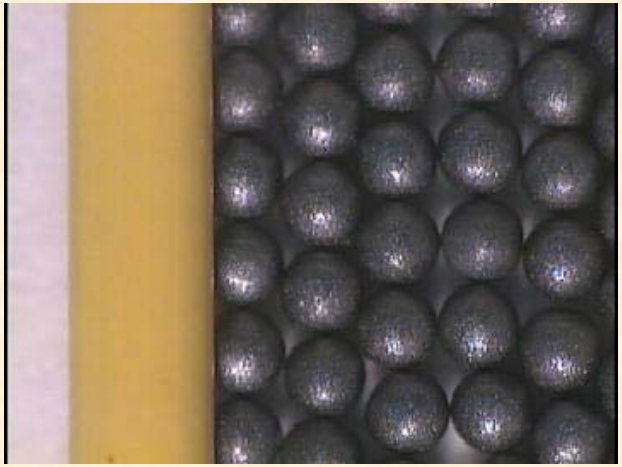
  - Substitutes not needed for UO_2/UC_2 or SiC
- A small quantity of TRISO-coated zirconia was available
  - Provided prototypical carbon layers for testing
  - UO_2 powder added to make system more realistic

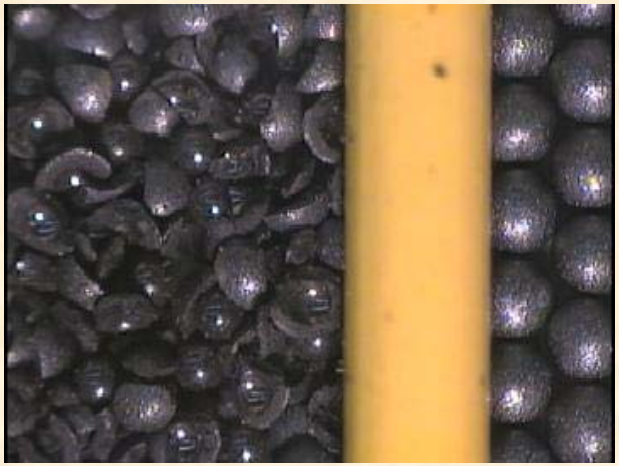
Summary of Experiments —continued—

- 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 $NaNO_3$ 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—

	Experimental D			Calculated D	
Test	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 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)