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GRIND-LEACH PROCESS FOR GRAPHITE-BASE  
REACTOR FUELS THAT CONTAIN COATED  
PARTICLES: LABORATORY DEVELOPMENT

L. M. Ferris

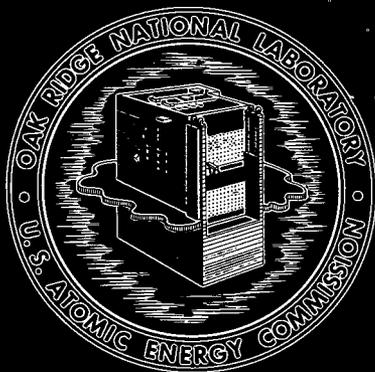
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CHEMICAL TECHNOLOGY DIVISION

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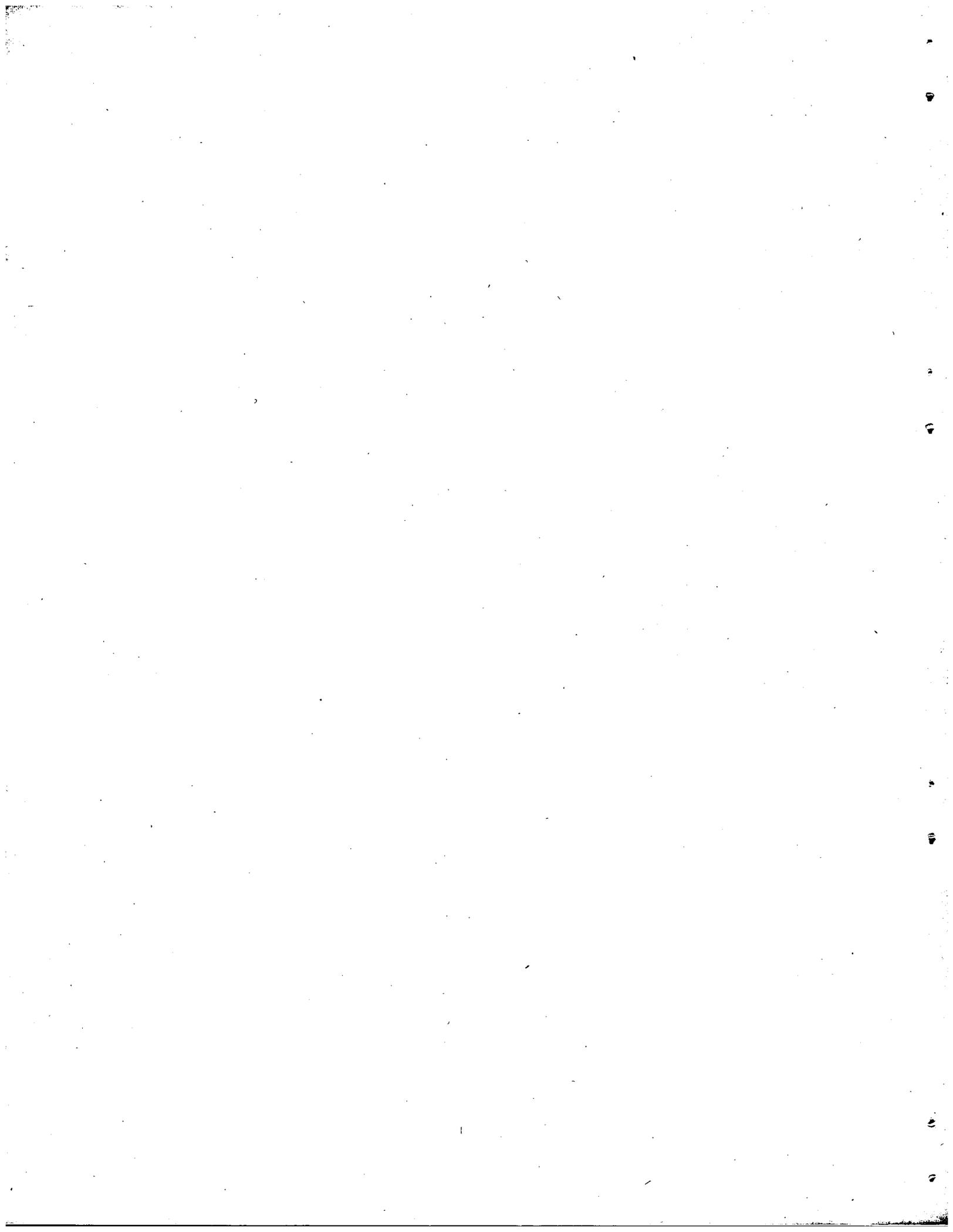
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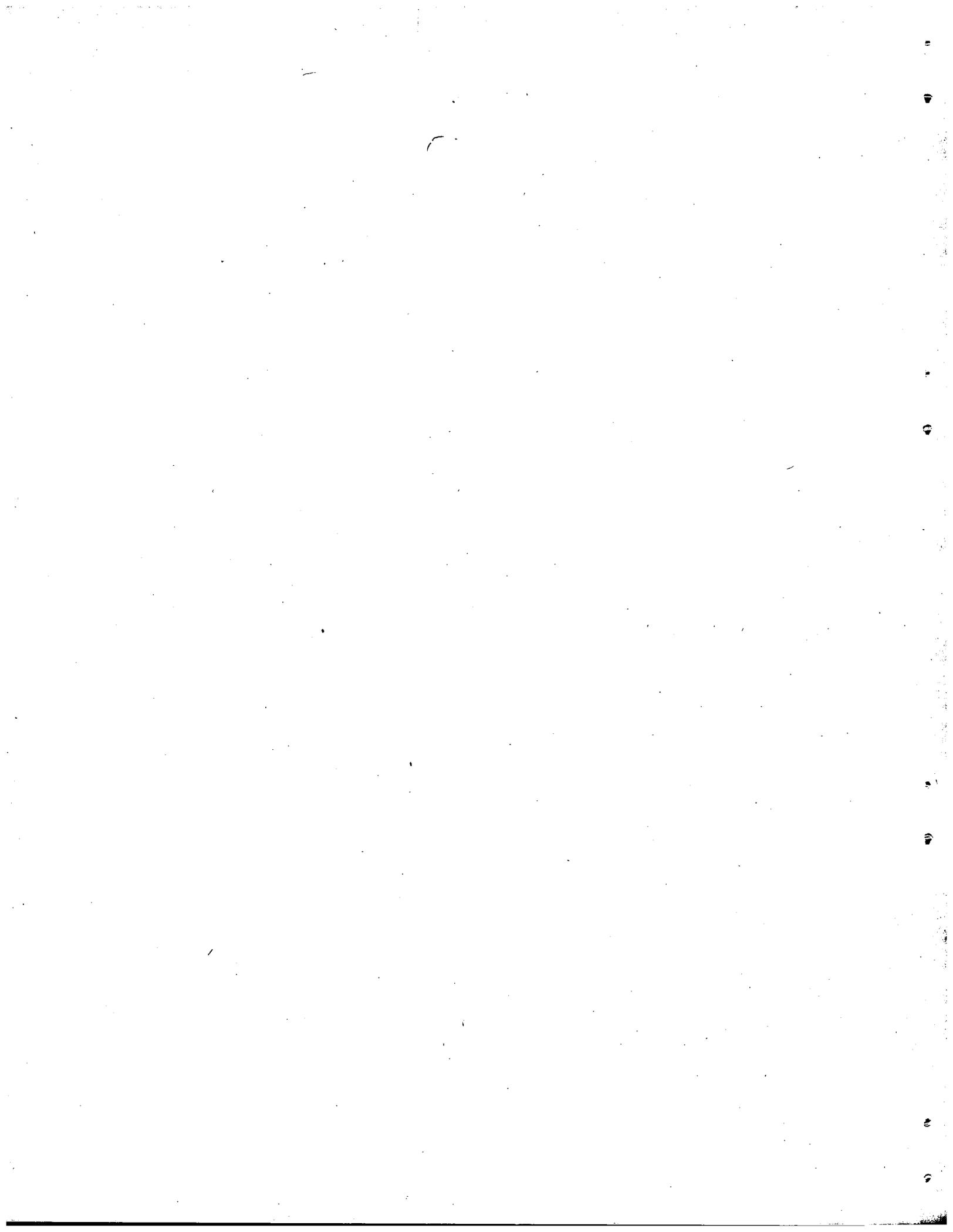


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GRIND-LEACH PROCESS FOR GRAPHITE-BASE REACTOR FUELS  
THAT CONTAIN COATED PARTICLES: LABORATORY DEVELOPMENT

L. M. Ferris

ABSTRACT

Leaching of crushed graphite-base reactor fuels that originally contained coated particles was studied on a laboratory scale in an effort to define the conditions necessary for the adequate recovery of uranium and thorium. All experiments were conducted with unirradiated prototype fuel samples. This study indicated that the grind-leach method is of only marginal usefulness for the processing of coated-particle fuels. Major chemical problems encountered were the difficulty in achieving high uranium and thorium recoveries and the formation of soluble organic compounds during leaching. The overall conditions required for adequate recoveries invariably made the leach solutions very dilute in uranium and thorium. These and other factors must be carefully evaluated before the process can be seriously considered for plant-scale use.

Most of the work was done with prototype Peach Bottom reactor fuel, which was composed of  $\text{ThC}_2\text{-UC}_2$  particles, each coated with a single layer of pyrocarbon, dispersed in a graphite matrix. A few experiments were conducted with crushed UHTREX fuel (graphite matrix containing  $\text{UC}_2$  particles that were coated with three layers of carbon).

In each instance, the fuel was ground fine enough to ensure rupture of the coated particles by rough-crushing it in a hammer mill and then pulverizing the resulting product in a double-roll crusher.

Recovery of 99.9% of the uranium and thorium from the crushed (-140 mesh) Peach Bottom fuel was achieved only after leaching the fuel twice (5 hr each leach) with boiling 5 to 15.8 M  $\text{HNO}_3$ . Recoveries were inadequate after a single 5- to 24-hr leach with the amount of reagent required to produce a solution 0.2 M in U + Th (if all the  $\text{ThC}_2\text{-UC}_2$  dissolved); usually 0.2 to 0.5% of the uranium and thorium remained in the graphite residue. Addition of HF to the nitric acid leachant did not enhance recoveries. Thorough washing of the residue after leaching was essential in obtaining maximum recoveries. During leaching, up to about 10% of the total carbon in the fuel was oxidized; however, the amount of carbon left in the leach solutions as soluble organic compounds generally corresponded to less than 1% of the carbon from the fuel. Uranium was not readily leached from crushed UHTREX fuel. Even after three 5-hr leaches with boiling 15 M  $\text{HNO}_3$ , more than 0.2% of the uranium remained with the graphite residue.

## 1. INTRODUCTION

During the past few years, several potential methods<sup>1-11</sup> for processing graphite-base fuels for high-temperature, gas-cooled reactors (HTGR's) have been studied at Oak Ridge National Laboratory (ORNL). Many of the techniques evaluated previously were inapplicable to the newer HTGR fuels that contain coated fuel particles; the two most promising methods are the burn-leach and the grind-leach processes. Initially, the burn-leach process was emphasized, and it has now been sufficiently developed that a plant-scale process for fuels containing carbon-coated carbide particles appears practicable. However, since its applicability to fuels that contain particles coated with materials such as SiC, BeO, or Al<sub>2</sub>O<sub>3</sub> is uncertain, the feasibility of the grind-leach process, which should be amenable to practically all types of graphite-base fuels, is being evaluated.

The grind-leach process was studied previously at ORNL<sup>1,3-6,12</sup> and elsewhere.<sup>13-17</sup> The early work at ORNL was discontinued when the method was found to be unsuitable for Rover fuels<sup>5</sup> and when the results of preliminary engineering experiments<sup>12</sup> indicated formidable problems if a hammer mill were used to grind the fuel finely. However, recent engineering-scale work<sup>18</sup> has shown that HTGR fuels can be ground efficiently and rapidly by, first, rough-crushing the fuel in a hammer mill and, then, pulverizing the resulting product in a roll crusher. The same study demonstrated that fuel crushed in such a manner could be leached and washed effectively.

The purpose of the experiments described in this report was to define conditions for achieving practically quantitative recovery of uranium and thorium from roll-crushed HTGR fuels. Most of the effort was devoted to unirradiated prototype Peach Bottom fuel<sup>19</sup> that contained pyrocarbon-coated ThC<sub>2</sub>-UC<sub>2</sub> fuel particles; however, some work was done with prototype UHTREX fuel<sup>20</sup> and with carbon-coated ThO<sub>2</sub> microspheres. At the outset of these studies it was assumed that ultimate decontamination and recovery of uranium and thorium, in the event of plant-scale application of the process, would be achieved by a solvent extraction method such as the Acid Thorex process;<sup>21</sup> hence, only leachants containing nitric acid as the major constituent were considered. The chief parameters investigated were nitric acid concentration, presence or absence of hydrofluoric acid in the leachant,

reaction temperature, reaction time, and number of leaches required for acceptable uranium and thorium recoveries. Similar work<sup>22</sup> with irradiated fuel specimens will be reported separately.

The author thanks C. T. Thompson and J. F. Land for conducting the experimental work; B. A. Hannaford, Unit Operations Section, for roll-crushing the fuel samples; and R. J. Bard, Los Alamos Scientific Laboratory, for supplying UHTREX fuel. Analyses were provided by the groups of W. R. Laing and L. J. Brady, Analytical Chemistry Division.

## 2. LITERATURE SURVEY OF ANTICIPATED HEAD-END PROCESS CHEMISTRY

As outlined in Sect. 1, a grind-leach process for graphite-base reactor fuels would involve the following sequence of steps: (1) rough-crushing of the fuel; (2) fine crushing or grinding of the product from step 1; (3) leaching of the crushed fuel to recover the uranium and thorium; and, (4) decontamination and final recovery of the uranium and thorium by a solvent extraction process. In the present study, it was assumed that uranium and thorium nitrates dissolved in nitric acid would produce the most desirable feed solution for the solvent extraction process. Therefore, only leachants containing nitric acid as the main constituent were considered. This selection gives rise to three areas of concern with respect to the leaching step: (1) the rate of reaction of graphite with nitric acid solutions; (2) the dissolution behavior of uranium and thorium carbides in nitric acid solutions; and (3) the dissolution behavior of uranium and thorium oxides in nitric acid solutions. A survey of the literature showed that high-density uranium and thorium oxides can be readily dissolved in nitric acid (nitric acid plus HF in low concentration for  $\text{ThO}_2\text{-UO}_2$ ), that powdered graphite should produce only a slight reaction during leaching, and that uranium and thorium carbides can be dissolved in concentrated nitric acid. However, it indicated that solutions resulting from the dissolution of carbides will contain significant quantities of soluble organic compounds.

### 2.1 Dissolution of Uranium and Thorium Oxides

It is generally known that all uranium oxides dissolve readily in hot nitric acid solutions. Similarly,  $\text{ThO}_2$  and  $\text{ThO}_2\text{-UO}_2$  are soluble in nitric

acid containing a small amount of HF as a catalyst. Perhaps the optimum dissolvent<sup>8</sup> for  $\text{ThO}_2$  and  $\text{ThO}_2\text{-UO}_2$  is boiling 13 M  $\text{HNO}_3$ --0.05 M HF that is 0.05 to 0.1 M in  $\text{Al}(\text{NO}_3)_3$ . The  $\text{Al}(\text{NO}_3)_3$  inhibits corrosion of the dissolver since it complexes fluoride ion. Based on the known dissolution behavior of the uranium and thorium oxides, no major chemical problems would be anticipated in their recovery from crushed graphite-base fuels.

## 2.2 Reaction of Graphite with Nitric Acid

A survey of the reaction of nitric acid with graphite was made previously.<sup>3</sup> Although the rate of reaction has not been quantitatively measured, the available literature does show that even finely powdered graphite is attacked only slowly by concentrated nitric acid. For example, digestion of finely powdered graphite for two weeks with refluxing fuming nitric acid (sp. gr. 1.5) containing 0.2% vanadic acid as a catalyst resulted in oxidation of only about 25% of the graphite.<sup>23</sup> Similarly, only about 3% of powdered (-100 mesh) type GBF graphite was oxidized after about 100 hr of digestion with boiling 90% (21.5 M)  $\text{HNO}_3$ .<sup>24</sup> As indicated by the prior survey<sup>3</sup> and by a study<sup>24</sup> of the reaction of graphite with 90%  $\text{HNO}_3$ , most of the oxidized graphite was converted to  $\text{CO}_2$ , with only a small fraction (less than 9% in the latter study) being converted to soluble compounds. The soluble compounds formed were mellitic (benzene hexacarboxylic) acid and other, higher-molecular-weight, polycarboxylic acids.<sup>3,24</sup>

Based on the scant evidence in the literature, the leaching of uranium and thorium from finely crushed graphite fuels should not result in significant oxidation of the graphite unless the leaching time is very long.

## 2.3 Reactions of Uranium and Thorium Carbides with Nitric Acid

The uranium carbides, UC,  $\text{U}_4(\text{C}_2)_3$ , and  $\text{UC}_{1.85}$ , react with boiling 1 to 16 M  $\text{HNO}_3$  to yield uranyl nitrate, soluble organic acids,  $\text{CO}_2$ , NO, and  $\text{NO}_2$ .<sup>25-29</sup> Little or no hydrogen, gaseous hydrocarbons, or CO is produced. Approximately 50 to 80% of the carbide carbon is converted to  $\text{CO}_2$ ; the remainder is converted to soluble organic polycarboxylic acids such as

oxalic acid, mellitic acid, and higher-molecular-weight species similar to those obtained in the oxidation of graphite. The rate of reaction of arc-melted uranium carbides increases regularly with increasing nitric acid concentration.<sup>29</sup> The carbides are practically passive in boiling 0.001 to 0.5 M HNO<sub>3</sub>,<sup>25</sup> but dissolution proceeds fairly rapidly in boiling 10 to 15 M HNO<sub>3</sub>.

Some studies of the reactions of the thorium carbides, ThC and ThC<sub>1.95</sub>, with nitric acid have been reported.<sup>27,30,31</sup> These reactions differed from the corresponding uranium carbide reactions in that the thorium carbides reacted rapidly with 0 to 1 M HNO<sub>3</sub> but were nearly inert in 2 to 8 M HNO<sub>3</sub>. Furthermore, gaseous hydrocarbons apparently were present in the off-gas from reactions with 0 to about 4 M HNO<sub>3</sub> but were not detected in the off-gas from reactions with more concentrated acid.<sup>30,31</sup> The rate of dissolution was fairly high in concentrated (11 to 15 M) HNO<sub>3</sub>, and the solutions thus produced contained organic polycarboxylic acids similar to those obtained from reaction of the uranium carbides with nitric acid. About 50 and 33% of the carbide carbon was found as CO<sub>2</sub> when ThC and ThC<sub>2</sub>, respectively, were allowed to react with 6 M HNO<sub>3</sub>.<sup>27</sup>

No studies of the reactions of nitric acid with mixed thorium-uranium carbides have been reported. However, previous work on the leaching of thorium-uranium carbides from graphite-base fuels<sup>3,4,8,13,15</sup> indicates that the mixed dicarbides do react with boiling, concentrated nitric acid. Thus, from the information available from the literature, we would expect the most efficient leaching of mixed carbides from crushed graphite fuel to be achieved by using concentrated nitric acid as the leachant. Furthermore, we would expect to find a significant fraction of the carbide carbon in the leach solution in the form of soluble organic polycarboxylic acids. There is some evidence<sup>26</sup> that the organic compounds could produce deleterious effects in subsequent process steps such as solvent extraction.

### 3. EXPERIMENTAL

#### 3.1 Fuel Samples

The unirradiated prototype Peach Bottom fuel used in these studies was initially in the form of compacts containing pyrocarbon-coated ThC<sub>2</sub>-UC<sub>2</sub>

particles dispersed in a graphite matrix. Each particle was 150 to 420  $\mu$  in diameter and was coated with a single layer of laminar pyrocarbon  $55 \pm 10 \mu$  thick. The unirradiated UHTREX fuel initially consisted of 3-ft-long, 1-in.-OD, 0.5-in.-ID, hollow cylinders containing 147- to 208- $\mu$ -diam triplex-coated UC<sub>2</sub> particles. The three coatings, all of carbon, were as follows: (1) a 27- $\mu$ -thick inner buffer layer of porous carbon; (2) a 35- $\mu$ -thick intermediate layer of isotropic pyrocarbon; and (3) a 40- $\mu$ -thick outer layer of granular pyrocarbon.

Before being used in leaching studies, the fuel compacts or cylinders usually were ground in a double-roll crusher, fine enough (100 to 140 mesh) to ensure rupture of practically all the particle coatings. This was confirmed by sieve analysis and/or microscopic examination. Grinding less finely generally left a significant fraction of the particles intact. One batch of fuel was ground in a Waring blender, the method that had been used previously for particle-size reduction in hot-cell studies.<sup>22</sup> The compositions and particle-size distributions of the crushed fuels are shown in Table 1 and Fig. 1. The particle-size distribution data usually gave straight-line plots on log-probability paper. The mean (50%) size obtained from such plots is the geometric mean,<sup>32,33</sup> the geometric standard deviation,  $\sigma_g$ , is obtained from either

$$\log \sigma_g = \log(84\% \text{ size}) - \log(50\% \text{ size}),$$

or

$$\log \sigma_g = \log(50\% \text{ size}) - \log(16\% \text{ size}).$$

In general, fuel roll-crushed to pass a 100- or 140-mesh screen had a geometric mean particle size of 40 to 50  $\mu$ . The fuel that was ground in a Waring blender had a mean particle size of about 26  $\mu$ .

Batch PB-2 of crushed fuel was used for most of the work. The tap density of this material was about 0.95 g/cc; the "fluff" density was about 0.57 g/cc. After the uranium and thorium were leached out and the material was dried at 100°C, corresponding values were about 0.77 and 0.47 g/cc respectively.

Several different types of coated particles (not dispersed in a graphite matrix) were also used in this work. These included two different batches of carbon-coated ThO<sub>2</sub> microspheres, fuel particles for use in advanced gas-cooled reactors. One batch (OR-520) was composed of 275- $\mu$ -diam

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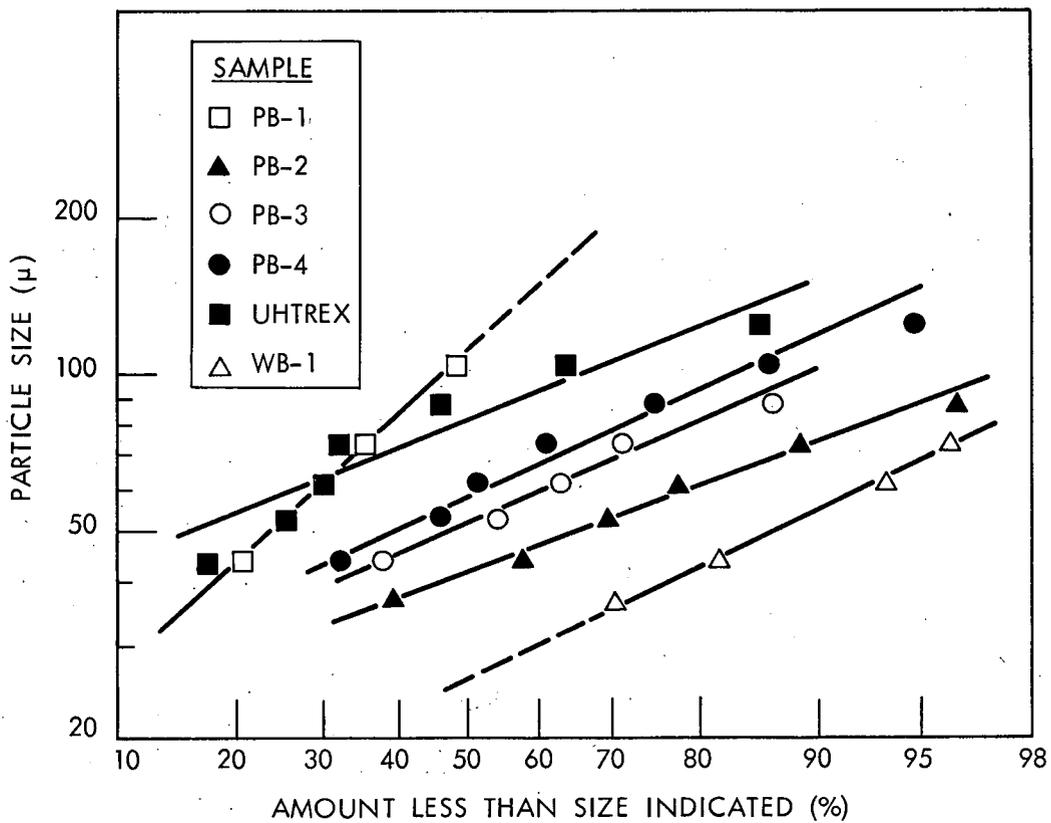


Fig. 1. Approximate Particle-Size Distributions for Crushed HTGR Fuel Samples Used in This Study.

Table 1. Uranium and Thorium Concentrations and Particle Size Distribution Data for Crushed HTGR Fuels Used in This Study

Sample	Maximum Particle Size (Mesh)	Average Uranium Conc. (%)	Average Thorium Conc. (%)	Geometric Mean Particle Size ( $\mu$ )	Geometric Standard Deviation ( $\sigma_g$ )
PB-1 <sup>a</sup>	50	3.77	16.0	110	2.64
PB-2 <sup>a</sup>	140	2.77	13.3	42	1.59
PB-3 <sup>b</sup>	100	1.70	8.11	52	1.79
PB-4 <sup>a</sup>	100	3.13	15.2	58	1.67
UHTREX	100	8.37	0	82	1.66
WB-1 <sup>a,c</sup>	140	2.66	13.4	26	1.81

<sup>a</sup> About 1.8% of these samples was carbide carbon, assuming that uranium and thorium were present as ThC<sub>2</sub>-UC<sub>2</sub>.

<sup>b</sup> About 1% of this sample was carbide carbon.

<sup>c</sup> This fuel sample was pulverized in a Waring blender instead of a roll-crusher.

ThO<sub>2</sub> kernels coated with a single, 45- $\mu$ -thick layer of dense pyrocarbon; the carbon content of these particles was about 23%. The other batch (OR-521) contained 275- $\mu$ -diam ThO<sub>2</sub> kernels and a duplex coating consisting of an inner, 40- $\mu$ -thick layer of porous carbon and an outer, 40- $\mu$ -thick layer of pyrocarbon; the carbon content of these particles was about 32%.

The three types of Dragon reactor<sup>34</sup> fuel particles used were: (1) Batch C-305: pyrocarbon-coated (U,Zr)C containing 14.68% uranium, 43.4% zirconium, and 40.02% carbon by analysis. The zirconium:uranium atom ratio was 7.7. Assuming the uranium and zirconium to be present as UC and ZrC, respectively, batch C-305 had the following composition: 15.42% UC, 49.11% ZrC, 6.45% carbon as carbide carbon, and 33 to 35% carbon as pyrocarbon coatings. (2) Batch C-349: pyrocarbon/silicon carbide/pyrocarbon triplex-coated (U,Zr)C containing 8.79% uranium, 23.7% zirconium, 11.38% silicon, and 54.59% carbon. The zirconium:uranium atom ratio was 7.0. Assuming the uranium, zirconium, and silicon to be present as UC, ZrC, and SiC, respectively, batch C-349 had the following composition: 9.23% UC, 26.82% ZrC, 16.25% SiC, 8.43% carbon as carbide carbon, and 46 to 48%

carbon as pyrocarbon coatings. (3) Batch C-522: pyrocarbon/silicon carbide/pyrocarbon triplex-coated (U,Th) $C_2$  containing 9.01% uranium, 26.4% thorium, 10.3% silicon. The thorium:uranium atom ratio was 2.92. Assuming the uranium and thorium to be present as  $UC_2$  and  $ThC_2$ , respectively, and the silicon to be present as SiC, batch C-522 had the following composition: 9.92%  $UC_2$ , 29.1%  $ThC_2$ , 14.7% SiC, 8.1% carbon as carbide carbon, and 46.3% carbon as pyrocarbon coatings.

### 3.2 Experimental Procedure

Two different types of leaching and washing experiments were made with crushed fuel. One technique consisted in digesting 2 to 10 g of crushed fuel with 10 to 30 ml of leachant in a 100-ml round-bottom flask fitted with a reflux condenser. During the digestion, the fuel was agitated constantly with a magnetic stirrer. Leachant was added to the crushed fuel, and the system was heated to the desired leaching temperature (if other than room temperature) only after the foaming from the rapid initial reaction had subsided (usually in less than 5 min). After leaching, the contents of the reaction flask were poured onto a medium-porosity sintered glass filter, and the liquid was collected by vacuum filtration. The residual fuel in the flask was removed by slurring it with small portions of the solution to be used as the first wash for the residue. After the residue and the wash solution had been completely transferred to the filter, the wash solution was left in contact with the residue for about 15 min with occasional stirring; then, the solution was collected by vacuum filtration. Each subsequent wash was conducted in the same way. If the residue was to be leached again, it usually was dried (either air-dried or in an oven at about 100°C) to facilitate transfer back to a boiling flask.

The other type of experiment performed involved use of pressure filtration in the removal of the product solution and the wash from the graphite after leaching. This simulated the washing of leached fuel in an engineering-scale leacher, and the data obtained on the effects of pressure gradient, washing temperature, and type of wash solution used were thought to be of some value in the preliminary design of engineering-scale equipment.

As discussed later (Sect. 4.3), the approximate permeability of the leached fuel to various solutions could also be measured.

In the experiments involving pressure filtration, a sample of fuel (usually 2.5 g) was leached for 5 hr with either boiling 13 M HNO<sub>3</sub> or 13 M HNO<sub>3</sub>--0.05 M HF. About 4 ml of leachant was used for each gram of fuel. After leaching, the contents of the reaction flask were transferred to a 1-cm-ID column for washing (Fig. 2). The transfer was accomplished by slurring the leached fuel with the supernate and transferring as much of the slurry to the column as possible. The leached graphite was allowed to settle in the column, and samples of the supernate were then pipetted off for use in slurring and transferring any solids remaining in the flask. The bed of leached graphite was supported in the column by a wad of glass wool and a small amount of 20-mesh alumina (Fig. 2).

After transfer of the leached fuel was complete, the leachate was removed and the residue was washed, with the pressure gradient across the graphite bed being kept nearly constant. Air pressure could be applied to the system to achieve any desired pressure gradient from 0 to 30 cm Hg per cm of bed height. A pressure gradient close to that desired was achieved by applying pressure to the system with stopcock A open and stopcocks B and C closed (Fig. 2). Virtually no compression of the bed occurred in this step. After the system was pressurized, the volume (height) of the graphite bed was noted, stopcock A was closed, and stopcocks B and C were opened simultaneously, allowing solution to flow from the column. As soon as stopcocks B and C were opened, a small amount of liquid from the reservoir dropped immediately into the column and a minor change in pressure occurred. The pressure gradient calculated from this pressure was the one used to correlate the data. Solution flowing from the column was collected in increments equal in volume to that of the bed of graphite. (Here, a bed volume is defined as the volume of the graphite bed that settles out from the product solution at 25°C under the pressure gradient established.) The settled density of the roll-crushed Peach Bottom fuel samples after leaching generally was about 0.7 g/cc. Since the unleached fuel was about 83% graphite, the settled volume (bed volume) of the residue after leaching a 2.5-g fuel sample was about 3 ml. A slight (generally less than 10%) compression of the bed occurred as soon as liquid began to flow from the

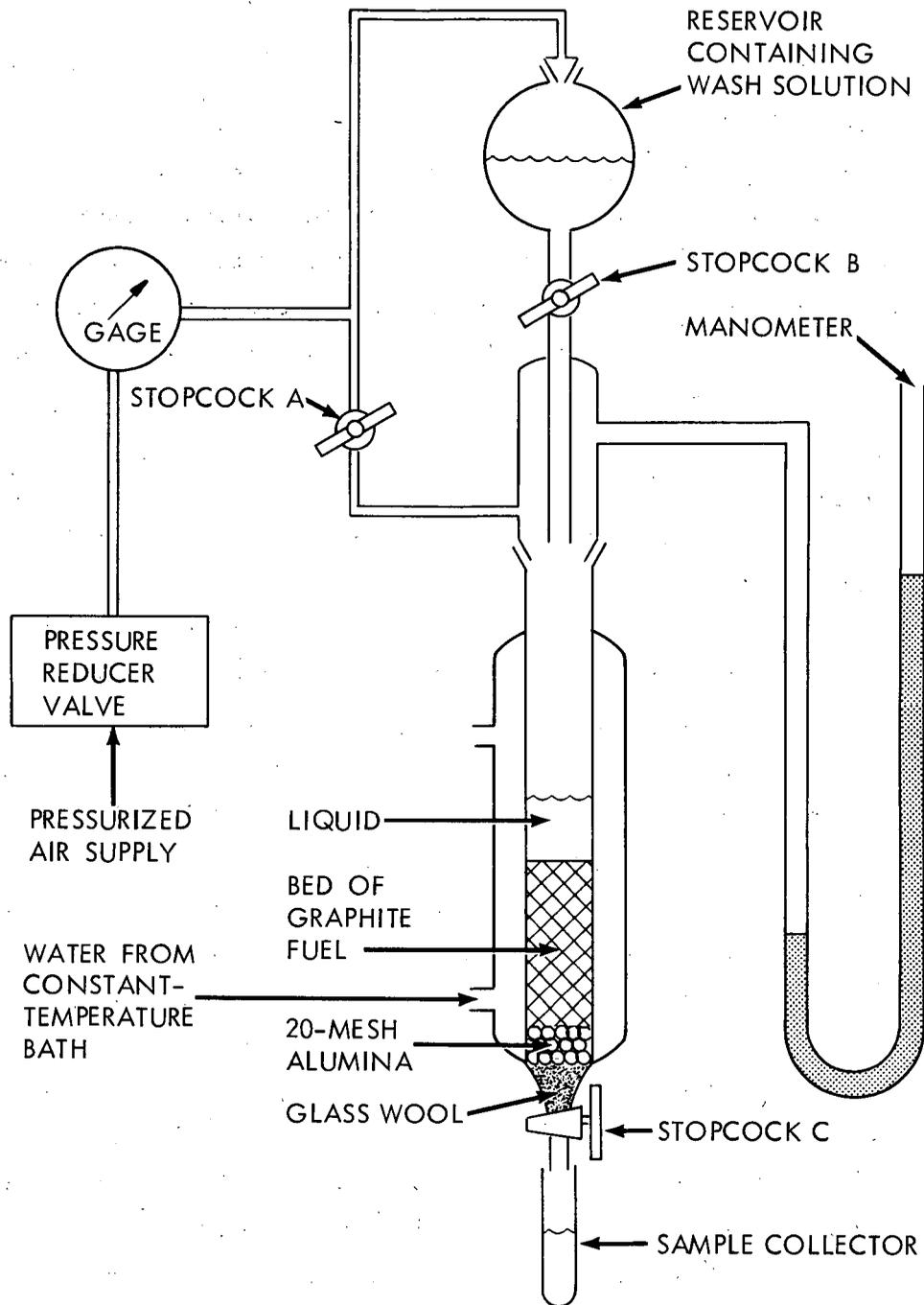


Fig. 2. Jacketed Column Used for Pressurized Washing of Leached Graphite Fuel Samples.

column; however, no further noticeable decrease in bed volume was detectable throughout the course of an experiment.

#### 4. RESULTS

##### 4.1 Leaching of Crushed Peach Bottom Fuel

Several different samples of unirradiated prototype Peach Bottom fuel (Table 1) that had been roll-crushed to fine powders were leached under various conditions in an effort to determine the optimum conditions for recovering uranium and thorium from this type of fuel. In the experiments described in this section, round-bottom flasks were used as reaction vessels and vacuum filtration was used to recover the leachate and wash solutions (see Sect. 3.2).

##### 4.1.1 Uranium and Thorium Recoveries in Single Leaches with Boiling Reagents

The leachants tested were 2 to 21.5 M  $\text{HNO}_3$  solutions and similar solutions that were either 0.05 M in HF or 0.05 M in both HF and  $\text{Al}(\text{NO}_3)_3$ . In each experiment, samples (crushed to -100 mesh to ensure rupture of the particle coatings) were leached with sufficient reagent to produce solutions 0.06 to 0.2 M in Th + U (if all the uranium and thorium dissolved); the residues were then washed with three portions of water, the volume of each portion being equal to the volume of leachant used. The amount of wash used corresponded to 10 to 18 bed volumes of fuel (see Sect. 3.2).

A single leach with any of the reagents tested did not provide adequate uranium and thorium recoveries. In 5-hr leaches with boiling 2 to 21.5 M  $\text{HNO}_3$ , uranium losses to the graphitic residue were generally between 0.2 and 0.5%, regardless of the acid concentration (Table 2). Increasing the reaction time to 24 hr did not improve the recovery. The behavior of thorium was similar to that of uranium, with the losses varying unsystematically from about 0.75 to 1.8%. The thorium:uranium atom ratios in the residues were generally in the range of 7 to 30, compared with a ratio of about 4.9 in the original fuel. The apparent selectivity in the leaching of the uranium is not understood at present.

Uranium losses to the residue after 5-hr leaches with boiling nitric acid solutions that were 0.05 M in HF were about the same as those

Table 2. Uranium and Thorium Losses to the Residues After a Single Leach of Crushed (-100 mesh) Peach Bottom Fuel with Boiling Reagent

Residues washed with 3 portions of water, each portion being equal to the volume of leachant used.

Expt.	Fuel Sample <sup>a</sup> (PB-)	Conc. in Leachant (M)			Leach Time (hr)	Losses to Residue (%)		(Th + U) Conc. in Leach Solution if All U and Th Dissolved (M)
		HNO <sub>3</sub>	HF	Al(NO <sub>3</sub> ) <sub>3</sub>		U	Th	
1	2	2.0	0	0	5	0.39	1.80	0.2
2	3	2.0	0	0	5	0.34	1.40	0.06
3	2	5.0	0	0	5	0.28	0.94	0.2
4	3	5.0	0	0	5	0.44	1.08	0.06
5	2	13.0	0	0	5	0.25	0.81	0.2
6	3	13.0	0	0	5	0.25	0.89	0.06
7	4	13.0	0	0	5	0.003	0.75	0.1
8	2	13.0	0	0	20	0.28	1.0	0.2
9	2	13.0	0	0	24	0.21	1.17	0.2
10	3	15.8	0	0	5	0.51	0.76	0.06
11	2	15.8	0	0	5	0.24	1.20	0.2
12	2	15.8	0	0	7	0.28	1.54	0.2
13	2	21.5	0	0	5	0.38	1.70	0.2
14	2	2.0	0.05	0	5	0.24	3.14	0.2
15	3	2.0	0.05	0	5	0.014	1.33	0.06
16	2	5.0	0.05	0	5	0.17	0.95	0.2
18	2	13.0	0.05	0	0.17	0.25	4.59	0.1
19	2	13.0	0.05	0	0.17	0.27	0.16	0.1
20	2	13.0	0.05	0	5	0.26	0.52	0.2
21	3	13.0	0.05	0	5	0.38	7.13	0.06
22	3	13.0	0.05	0	5	0.29 <sup>b</sup>	8.30 <sup>b</sup>	0.06
23	2	13.0	0.05	0	5	0.30 <sup>b</sup>	0.55 <sup>b</sup>	0.2
24	2	13.0	0.05	0	5	0.16 <sup>c</sup>	0.13 <sup>c</sup>	0.2
25	2	13.0	0.05	0	20	0.51	0.76	0.2
26	2	13.0	0.05	0	24	0.17	0.99	0.2
27	2	2.0	0.05	0.05	5	0.25	2.31	0.2
28	3	2.0	0.05	0.05	5	0.37	1.38	0.06
29	2	5.0	0.05	0.05	5	0.23	0.78	0.2
30	3	5.0	0.05	0.05	5	0.36	0.96	0.06
31	2	13.0	0.05	0.05	5	0.18	0.63	0.2
32	3	13.0	0.05	0.05	5	0.27	0.68	0.06

<sup>a</sup> See Table 1 for compositions of the fuel samples.

<sup>b</sup> Residue washed with hot (80 to 90°C) water.

<sup>c</sup> Residue washed with 10 M HNO<sub>3</sub> at room temperature.

resulting from leaching with nitric acid alone (Table 2). The thorium loss values were highly scattered but, in general, were higher (up to 8.3%) than those obtained by leaching with nitric acid. Since the highest thorium losses occurred in systems that were the most dilute in thorium and that had the highest fluorine:thorium atom ratios ( $>1$ ), it is possible that they may have been caused, at least partly, by precipitation of insoluble  $\text{ThF}_4$ ; however, no direct evidence for the presence of  $\text{ThF}_4$  in the residues was obtained.

Most of the thorium and uranium dissolved in the first few minutes of leaching (see expts. 18 and 19, Table 2). The organic compounds formed in this initial, rapid reaction apparently had surfactant properties; for example, when solutions resulting from the 10-min leaches were shaken, large quantities of foam were produced. The presence of the organic compounds in solution, coupled with the initial high rate of gas evolution (nitrogen oxides) from the dissolution of the mixed dicarbide, undoubtedly accounts for the frothing of the system (Sect. 3.2). The organic compounds that cause this soapy effect apparently are partially oxidized by nitric acid over a period of time since no foam was generated when solutions from 5-hr leaches were shaken.

In 5-hr leaches with nitric acid solutions that were 0.05 M in both HF and  $\text{Al}(\text{NO}_3)_3$ , uranium and thorium losses to the residues were about the same as those obtained by leaching with nitric acid alone (Table 2, expts. 27-32).

A few leaching experiments were made with prototype Peach Bottom fuel that was roll-crushed to only 50 mesh (sample PB-1). Apparently all the fuel particles were not broken during crushing since the uranium losses to the residues after 5-hr leaches (Table 3) were about twice those obtained when finely ground samples were leached (Table 2). Why the thorium losses were not proportionately as high (they were only 0.7 to 1.1%) is not obvious.

In each of the experiments discussed (except those made with sample PB-1), the amounts of uranium and thorium found in the leachate, first wash, second wash, and third wash, respectively, were about 70 to 90%, 9 to 26%, 0.1 to 3%, and 0.005 to 0.3% (Table 4). These washing data do not aid in explaining why the thorium losses were, for the most part, higher

Table 3. Leaching of Peach Bottom Fuel (Sample PB-1)  
That Was Roll-Crushed to Only -50 Mesh

5-g samples leached with 19 ml of boiling reagent; then residue washed with three 19-ml portions of water

Expt.	Concentration in Leachant (M)		Leaching Time (hr)	Losses to Residue (%)	
	HNO <sub>3</sub>	HF		Uranium	Thorium
33	4.0	0	5	1.28	1.11
34	4.0	0.05	5	0.91	0.81
35	13.0	0	5	1.10	0.87
36	13.0	0	20	0.45	1.06
37	13.0	0.05	5	1.08	0.74
38	13.0	0.05	20	0.54	0.90

Table 4. Amounts of Uranium and Thorium Recovered by Washing  
Residues After a Single Leach with Boiling Reagent

Leachate removed by vacuum filtration; then residue washed with three portions of water, each portion being equal to the volume of leachant used

Experiment	Percentages of Uranium and Thorium Recovered in							
	Leachate		First Wash		Second Wash		Third Wash	
	Uranium	Thorium	Uranium	Thorium	Uranium	Thorium	Uranium	Thorium
1	74.0	72.0	25.4	26.0	0.11	0.15	0.02	0.02
2	84.1	84.0	15.0	13.8	0.52	0.77	0.04	0.06
3	72.8	72.4	24.9	24.4	1.80	2.01	0.24	0.26
4	87.6	87.6	11.5	10.7	0.44	0.61	0.03	0.02
5	81.3	80.0	17.7	18.2	0.72	1.02	0.007	0.005
6	81.7	81.7	17.4	16.6	0.56	0.73	0.08	0.06°
10	90.4	90.1	8.75	8.84	0.24	0.24	0.12	0.02
11	77.1	77.2	20.6	19.3	1.87	2.22	0.16	0.08
12	85.8	84.6	13.3	13.6	0.50	0.27	0.06	0.03
14	72.0	70.8	25.4	24.7	2.17	1.17	0.13	0.12
15	89.3	88.4	10.0	9.35	0.56	0.88	0.04	0.04
16	78.7	83.4	20.4	14.8	0.65	0.75	0.06	0.05
17	85.7	85.3	13.2	13.0	0.59	0.75	0.04	0.04
20	76.4	76.0	22.8	23.0	0.53	0.49	0.01	0.005
21	85.4	77.6	13.5	14.1	0.70	1.11	0.04	0.05
22	86.8	78.9	11.0	11.9	1.65	0.79	0.24	0.09
23	79.8	78.2	17.7	19.0	2.16	2.14	0.06	0.05
24	81.0	76.7	16.2	20.2	2.61	2.89	0.07	0.08
27	79.5	76.7	19.8	20.5	0.44	0.49	0.01	0.005
28	86.9	87.4	12.2	10.6	0.49	0.58	0.04	0.03
29	72.4	73.0	25.9	24.6	1.22	1.46	0.16	0.17
30	88.3	88.2	10.7	10.0	0.52	0.79	0.08	0.07
31	79.0	79.7	19.7	18.1	0.89	1.36	0.23	0.22
32	81.1	82.2	18.0	16.2	0.53	0.76	0.04	0.06

<sup>a</sup>See Table 2 for leaching conditions.

than the uranium losses. Thorium was washed from the residues about as rapidly as the uranium; usually, the amount found in the third wash was nearly negligible compared with the loss to the residue.

It should be noted that the removal of the leachate and wash solutions by vacuum filtration was slow because of the fineness of the crushed graphite fuel. Filtration was especially difficult after leaching with 90%  $\text{HNO}_3$  since the latter apparently caused a further reduction in particle size.

#### 4.1.2 Uranium and Thorium Recoveries in Single Leaches at Temperatures Below the Boiling Point

Five-hour leaches of sample PB-2 were made to determine the effects of leaching temperature, nitric acid concentration, and presence of HF in the leachant on the recovery of uranium and thorium. Leaching with either 13  $\text{M}$   $\text{HNO}_3$  or 13  $\text{M}$   $\text{HNO}_3$ --0.05  $\text{M}$  HF at 25°C resulted in uranium and thorium losses of about 13 to 15% (Table 5). Leaching with 13 to 16  $\text{M}$   $\text{HNO}_3$  at 50°C, or with 2 to 16  $\text{M}$   $\text{HNO}_3$  at 75°C, resulted in losses that were as low as those obtained with boiling reagents. The nitric acid concentration had practically no effect on losses at 75°C; however, at 50°C, uranium and thorium losses decreased from about 36% to 0.3 to 0.4% as the nitric acid concentration was increased from 2 to 15.8  $\text{M}$ .

Leaching at 50 and 75°C with nitric acid solutions that were 0.05  $\text{M}$  in HF produced surprising results. The uranium losses after leaching at 50°C with solutions that were 5 to 16  $\text{M}$  in  $\text{HNO}_3$ , or at 75°C with solutions that were 2 to 16  $\text{M}$  in  $\text{HNO}_3$ , were generally lower than those obtained with solutions that did not contain HF (Table 5). However, at both 50 and 75°C, the thorium losses were significantly higher than those obtained with nitric acid alone and increased at each temperature with increasing nitric acid concentration of the leachant (Table 5). In general, thorium losses decreased with increasing temperature, other conditions being the same.

#### 4.1.3 Uranium and Thorium Recoveries After Multiple Leaches

Multiple leaching of roll-crushed Peach Bottom fuel was investigated because adequate uranium and thorium recoveries generally were not achieved in a single leach. The results, summarized below, showed that two leaches accompanied by suitable water washes resulted in uranium and thorium

Table 5. Uranium and Thorium Recoveries From Crushed Peach Bottom Fuel After a Single 5-hr Leach at Temperatures Below the Boiling Point

2.5-g samples of PB-2 leached with 18 ml of reagent; then residue washed with three volumes of cold water

Experiment	Conc. in Leachant (M)		Temperature (°C)	Losses to Residue (%)	
	HNO <sub>3</sub>	HF		Uranium	Thorium
39	13.0	0	25	15.2	14.3
40	2.0	0	50	36.1	36.5
41	5.0	0	50	5.23	5.10
42	13.0	0	50	0.37	0.74
43	15.8	0	50	0.33	0.45
44	2.0	0	75	0.52	1.34
45	5.0	0	75	0.34	0.56
46	13.0	0	75	0.27	0.49
47	15.8	0	75	0.24	0.19
48	13.0	0.05	25	12.9	13.5
49	2.0	0.05	50	1.38	2.77
50	5.0	0.05	50	0.30	1.05
51	13.0	0.05	50	0.17	4.06
52	15.8	0.05	50	0.074	7.20
53	2.0	0.05	75	0.26	1.85
54	5.0	0.05	75	0.12	4.94
55	13.0	0.05	75	0.09	4.49
56	15.8	0.05	75	0.18	5.13

recoveries of about 99.9%. Two different procedures were used: (A) The fuel sample was leached for 5 hr, and the resulting solution was removed by vacuum filtration; then the residue was leached again for 5 hr with an equal volume of fresh reagent, the solution was removed by vacuum filtration, and the final residue was washed with three volumes of water. Each wash solution was removed by vacuum filtration. (B) The fuel sample was

leached for 5 hr, and the solution was removed; then the residue was washed with two volumes of water, each solution being recovered by vacuum filtration. The residue was leached again with an equal volume of fresh reagent and the solution was removed; finally, the residue was washed with three volumes of water in the manner just described.

The results obtained (Table 6) showed that two leaches at 25°C did not produce the desired uranium and thorium recoveries. In two experiments at 50°C, the maximum losses of uranium and thorium were 0.1 and 0.28%, respectively, using 13 M HNO<sub>3</sub> as the leachant. With boiling 3 to 5 M HNO<sub>3</sub>, uranium and thorium losses were 0.2 to 0.4%, irrespective of the leaching procedure employed. Use of procedure B with boiling 13 M HNO<sub>3</sub> as the leachant generally resulted in uranium and thorium losses of less than 0.1%, and 0.12% or less, respectively. The presence of HF in the leachant had no apparent effect on the recoveries. The use of procedure A with either boiling 13 M HNO<sub>3</sub> or 13 M HNO<sub>3</sub>--0.05 M HF as leachant resulted in slightly higher (0.12 to 0.15%) uranium losses and slightly lower (0.025 to 0.044%) thorium losses than those obtained with procedure B.

The above results show that adequate uranium and thorium recoveries from crushed, unirradiated Peach Bottom fuel can be achieved in two successive leaches with boiling 13 M HNO<sub>3</sub> and that washing with water between leaches (procedure B) helps achieve higher uranium recoveries.

#### 4.1.4 Carbon, as Soluble Organic Compounds, in Leach Solutions

As the discussions in Sects. 2.2 and 2.3 indicated, soluble organic compounds are expected to be present in the product solutions from a grind-leach process for graphite-base fuels. These organic compounds are produced by the reaction of nitric acid with both graphite (matrix and particle coatings) and Th-U carbide fuel particles. In the experiments discussed in this report, the amount of carbon in leach solutions, from all sources, was determined by a wet oxidation method.<sup>35</sup> The amount of graphite (matrix and particle coatings) oxidized was assumed to be the difference between the amount of graphite present initially in the fuel (calculated from the fuel composition) and the weight of the dry residue after leaching. The values thus obtained should be slightly low since the residues were not pure graphite. Each residue contained small

Table 6. Uranium and Thorium Losses to Residue After Two  
Leaches of Roll-Crushed Peach Bottom Fuel

Sample PB-2 used in all experiments; duration of each leach, 5 hr

Experiment	Concentration in Leachant (M)		Procedure	Temperature (°C)	Volume of Leachant per gram of fuel (ml/g) <sup>a</sup>	Loss to Residue (%)	
	HNO <sub>3</sub>	HF				Uranium	Thorium
57	13	0	A <sup>b</sup>	25	7.2	0.45	0.18
58	13	0	A	25	7.2	0.33	0.037
59	13	0.05	A	25	7.2	0.86	13.0
60	13	0.05	A	25	7.2	0.73	2.23
61	13	0	A	50	7.2	0.002	0.28
62	3	0	A	bp <sup>c</sup>	3.6	0.18	0.41
63	13	0	A	bp	3.6	0.12	0.025
64	13	0.05	A	bp	3.6	0.15	0.044
65	21.5	0	A	bp	3.6	0.14	0.65
66	21.5	0	A	bp	3.6	0.12	0.81
67	13	0	B <sup>d</sup>	50	7.2	0.10	0.13
68	3	0	B	bp	3.6	0.21	0.28
69	5	0	B	bp	3.6	0.12	0.17
70	5	0	B	bp	3.6	0.24	0.30
71	5	0.05	B	bp	3.6	0.009	0.07
72	13	0	B	bp	3.6	0.057	0.12
73	13	0	B	bp	3.6	0.006	0.07
74	13	0	B	bp	3.6	0.084	0.07
75	13	0.05	B	bp	3.6	0.06	0.05
76	13	0.05	B	bp	3.6	0.009	0.07

<sup>a</sup> The same volume of reagent was used in each leach.

<sup>b</sup> Procedure A consisted in leaching of the sample, removing the solution by vacuum filtration, leaching the sample again with an equal volume of fresh reagent, recovering the solution by vacuum filtration, and finally, washing the residue with three volumes of water.

<sup>c</sup> Boiling point of the reagent.

<sup>d</sup> Procedure B consisted in leaching the sample, removing the solution by vacuum filtration, washing the residue with two volumes of water; then, the procedure was repeated, except that the final residue was washed with three volumes of water.

quantities of uranium and thorium and probably also a small amount of sorbed water.

~~No oxidation of graphite (matrix and particle coatings) was detectable in experiments where crushed Peach Bottom fuel was leached for 5 hr with 13 M HNO<sub>3</sub> at 25°C, or with 2 and 5 M HNO<sub>3</sub> at the boiling point (Table 7).~~ Practically the same results were obtained under the same conditions with nitric acid solutions that were 0.05 M in Al(NO<sub>3</sub>)<sub>3</sub> and/or HF. However, organic compounds, presumably produced by reaction of the ThC<sub>2</sub>-UC<sub>2</sub> particles with nitric acid, were found in the leach solutions. The amount of carbon found in solution after leaching under the conditions noted above corresponded to between 12 and 50% of the carbide carbon and 0.24 and 1.1% of the total carbon in the fuel (Table 7).

Measurable oxidation of the graphite occurred when crushed Peach Bottom and UHTREX fuel samples were leached with boiling solutions that were 13 to 21.5 M in HNO<sub>3</sub>. With boiling 13 M HNO<sub>3</sub> solutions, as much as 2.6% of the graphite was oxidized in 5 hr (Table 7). Leaching for 24 hr increased this amount to 5 to 12%. As much as 5.5% and 9.4% of the graphite were oxidized in 5-hr leaches with boiling 15.8 and 21.5 M HNO<sub>3</sub> respectively. Despite the relatively large fraction of graphite oxidized, usually less than 1% of the original carbon in the fuel was found in the leach solution as soluble species; this indicates that the main oxidation products were CO<sub>2</sub> and CO.

As expected, more graphite was oxidized in two leaches than in one. Up to 3.8% of the graphite was oxidized in two 5-hr leaches of crushed Peach Bottom fuel at room temperature (Table 8). In experiments where crushed Peach Bottom or UHTREX fuel samples were leached twice for 5 hr with boiling solutions, the amount of graphite oxidized increased from about 1 to 17% as the HNO<sub>3</sub> concentration in the leachant was increased from 3 to 21.5 M. However, the amount of carbon found in the leach solutions still generally corresponded to less than 1% of the carbon in the fuel.

The above results show that, when crushed graphite-base fuels are leached, significant amounts of soluble organic compounds will be present in the product solutions. Since measurable oxidation of the graphite matrix itself occurs, the presence of organic compounds is not dependent

Table 7. Carbon Present in Leach Solutions As a Result of Oxidation of Graphite and Dissolution of Carbide Particles After Single Leach of Crushed Fuel

Expt.	Fuel Sample (PB-)	Conc. in Leachant (M)			Leach Conditions		Graphite Oxidized <sup>a</sup> (%)	Carbon in Leach Solution	
		HNO <sub>3</sub>	HF	Al(NO <sub>3</sub> ) <sub>3</sub>	Temp. (°C)	Time (hr)		% of Total	% of Carbide Carbon <sup>b</sup>
39	2	13	0	0	25	5	c	0.27	14
48	2	13	0.05	0	25 <sup>d</sup>	5	c	0.24	12
1	2	2	0	0	bp	5	c	0.56	24
3	2	5	0	0	bp	5	c	0.71	31
5	2	13	0	0	bp	5	0	0.30	13
6	3	13	0	0	bp	5	c	0.35	30
7	4	13	0	0	bp	5	2.0	0.32	13
8	2	13	0	0	bp	20	6.0	1.4	73
9	2	13	0	0	bp	24	5.0	0.84	43
79	UHTREX	13	0	0	bp	5	2.6	0.39	42
10	3	15.8	0	0	bp	5	5.5	0.06	5
11	2	15.8	0	0	bp	5	2.8	0.06	3
13	2	21.5	0	0	bp	5	9.4	1.6	87
14	2	2	0.05	0	bp	5	c	1.1	50
16	2	5	0.05	0	bp	5	c	0.71	32
20	2	13	0.05	0	bp	5	2.6	0.48	22
21	3	13	0.05	0	bp	5	c	0.24	22
25	2	13	0.05	0	bp	20	12	1.3	64
26	2	13	0.05	0	bp	24	5.5	0.88	46
27	2	2	0.05	0.05	bp	5	0.29	0.57	27
29	2	5	0.05	0.05	bp	5	c	0.79	35
31	2	13	0.05	0.05	bp	5	0.79	0.36	16

<sup>a</sup>Based on initial composition of fuel and the assumption that the residue after leaching was pure graphite.

<sup>b</sup>Calculated on the assumption that uranium and thorium were present initially as UC<sub>2</sub> and ThC<sub>2</sub>.

<sup>c</sup>Weight of residue was greater than the calculated initial weight of graphite.

<sup>d</sup>Boiling point of the leachant.

Table 8. Carbon Found in Leach Solutions As a Result of Oxidation of Graphite and Dissolution of Carbide Particles in Two 5-hr Leaches of Crushed Fuel

Expt.	Fuel Sample (PB-)	Conc. in Leachant (M)		Temp. (°C)	Leach Procedure <sup>a</sup>	Graphite Oxidized <sup>b</sup> (%)	Carbon in Leach Solutions	
		HNO <sub>3</sub>	HF				% of Total	% of Carbide Carbon <sup>c</sup>
57	2	13	0	25	A	3.8	0.87	47
58	2	13	0	25	A	3.1	0.09	5
59	2	13	0.05	25	A	0.05	0.74	40
60	2	13	0.05	25	A	1.4	0.20	12
61	2	13	0	50 <sup>d</sup>	A	2.5	0.22	12
62	2	3	0	bp	A	1.1	0.40	20
80	UHTREX	5	0	bp	A	2.7	0.11	13
63	2	13	0	bp	A	3.9	0.66	35
81	UHTREX	13	0	bp	A	5.8	0.31	29
64	2	13	0.05	bp	A	4.3	0.74	40
65	2	21.5	0	bp	A	14	1.1	60
66	2	21.5	0	bp	A	17	1.5	79
67	2	13	0	50	B	2.0	0.64	33
68	2	3	0	bp	B	5.3	0.10	6
69	2	5	0	bp	B	5.1	0.04	2
70	2	5	0	bp	B	1.5	0.46	24
71	2	5	0.05	bp	B	1.7	0.33	17
72	2	13	0	bp	B	4.6	1.2	64
73	2	13	0	bp	B	3.0	0.36	19
74	2	13	0	bp	B	6.5	0.09	5
75	2	13	0.05	bp	B	3.3	1.2	65
76	2	13	0.05	bp	B	3.2	0.41	21

<sup>a</sup> See Table 6 for description of leaching procedures employed.

<sup>b</sup> Based on initial composition of the fuel and the assumption that the residue after leaching was pure graphite.

<sup>c</sup> Calculated on the assumption that uranium and thorium were present initially as UC<sub>2</sub> and ThC<sub>2</sub>.

<sup>d</sup> Boiling point of the leachant.

on the type of fuel particle (carbide or oxide). Preliminary experiments reported in Sect. 4.4 indicate that some oxidation of particle coatings, especially those of porous carbon, will also occur. Thus, it appears that organic compounds will always be present in the leach solutions, regardless of the type of fuel particle and despite separation of the carbon-coated fuel particles from the graphite matrix before leaching.

#### 4.2 Leaching of UHTREX Fuel

A few leaching tests were made with prototype UHTREX fuel<sup>20</sup> that had been roll-crushed to -100 mesh (Sect. 3.1, Table 1). Round-bottom flasks were used as reaction vessels, and vacuum filtration was used to recover solutions.

In three experiments, samples of crushed fuel were leached for 5 hr with the amount of boiling nitric acid sufficient to produce solutions 0.2 M in uranium (if all the  $UC_2$  dissolved). After leaching, the residues were washed with three volumes of water. As the  $HNO_3$  concentration was increased from 2 to 13 M (Table 9), uranium losses to the residues decreased from 29 to 0.9% and the amount of the total carbon from the fuel found in solution increased from 0.03 to about 0.4%. Carbon, as soluble organic compounds, was present in each product solution.

Adequate uranium recovery was not achieved even when the fuel was leached three times with boiling 13 M  $HNO_3$ . After two 5-hr leaches, the uranium loss to the residue was 0.4%; greater than 0.2% of the uranium still remained in the residue after three leaches (Table 9). About 6% of the graphite (matrix plus particle coatings) in the fuel was oxidized in two or three leaches; however, less than 0.6% of the total carbon from the fuel was found in the leach solutions.

The low uranium recoveries obtained with UHTREX fuel were surprising in light of the results obtained with Peach Bottom fuel (Sect. 4.1). The difference in behavior may be attributed to the porous carbon surrounding the  $UC_2$  particles in the UHTREX fuel; in contrast, the  $ThC_2-UC_2$  particles in the Peach Bottom fuel were surrounded only by pyrocarbon. It is conceivable that some  $UC_2$  diffused into the porous carbon during manufacture of the UHTREX fuel and that this carbide was much less accessible to attack by nitric acid than the  $UC_2$  constituting the main part of the fuel particle.

Table 9. Uranium Losses to Residue After Leaching  
of Roll-Crushed UHTREX Fuel with Boiling Nitric Acid

Expt.	HNO <sub>3</sub> Conc. (M)	Leach Method <sup>a</sup>	Uranium Loss to Residue (%)	Graphite, Oxidized <sup>b</sup> (%)	Carbon in Leach Solutions	
					% of Total	% of Carbide Carbon <sup>c</sup>
77	2	I	28.6	--	0.03	4.4
78	5	I	15.1	--	0.11	14
79	13	I	0.93	--	0.38	42
80	5	II	0.78	--	0.11	13
81	13	II	0.40	6	0.31	29
82	13	III	0.24	6	0.58	58

<sup>a</sup> Method I consisted of leaching a 5-g fuel sample for 5 hr with 10 ml of acid. After leaching, the residue was washed with three 10-ml portions of water.

Method II consisted of leaching a 5-g fuel sample for 5 hr with 10 ml of acid, removing the leach solution by vacuum filtration, and leaching the residue again for 5 hr with 10 ml of fresh acid before water-washing the residue.

Method III consisted of three acid leaches; only the last leach was followed by a water wash.

<sup>b</sup> Based on initial composition of the fuel and the assumption that the residue after leaching was pure graphite.

<sup>c</sup> Calculated on the assumption that uranium was present initially as UC<sub>2</sub>.

#### 4.3 Washing of Leached Fuel: Column Experiments

##### 4.3.1 Permeability of Graphite Residues to Water and Nitric Acid

As outlined in Sect. 3.2, column experiments with leached fuel samples were conducted under various pressure gradients to determine the permeability of graphite residues to both leach and wash solutions and to estimate the minimum amounts of various wash solutions required to effect practically quantitative removal of solubilized uranium and thorium from a bed of leached fuel. The results of these experiments should be used only as first approximations because of the small scale of the equipment used (a 1-cm-ID column, Fig. 2). More reliable measurements have been made in larger equipment.<sup>36,37</sup>

These latter studies resulted in correlation of the permeability of typical leached fuel beds with the pressure gradient across the bed, the viscosity of the solution flowing through the bed, and the temperature.

In most of the experiments discussed below, 2.5-g portions of sample PB-2 were leached for 5 hr with 10 ml of either boiling 13 M HNO<sub>3</sub> or boiling 13 M HNO<sub>3</sub>--0.05 M HF. Transfer of the resultant solution and residue to the column (see Sect. 3.2) gave a settled graphite bed about 3.5 cm high, with a cross-sectional area of about 0.8 cm<sup>2</sup>. The leach solution was removed, and the bed was washed using pressure filtration. A different pressure gradient — pressure drop across the graphite bed (cm Hg) divided by the bed height (cm) — was used in each experiment. At each pressure gradient, the permeability of the graphite bed to the leach and wash solutions was determined by measuring the respective solution flow rates. At the beginning of each run, leach solution flowed from the column at a nearly constant rate. As wash solution began to flow through the column, an abrupt change in flow rate occurred if the composition of the wash solution was markedly different than that of the leach solution. After the change, when only wash solution was flowing through the column, the flow rate again became practically constant.

As expected, the permeability of the bed varied with pressure gradient, temperature, the composition of the solution, and, apparently, the particle-size distribution of the crushed graphite. For example, the rate at which leach solution was forced from the column at 25°C increased from about 0.4 to about 3 ml min<sup>-1</sup> cm<sup>-2</sup> as the pressure gradient across the column was increased from 1 to about 25 cm Hg per centimeter of bed (Table 10 and Fig. 3). The permeability of the graphite to 10 M HNO<sub>3</sub> at 25°C was about the same as its permeability to leach solutions. This was expected since the leach solutions were similar in composition (about 11 M in HNO<sub>3</sub> and only about 0.2 M in U + Th). The graphite was much more permeable to water than to nitric acid, presumably because of the lower viscosity of water.<sup>36,37</sup> Under all pressure gradients used at 25°C, water usually was forced from the column at rates that were slightly less than twice those achieved with nitric acid (Fig. 3). Increasing the temperature from 25 to 75°C increased the permeability by about a factor of 3, other conditions being the same.

Table 10. Permeability of Crushed Graphite Fuel to  
Water and Nitric Acid in a 1-cm-ID Column

Sample used: PB-2; initial bed height: about 3.5 cm

Expt.	Wash	Temp. (°C)	$\Delta P/h$ (cm of Hg per cm of bed)		Avg. Flow Rate (ml min <sup>-1</sup> cm <sup>-2</sup> )	
			Leach Solution Removal	Wash	Leach Solution Removal	Wash
83 <sup>a,b</sup>	Water	25	0.70	0.72	0.36	0.59
84 <sup>b</sup>	Water	25	0.76	0.76	0.45	0.86
85 <sup>b</sup>	Water	25	1.57	1.69	0.72	1.21
86 <sup>c</sup>	Water	25	2.14	2.50	1.68	2.85
87 <sup>c</sup>	Water	75	2.14	2.42	3.08	4.32
88 <sup>b,d</sup>	Water	25	5.16	5.44	0.26	1.81
89 <sup>b</sup>	Water	25	5.58	5.78	1.28	2.57
90 <sup>c,e</sup>	Water	25	10.8	14.6	0.52	0.91
91 <sup>b</sup>	Water	25	11.0	12.1	3.04	4.99
92 <sup>b</sup>	Water	25	22.2	30.3	3.40	7.58
93 <sup>c</sup>	10 <u>M</u> HNO <sub>3</sub>	25	2.08	2.42	2.80	3.34
94 <sup>c</sup>	10 <u>M</u> HNO <sub>3</sub>	25	2.08	2.42	---	1.78
95 <sup>c</sup>	10 <u>M</u> HNO <sub>3</sub>	25	2.14	2.42	1.05	1.26
96 <sup>b</sup>	10 <u>M</u> HNO <sub>3</sub>	25	11.6	12.3	2.38	3.0
97 <sup>b</sup>	10 <u>M</u> HNO <sub>3</sub>	25	23.8	25.7	3.51	4.08
98 <sup>c</sup>	10 <u>M</u> HNO <sub>3</sub>	50	2.50	2.78	1.86	2.01
99 <sup>c</sup>	10 <u>M</u> HNO <sub>3</sub>	75	2.08	2.42	3.10	3.20
100 <sup>c</sup>	10 <u>M</u> HNO <sub>3</sub>	75	2.08	2.42	2.87	3.01
101 <sup>c</sup>	10 <u>M</u> HNO <sub>3</sub>	75	12.2	14.1	---	17.7

<sup>a</sup> Assume that  $\Delta P =$  hydrostatic pressure of water in the reservoir plus hydrostatic pressure of liquid in column. Further assume that the hydrostatic pressure in the column is equal to that of a column of water with a height equal to that of the bed height plus the height of liquid above the bed. Then,  $\Delta P = h \rho$ .

<sup>b</sup> The fuel was leached with boiling 13 M HNO<sub>3</sub>--0.05 M HF.

<sup>c</sup> The fuel was leached with boiling 13 M HNO<sub>3</sub>.

<sup>d</sup> The initial bed height in this experiment was about 16 cm.

<sup>e</sup> Fuel for this experiment was powdered in a Waring blender (sample WB-1).

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The permeability of leached fuel that initially had been pulverized in a Waring blender (sample WB-1) was much lower than that of material that had been crushed in a roll-crusher (Table 10, experiments 90 and 91). This

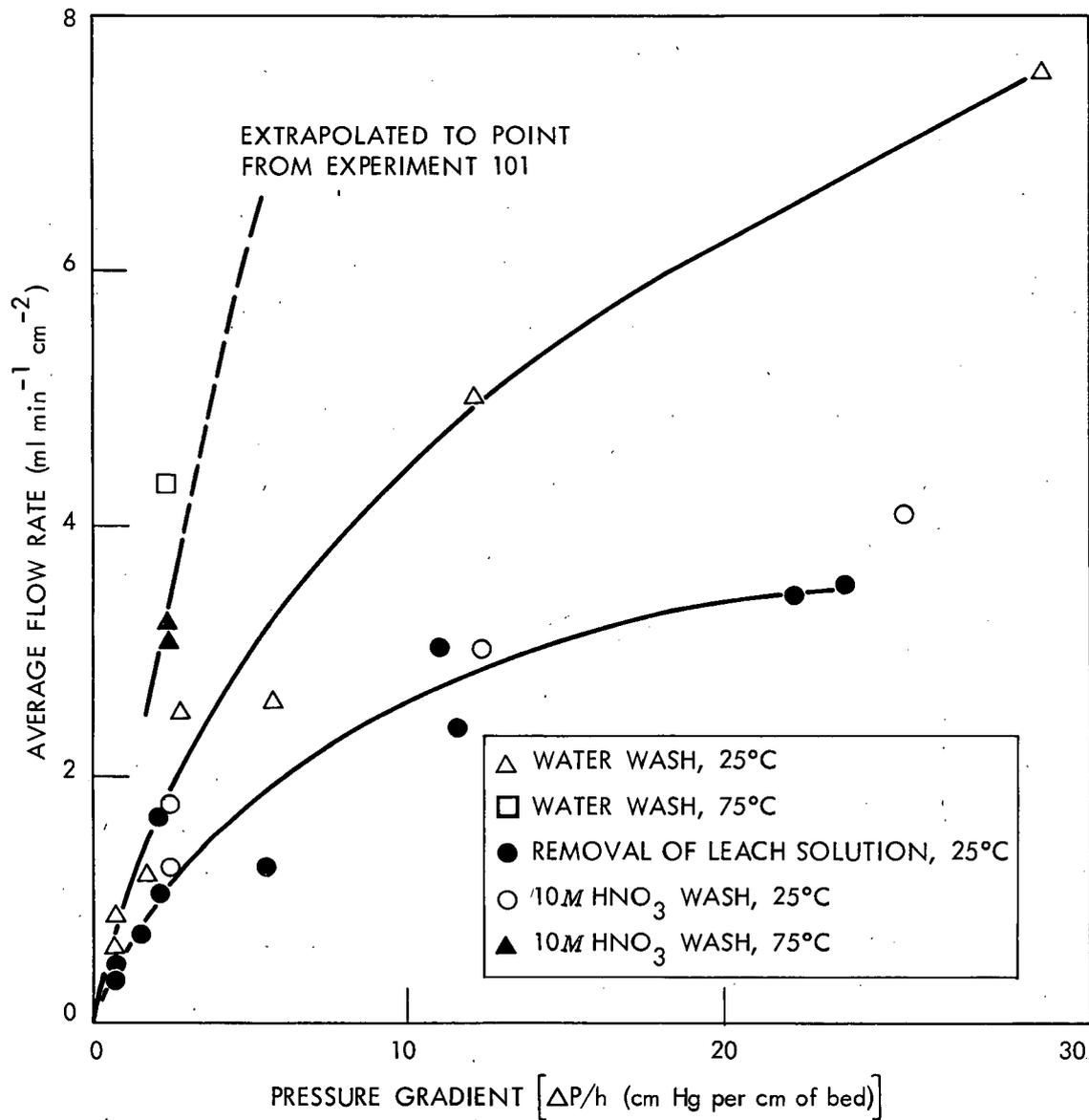


Fig. 3. Permeability of Leached PB-2 Samples as Determined from Experiments in a 1-cm-ID Column. Bed height in each experiment, about 3.5 cm; bed volume in each experiment, about 3 ml.

behavior was not unexpected because the mean particle size of sample WB-1 was about half that of the roll-crushed PB-2 sample (Table 1).

It was expected that the flow rate at a given pressure gradient would be nearly constant for all bed heights, assuming that compression of the beds did not occur. However, this was not the case (experiments 88 and 89, Table 10). No noticeable bed compression was noted in experiment 88, where the bed height was 16 cm; on the other hand, the flow rate was markedly lower than that obtained in experiment 89, in which a 3.5-cm bed was used. The pressure gradients in the two experiments were about the same.

#### 4.3.2 Removal of Uranium and Thorium from the Column

In each column experiment, a total of about 26 bed volumes of solution was passed through the graphite bed. The thorium and uranium concentrations in the effluent solution remained nearly constant until three to four bed volumes of solution had been eluted from the column; then, their concentrations in the effluent solution decreased markedly (Fig. 4). (Three bed volumes corresponded roughly to the volume of acid used to leach the fuel.) When the bed was washed with water, only 1 to 2% of the uranium and thorium remained in the graphite bed after four bed volumes of effluent solution had been collected (Fig. 5). Passage of another two to four bed volumes of water through the column resulted in nearly quantitative removal of the solubilized uranium and thorium. Only traces of thorium and uranium were removed by washing with an additional 10 to 15 bed volumes of water (Fig. 5). Uranium and thorium were eluted at practically the same rate, indicating that neither element was preferentially sorbed by the graphite. In experiments where the bed was washed with water, uranium and thorium losses to the residue averaged about 0.3 and 0.5% respectively. Using hot (75°C) water instead of cold water did not appear to be advantageous, except that higher flow rates could be attained at higher temperatures. Uranium and thorium losses to the residue after washing with water at 75°C were about the same as those obtained after washing at 25°C. These data indicate that a leach solution would be diluted to about half its original concentration by washing the graphite residue with water, and that practically all the uranium and thorium solubilized during the leach could be quantitatively recovered.

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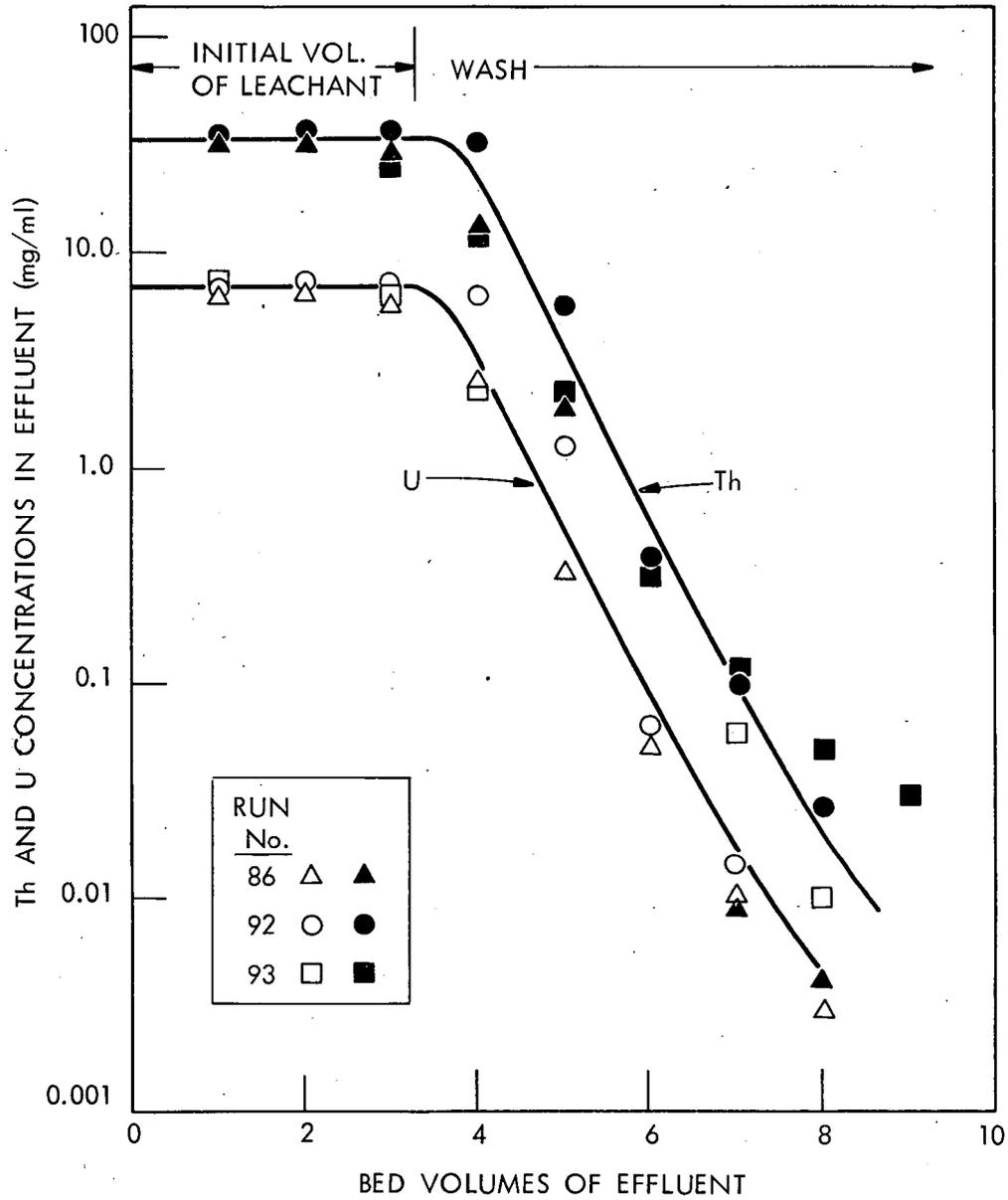


Fig. 4. Typical Elution Curves for Thorium and Uranium from Column Washing Experiments.

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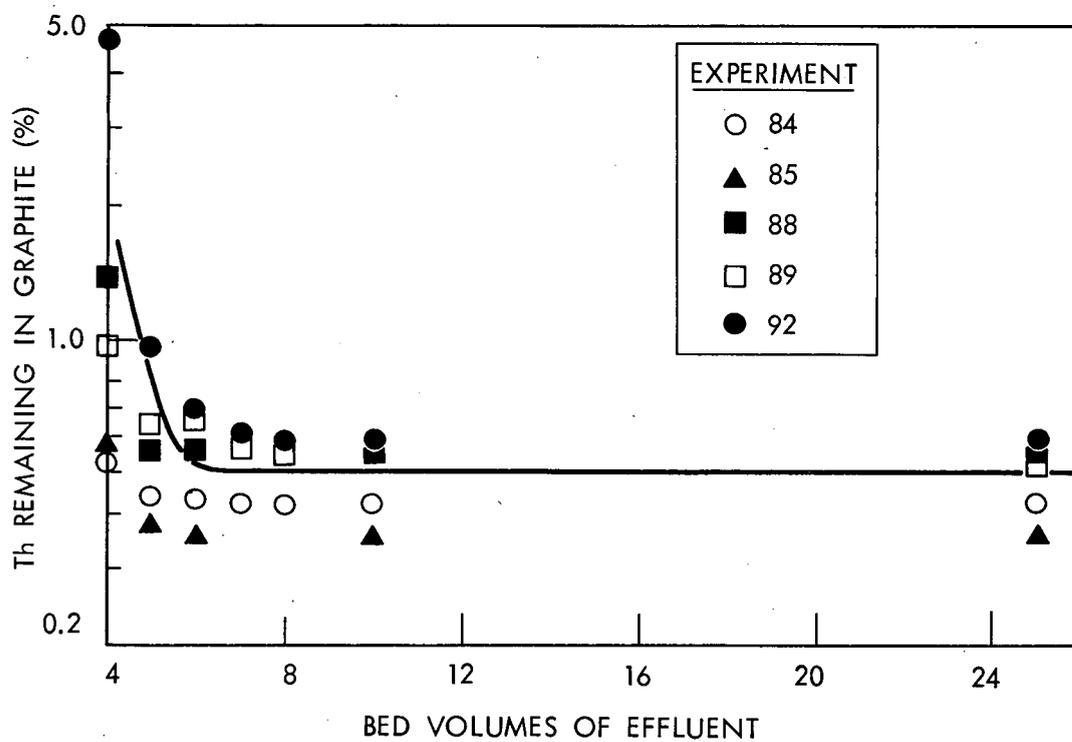
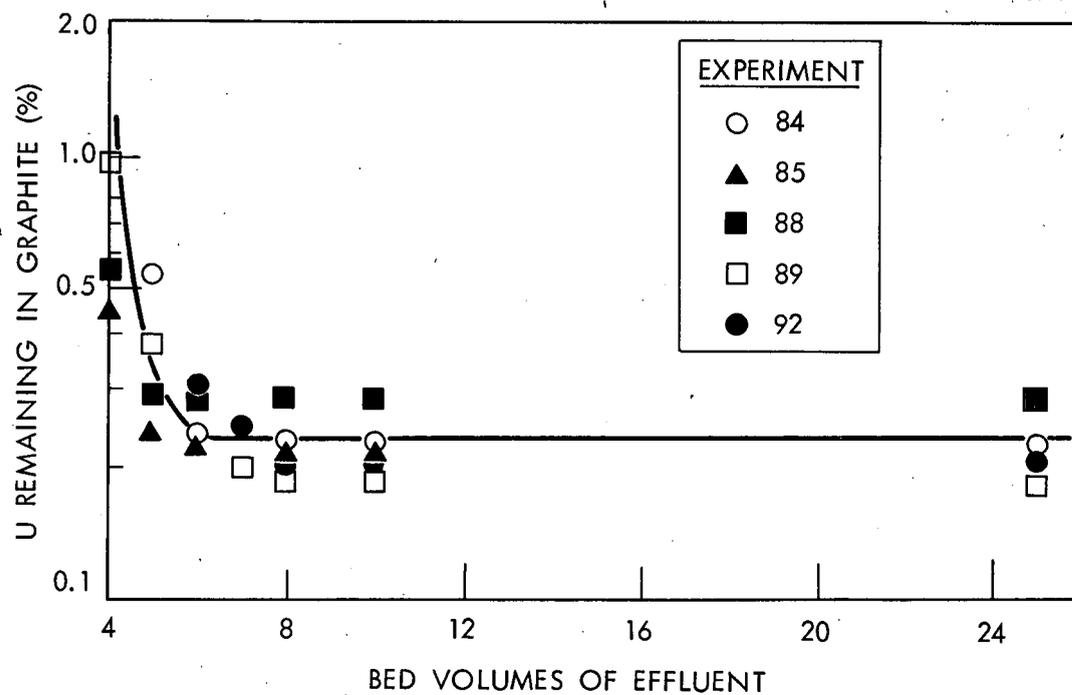


Fig. 5. Uranium and Thorium Retention in Graphite Residue During Water Washing of Leached PB-2 Samples in Column Experiments.

Removal of the leach solution (about three bed volumes) and washing of the bed with two to four bed volumes of 10 M  $\text{HNO}_3$  at 25°C gave results similar to those obtained with water (Figs. 6 and 7). Washing with an additional 10 to 15 bed volumes of 10 M  $\text{HNO}_3$  at 25°C had little further effect on the amount of uranium removed from the bed (Fig. 6) but was beneficial in removing more of the thorium (Fig. 7). After passage of about 20 bed volumes of 10 M  $\text{HNO}_3$  through the column, less than 0.1% of the thorium from the fuel remained with the graphite residue (Fig. 7).

Washing with 10 M  $\text{HNO}_3$  at 50 and 75°C gave markedly different and surprising results. During elution of the first three to four bed volumes of solution (roughly the volume of the leachant), the uranium and thorium recoveries amounted to only about 95% (Figs. 6 and 7). Furthermore, washing with two to four bed volumes of hot acid was less effective than washing with the same volume of hot or cold water or with 10 M  $\text{HNO}_3$  at 25°C. With water or 10 M  $\text{HNO}_3$  at 25°C, the amounts of uranium and thorium remaining in the bed generally were about 0.3 and 0.5%, respectively, after a total of six to eight bed volumes of effluent solution had been collected. When the bed was washed with 10 M  $\text{HNO}_3$  at 50 or 75°C (other conditions being equal), 1 to 9% of each was retained, the maximum retention occurring at 75°C (Figs. 6 and 7). No explanation for this behavior is readily apparent. Despite the inefficient removal of uranium and thorium with three to four bed volumes of hot 10 M  $\text{HNO}_3$  wash, final uranium and thorium losses that were somewhat lower than those achieved by water washing were obtained by washing the bed with a total of about 20 bed volumes of hot 10 M  $\text{HNO}_3$  (Figs. 6 and 7).

#### 4.4 Leaching of Crushed Carbon-Coated $\text{ThO}_2$ Particles

The use of carbon-coated  $\text{ThO}_2$ - $\text{UO}_2$  and  $\text{ThO}_2$  microspheres as fissile and fertile particles, respectively, is currently receiving study in connection with graphite-base fuels for advanced high-temperature, gas-cooled reactors. Consequently, preliminary leaching experiments were made to determine the effect, if any, of the carbon coatings on the dissolution of the oxide in boiling 13 M  $\text{HNO}_3$ --0.05 M HF.

Samples of carbon-coated  $\text{ThO}_2$  particles (batches OR-520 and OR-521

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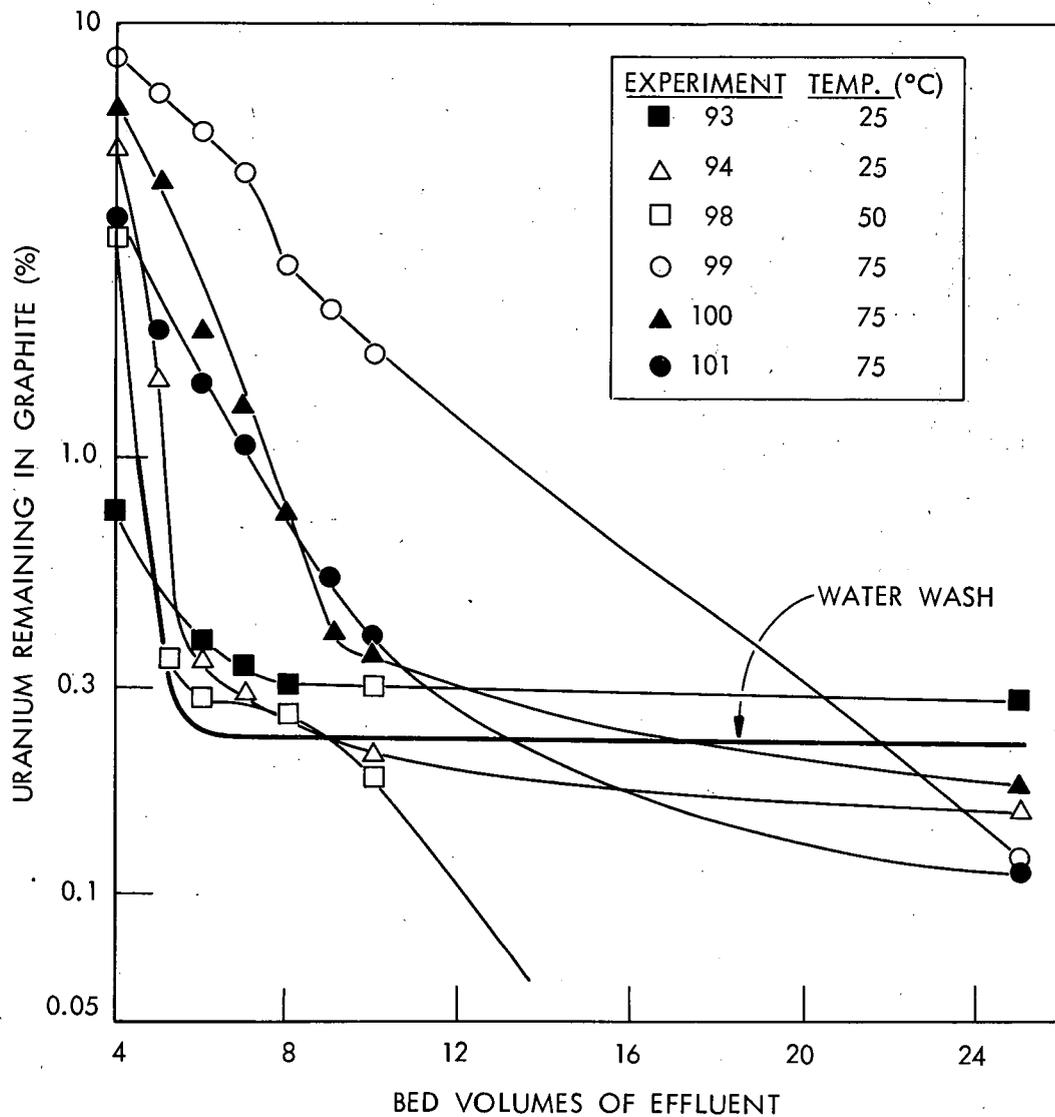


Fig. 6. Curves from Column Washing Experiments Showing That Elution of Uranium Was Slower with a Hot 10 M HNO<sub>3</sub> Wash than with Water.

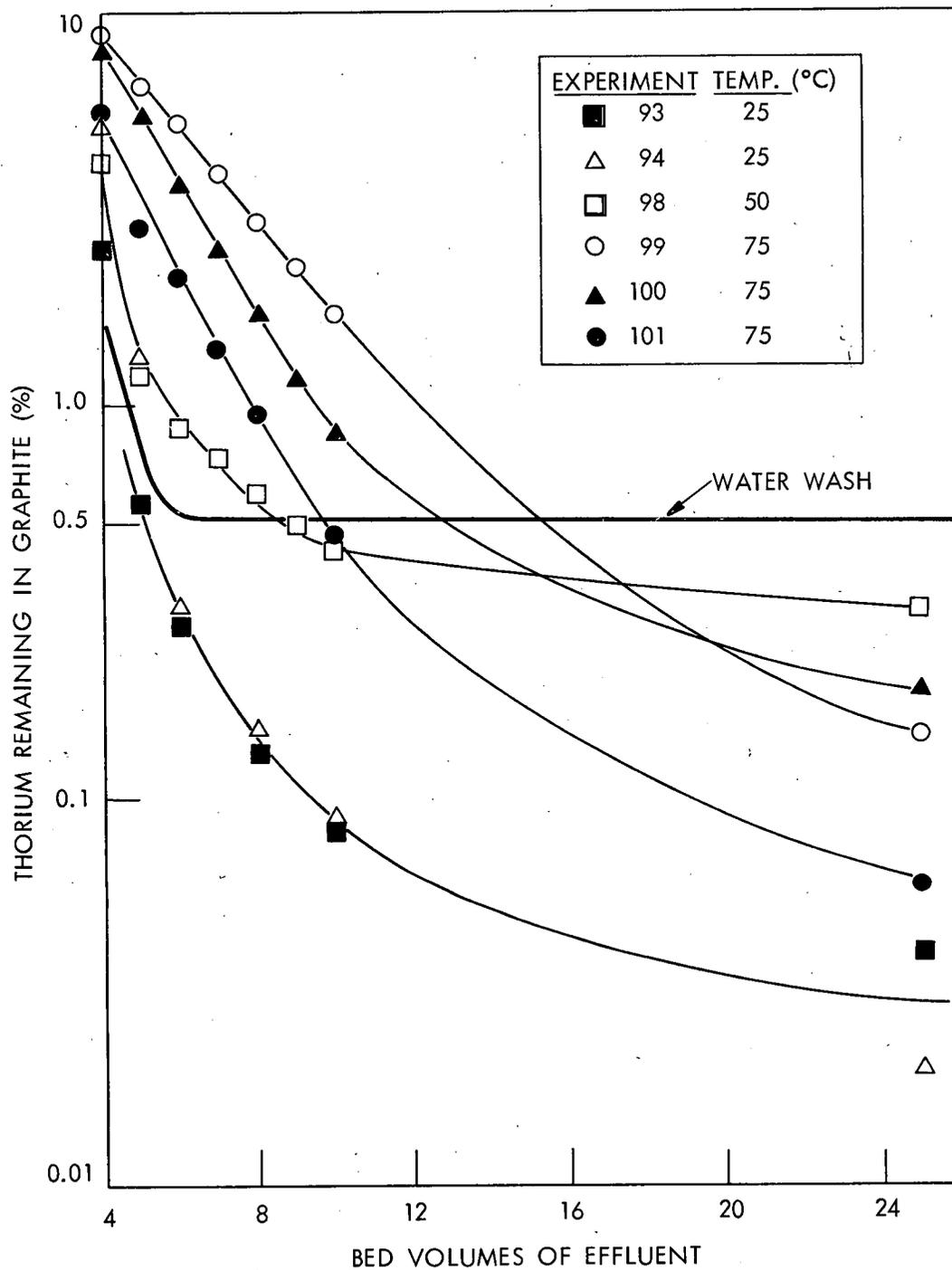


Fig. 7. Curves from Column Washing Experiments Showing That Elution of Thorium Was Slower with a Hot 10 M  $\text{HNO}_3$  Wash than with Water.

described in Sect. 3.1) were crushed to -100 mesh to ensure rupture of the particle coatings and then were leached for 5 hr with the amount of boiling 13 M  $\text{HNO}_3$ --0.05 M HF required to produce a solution 0.5 M in thorium (if all the  $\text{ThO}_2$  dissolved). In all cases, leaching of the  $\text{ThO}_2$  was practically quantitative; the thorium losses to the carbon residues were less than 0.01%. The solution resulting from the leaching of batch OR-520 (single carbon coating) was faint amber in color and contained only a trace of soluble organic compounds (0.1% of the original carbon). The solution obtained by leaching batch OR-521 (duplex coating) was red-brown in color, but analysis showed only 0.3% of the original carbon in solution. However, because of the differences in the carbon contents of the particles, the carbon concentration in this solution (about 0.2 mg/ml) was four times greater than that for batch OR-520.

These preliminary experiments indicate that significant quantities of soluble organic compounds can be expected in the leachate when graphite fuel containing oxide particles is leached, especially if one of the coatings is of porous carbon. If the coating is entirely of pyrocarbon, the bulk of the organic compounds in solution will probably come from the reaction of finely powdered graphite with nitric acid (see Sect. 4.1.4).

#### 4.5 Studies with Dragon Fuel Particles

Processing methods for Dragon reactor fuel<sup>34</sup> were evaluated cursorily, using the coated  $\text{ThC}_2$ - $\text{UC}_2$  and  $\text{UC-ZrC}$  particles described in Sect. 3.1. Experiments described below, with unirradiated particles, indicated that adequate uranium and thorium recoveries could be achieved either by a grind-leach method or by crushing the fuel particles fine enough to ensure rupture of coatings and then burning and leaching the resulting product.

The grind-leach method was not tested here with coated  $\text{ThC}_2$ - $\text{UC}_2$  particles since Dragon Project work<sup>15,16</sup> had shown that excellent uranium and thorium recoveries from unirradiated fuel could be achieved by leaching crushed fuel with nitric acid. However, a few experiments were conducted with carbon-coated  $\text{UC-ZrC}$  particles to determine whether HF was required in the leachant to effect adequate uranium recovery. The fuel particles (batch C-305, Sect. 3.1) were crushed to -140 mesh to ensure their rupture. Leaching of the crushed fuel for 7 hr with the amount of boiling 13 M  $\text{HNO}_3$

required to produce a solution about 0.1 M in uranium resulted in solubilization of about 99.2% of the uranium; however, most of the zirconium was precipitated as the oxide. Practically complete solubilization of both uranium and zirconium was achieved when the crushed fuel was leached for 7 hr with sufficient boiling 13 M  $\text{HNO}_3$ --0.1 M  $\text{HF}$  to give an overall fluorine:zirconium atom ratio of about 5. However, the leach solution under these conditions was only about 0.003 M in uranium.

A conventional burn-leach process,<sup>7,8</sup> in which the fuel is only rough-crushed prior to burning at 700 to 750°C, does not appear practicable for Dragon (or other) fuels that contain particles whose coatings contain SiC. The SiC reportedly<sup>16</sup> is not attacked by oxygen at temperatures below about 1500°C. The inertness of SiC to oxygen in the temperature range of 700 to 1500°C was confirmed in this Laboratory using particles from both batches C-522 and C-349 (Sect. 3.1) as test specimens.

A possible processing method for fuels containing SiC-coated particles consists in crushing the fuel fine enough to ensure rupture of the particle coatings, burning the crushed fuel to convert matrix graphite and pyrocarbon particle coatings to CO and CO<sub>2</sub> and to convert the carbide kernels to oxide, and, finally, leaching of the residue to recover uranium and thorium. Unirradiated fuel particles (pyrocarbon/silicon carbide/pyrocarbon triplex-coated ThC<sub>2</sub>-UC<sub>2</sub>; batch C-522, Sect. 3.1) were crushed to -100 mesh to ensure rupture of the particle coatings. The crushed particles were allowed to react with oxygen for 5 hr at 800°C. The weight of combustion residue was about that expected for the appropriate mixture of SiC, ThO<sub>2</sub>, and U<sub>3</sub>O<sub>8</sub>, indicating that the pyrocarbon coatings and the ThC<sub>2</sub>-UC<sub>2</sub> kernels had been oxidized. The combustion residue was then leached for 7 hr with the amount of boiling 13 M  $\text{HNO}_3$ --0.05 M  $\text{HF}$  required to produce a solution 0.2 M in U + Th. Analysis of the residue after leaching showed uranium and thorium losses of 0.05 and 0.11% respectively. About 0.1% of the silicon was found in the leach solution. The weight of the residue left after leaching corresponded closely to the weight of SiC in the sample. Chemical analysis confirmed that the residue was mainly SiC; the silicon concentration in the residue was 65%, compared with the 70% expected for pure SiC.

In other experiments, combustion of pyrocarbon-coated UC-ZrC particles (batch C-305) was complete in less than 7 hr at 750°C, yielding a ZrO<sub>2</sub>-U<sub>3</sub>O<sub>8</sub>

product. Leaching of this product for 7 hr with boiling 15.8 M  $\text{HNO}_3$  resulted in solubilization of only about 12% of the uranium and less than 1% of the zirconium. However, complete dissolution could be achieved in 7 hr in boiling 13 M  $\text{HNO}_3$ --0.1 M HF when the fluorine:zirconium atom ratio was about 5.

#### 4.6 Removal of Soluble Organic Compounds from Leach Solutions

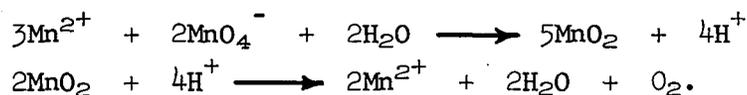
As mentioned in Sects. 2.2, 2.3, and 4.1.4, leaching of graphite-base fuels, especially those containing carbide fuel particles, results in the formation of significant quantities of soluble organic compounds. Earlier studies showed that these compounds could have a deleterious effect in subsequent solvent extraction processing. In experiments with solutions produced by dissolving either UC or UC-PuC in nitric acid, the organic compounds caused emulsions and increased settling times of the mixed phases during extraction of the uranium and plutonium with 20% TBP--80% kerosene<sup>26</sup> or with 30% TBP--70% Adakane.<sup>38</sup> Recently, studies were conducted<sup>39,40</sup> using the Thorex extraction process for recovering uranium and thorium from solutions produced by leaching crushed, unirradiated Peach Bottom fuel. Use of the conventional extraction process, in which the feed is acid-deficient, resulted in the formation of heavy emulsions. However, when the feed was made 2 to 5 M in  $\text{HNO}_3$ , good extraction behavior resulted. No emulsions formed, uranium and thorium were readily extracted into 30% TBP--70% dodecane solution, and the organic compounds remained in the aqueous phase. These experiments indicated that, by merely modifying existing solvent extraction processes, uranium and thorium can be separated from the undesirable organic compounds derived from carbides and graphite. However, prior to these studies, other methods for the removal or destruction of the organic compounds were studied briefly.

##### 4.6.1 Oxidation with $\text{KMnO}_4$

Earlier work<sup>38</sup> had indicated that oxidation with  $\text{KMnO}_4$  in acid solution would be a feasible method for destroying the soluble organic compounds in leach solutions. Since the addition of solid  $\text{KMnO}_4$  to the system did not seem practical for plant-scale use,  $\text{KMnO}_4$  was added to the system as part of

the wash solution after leaching the crushed fuel. Crushed Peach Bottom fuel samples (PB-2; Sect. 3.1) were leached for 5 hr with the volume of either boiling 13 or 15.8 M HNO<sub>3</sub> that was required to produce solutions 0.1 M in U + Th (if all the ThC<sub>2</sub>-UC<sub>2</sub> dissolved). The residues were then washed at 25°C with the appropriate amounts of water and 0.47 M KMnO<sub>4</sub> solution to produce final solutions that were 1.5 to 3 N in H<sup>+</sup> and 0.01 M in U + Th. The initial KMnO<sub>4</sub> concentration in the solutions was varied from 0.09 to about 0.4 M; this corresponded to initial KMnO<sub>4</sub>:carbon ratios in solution of approximately 5 to 20. Each solution was refluxed for 2 hr; then the MnO<sub>2</sub> formed was recovered by vacuum filtration and washed thoroughly.

In most instances, the amount of carbon, as soluble organic compounds, remaining in solution after the acid KMnO<sub>4</sub> oxidation corresponded to less than 0.2% of the total carbon in the fuel (Table 11). This amount of carbon is equivalent to about 10% of the carbide carbon, assuming that the uranium and thorium were present in the fuel as UC<sub>2</sub> and ThC<sub>2</sub> respectively. The amount of carbon in the final solutions was often below the limit of detection (about 3% of the carbide carbon). Since up to 50% of the carbide carbon was present in the leach solution prior to permanganate oxidation, the results indicate that at least 60% of the soluble organic compounds were oxidized under the conditions used. In every experiment except one, 85 to 92% of the manganese was converted to MnO<sub>2</sub>, regardless of the initial KMnO<sub>4</sub> concentration (Table 11); this can probably be attributed to the decomposition of KMnO<sub>4</sub>, which is catalyzed by MnO<sub>2</sub> in acid solution.<sup>41</sup> Apparently, a sequence of reactions similar to the following<sup>42</sup> occurs, starting with acid KMnO<sub>4</sub> solution and enough organic material to produce some MnO<sub>2</sub>:



Because of the autocatalytic decomposition of KMnO<sub>4</sub> under the conditions used, the overall stoichiometry of the reaction involving the organic compounds could not be determined. The results indicate, however, that relatively efficient oxidation can be achieved when the initial KMnO<sub>4</sub>:carbon mole ratio in solution is as low as about 5.

Table 11. Effectiveness of  $\text{KMnO}_4$  in Oxidizing Soluble Organic Compounds  
 After Leaching Sample PB-2 with Nitric Acid  
 Digestion time: 2 hr

Expt.	H <sup>+</sup> Conc. Before Digestion (N)	KMnO <sub>4</sub> Conc. Before Digestion (M)	Amount of Mn Converted to MnO <sub>2</sub> (%)	Carbon in Final Solution		Uranium and Thorium Losses (%)			
				% of Total Carbon	% of Carbide Carbon	To MnO <sub>2</sub> Cake		To Graphite Residue	
						U	Th	U	Th
102	2.2	0.12	71	0.36	18	0.01	1.40	0.37	1.05
103	~ 3	0.19	92	0.46	23	0.12	4.53	0.21	0.79
104	~ 3	0.3	--	0.20	10	0.11	3.36	0.37	1.40
105	~ 3	0.3	--	0.18	9	0.07 <sup>a</sup>	3.06 <sup>a</sup>	0.26	0.14
106	2.3	0.09	85	0.12	6	0.07	2.35	0.19	1.05
107	2.2	0.19	89	<0.06	<3	0.62	5.34	0.20	0.99
108	1.8	0.28	89	<0.06	<3	1.11	8.14	0.26	0.81
109	1.5	0.38	90	<0.06	<3	0.22	8.45	0.31	0.78

<sup>a</sup> MnO<sub>2</sub> precipitate washed with warm 2 M HNO<sub>3</sub> in this experiment.

Although  $\text{KMnO}_4$  oxidation was relatively effective in destroying the soluble organic compounds, the method has the disadvantages that a solid ( $\text{MnO}_2$ ) is produced and that this solid sorbs significant amounts of uranium and thorium. In the experiments reported here, the amount of uranium sorbed varied from 0.01 to about 1.0% and the amount of thorium sorbed varied from 1.4 to greater than 8% (Table 11). In general, the largest amounts were sorbed in experiments where the  $\text{KMnO}_4$  concentration was the highest; obviously, more  $\text{MnO}_2$  was produced here than in experiments where the initial  $\text{KMnO}_4$  concentration was lower. Both water and warm 2 M  $\text{HNO}_3$  were inefficient in removing the sorbed uranium and thorium. If  $\text{KMnO}_4$  oxidation were to be used as part of a grind-leach process, the  $\text{MnO}_2$  precipitate would probably have to be dissolved in nitric acid--sodium nitrite solution<sup>43</sup> and then the resulting solution would have to be blended with the solvent extraction feed solution to ensure complete recovery of uranium and thorium. Thus a method other than acid permanganate treatment would be desirable, not only for more efficient removal of the soluble organic compounds but also to avoid handling of an  $\text{MnO}_2$  filter cake.

#### 4.6.2 Oxidation with $\text{K}_2\text{Cr}_2\text{O}_7$

Potassium dichromate, in fairly concentrated nitric acid solutions, proved to be an effective oxidant for the soluble organic compounds present in leach solutions. Tests were made with two feed solutions prepared by leaching crushed Peach Bottom fuel. Solution GL-3 was 9.67 N in  $\text{H}^+$  and contained 63.4 mg of thorium, 13.4 mg of uranium, and 1.45 mg of carbon per milliliter. The other solution, GL-3-D, was 2.35 N in  $\text{H}^+$  and contained 15.4 mg of thorium, 3.3 mg of uranium, and 0.52 mg of carbon per milliliter.

Making solution GL-3 (9.67 N in  $\text{H}^+$ ) 0.1 M in  $\text{K}_2\text{Cr}_2\text{O}_7$  and refluxing the system for 1 hr resulted in the oxidation of about 99% of the organic compounds in solution. When the  $\text{K}_2\text{Cr}_2\text{O}_7$  concentration was reduced to 0.05 M, oxidation of 99% of the organic compounds in solution required about 4 hr. In similar tests with solution GL-3-D (2.35 N in  $\text{H}^+$ ), only up to 85% of the organic compounds were oxidized in 4 hr when the  $\text{K}_2\text{Cr}_2\text{O}_7$  concentration was 0.1 M. These results indicate that dichromate oxidation is most effective

when the acid concentration of the solution is high. This method has the advantage that no solids are formed as reaction products; however, the chromium added to the system would ultimately pass into the solvent extraction and waste systems.

#### 4.6.3 Oxidation with Hydrogen Peroxide

To test this method, small amounts of either 30 or 50%  $H_2O_2$  solution were added every 15 min over a 2.5-hr period to boiling samples of both solutions GL-3 and GL-3-D (see Sect. 4.6.2). The total volume increase during each experiment was about 15%. Only 40 to 60% of the organic compounds were oxidized by this method. Addition of a single large quantity of  $H_2O_2$  before digestion was even less effective than the periodic addition of the peroxide.

#### 4.6.4 Oxidation with Mercuric Ion

Mercuric ion was not very effective as an oxidant for the soluble organic compounds. In tests where solutions GL-3 and GL-3-D (see Sect. 4.6.2) were made 0.1 M in  $Hg(NO_3)_2$  and then refluxed for 5 hr, less than 40% of the organic compounds were oxidized.

#### 4.6.5 Oxidation with Ceric Ion

Ceric ion, as  $(NH_4)_2Ce(NO_3)_6$ , was added to solution GL-3. Aliquots of this solution were made 0.01 and 0.05 M in  $Ce^{4+}$ , respectively, and the resulting solutions were refluxed for 5 hr. Only 50 to 60% of the carbon was oxidized.

#### 4.6.6 Oxidation with Ozone

~~Oxygen was bubbled for 7 hr through an ozone generator~~ (efficiency unknown) and then through solution GL-3 at room temperature. About 74% of the soluble organic compounds were oxidized.

#### 4.6.7 Pressurized Aqueous Combustion

Autoclaving of leach solutions, using an oxygen overpressure, did not appear promising for the rapid oxidation of the soluble organic species.

Aliquots of solution GL-3-D were loaded into an autoclave, along with sufficient oxygen to give an initial oxygen:carbon mole ratio of at least 3. Oxidation of the soluble organic compounds in this system was slow at both 150 and 200°C. At 150°C (total pressure of about 125 psi), less than 40% of the carbon was oxidized in 5 hr; at 200°C (total pressure of about 300 psi), the amount oxidized increased from 30 to 84% as the reaction time was increased from 1 to 5 hr.

#### 4.6.8 Anion Exchange

Since the soluble organic compounds are apparently polyfunctional acids, they would be expected to sorb on anion exchange resins, particularly from solutions with low acid concentrations. On the other hand, the tendency for uranium and thorium to sorb decreases with decreasing acidity. Preliminary experiments with typical leach solutions at 25°C, using Dowex-1 X4 nitrate-form resin, showed that distribution coefficients (DC's) for the organic species were 50 or greater when the nitric acid concentration of the solution was 3 M or less; the DC's for thorium and uranium were about 3 or less. Visually, the highly colored organic compounds appeared to sorb rapidly on the resin. However, experiments that were designed to determine the capacity of the resin under flow conditions showed that this was not the case. In these tests, the feed, which was produced by leaching crushed Peach Bottom fuel, was 3.1 M in HNO<sub>3</sub> and contained 1.9 mg of uranium, 9.5 mg of thorium, and 0.52 mg of carbon per milliliter. In separate experiments, this solution was fed onto a 1-cm-ID column of Dowex 1-X4 resin at rates of about 0.5 and 1.5 ml min<sup>-1</sup> cm<sup>-2</sup>. In each instance, uranium, thorium, and carbon (as soluble organic compounds) appeared in the effluent solution almost immediately. Saturation of the resin with uranium occurred after passage of about 6 bed volumes (a bed volume was about 6 ml) of feed through the column. After the passage of about 13 bed volumes, the resin was nearly saturated with thorium. However, in both experiments the carbon concentration in the effluent was still only about half that in the feed and was still increasing after passage of about 13 bed volumes of the feed through the column. The approximate loading at this point corresponded to only about 2 mg of carbon per milliliter of resin. This work shows that the organic compounds are sorbed

slowly at 25°C and that use of anion exchange for removal of these species from solution is of only marginal value.

#### 4.6.9 Sorption on Activated Alumina and Charcoal

Feed solutions for these experiments were prepared by leaching crushed Peach Bottom fuel; they were 1.5 to 4 M in HNO<sub>3</sub> and contained 9 to 12 mg of thorium, 2 to 3 mg of uranium, and 0.5 to 1 mg of carbon per milliliter. Equilibration for 24 hr at 25°C with Alcoa grade F-20 activated alumina (5 ml of feed per gram of Al<sub>2</sub>O<sub>3</sub>) resulted in no detectable sorption of uranium or thorium. The distribution coefficient (DC) for carbon, which is defined as:

$$DC = \frac{\text{mg of carbon per gram of sorbent}}{\text{mg of carbon per ml of solution}},$$

varied from 3 to 4.

In similar tests with Norit A decolorizing charcoal (0.5 g of charcoal per 10 ml of feed), the DC for carbon increased from 128 to 240 as the HNO<sub>3</sub> concentration of the solution decreased from 3 to 1.6 M. However, sorption of uranium was also significant; the DC for uranium increased from 2.5 to 11 under the same conditions. No sorption of thorium was noted.

### 5. DISCUSSION AND CONCLUSIONS

The results presented in this report show that a grind-leach process for recovering the uranium and thorium from graphite-base reactor fuels that contain coated particles is only marginally feasible. Assuming that most of the disadvantages could be overcome, the main steps of this process would be as follows: (1) rough-crushing of the fuel in a hammer mill; (2) roll-crushing to reduce the particle size of the fuel to that required for rupture of all the particle coatings; (3) leaching of the crushed fuel; (4) separating the leach solution from the residual graphite; (5) washing the residual graphite to ensure maximum uranium and thorium recoveries; (6) separating the soluble organic compounds from the uranium and thorium by solvent extraction; (7) separating the uranium and thorium from fission products and recovering the uranium and thorium by additional cycles of solvent extraction; (8) fabricating new fuel particles by recycling the

recovered uranium and thorium via a sol-gel process; and (9) disposing of the waste graphite. This procedure is summarized in the ensuing paragraphs.

### 5.1 Crushing of the Fuel

Fine-grinding of graphite-base fuels was once thought to be a difficult engineering problem.<sup>12</sup> However, Hannaford has shown<sup>18,36,40,44</sup> that unirradiated fuels can be effectively and rapidly powdered by first rough-crushing the fuel in a hammer mill and then pulverizing the product in a double-roll crusher. A -6 mesh product was easily obtained by hammer-milling. After being passed through the roll-crusher three times at successively closer roll spacings (40, 3, 2 mils), this product was reduced to -140 mesh. Crushing rates of up to 50 kg/hr were achieved in the first two passes; the maximum rate achieved in the third pass was about 10 kg/hr. Although these studies indicate that crushing of actual fuels should present no major problems, additional work with fuels containing oxide particles and with irradiated fuels, for example, would be desirable.

In some proposed HTGR fuels, the graphite elements contain holes filled with fuel particles, which may be either loose or bonded together. In either case, separation of the fuel particles from the bulk of the graphite appears possible; therefore, only the fuel particles, and not the entire fuel element, would have to be crushed.

### 5.2 Leaching of Crushed Fuel

Achievement of high uranium and thorium recoveries appears to be a major chemical problem in the grind-leach process for graphite-matrix fuels. The laboratory work summarized in this report showed that acceptable (99.9%) uranium and thorium recoveries could not be achieved in a single leach. Multiple leaching gave acceptable recoveries from Peach Bottom fuel but not with UHTREX fuel. Engineering-scale studies<sup>18,36</sup> with crushed, unirradiated Peach Bottom fuel also indicated that adequate recoveries were difficult to attain. In the engineering work, a total of nearly 4 kg of crushed fuel (-140 mesh) was added incrementally (75 g/min) to 8 liters of 13 M HNO<sub>3</sub>--0.05 M HF contained in a 4-in.-diam leacher. Slow addition of fuel was necessary to prevent excessive foaming. After admittance to the leacher,

the fuel was leached for 7 hr by continuously circulating the nearly boiling acid upward through the bed of fuel. The leachate was then removed from the system, and the residual graphite was washed with a total of about 7 liters of water. The composite solution (leachate plus washes) was about 6 M in  $\text{HNO}_3$  and 0.2 M in U + Th, and contained 0.5 g of carbon per liter. Uranium and thorium losses to the residue were 0.35 and 0.67% respectively. Higher recoveries were achieved by washing with concentrated nitric acid instead of water;<sup>40</sup> this, in effect, constituted a second leach of the fuel. No engineering-scale studies of the leaching of UHTREX or similar fuel have been reported.

The inability to achieve high uranium and thorium recoveries has also been encountered in recent experiments<sup>40,45</sup> with irradiated Peach Bottom and AVR<sup>46</sup> fuel specimens. The fuel samples were crushed in a Waring blender before being leached with several portions of either 13 M  $\text{HNO}_3$  or 13 M  $\text{HNO}_3$ --0.05 M HF. Each residue was exhaustively washed with water after leaching. The average uranium and thorium losses were 1.1 and 2%, respectively, and were independent of the type of fuel and irradiation level, which varied from about 8000 to 55,000 Mwd/ton (U+Th). Retention of fission products, mostly ruthenium and rare earths, by the graphite residue was as high as 10%, based on the gross-gamma activity.

Assuming that the conditions determined for adequate recovery of uranium and thorium from unirradiated fuels will also apply to their recovery from irradiated fuels, then nitric acid alone, as dilute as 5 M, could be used as the leachant for fuels containing carbide fuel particles and the leaching could be conducted at temperatures below the boiling point. Nitric acid containing HF in low concentration would be required for fuels that contained  $\text{ThO}_2$  or  $\text{ThO}_2\text{-UO}_2$  particles. If multiple leaching were used, the leachate from the second leach of one batch of fuel could probably be used as the reagent for the first leach of a fresh batch of fuel.

### 5.3 Washing of Leached Fuel

Maximum uranium and thorium recoveries are achieved only with thorough washing of the graphite residue after leaching of the fuel. The work described in this report showed that, if the residue were washed in a column, the

leachate would probably not be diluted by more than a factor of 2. Practically the same results were obtained in engineering-scale experiments.<sup>18,36</sup> Higher uranium and thorium recoveries<sup>40</sup> were obtained by washing with concentrated nitric acid instead of water.

Conditions for washing leached fuel on a plant scale must be carefully evaluated because of the relatively low permeability of crushed graphite to nitric acid and water and because of the criticality problems inherent in the system. If washing is to be done in small-diameter vessels, where criticality is no problem, pressure filtration will probably be required to ensure an adequate wash throughput. Vacuum filtration could probably be used, but the filter vessel necessarily would have to be of large diameter and the depth of the bed would have to be kept small to provide both the desired flow rate and criticality control.

#### 5.4 Treatment of Soluble Organic Compounds in Leach Solutions

As discussed in Sect. 4.6, soluble organic compounds are found in solution after leaching graphite-base fuels, particularly those that contain carbide fuel particles. The compounds could possibly be removed from solution by oxidation prior to solvent extraction of the uranium and thorium (see Sect. 4.6), but none of the oxidation methods tested proved to be highly efficient. Removal by solvent extraction appears to be a much simpler and more effective method.<sup>39,40</sup> The uranium and thorium would be extracted from a feed solution that was 2 to 5 M in  $\text{HNO}_3$ , leaving the organic species in the aqueous phase. Decontamination from fission products, in the case of irradiated fuel, is not expected to be high in this step (the gross-gamma decontamination factor was about 350 in preliminary experiments); however, the desired degree of purification of the uranium and thorium could be achieved in subsequent extraction cycles.

#### 5.5 Fuel Recycle

The best method for recycling uranium and thorium back to HTGR reactor fuel has not yet been determined, and will probably depend on the type of fuel particle desired. One general method, the sol-gel process,<sup>36,47</sup> could be used to produce either carbide or oxide particles from nitrate solutions.

In one approach,<sup>47</sup> heavy-metal oxide sols would be mixed with a carbon sol and then the resulting sol would be used to produce gelled microspheres that, on firing at high temperature, would yield carbide microspheres directly. In another approach,<sup>48</sup> oxide microspheres would be produced separately by a sol-gel method and then converted to carbide microspheres by firing in an inert atmosphere at high temperatures (up to 2100°C) in a bed of carbon "flour."

### 5.6 Disposal of Graphite Waste

This aspect of a grind-leach process has not yet received much attention. Based on recent hot-cell work,<sup>40,45</sup> self-heating of the leached graphite as a result of the large fraction of fission products left unleached may preclude simple canning and burial as a means of waste disposal. More elaborate disposal methods will probably have to be developed; for example, the waste graphite could be burned in a fluidized bed of alumina, which would allow the fission product concentration in the bed to increase until disposal of the alumina, either by canning and burial or incorporation into a glass, would become necessary. One possible advantage in this method is a reduction in the amount of solid material that would ultimately require disposal. On the other hand, if combustion is to be used as one step in a process for graphite-base fuels, it probably should be used as the first, rather than the last step, considering the highly successful development of the burn-leach process.<sup>7-9,40,44,45</sup>

### 5.7 Conclusions

It must be concluded from the data presented here that the practicality of a grind-leach method for processing graphite-base fuels is open to serious question. The method has severe limitations even with unirradiated fuels, and the unfavorable results reported for the first experiments with irradiated specimens make the feasibility of the process even more dubious. Even with more development, the process probably cannot compete with the burn-leach approach. Development of procedures for the fine crushing of graphite fuels has not been entirely ineffectual, however, since crushing of fuel containing particles coated with SiC or a similar ceramic appears to be essential as the first step in a burn-leach process for these fuels.

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