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URANIUM CARBIDES WITH NITRIC

ACID AT 90°C

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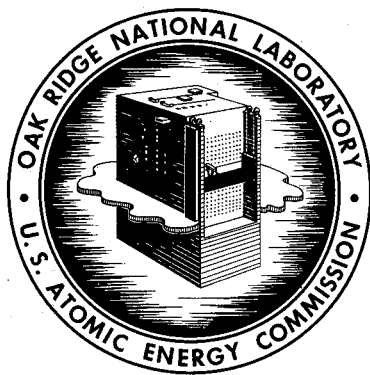
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CONTENTS

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ABSTRACT

The uranium carbides, UC, $U_4(C_2)_3$, and $UC_{1.85}$, dissolved in 2 to 16 $\underline{M}$ HNO_3 in 10 hr or less at 90°C, yielding off-gases comprised mainly of NO_2, NO, and CO_2. The off-gas compositions varied with the acid concentration: in dilute (2 to 4 $\underline{M}$) acid, NO was the main nitrogen oxide present, whereas NO_2 predominated at higher acid concentrations. Traces of N_2O were found, but no CO, H_2, or gaseous hydrocarbons were detected. The carbides were almost completely passive in very dilute (0.001 to 0.5 $\underline{M}$) acid. Between 30 and 50% of the carbide carbon was converted to species soluble in nitric acid irrespective of the carbide, reaction time, or variation of acid concentration between 2 and 16 $\underline{M}$.

1. INTRODUCTION

Uranium carbides can be used in several different forms as fuels for nuclear reactors. For example, the first and second cores of the Hallam reactor[1] contain elements of cast uranium monocarbide (UC) rods clad in stainless steel with a sodium bond. In the Peach Bottom reactor,[2] uranium dicarbide[3,4] ($UC_{1.85}$) is used as the fuel. The element consists of pyrolytic carbon-coated Th-U dicarbide particles (100 to 400 μ in diameter) dispersed in a graphite matrix. Uranium sesquicarbide, $U_4(C_2)_3$, is stable up to about 1780°C[5,6,7] but has not yet been proposed for use in a fuel element.

At Oak Ridge National Laboratory (ORNL), various processing methods involving the use of nitric acid are being studied for both the Hallam-type[8,9] and the graphite-base fuels.[10,11] As part of the development of these processes, a basic study of the reactions of uranium carbides with nitric acid is being made. This report contains results of studies on the effect at 90°C of nitric acid concentration on the rates of reaction and the volumes and compositions of the off-gases.

There is general qualitative agreement that uranium carbides dissolve in nitric acid (in concentrations of at least 2 $\underline{M}$), yielding nitrogen oxides and soluble organic polyacids which oxidize very slowly in nitric acid.[12-16] Simpson and Heath[12] did not find carbon-containing compounds in the off-gas from the reaction of UC with 6 $\underline{M}$ HNO_3, and they inferred that all the carbide carbon remained in solution. On the other hand, Donaldson et al.,[14] reported that at least 33% of the carbide carbon was converted to CO_2 in reactions of UC with 2 to 12 $\underline{M}$ HNO_3. Pausen et al.,[13] found about 30% of the carbide carbon as CO_2 in reacting the three uranium carbides with 6 $\underline{M}$ HNO_3. No prior attempt was made to analyze the off-gases quantitatively for components other than CO_2. Therefore, the objective of the present work was to resolve the discrepancies in the carbon balances and to determine whether or not hydrogen and hydrocarbons were also formed during the reaction, particularly in solutions of low nitric acid concentration. Reactions of the carbides with pure water yielded off-gases containing only hydrogen and hydrocarbons.[3,5,17] Thus, the possibility of producing potentially explosive mixtures containing hydrogen, hydrocarbons, and nitrogen oxides with dilute nitric acid could not be overlooked.

2. EXPERIMENTAL

2.1 Materials

The uranium carbides used in this study were prepared by arc-melting high-purity uranium and spectroscopic-grade carbon, as described elsewhere.[3,5,17] The mono- and dicarbides (UC and $UC_{1.85}$, respectively) were formed directly. After arc-melting, the $UC_{1.5}$ composition was heat-treated

for 60 hr at 1600°C to form the sesquicarbide $(U_4(C_2)_3)$. Metallographic and x-ray diffraction analysis supported the chemical analyses (Table 1) in showing that both the mono- and sesquicarbides were at least 95% pure. Specimen UC_2-18A can be considered as a $UC_{1.85}$-C mixture containing about 13 mole % (0.7 wt %) carbon. Nitrogen, oxygen, and tungsten (a contaminant from the arc-melting step) concentrations were less than 60 ppm, 0.05%, and 0.2%, respectively, in all samples.

Table 1. Compositions of the Carbide Specimens

| Carbide | Specimen | Uranium (%) | Carbon (%) | | Combined-C/U Atom Ratio |
			Total	Free	
UC	ORNL-1B	95.3	4.64	0.02	0.96
$U_4(C_2)_3$	U_2C_3-2A	93.0	7.00	0.06	1.48
$UC_{1.85}$	UC_2-18A	90.8	9.12	0.70	1.84

2.2 Procedure

All reactions were conducted at 90°C, using 1- to 4-g carbide specimens in an apparatus identical to that used in studies of the hydrolysis of uranium carbides.[3,5,17] A small amount of silicone oil was used to cover the mercury on the reaction side of the manometer to minimize the reaction of the mercury with the nitrogen oxides evolved. The amount of nitric acid used was such that the uranium concentration in the final solution was about 0.2 $\underline{M}$. The reactions were usually allowed to proceed until the rates of gas evolution were less than about 2 ml/hr. The reaction times were sufficiently long for complete dissolution of the carbides but not long enough for complete oxidation of the soluble organic species. The evolved gases were first collected in the gas buret, where the volume was measured, and then were transferred to evacuated sample bulbs. Generally, several bulbs were filled during an experiment. The volume of gas in all but the last of these was determined with the gas buret. The last sample taken was that of the gas remaining in the apparatus. Since

complete collection of the gas was impossible, a presumably representative sample was transferred into an evacuated bulb by using the gas buret as a Toepler pump. Gas volumes were corrected to 25°C and 1 atm pressure, assuming ideal gas behavior. The amount of each component in the last sample was calculated from the volume of the apparatus and the gas-chromatographic analyses (Sec 2.3). The amounts of each component in the other samples were calculated from the volumes determined with the gas buret (after correction) and the analyses. Nitrogen was found in nearly all the gas samples; however, since its concentration was nearly constant at 2 to 5%, its presence was attributed to air contamination.

The gas samples were analyzed by gas chromatography for the nitrogen oxides and carbon oxides. The procedure was: Mixtures of the nitrogen oxides and carbon oxides, in helium carrier gas, were resolved on a 2.5-m-long by 0.5-cm-ID Pyrex column containing Linde 5A molecular sieve. The instrument used for analysis was a Burrell Kromo-tog model K-2 with a thermistor-type detector. After loading the gases on the column, oxygen, nitrogen, and NO were eluted successively with helium at 25°C. The temperature of the column was then raised rapidly to 200°C where NO_2 (including dissociated N_2O_4), N_2O, and CO_2 were eluted successively. Since NO and CH_4 could not be differentiated on this column, samples of the gases were tested by mass spectroscopy to ensure that NO was the component being determined. In addition, most of the samples were tested for C_2- to C_8-hydrocarbons with the chromatographic columns used to analyze the hydrocarbon mixtures evolved in the hydrolysis of uranium carbides.[18] The columns were calibrated with standard gas mixtures, and the results were reported as the volume percentage of each component corrected to 25°C and 1 atm.

Analysis of the nitrogen oxides posed special problems because of the $N_2O_4 \rightleftharpoons 2NO_2$ equilibrium. At 25°C, where the gas samples were collected, both NO_2 and N_2O_4 were present; however, no satisfactory method was found for analyzing the gases at 25°C and determining the amounts of both NO_2 and N_2O_4. Therefore, in the chromatographic method selected, the total amount of nitrogen (IV) present in the mixture was determined as NO_2 at 200°C, where the amount of N_2O_4 was negligible. Because all

nitrogen (IV) was reported as NO_2, the sum of the volume percentages of the various gases frequently exceeded 100%. To further complicate the problem, the volume of the sample that was injected into the chromatograph had to be measured at a reduced pressure (about 500 mm Hg). The data of Verhoek and Daniels[19] were used to correct this volume for the effect of pressure on the $N_2O_4 \rightleftharpoons 2NO_2$ equilibrium.

The solution resulting from each experiment was analyzed for uranium, nitrogen, H^+, and carbon so that appropriate balances could be made. Nitrogen was determined by the Kjeldahl method, and carbon in solution by a wet combustion method.[20] Other analytical procedures have been described elsewhere.[3,5,17]

3. RESULTS

3.1 Passivation in Dilute Nitrate Systems

Since reaction of the uranium carbides with water resulted in the evolution of only hydrogen and hydrocarbons,[3,5,17] and since other work[12-14] suggested that only nitrogen oxides and carbon oxides could be expected in the off-gas from reaction with nitric acid, the initial studies were made with pieces of the as-cast carbides to determine whether mixtures of hydrogen, hydrocarbons, and the oxide gases were evolved with 0 to 2 $\underline{M}$ HNO_3. Quite unpredictably, the uranium carbides were almost completely passive in boiling 0.001 to 0.5 $\underline{M}$ HNO_3 over 24-hr periods (Table 2). In the very dilute solutions no gas was evolved, and the surfaces of the originally shiny specimens turned black. In some cases, the specimen crumbled to a powder, but no reaction occurred. This phenomenon was not limited to nitric acid solutions but occurred in many dilute nitrate solutions (Table 2). Although not understood at present, it appears from the latter tests that the nitrate ion is the cause of passivation and that this tendency to promote passivation is overcome only when the H^+ concentration is greater than about 1 $\underline{M}$. More work will be required before this behavior is understood.

Table 2. Behavior of the Uranium Carbides in Boiling Dilute
Nitrate Solutions

Carbide	Boiling Solution	NO_3^- Conc. (M)	Test Period (hr)	Results
UC	HNO_3	0.001	24	Crumbled, but no reaction
		0.01	24	No reaction, surface black
		0.05	24	No reaction, surface black
		0.5	24	Very slow reaction
		1.0	24	Slow reaction
	$NaNO_3$	0.05	24	Crumbled, but no reaction
	$Ca(NO_3)_2$	0.05	24	No reaction
	$UO_2(NO_3)_2$	0.1	6	No reaction
		0.37	24	No reaction, surface black
	$Al(NO_3)_3$	0.05	24	No reaction
	$Th(NO_3)_4$	0.05	24	No reaction
$U_4(C_2)_3$	HNO_3	0.001	24	No reaction, surface black
		0.01	24	No reaction, surface black
		0.025	24	No reaction, surface black
		0.05	24	No reaction, surface black
		0.1	24	No reaction, surface black
		0.5	24	Very slow reaction
$UC_{1.85}$	HNO_3	0.001	24	Reaction within 30 min
		0.01	24	No reaction
		0.025	24	No reaction
		0.05	24	No reaction
		0.1	24	No reaction
		0.5	24	No reaction, surface black

3.2 Effect of Nitric Acid Concentration on the Rate of Reaction

Reaction does occur at measurable rates when the nitric acid concentration is between 2 and 16 M (Figs. 1 and 2). Visual observation indicated that dissolution of the carbide in nitric acid was complete at about the same time that the slope of the gas-volume-vs-time plot changed abruptly. Slow gas evolution continued beyond this point owing to the oxidation of the nitric acid-soluble organic species. With 1- to 4-g pieces, the time required for complete dissolution of UC (but not oxidation of all of the soluble organic species) at 90°C decreased from about 10 to 1.5 hr as the
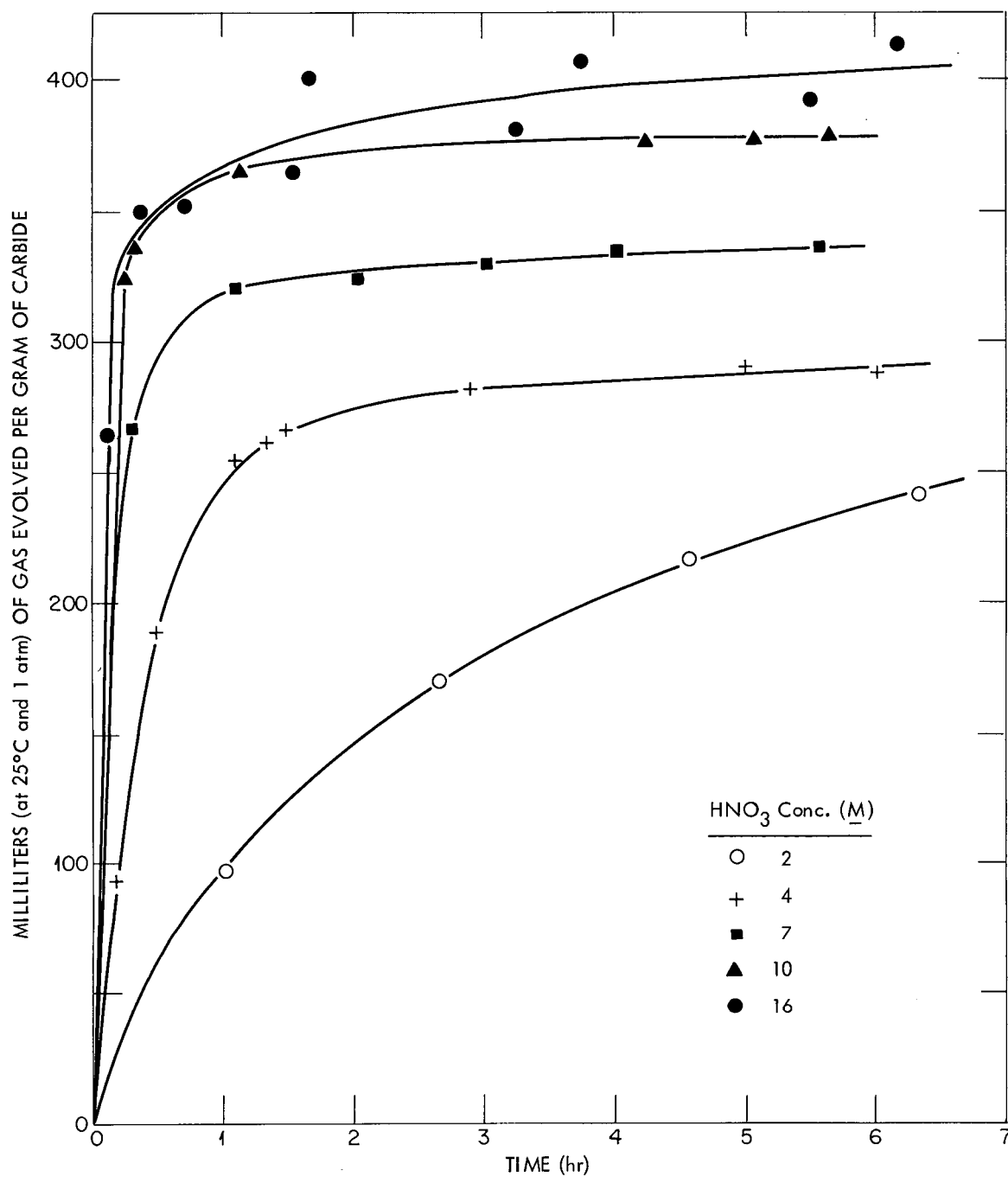
Fig. 1.   Gas Evolution in the Reactions of 1- to 4-g Specimens of Uranium Monocarbide with Nitric Acid Solutions at 90°C.
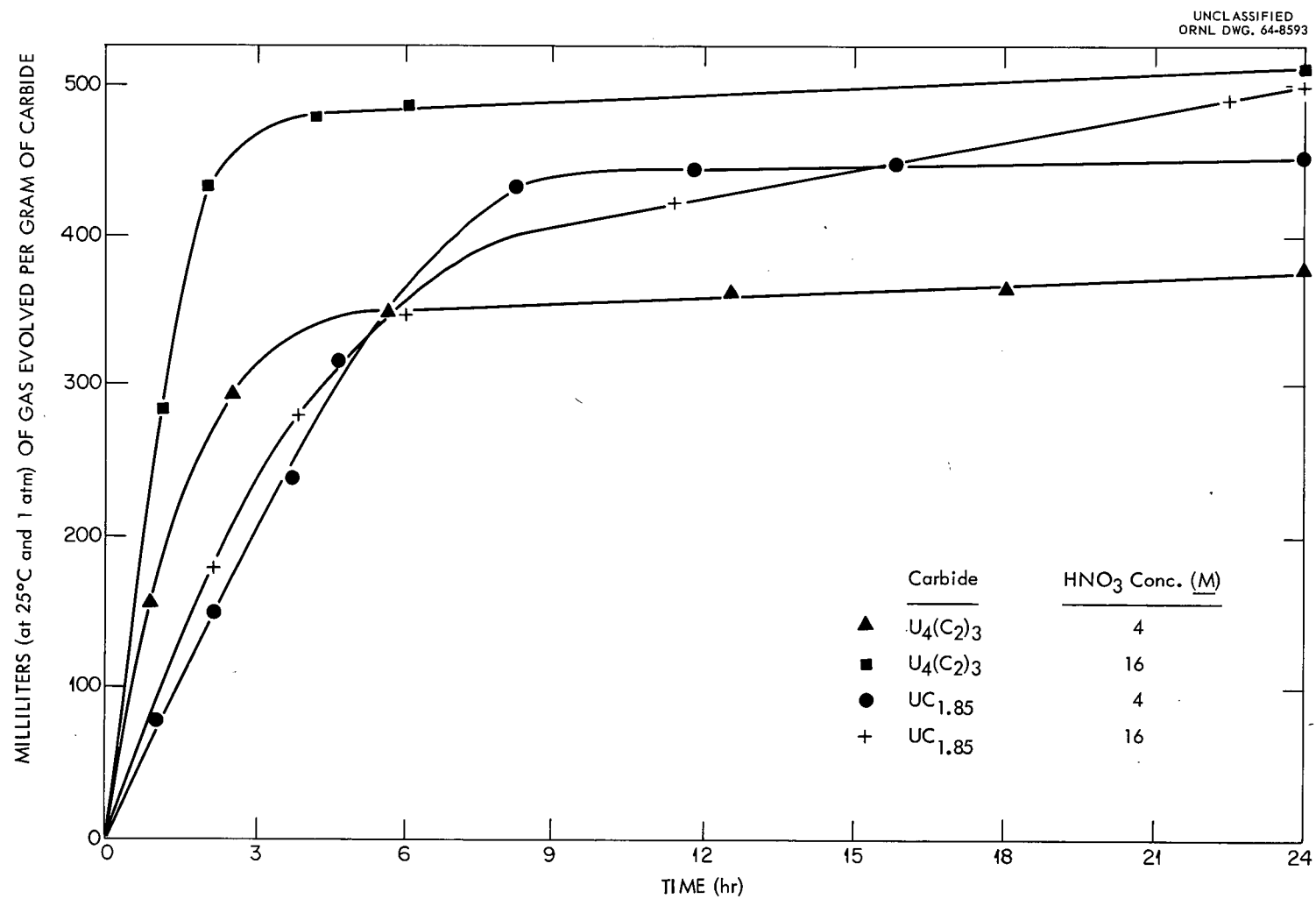
Fig. 2. Effect of Time and Nitric Acid Concentration on the Gas
Evolution in the Reactions of 1- to 4-g Uranium Sesquicarbide and Dicarbide
Specimens with Nitric Acid Solutions at 90°C.

nitric acid concentration increased from 2 to 16 $\underline{M}$ (Fig. 1). With the sesquicarbide, reaction was complete in about 5 hr with both 4 and 16 $\underline{M}$ HNO_3 (Fig. 2). The dicarbide reacted more slowly than either the mono- or sesquicarbides; complete solubilization of the uranium required about 8 hr in both 4 and 16 $\underline{M}$ HNO_3 (Fig. 2).

3.3 Approximate Volumes and Compositions of the Gases Evolved

The volume of gas (at 25°C and 1 atm) evolved per gram of monocarbide (determined from the nearly flat portions of the curves) increased from about 300 to 400 ml as the nitric acid concentration increased from 2 to 16 $\underline{M}$ (Fig. 1, Table 3). With the sesquicarbide and dicarbide, the volume of gas evolved increased from about 380 and 450 ml/g, respectively, to about 500 ml/g as the nitric acid concentration increased from 4 to 16 $\underline{M}$ (Fig. 2, Table 3).

The overall compositions of the gases evolved show that NO was the chief nitrogen oxide from dilute nitric acid, whereas NO_2 was the main component evolved from more concentrated acid (Table 3). In most experiments, the N_2O/CO_2 mole ratio in the gas was between 0.1 and 0.3, irrespective of the carbide dissolved or the acid concentration. It is significant to note that no CO, hydrocarbons, or hydrogen were detected in the off-gases from any run.

As might be expected from the nature of the reaction (rapid dissolution of the carbide followed by slow oxidation of the soluble organic species), the composition of the off-gas changed as the reaction proceeded. With dilute (2 and 4 $\underline{M}$) HNO_3 the NO/CO_2 mole ratio in the gas from UC was initially about 6, but decreased to about unity in the later stages of reaction (Table 3). The NO/CO_2 ratio was nearly constant during the first hours of reaction while the carbide was dissolving and then decreased as the soluble organic compounds were oxidized. Similar behavior was noted for the sesquicarbide and dicarbide in 4 $\underline{M}$ HNO_3. During dissolution of UC in 10 and 16 $\underline{M}$ HNO_3, the NO_2/CO_2 mole ratio was initially 10 to 20, but decreased in the final stages of reaction to about 3 (Table 3). Little NO was formed in the initial phase of reaction, but significant

Table 3. Volumes, Approximate Compositions, and Changes in Gas
Composition with Time in the Reaction of Uranium
Carbides with Nitric Acid at 90°C

Expt.	Carbide	HNO_3 Conc. (M)	Ml of Gas Evolved per g of Carbide[a]	Reaction Time Interval (hr)	Mole Ratio in Gas[b]		
					NO/CO_2	NO_2/CO_2	N_2O/CO_2
1	UC	1.98	301	0-1	7.3	0.5	0.27
				1-3.5	7.0	0.4	0.30
				3.5-30	4.7	0.3	0.27
				30-97	1.3	0.3	0.24
				Overall Comp.	4.3	0.30	0.26
2	UC	3.98	315	0-0.17	5.2	0.7	0.19
				0.17-0.48	7.1	1.0	0.23
				0.48-1.1	5.9	0.6	0.23
				1.1-29.7	2.7	0.2	0.18
				29.7-53.3	0.9	0.1	0.11
				Overall Comp.	3.5	0.43	0.17
3	UC	3.98	325	0-0.18	6.0	1.4	0.20
				0.18-0.5	5.2	1.1	0.20
				0.5-1.3	4.0	0.4	0.17
				1.3-30	3.3	0.6	0.23
				30-70	0.8	0.2	0.11
				Overall Comp.	2.7	0.52	0.16
4	UC	6.98	336	0-5.6	8.9	9.6	0.33
				Residue[c]	3.9	5.8	0.27
				Overall Comp.	5.7	7.1	0.29
5	UC	9.85	377	0-0.28	0.3	17.6	0.27
				0.28-5.1	2.5	10.9	0.21
				Overall Comp.	1.5	14.0	0.24
6	UC	9.85	377	0-0.32	2.1	16.6	0.17
				0.32-5.6	2.9	10.4	0.24
				Overall Comp.	2.6	12.9	0.21
7	UC	9.85	335	0-5.5	2.7	10.5	0.14
				Residue[c]	1.7	3.0	0.10
				Overall Comp.	2.0	5.0	0.11

Table 3. Volumes, Approximate Compositions, and Changes in Gas
Composition with Time in the Reaction of Uranium
Carbides with Nitric Acid at 90°C
(Continued)

Expt.	Carbide	HNO_3 Conc. ($\underline{M}$)	Ml of Gas Evolved per g of Carbide[a]	Reaction Time Interval (hr)	Mole Ratio in Gas[b]		
					NO/CO_2	NO_2/CO_2	N_2O/CO_2
8	UC	9.85	374	0-6.0	5.6	10.3	0.11
				Residue[c]	3.0	2.2	0.13
				Overall Comp.	3.5	3.8	0.12
9	UC	15.6	391	0-0.72	0.2	16.3	0.10
				0.72-5.5	1.8	17.8	0.10
				Overall Comp.	1.0	17.1	0.10
10	UC	15.6	413	0-0.38	0	23.8	0.18
				0.38-6.2	3.7	20.0	0.10
				Overall Comp.	2.1	21.5	0.14
11	$U_4(C_2)_3$	3.98	378	0-5.7	10.0	1.0	0.34
				5.7-24	3.8	2.6	0.44
				Overall Comp.	5.3	1.6	0.28
12	$U_4(C_2)_3$	15.6	508	0-1	0	13.7	0.10
				1-24	2.7	5.0	0.13
				Overall Comp.	2.5	5.7	0.13
13	$UC_{1.85}$	3.98	451	0-4.7	5.2	1.1	0.18
				4.7-24	3.3	0.4	0.15
				Overall Comp.	3.7	0.6	0.15
14	$UC_{1.85}$	15.6	501	0-3.9	0	6.8	0.38
				3.9-24	1.3	2.7	0.11
				Residue[c]	2.8	7.6	0.10
				Overall Comp.	1.6	5.0	0.10

[a]Volume at 25°C and 1 atm pressure; in general, the volume given is that obtained from the essentially flat portion of a volume-time plot.

[b]No hydrocarbons detected in the gas by gas-chromatographic or mass-spectrographic analysis. All nitrogen (IV) is reported as NO_2.

[c]Residue refers to a sample of the gas remaining in the apparatus.

quantities were formed during oxidation of the organic species. Similar results were obtained with the sesquicarbide and dicarbide in 16 $\underline{M}$ HNO_3.

3.4 Carbon Balances

Carbon balances were made on the system by adding the amounts found in the gas and solution by analysis and comparing this total to the amount of carbon originally present in the carbide. The wet combustion technique for carbon in solution[20] gave about a 90% accuracy when used with standard solutions containing nitric acid and either pyromellitic or mellitic acids (Table 4), and even better results with more easily oxidized species.[21] Consequently, although the overall carbon balances for the experiments varied between 70 and 130% (Table 5), the amount of carbon in solution is probably fairly accurate. Despite the large variations in reaction time, acid concentration, and type of carbide, between 30 and 50% of the carbide carbon remained in solution (Table 5). The lower values did result from the longer runs.

In two runs, the amount of carbon in solution was also determined by extracting the uranium with tributyl phosphate, evaporating the organic-bearing raffinate to dryness at room temperature, and analyzing the resulting solids for carbon. The amounts of carbon in solution determined in this manner agreed reasonably well with those obtained by the wet oxidation technique (Table 6).

Table 4. Carbon Analyses of Standard Nitric Acid Solutions
Containing Known Quantities of Pyromellitic and Mellitic Acids

Solution	Carbon Concentration (mg/ml)		C Found/C Calculated
	Calculated	Found	
Pyromellitic acid in 1 $\underline{M}$ HNO_3	0.26	0.23	0.88
		0.25	0.96
		0.25	0.96
Pyromellitic acid in 2 $\underline{M}$ HNO_3	0.50	0.46	0.92
		0.47	0.94
		0.47	0.94
Pyromellitic acid in 4 $\underline{M}$ HNO_3	1.02	0.93	0.91
		0.92	0.90
		0.92	0.90
Mellitic acid in 2 $\underline{M}$ HNO_3	0.88	0.80	0.91

Table 5. Carbon Distribution in Nitric Acid Dissolution of Uranium
Carbides at 90°C, Based on CO_2 Content of the Off-Gas and
Carbon Analyses of the Solutions

Expt.	Carbide	HNO_3 Conc. ($\underline{M}$)	Reaction Time (hr)	Amount of Carbide Carbon (%)		Carbon Balance (%)
				In Gas	In Solution	
1	UC	1.98	97.	52.4	31.4	83.8
2	UC	3.98	53.	60.0	33.8	93.8
3	UC	3.98	70.	85.8	33.8	120.
4	UC	6.98	5.6	23.9	42.1	66.0
5	UC	9.85	5.0	27.8	46.2	74.0
6	UC	9.85	5.5	86.2	49.8	136.
7	UC	9.85	5.6	25.2	48.7	73.9
8	UC	9.85	6.0	77.8	47.8	126.
9	UC	15.6	5.5	30.4	46.4	76.4
10	UC	15.6	6.2	24.2	40.9	65.1
11	$U_4(C_2)_3$	3.98	24.	40.3	45.0	85.3
12	$U_4(C_2)_3$	15.6	24.	48.8	35.0	83.8
13	$UC_{1.85}$	3.98	24.	50.9	40.5	91.4
14	$UC_{1.85}$	15.6	24.	56.3	45.9	102.

Table 6. Comparison of Carbon in Solids Not Extracted by
Tributyl Phosphate with Carbon in Nitric Acid Solution

Experiment	Amount of Carbon in Solution (% of Carbide Carbon)	
	By Wet Combustion	By Analysis of Solids After Removal of U by Extraction
1	31.4	39.4
2	33.8	38.5

3.5 Nitrogen Balances

Nitrogen balances were made on the system by adding the amounts of
nitrogen found in the gas and in the final solution and comparing this
total to that present in the original nitric acid solution. The overall
nitrogen balances were generally between 90 and 110% (Table 7). However,
under the conditions employed, most of the original nitrogen remained

Table 7. Nitrogen Balances in Reaction of Uranium Carbides
with Nitric Acid Solutions at 90°C

| | Nitrogen (mmoles) | | | Millimole Ratios | |
| | In Original HNO_3 | In Final Solution | In Gas | N in Gas + N in Solution / N in Original HNO_3 | N in Gas / N in Original HNO_3 Minus N in Final Solution |
Expt.					
1	99	55.9	41.4	0.98	0.96
2	199	148.6	41.0	0.95	0.81
3	199	137.5	46.2	0.92	0.75
4	87.2	73.8	13.3	1.0	0.99
5	123	95.8	19.7	0.94	0.72
6	123	94.9	25.7	0.98	0.91
7	123	87.1	17.6	0.85	0.49
8	123	94.6	25.0	0.97	0.88
9	194	152	23.8	0.91	0.56
10	194	163	24.9	0.97	0.80
11	49.8	37.9	15.8	1.08	1.34
12	194	151	24.5	0.90	0.56
13	49.8	35.9	20.2	1.13	1.46
14	194	134	28.1	0.84	0.47

in solution (the final solutions contained only about 0.2 $\underline{M}$ uranium).
Therefore, a large error in the gas-chromatographic analysis causes only
a minor perturbation in the overall balance. The amount of nitrogen lost
by the solution (initial nitrogen content minus the nitrogen content of
the final solution) differed from the amount found by gas analyses by as
much as 50% (Table 7, last column).

3.6 Uranium and Ionic Balances

Uranium balances were calculated from the amounts of uranium present
in the original carbide and the uranium found in the final solution. In
all cases, the uranium balance was 100 ± 5%.

Ionic balances were made on the final solution ignoring the dissolved
organic species so that $[H^+] + 2[UO_2^{++}] = [NO_3^-]$, where the quantities in
brackets are molar concentrations. In general, the anion $[NO_3^-]$ to cation
($[H^+] + 2[UO_2^{++}]$) molar ratio was between 0.92 and 1.02. These results
account for the good overall nitrogen balances (Sec 3.5) obtained and

indicate that the analysis of the solution is reasonably accurate. These results emphasize again that the major error in the nitrogen balances is to be found in the gas-chromatographic analyses.

3.7 Acid Consumption

The amount of nitric acid consumed per mole of carbide dissolved is readily calculated from the change in hydrogen ion concentration and the weight of carbide used. This was done for all experiments. The results showed that the number of moles of nitric acid consumed per mole of UC increased from about 4 to 10 as the nitric acid concentration increased from 2 to 15.6 $\underline{M}$. With the sesquicarbide and dicarbides, about 4 moles of acid were consumed per mole of carbide when the acid concentration was 4 $\underline{M}$, but in 15.6 $\underline{M}$ HNO_3, 12 and 18 moles, respectively, were consumed.

4. CONCLUSIONS AND DISCUSSION

The uranium carbides dissolved readily in 2 to 16 $\underline{M}$ HNO_3 producing uranyl nitrate, carbon dioxide, nitrogen oxides, and nitric acid-soluble organic polyacids (containing 30 to 50% of the carbide carbon). No hydrogen or gaseous hydrocarbons were found. Therefore, a conventional off-gas treatment system could be used in processes involving the direct dissolution of uranium carbide fuels without fear of hydrogen explosions or the formation of potentially explosive nitro-organics. The major drawback to such a process is the deleterious effect of the soluble organic species in the stripping step after solvent extraction using modified Purex conditions.[9] The good agreement between direct analyses for carbon in solution and those obtained by analyzing the organic solids after extraction of the uranium from the nitric acid solution with tributyl phosphate shows that little, if any, of the organic species are extracted with the uranium. Consequently, solvent cleanup and recycle could probably be conducted conventionally. The rates of reaction obtained in this study with arc-melted carbides were similar to those obtained earlier[9] with other batches of carbide.

The results reported here are in general agreement with those of
Pausen, et al.,[13] and of Donaldson, et al.,[14] although we found nearly
twice as much CO_2 (an average of 50% by direct analysis or 60% by dif-
ference between total carbon and carbon in solution vs 30 and 33%, res-
pectively). These results are not in agreement with the observations of
Simpson and Heath,[12] who found no carbon-containing compounds in the gas
and assumed that all of the carbide carbon remained in solution.

The passivity (or extremely low rate of reaction) of the carbides
with dilute nitrate systems was most surprising. This could have a
serious effect on a scrap-recovery process involving hydrolysis of UC
followed by nitric acid dissolution of the $UO_2 \cdot xH_2O$ formed. If all the
nitric acid were not washed from the system after a dissolution, passiva-
tion of the next fuel charge could occur. The mechanism for this pas-
sivation is obscure at this point.

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