

PROCESSING OF SPENT TRISO-COATED GEN IV REACTOR FUELS

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Abstract

The crush-leach process was investigated as a method to treat GEN IV TRISO-coated reactor fuels. The method retains the bulk of the carbon components in elemental form, which is favorable for achieving waste reduction goals. A literature review identified the potential problems with this technique. Leaching of simulated crushed TRISO-coated fuel and extraction behavior of the separated leaching solution were tested at the laboratory scale. Very finely divided carbon used in the preparation of simulants was difficult to separate by filtering, indicating the need to carefully control particle size and/or use alternative solid-liquid separation methods. In the solvent extraction tests, the production of foams or emulsions was not observed. Measured distribution ratios for uranium were slightly larger than predicted by accepted models. This increase may be due to small concentrations of organics, but the experimental results are not conclusive. Although the data do not strongly indicate effects by a contaminating organic agent, the organic species may exist in small concentrations.

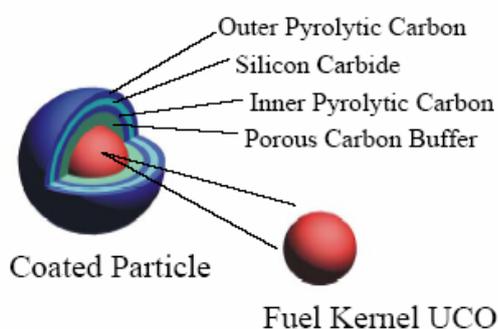
Introduction

There has been renewed interest in coated-particle nuclear fuels for high-burnup and high-temperature applications. New versions of tristructural-isotropic (TRISO)-coated fuels are comprised of an oxide or oxycarbide fuel kernel coated with a porous carbon layer, a strong pyrolytic carbon layer, and a very tough silicon carbon (SiC) layer. The SiC layer is usually coated with another pyrolytic carbon layer to provide a bonding surface with the carbon matrix used to fabricate fuel compacts. Additional layers of one of these three types may be used to improve certain performance objectives. The fuel compacts are loaded into a machined graphite fuel element. The construction of high-temperature gas-cooled reactor (HTGR) fuel is illustrated in Figure 1. Because only a relatively small amount of fuel in a “sea” of carbon will contain ^{14}C after burnup, processing these fuels to recover the fissile materials presents special problems.

Background

Historical approaches to processing TRISO-coated fuel involved crushing and burning operations, which would size reduce the fuel elements (thereby increasing the surface area), breach the SiC layer, oxidize the metal carbide, and remove the carbon components from the fuel as gaseous carbon dioxide. The fuel was then easily separated from the remaining SiC fragments by dissolution in nitric acid.¹ The primary disadvantage of this method is the need to capture and sequester the ¹⁴C-containing CO₂. Sequestration using calcium hydroxide results in a large increase in the mass and volume of waste compared with that of the original carbon. An alternative crush-leach process was also developed. Disadvantages were reported to be production of soluble organic acids, which interfered with the solvent extraction process, and large quantities of dissolver solution with low uranium concentrations, which were not optimal for the solvent extraction step.²

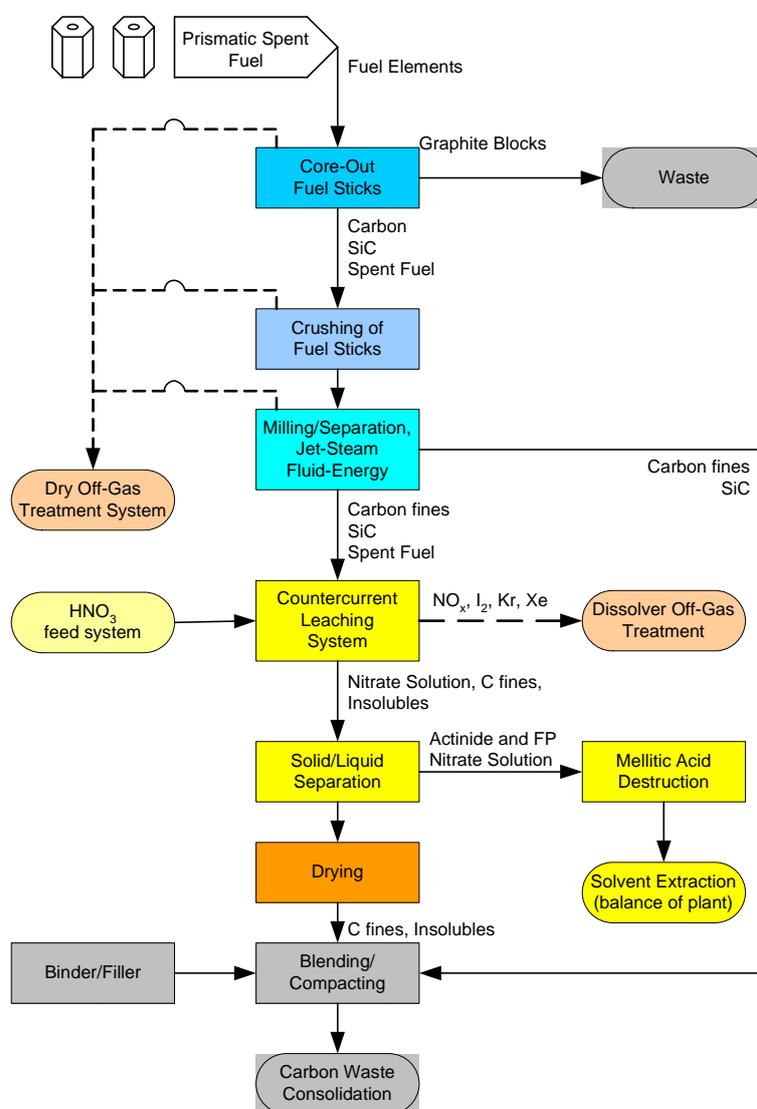
Figure 1. **Configuration of HTGR fuels: individual particle, group of particles, compacts, and fuel element**



An updated crush-leach process has been proposed to separate the carbon from the fuel without oxidation of the carbon component.³ The process is illustrated in Figure 2. It relies on removing the fuel compacts from the graphite-block fuel element, grinding the fuel compacts to a very small particle size, and leaching the fuel components from the finely divided carbon using methods similar to those industrialized for graphite purification. The residual carbon waste and any undissolved residues can be consolidated into a compact waste form that has excellent characteristics.⁴

The present fuel form and processing concepts for a crush-leach process potentially alleviate many of the problems. Removal of the fuel compacts from the graphite block prior to grinding eliminates the graphite as a reactant in the subsequent leaching process, reducing greatly a source of the soluble organic species. Separation of the compacts from the graphite block effectively increases the heavy metal concentration in the solid. Thus, a smaller volume of leaching solution per unit mass of crushed fuel is required to recover the fuel components. The fuel form is a mixture of UO_2 and UC_2 , with the carbide being less than about 30 mol %. Compared with all-carbide fuels, there should be smaller quantities of organics produced from the metal carbide carbon. The particle coatings themselves include pyrolytic carbons deposited by the decomposition of hydrocarbons. These deposited carbons may have a graphitic ring structure and will remain as a potential precursor to the soluble organic compounds.⁵ Overall, the compounds that give rise to soluble organic species are significantly reduced by the mechanical head-end of the conceptual process.

Figure 2. **Proposed flow sheet for updated crush-leach process**



Objectives

This paper presents information on experiments for the leaching step. The most important phenomenon investigated was the production of organic acids (e.g., carboxylic acids) from the reaction of nitric acid with the metal carbide and buffer carbon components that could interfere with the solvent extraction process.

Description of Experiments

TRISO-coated fuel particles consist of a uranium dioxide or a uranium oxycarbide (UCO, a mixture of UO_2 and UC_2) coated with three different types of layers using chemical vapor deposition methods. The three types of layers are a low-density pyrolytic carbon (buffer), high-density pyrolytic carbon, and SiC. The pyrolyzed carbon mastic (filler carbon) used to make the compacts also needed to be considered. Surrogates were prepared in two different ways. The first method involved using readily available chemicals in the proper proportions. Silicon carbide fines (Carborundum Company, grit No. 120) with particle sizes of $<116 \mu\text{m}$ were used to simulate crushed SiC shells. The carbon layers were more difficult to simulate. Carbon black (high purity, Cabot Mogul[®]L) having particle sizes less than 24 nm and a bulk density of 15 lb/ft^3 was substituted for the low-density pyrolytic carbon and the pyrolyzed filler carbon. This material is finer than is necessary or likely to be made by grinding TRISO fuel. However, it would enhance the reactions with nitric acid and thus provide a conservative case with respect to formation of organic carbon by-products. Finely divided activated carbon (Mallinckrodt U.S.P., lot 439Y25611) was substituted for the high-density pyrolytic carbon. Small quantities of UO_2 and UCO were prepared and were therefore chemically identical to the actual fuel materials.

The second method involved the use of coated zirconia particles manufactured at the Oak Ridge National Laboratory. Two types of coated particles were available: a sample that included all three TRISO layers [i.e., low-density pyrolytic (buffer) carbon, high-density pyrolytic carbon, and SiC] and a sample that was similar but did not possess the SiC layer. The characteristics of the triple-coated material are given in Table 1 for reference. The carbon coatings in these particles are prototypic with respect to their chemical and physical characteristics. To perform leaching tests on material simulating ground TRISO-coated fuel, samples of these coated particles were ground to ensure that all the layers were broken. A quantity of uranium dioxide powder was added to the solids mixture equivalent to the quantity that would have been in the particles if the zirconia had been urania. Test samples were made from each of the two types of particles provided.

The leaching equipment consisted of a simple Pyrex[®] reaction vessel fitted with a spiral-wound reflux condenser. The temperature of the reaction was maintained with a water bath heated on a combination hot plate–stirrer. Temperature was monitored with a type-K thermocouple attached to an Omega digital display. The best experimental technique was found through experience. The solids were added to the reaction vessel along with a volume of deionised water. A Teflon coated stir-bar was used to slurry the solids and water. Mixing was allowed to continue for 5 min to ensure wetting of the solids. A volume of concentrated nitric acid equal in volume to the water was then slowly added to the mixture. The feed port on the vessel was closed so that off-gas was vented only through the reflux condenser. Adjustments to the hot plate were used to bring the reaction mixture to the desired temperature of around 98°C (while the water bath boiled) and to maintain this temperature. Reaction was rapid, but leaching was allowed to continue up to about 3 hours. The remaining free nitric acid was about 7 M in all tests.

Table 1. The constituents of the TRISO-coated zirconia fuel surrogate based on particle characteristics^a

Layer	Material	Dimension	Density (g/cm ³)	Volume (cm ³)	Mass (g)	wt %
Kernel	Zirconia	500 μm (diam)	5.6	6.54E-05	3.67E-04	43.6
Buffer layer	Porous carbon	100 μm (thickness)	0.95	1.14E-04	1.08E-04	12.9
I-PyC	Pyrolytic carbon	40 μm (thickness)	1.9	6.89E-05	1.31E-04	15.6
SiC	Silicon carbide	35 μm (thickness)	3.2	7.31E-05	2.34E-04	27.9
Coated particle as a whole		850 μm (total diam)	2.61	3.22E-04	8.40E-04	100.0
	Zirconia				3.67E-04	43.6
	Carbon				2.39E-04	28.5
	SiC				2.34E-04	27.9
	Total				8.40E-04	100.0

^a Density of each layer is from various references and is used together with the dimensions to calculate the volume, mass, and weight fractions of each constituent.

When the reaction was complete, the slurry was permitted to cool to ~40°C (requiring a time of ~2 h) before filtration or centrifugation. This was necessary to safely handle the solutions and equipment.

Solvent extraction shake-out tests were conducted using a 1:1 ratio of aqueous to organic phases. The tests were performed at room temperature (~23°C). Mechanical pipettes were used to measure aliquots (usually 5 mL) of each phase into a small vial. The vial was capped and shaken by hand for about 1 min to ensure good mixing of the phases. After allowing the phases to separate for about 2 min, the aqueous phase was sampled using the mechanical pipette to obtain an accurate volume of solution for measurement.

The concentration of free acid in the filtered leachate solutions was measured by titrating a sample to a pH of 3.2 with 1.0 M sodium hydroxide solution (JT Baker analyzed solution, lot A25P00, concentration accurate to 0.1%). A Thermo Orion (model 720) pH meter was used to monitor the progress of the titration. Uranium does not precipitate at this value of pH, and values of pH above about 10 are required to precipitate mellitic acid. Uranium concentrations in the filtered leachate solutions and UREX raffinate were measured with inductively coupled plasma–atomic emission spectroscopy (ICP-AES) using a Jarrell Ash (model 61 E) Trace ICP-AES. Accuracy of the measurement was estimated at ±10%.

The presence of soluble organic by-products was detected by two methods: observation of solution characteristics and uncharacteristic distribution coefficients for uranium in solvent extraction. Observation included noting the color of the filtered solution, which is normally yellow for uranyl nitrate solutions. The soluble organic species previously reported in the literature would impart an amber hue to the solution. Shaking the sample would result in formation of persistent foam if the organic compounds were present. A third method of detection, using Fourier-transform infrared (FTIR) analysis, was inconclusive.

The transmittance of various wavelengths of light through the sample was tested as a means to ascertain the presence of carboxylic acids. A sodium nitrate solution was prepared to simulate the matrix that would result after the leachate solution was neutralized with sodium hydroxide. Neutralization to a pH of around 7 converts the free nitric acid to sodium nitrate and precipitates the uranium while leaving the organic species in solution. Test solutions were prepared containing mellitic acid (TCI America, lot OGN01) in concentrations ranging from 0 to 1 wt%. The results indicated that transmittance at a wavenumber of about 2500cm^{-1} was measurable but very low (<5%). The transmittance decreased further with increasing mellitic acid concentration, but they were much too low for quantitative analysis.

A solvent extraction test was used to qualitatively assess the presence of soluble organics. The performance of simple shake-out tests was observed with respect to foaming and formation of slow-breaking emulsions. The distribution coefficients were then measured and compared with values calculated with accepted models (AMUSE and SEPHIS).

General qualitative observations

Leaching of the uranium from the surrogate samples appeared to be rapid. Samples without the carbon component could be observed clearly, with the expected brown NO_x fumes evolving from the solution. Addition of the finely divided carbon (carbon black and activated carbon) gave the slurry the color of black ink and made observation difficult. It was necessary to infer the progress of the reaction from the clarity of the NO_x fumes above the reacting mixture. Separation of the residual solids by filtration was difficult—the filter often clogged. The mixture could be separated with centrifugation. After separation of the solids from the leachate solution, the solution was generally the yellow of uranyl nitrate solution. In one case, however, dissolution of TRISO-coated zirconia yielded a greenish solution. Because the kernels were manufactured from yttria-stabilized zirconia, the yellow color could have been altered by dissolution of a small quantity of yttria. Pure yttrium nitrate solution is usually a red-brown color.

Some foaming of the solution was noted during the leaching operation. However, the foam was not stable and did not accumulate. It is anticipated that foaming will not be a problem for the leaching step. After separating the leachate from the solids, the leachate was shaken vigorously. No foaming of the solution was noted, indicating a low concentration of soluble organics.

Analysis for mellitic acid

FTIR analysis of actual leachate solutions for mellitic acid was inconclusive. Samples of leachates from tests with solids containing only carbon components and graphite exhibited transmittances between those of the control samples having mellitic acid concentrations of 0.75% and 1.0%. The overall absorbance by the water matrix was too high to permit transmittance values in a range significantly different from signal noise. Isolation and identification of the soluble organics would itself be a significant research task.

Solvent extraction behaviour

It was inferred from the literature that the by-product soluble organic species, mellitic acid in particular, would affect the distribution coefficients of uranium in the UREX process. The underlying causes would be (i) foaming, (ii) emulsion formation, or (iii) chemical interactions. Foaming would cause difficulty in phase separation, contaminating the organic phase with aqueous phase. Emulsions might be either organic-phase continuous or aqueous-phase continuous, contaminating the organic with aqueous phase or the aqueous with organic phase, respectively. Contamination of the organic phase with aqueous usually leads to lowered decontamination factors. On the other hand, contamination of the aqueous phase with organic phase usually leads to lowered heavy metal recovery and apparently-low distribution ratios. Chemical interactions would have similar effects. The organic could complex with the metal ion in the aqueous phase and lower the distribution ratio. It could also interact with the extractant, either lowering or enhancing its extracting power.

Shake-out tests were performed with filtered leachate solution and UREX solvent in a 1:1 phase ratio. No foaming was noted during the test, and the phases readily separated. Neither phase was cloudy as would be expected if an emulsion formed. The distribution ratios were calculated from measured aqueous-phase concentrations. An aqueous aliquot was analyzed for the free acid and uranium concentrations. A separate aliquot was contacted with the solvent in the stated ratio, and the separated aqueous phase was then analyzed for uranium concentration. Assuming the phases do not change volume upon extraction, the distribution ratio may be calculated from

$$D = \frac{[U]_{org}}{[U]_{aq}} = \frac{[U]_{aq,precontact}}{[U]_{aq,postcontact}} - 1. \quad (1)$$

Both the nitric acid and uranium concentrations were measured in the filtered leachate solution. Only the uranium concentration was measured in the aqueous phase after equilibration with the UREX solvent. The titration was estimated to result in little error in the measured free nitric acid concentration. Analyses of uranium concentrations with ICP-AES were estimated to be in error by up to 10%. Based on this error band, high and low values for the uranium distribution ratio were calculated and are listed in Table 2 along with the nominal value calculated directly from the data.

Equilibration of fresh UREX solvent with aqueous solutions having the measured uranium and nitric acid concentrations was modeled with both the AMUSE (ver. 3.02e) and SEPHIS (Mod 4) codes. The calculated distribution ratios are listed in Table 2 with the experimental values. As shown in the table, the nominal measured distribution ratios are similar to, but larger than, those predicted by either model. The lower experimental values are very close to the model predictions but are generally slightly higher. These data indicate that the aqueous phase is not contaminated with organic phase, due to the action of soluble organic species arising from the carbon constituents. Otherwise, the measured distribution coefficients would be lower than those predicted by the models.

Table 2. Comparison of experimental and calculated uranium distribution ratios

Test	Material Leached	Experimental D			Calculated D	
		Low	High	Nominal	AMUSE 3.02e	SEPHIS Mod 4
A	UO ₂ (pure)			Not meas.		
B	UO ₂ (pure)	5.30	8.42	6.70	5.69	5.38
C	UO ₂ + C + SiC + C _{activated}					
D	UO ₂ + C + SiC + C _{activated}	27.97	42.28	34.41	26.9	27.35
E	UCO ^a	6.10	9.61	7.68	5.45	4.93
F	UCO ^a + C + SiC + C _{activated}	28.95	43.74	35.60	26.3	25.38
G	C + SiC + C _{activated}			n/a		
H	Graphite			n/a		
I	Zr-TRISO + UO ₂	16.82	25.62	20.78	12.1	11.31
J	Zr-BISO + UO ₂	10.89	16.75	13.53	10.0	9.55
K	UCO ^b	8.50	13.19	10.61	6.23	5.94
L	UCO ^b + C + SiC + C _{activated}	33.07	49.89	40.64	27.9	29.69

^a The UO₂-UC₂ mixture was 15 mol % UC₂.

^b The UO₂-UC₂ mixture was 30 mol % UC₂.

The reason for the systematically higher measured distribution ratios needs to be understood. It could be due to one or more of the following: (1) the phases change volume appreciably upon equilibration, violating the assumptions built into Eq. 1; (2) there are systematic errors in the experimental methodology; (3) the computer models deviate from reality at the high nitric acid concentrations around 7 M, as in these leachate solutions; or (4) an organic compound is formed that alters the uranium extraction behavior. The latter could be caused by an organic compound that distributes to the organic phase and enhances the extraction of uranium by tri-*n*-butyl phosphate (TBP). However, the control sample prepared with pure UO₂ also exhibited a high distribution ratio. It is likely that either postulate 2 or 3 is the cause of the deviations from the models.

Based on the literature, an organic compound produced by reaction of the nitric acid with the carbonaceous materials would be a likely cause of the higher-than-expected distribution ratios. Long reaction times were reported in the literature. Thus, it may be that the short leaching times used in these experiments were insufficient to produce quantities that would interfere with solvent extraction. In addition, the final high nitric acid concentration in the filtered leachate could have oxidized any organic compounds during the solution cool-down period before the solvent extraction test. However, the data do not strongly indicate effects by a contaminating organic agent.

Conclusions

Very finely divided carbon was used in the preparation of simulants for crushed GEN IV fuel. Mixing the nitric acid with the fines as a slurry led to rapid and effective leaching of the heavy metal. No problems with foaming during dissolution were noted. However, the residual fines could not be easily separated from the leachate solution by filtration. This indicates the need to carefully control particle size during milling and/or carefully select solid-liquid separations equipment.

Solvent extraction shake-out tests with clarified leachate did not indicate any physical or mechanical problems. The production of foams or emulsions was not observed. Measured distribution ratios for uranium were slightly larger than predicted by accepted models such as AMUSE and SEPHIS. The most likely reasons for the deviations are systematic errors in the experimental methodology or the computer models deviate from reality at the high nitric acid concentrations around 7 M. The data do not strongly indicate effects by a contaminating organic agent, or the organic species may exist in small concentrations. Such an organic species could affect the extraction behavior of the solvent if it accumulates over time.

REFERENCES

- [1] M. Benedict, T. H. Pigford, and H. W. Levi, *Nuclear Chemical Engineering*, 2nd ed., McGraw-Hill Book Co., New York, 1981.
- [2] L. M. Ferris, *Grind-Leach Process for Graphite-Base Reactor Fuels that Contain Coated Particles: Laboratory Development*, ORNL-4110, Union Carbide Corp., Oak Ridge National Laboratory, Oak Ridge, Tennessee, June 1967.
- [3] B. B. Spencer, G. D. Del Cul, C. W. Forsberg, E. D. Collins, and W. S. Rickman, "Processing of TRISO-Coated Fuel in Support of High-Temperature Gas-Cooled Reactors," *Transactions of the American Nuclear Society and Embedded Topical Meeting: Decommissioning and Spent-Fuel Management* (San Diego, California), Vol. 88, pp. 376–377, June 1–5, 2003, presented June 3, 2003.
- [4] C. W. Forsberg, G. D. Del Cul, B. B. Spencer, and E. D. Collins, "A New Repository Waste Form: Graphite-Carbon High-Level Waste," *Proc. of the 2003 International High-Level Radioactive Waste Management Conference*, Las Vegas, Nevada, March 30–April 2, 2003.
- [5] K. Kamegawa, K. Nishikubo, M. Kodama, Y. Adachi, and H. Yoshida, "Oxidative Degradation of Carbon Blacks with Nitric Acid II. Formation of Water-Soluble Polynuclear Aromatic Compounds," *Carbon*, 40, 1447–1455, 2002.