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CHEMICAL PROCESSING OF COATED PARTICLE FUELS[*]

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ABSTRACT

Laboratory studies on the processing of graphite-base fuel elements containing pyrolytic carbon- or Al_2O_3-coated particles are reviewed. Potential processes for recovering uranium and thorium from irradiated elements include grinding followed by acid leaching, and, burning and subsequent dissolution of the oxide ash. Disintegration in 90% HNO_3 was briefly evaluated as a method for determining the integrity of coated particles dispersed in graphite matrices.

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CHEMICAL PROCESSING OF COATED PARTICLE FUELS

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INTRODUCTION

The purpose of this report is to summarize work conducted by the ORNL Chemical Technology Division on the chemical processing of coated particle reactor fuel elements such as those proposed for the HTGR and the PBR. Chemical processing of irradiated elements is only one of the many steps in the over-all fuel cycle and consists of dissolution of the fuel values, uranium and thorium, followed by a decontamination procedure to effect separation of these elements from the fission products. Currently, extraction of the uranium and thorium from nitric acid solutions with tributyl phosphate is the best method for achieving the desired decontamination.

Initial laboratory work has been concentrated on graphite-base fuels which contain either carbon- or alumina-coated particles. At least five processing methods for these fuels are being evaluated. They are Grind-Leach ([1],[2]), Combustion-Dissolution ([2]), the 90% HNO_3 technique ([2],[3]), anodic disintegration, and Chloride Volatility ([4]). A brief description of these techniques and a summation of data obtained so far are given in the following sections.

POTENTIAL PROCESSING METHODS

Grind-Leach Process - This process involves mechanically grinding the fuel elements fine enough to ensure rupture of the particle coatings, and, then, leaching the resulting powder with nitric acid or HNO_3-HF to recover the uranium and thorium. This technique is applicable to all types of graphite-base fuel elements, the extent of grinding being dependent primarily on the size of the coated particles. In principle, the technique is applicable to other types of high-temperature reactor fuels, e.g., those having Al_2O_3 or BeO matrices. When grinding is fine

enough, 200 mesh for most coated particle fuels, uranium and thorium recoveries are almost quantitative when the powder is leached for 6-8 hr with the suitable boiling reagent (Table 1).

Table 1. URANIUM AND THORIUM RECOVERY FROM GRAPHITE FUELS
BY THE GRIND-LEACH PROCESS

(Fuel ground to 200 mesh and leached for 6-8 hr with boiling reagent.)

| Fuel | Fuel Comp., % | | Leachant | Recoveries, % | |
	Uranium	Thorium		Uranium	Thorium
Uncoated UO_2-ThO_2	1.2	8.0	13 $\underline{M}$ HNO_3-0.04 $\underline{M}$ HF-0.1 $\underline{M}$ $Al(NO_3)_3$	99.9	99.9
Uncoated UC_2-ThC_2	1.5	7.2	13 $\underline{M}$ HNO_3-0.04 $\underline{M}$ HF-0.1 $\underline{M}$ $Al(NO_3)_3$	90	88
Al_2O_3-coated UO_2	8.0	---	15.8 $\underline{M}$ HNO_3	99	---
Pyr-C-coated UC_2-ThC_2	9.7	33.8	15.8 $\underline{M}$ HNO_3	98.8	99.9
Pyr-C-coated UC_2-ThC_2	9.6	33.5	13 $\underline{M}$ HNO_3-0.04 $\underline{M}$ HF-0.1 $\underline{M}$ $Al(NO_3)_3$	99.4	99.9

Several engineering problems need to be solved before this method can be considered practicable. Studies of the feasibility of fine grinding of fuels containing refractories and abrasives such as SiC and Al_2O_3 must be made. Methods for filtering or centrifuging large volumes of graphite slurries and for adequately washing graphite beds must be developed.

Combustion-Dissolution Process - Combustion, in oxygen, of graphite-base fuels followed by dissolution of the oxide ash leads to quantitative recovery of uranium and thorium from fuels containing carbon-coated particles (Table 2). This technique may also be applicable to fuels containing BeO-coated particles using dissolution techniques developed for sintered BeO (5). Alumina-coated particle fuels present a nearly impossible situation because of the inertness of sintered Al_2O_3. The graphite matrix burns readily, but the coated particles are virtually unaffected by the combustion. Fuels which are coated with materials such as SiC or contain impurities such as iron yield combustion residues from which

Table 2. URANIUM AND THORIUM RECOVERY FROM GRAPHITE FUELS BY THE

COMBUSTION-DISSOLUTION PROCESS

(Fuel burned in oxygen at 750-850°C; ash leached 6-10 hr

in boiling reagent.)

Fuel	Fuel Comp., %				Leachant	Recoveries, %	
	U	Th	Si	Fe		U	Th
Uncoated UC_2-ThC_2	1.7	8.0	--	--	13 $\underline{M}$ HNO_3-0.04 $\underline{M}$ HF-0.1 $\underline{M}$ Al$(NO_3)_3$	100	100
Pyr-C-Coated UC_2-ThC_2	9.9	33.0	--	--	13 $\underline{M}$ HNO_3-0.04 $\underline{M}$ HF-0.1 $\underline{M}$ Al$(NO_3)_3$	100	100
Al_2O_3-Coated UO_2	8.0	--	--	--	10 $\underline{M}$ HNO_3	9.9	--
Uncoated UC_2	3.7	--	--	0.1	10 $\underline{M}$ HNO_3	99.8	--
Uncoated UC_2	0.7	--	--	0.4	10 $\underline{M}$ HNO_3	98.0	--
Uncoated UO_2	7.0	--	2.0	--	10 $\underline{M}$ HNO_3	99.6	--
Uncoated UO_2	6.8	--	20.3	--	10 $\underline{M}$ HNO_3	97.8	--

quantitative leaching of the uranium and thorium is difficult. For example, the ash from a siliconized-SiC coated PBR fuel sphere, when leached with boiling 10 $\underline{M}$ HNO_3, retained 2% of the uranium in insoluble form (Table 2).

The combustion process is not without its shortcomings. Because of the high temperatures involved the choice of materials for burner construction is severely limited, and CO, which can form explosive mixtures with oxygen, is formed in preference to CO_2 unless an excess of oxygen is present. Methods for safely disposing of the radioactive off-gas will have to be developed. The ash from thorium-bearing fuels can be dissolved only in nitric acid containing small amounts of fluoride ion, a somewhat corrosive solution. Because of the markedly different thermal and environmental conditions imposed in the two steps of the process, it is doubtful that a single vessel can be used for the combustion and dissolution.

Low temperature combustion may alleviate many of these problems. Scouting work in this area has indicated that the ignition temperature can be lowered several hundred degrees using catalysts such as manganese, copper, or lead. For example, United Carbon Products spectroscopic grade graphite ignites only at 720°C or higher in a stream of pure oxygen; the ignition temperature, however, can be lowered to about 345°C by pre-soaking the graphite in 0.07 M lead acetate solution (Table 3). Furthermore, the catalytic effect is noticeable below the ignition temperature. Untreated graphite showed at most a 0.4% weight loss when exposed for 3 hr to a stream of oxygen at 460°C, but a piece of graphite which had been soaked for 3 minutes in 0.25 M KMnO₄ solution lost 34% of its weight under the same conditions (Table 3). Further work on such catalysts is now in progress.

Table 3. CATALYSIS OF THE COMBUSTION OF UNITED CARBON PRODUCTS GRAPHITE[*]

Catalyst[**]	Ignition Temp., °C	Comb. Temp., °C	Time, hr	Weight Loss, %
None	720			
		311	3	0.00
		334	3	0.00
		459	3	0.37
		459	3	0.05
		471	3	0.23
0.07 M Lead acetate	345			
		311	3	3.2
		334	3	6.0
0.25 M KMnO₄	482			
		448	3	33.6
		459	3	34.4
3.15 M Cu(NO₃)₂	482			
		459	3	13.5
		471	3	11.9

[*] United Carbon Products Co. Ultra Purity Spectroscopic graphite. Lot No. 5387. Density, 1.55 g/cc.

[**] Each specimen soaked for 3 minutes in the indicated solution.

90% HNO$_3$ Process - Graphite matrices are readily disintegrated in 90% HNO$_3$ (21.5 M) at temperatures from 25°C to the boiling point, about 93°C. Unfortunately, only the matrix is affected; both carbon- and alumina-coated particles are unaffected. For example, when specimens containing coated particles were disintegrated to powder (mean particle size about 700 microns) in boiling 90% HNO$_3$, less than 7% of the uranium and thorium was solubilized (Table 4). This technique, therefore, does not appear applicable to the processing of graphite-base fuels containing coated particles.

Table 4. URANIUM AND THORIUM RECOVERY FROM GRAPHITE FUELS BY THE 90% HNO$_3$ PROCESS

(Fuel disintegrated and leached twice for 4 hr with boiling 21.5 M HNO$_3$)

Fuel	Fuel Comp., %		Recoveries, %	
	Uranium	Thorium	Uranium	Thorium
Uncoated UC$_2$	3.0	--	99.4	--
Uncoated UC$_2$	15.2	--	99.9	--
Uncoated UC$_2$-ThC$_2$	1.3	15.0	99.9	99.8
Pyr-C-coated UC$_2$-ThC$_2$	9.7	33.5	6.5	4.6
Al$_2$O$_3$-coated UO$_2$	8.0	--	0.8	--

Since graphite fuel compacts are disintegrated by boiling 90% HNO$_3$ but the fuel particles generally are unattacked, this technique was evaluated briefly as a destructive method for determining the integrity of the coated fuel particles. A similar technique based on electrolytic disintegration has been used at Battelle Memorial Institute (6). The amount of uranium (and/or thorium) dissolved during the acid treatment would reflect the number of particle coatings which were defective (or which were susceptible to oxidation). Graphites, in general, are oxidized very slowly in concentrated nitric acid. ORNL studies with type GBF graphite showed that digestion of powdered samples for periods of up to 100 hr resulted in oxidation of less than 2% of the carbon. Amorphous carbons, however, are oxidized at a much higher rate. As a result, carbon coatings which are not highly graphitized probably will be oxidized.

Two batches of carbon-coated UC_2 particles were tested using the 90% HNO_3 technique. In two, 6-hr leaches with boiling acid, only 1-2% of the uranium was dissolved from batch 3M-D (Table 5); however, about 48% of the uranium was dissolved from batch NCC-J. Since the weight losses were about those expected from the amounts of uranium dissolved assuming no carbon oxidized, it is concluded that these leaching results reflect the degree to which the particle coatings were defective. The ultimate usefulness of this technique will be determined only after more intensive study. Corroboration of leaching results by those of another independent method would be highly desirable.

Table 5. EVALUATION OF CARBON COATINGS ON UC_2 PARTICLES
USING 90% HNO_3

(Each sample leached twice for 6 hr with boiling 21.5 $\underline{M}$ HNO_3.)

| Type of Particle | Uranium Content of Sample, % | Uranium Solubilized,% | | Wt. Loss, % | |
		First Leach	Second Leach	Calcd.	Found
3M-D	69.24	0.34	2.5	1.9	0
3M-D	68.58	0.33	1.0	0.9	0
NCC-J	44.00	11.8	35.8	21	16.9
NCC-J	43.86	11.5	36.4	21	17.2

Anodic Disintegration - Electrolytic disintegration in hot ($93°C$) 15.8 $\underline{M}$ HNO_3 did not result in satisfactory recovery of uranium from graphite fuel specimens containing pyrolytic carbon-coated uranium carbide fuel particles. The graphite matrix was readily disintegrated, but the particle coatings were not markedly affected; that is, less than 2% of the uranium was found in solution. Similar results were obtained at BMI with fuels containing Al_2O_3-coated UO_2 particles (6).

Chloride Volatility Process - Very little work has been done on Chloride Volatility processing of coated particle fuels. Two variations are being studied. In the first, uranium would be converted to a volatile chloride using one of several reagents such as CCl_4, Cl_2, or $COCl_2$ and sublimed away from the graphite matrix (graphite reacts only very slowly

with chlorinating agents even at relatively high temperatures). The re-
covered uranium chloride would either be fluorinated to UF_6 or dissolved
in an aqueous solution preparatory to solvent extraction. Chlorination
techniques are also applicable to the recovery of uranium from combustion
ashes.

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