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RECOVERY OF URANIUM AND THORIUM FROM GRAPHITE FUELS. I. LABORATORY DEVELOPMENT OF A GRIND-LEACH PROCESS

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operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

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Chemical Development Section B

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ABSTRACT

A grind-leach method is presented for the recovery of uranium from uranium-graphite fuel elements. With unirradiated graphitized high-density reimpregnated fuel ground to -200 mesh containing 5.5-14 wt % uranium and less than 0.4% iron, 99.9% or more of the uranium was recovered with two leaches of boiling 15.8 M HNO_3 and thorough washing of the graphite residue. Yields were 0.1-0.2% lower when the fuel was ground to only -4 +8 mesh. Uranium recovery decreased rapidly with decreasing uranium concentration in the fuel, rendering the grind-leach method unsuitable for fuels containing less than 3% uranium. The gases evolved during leaching were a mixture of nitrogen oxides. No volatile carbon-containing gas was found. Preliminary data indicated that about 3.2 moles of nitric acid was consumed per mole of metal when oxygen was excluded from the system, suggesting that, in fuel specimens which had been exposed to the laboratory atmosphere for months, the uranium was present as UO_2 rather than UC_2.

Leaching of -200 mesh samples of 1.5% uranium—7.2% thorium—graphite fuel with boiling 15.8 M HNO_3 resulted in maximum uranium and thorium recoveries of about 90%. Leaching with 15.8 M HNO_3—0.04 M NaF—0.04 M $Al(NO_3)_3$ offered no advantages. Combustion of the fuel followed by dissolution of the uranium and thorium oxide products in boiling 13 M HNO_3—0.04 M NaF—0.04 M $Al(NO_3)_3$ resulted in essentially quantitative recovery of the metals.

A survey of processing methods indicated that combustion and digestion or particle size disintegration and leaching are the better possibilities for graphite fuels.

CONTENTS

1.0 INTRODUCTION

A general study of the recovery of uranium and thorium from graphite reactor fuels has been undertaken. Interest in this new class of fuels has grown with the development of gas-cooled power reactor concepts such as the proposals by General Atomics (Philadelphia Electric),[1] Sanderson and Porter (Pebble Bed Reactor),[2] and Los Alamos (Turret Reactor).[3] Potential methods for processing of graphite fuels were surveyed and evaluated. Mechanical grinding and leaching with nitric acid is the method currently being investigated experimentally on a laboratory scale for uranium-graphite fuels. Studies on the effects of initial uranium concentration, particle size, acid concentration, reflux time, successive leaches, washing technique, and Soxhlet extraction on the recovery of uranium from graphitized fuels containing 0.7 to 14 wt % uranium were completed, and a study of the stoichiometry of the reaction, with particular attention to the gaseous products, was started. Since the General Atomics fuel may be clad with stainless steel, the rate at which uranium and thorium dissolved in two decladding reagents—dilute aqua regia and sulfuric acid—was determined. Leaching of 1.5% uranium—7.2% thorium—graphite fuel with boiling 15.8 M HNO_3 and 13 M HNO_3—0.04 M NaF—0.04 M $Al(NO_3)_3$ was surveyed. Combustion of the fuel followed by dissolution of the uranium and thorium oxides in 13 M HNO_3—0.04 M NaF—0.04 M $Al(NO_3)_3$ was studied briefly. All tests were made with unirradiated prototype fuels.

The authors wish to thank J. M. Blickensderfer for performing some of the leaching experiments. Chemical analyses by the groups of G. R. Wilson, W. R. Laing, and P. F. Thomason of the ORNL Analytical Chemistry Division are acknowledged. Special credit is due A. D. Horton for the gas chromatographic analyses, W. L. Belew for infrared and visible spectrographic gas analyses, and H. Kubota for weak acid determinations.

2.0 URANIUM-GRAPHITE FUELS

The uranium-graphite fuel specimens used in this study were prepared by mixing UO_2 (325 mesh) with graphite flour (Great Lakes Carbon 1008-58) and a liquid resin binder, pressing into plates, curing at 180°C to set the resin, impregnating with more resin to increase the density, coking at 800°C (under vacuum to remove CO_2, from UO_2-carbon reaction) and finally graphitizing at 2400°C. At this temperature the uranium is converted to UC_2; however, since uranium dicarbide reacts rapidly with moisture, the uranium in the fuel samples was probably present as the oxide.

2.1 Grind-Leach Flowsheet

A flowsheet based on the grind-leach technique as the primary method for uranium recovery from uranium-graphite fuels containing 2-14 wt % uranium, <0.4 wt % iron, is given in Fig. 2.1. When fuel specimens containing 5.5-14 wt % uranium and <0.4 wt % iron were ground to -200 mesh, 99.9% or more of the uranium was recovered in two 4-hr leaches with boiling

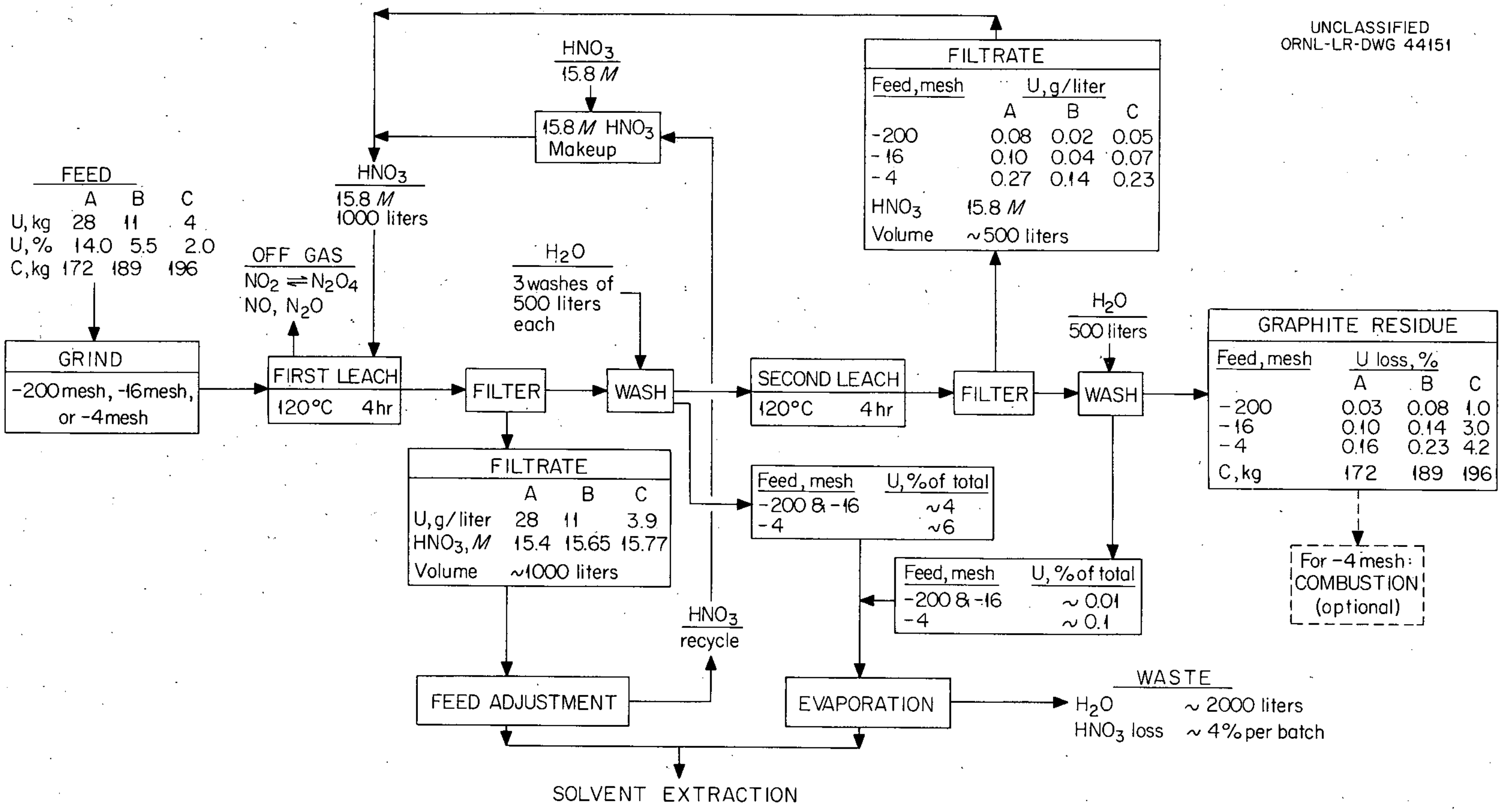

Fig. 2.1. Flowsheet for recovery of uranium from graphite fuel (<0.4 wt % Fe) by a grind-leach method.

15.8 M HNO_3 and thorough washing of the graphite residue. If higher uranium losses may be tolerated, coarser grinding is feasible. The uranium loss to the graphite residue was decreased 0.1-0.2% by decreasing the particle size of 5.5-14 wt % uranium fuels from -4 +8 mesh to -200 mesh. The uranium recovery from 2 wt % fuel increased 3.2% when the particle size was decreased from -4 +8 to -200 mesh. Iron concentrations above 0.4 wt % in the fuel appeared to lower yields (Sect. 2.2a). In laboratory experiments (Sect. 2.3) about 3.2 moles of nitric acid was consumed per mole of metal (uranium + iron), yielding a mixture of nitrogen oxides as the gaseous products. No volatile carbon-containing gases were found.

The processes proposed for the three particle sizes are essentially the same. Flowsheet conditions were calculated for a fuel charge of 200 kg, since the amount of nitric acid required is dependent on the total amount of material present, because of the high absorption capacity of the graphite, rather than the amount of uranium. The fuel is ground before digestion with boiling 15.8 M HNO_3 for 4 hr at an acid volume/fuel weight ratio of 5 liters/kg. The filtered product solution is 15.4-15.77 M HNO_3 containing 28 to 4 g of uranium per liter. A suitable solvent extraction feed solution may be obtained by evaporating the excess nitric acid and diluting with water. The distillate may be recycled to the dissolver after the addition of relatively small quantities of 15.8 M HNO_3, since the nitric acid concentration in the filtered solution, 15.4-15.77 M, is higher than the maximum-boiling, azeotropic concentration of 15.3 M. Because the graphite matrix tends to retain solution to the extent of 10 to 20% of the graphite weight even after vacuum filtration, ~4% of the total uranium recovered is found in the wash solutions. A second nitric acid leach (2.5 liters of acid per kilogram of fuel) of -16 mesh fuel solubilizes 0.2% of the total uranium found in 5.5-14 wt % samples and 0.8% of the uranium in 2 wt % specimens. With -4 +8 mesh particles, the second leach solubilizes 1% of the total uranium from 5.5-14 wt % samples and 6% from the 2 wt % specimens.

The filtrate from the second nitric acid leach is dilute in uranium and has essentially the same nitric acid concentration as the original reagent. This solution could probably be used to leach the next batch of fuel, thus eliminating the distillation of large volumes of nitric acid at this point. Although the laboratory experiments have all been with 15.8 M HNO_3, rather than the azeotropic 15.3 M, it may be possible to operate the process with recycled 15.3 M acid and additions of 15.8 M acid as necessary to maintain the total volumes without noticeable increase in the uranium losses. If the nitric acid concentration is only 12 M, the uranium recovery from 14 wt % fuel specimens will decrease 0.1% under the flowsheet conditions proposed for -16 mesh fuel and 1.0% from 2 wt % fuel. Changing the acid volume/fuel weight ratio from 5 to 2.5 liters/kg in the first leach of a flowsheet for -16 mesh material lowers the uranium recovery 0.1% from 5.5-14 wt % uranium specimens in the first leach plus washes; however, the second leach recovery increases by a corresponding amount so that over-all recovery is essentially the same. The amount of uranium in the wash solutions increases when less acid is used. It is doubtful whether the acid volume/fuel weight ratio can be decreased much below 2.5 liters/kg and still cover all the graphite with acid. Although water was always used for washing the residues in the laboratory, nitric acid could be substituted in the process to eliminate carry-over of water between the washing and leaching steps, with subsequent lowering of the nitric acid concentration. Exact washing conditions will depend on the efficiency of the filter.

It may be desirable to use a combination of grind-leach—combustion-digestion, particularly with 2 wt % uranium fuel where at best the uranium recovery is only 99.0% by a grind-leach method. Coarse grinding to -4 mesh followed by two leaches would remove 96% of the uranium and probably the major portion of the fission products. The graphite residue could then be burned at leisure, with the hazard from volatile radioactive fission products greatly decreased by leaching before the combustion. Uranium losses should be strictly handling losses.

2.2 Leaching Tests on Uranium-Graphite Fuel

When graphite fuel specimens containing more than 5% uranium and less than 0.4% iron were ground to -200 mesh and leached with two portions of boiling 15.8 M HNO_3, 99.9% or more of the uranium was recovered. Below about 3% uranium in graphite, the uranium recovery from these admixture high-density graphitized fuels decreased so rapidly with decreasing uranium concentration, even at -325 mesh, that the grind-leach process as the only method of uranium recovery will not be applicable (Fig. 2.2). Losses with -200 mesh samples of graphite fuels containing 3 to 5% uranium will be about 0.5% to 0.1%, based on the general curve (Fig. 2.2). The amount of uranium recovered from ground uranium-graphite fuel samples increased with decreasing particle size, increasing nitric acid concentration of the leach, increasing number of water washes, increasing number of acid leaches, and increasing reflux time up to 4 hr. Except where other leaching procedures were being tested, the leaching method consisted in refluxing 10-g samples of fuel with 50 ml of 15.8 M HNO_3 for 4 hr, washing the residue with three 25-ml portions of cold water, digesting the residue another 4 hr with 25 ml of fresh acid, and finally washing once with 25 ml of water. Washing was achieved by contacting the residue with each volume of water for 15 min and then filtering under vacuum.

a. Leaching of Fuel Containing >5% Uranium

Effects of Particle Size, Water Washes, Second Nitric Acid Leach, and Acid Volume. The uranium loss to the graphite residue was reduced to 0.1-0.2% by reducing the particle size from -4 +8 to -200 mesh (Table 2.1). Significant amounts of uranium were found in the water washes after the first leach, 0.2% in the third wash of -16 mesh material and 0.6% in the third wash of -4 +8 mesh samples. The second nitric acid leach recovered 0.2% of the total uranium from -16 mesh samples, 0.9% from -4 +8 mesh. Decreasing the amount of acid used in the first leach to 25 ml per 10-g

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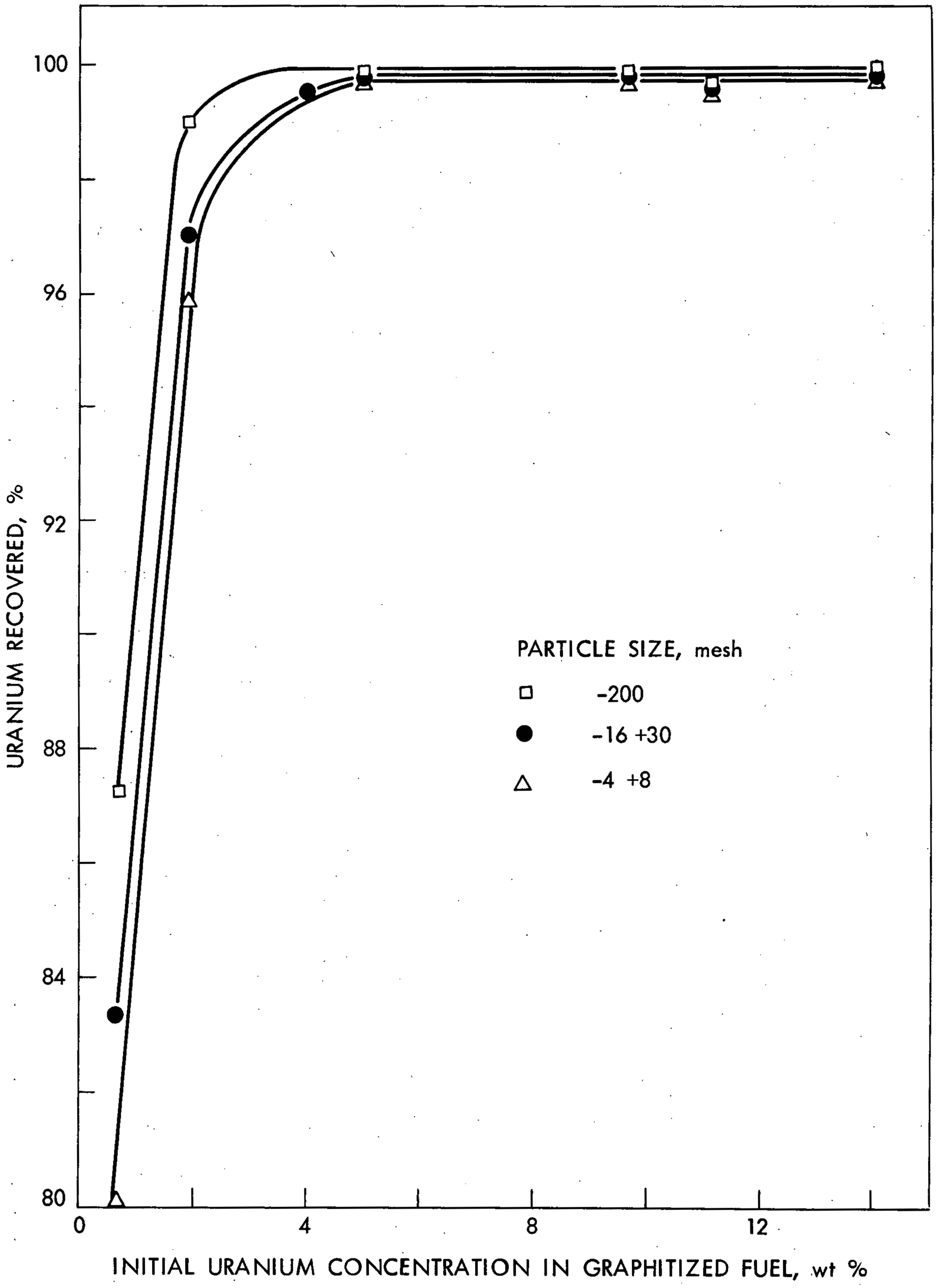

Fig. 2.2. Uranium recovery as a function of initial uranium concentration in admixture high-density graphitized fuels after leaching with two portions of boiling nitric acid. First leach 50 ml of acid per 10-g sample, 4 hr reflux; second leach 25 ml of acid per 10-g sample, 4 hr reflux; thorough water washes after each leach.

Table 2.1. Recovery of Uranium from 5.5-14 wt % Uranium-Graphite Fuel Specimens by Leaching with Boiling 15.8 M HNO_3

Leaching procedure: 10-g sample digested 4 hr with 50 ml of boiling 15.8 M HNO_3 and filtered, and residue washed three times with water; digested again with 25 ml of boiling 15.8 M HNO_3 and washed once with water

Run No.	U in Fuel, %	Fe in Fuel, %	Particle Size, mesh	Uranium Recovered, %: 1st HNO_3 Leach + 2 Water Washes	3rd Water Wash	Total Solubilized 1st Leach + 3 Washes	2nd HNO_3 Leach + 1 Water Wash	Graphite Residue[a]	Total Solubilized[b]
29	5.41	0.25	-4+8	98.04	0.50	98.54	1.24	0.231	99.77
24	5.49	0.24	-16+30	99.67	0.06	99.73	0.13	0.138	99.86
23	5.47	0.24	-16+30	99.43[c]	0.20[c]	99.63[c]	0.22[c]	0.148	99.85[c]
30	5.33	0.27	-200	99.81	0.04	99.85	0.08	0.077	99.92
26	9.46	0.07	-4+8	98.31	0.69	99.00	0.82	0.18	99.82
14	9.76	0.06	-16+30	99.59	0.10	99.69	0.20	0.121	99.88
13	9.73	0.07	-16+30	98.87[c]	0.72[c]	99.59[c]	0.31[c]	0.132[c]	99.87[c]
31	10.51	0.17	-200	99.71	0.07	99.78	0.13	0.098	99.90
18	11.06	0.76	-4+8	98.19	0.38	99.57	0.87	0.51	99.49
15	11.14	0.69	-16+30	99.10	0.23	99.33	0.19	0.43	99.57
16	11.20	0.67	-16+30	99.20	0.21	99.41	0.15	0.43	99.57
17	11.16	0.68	-16+30	99.01[c]	0.16[c]	99.17[c]	0.32[c]	0.49[c]	99.51[c]
27	12.43	1.04	-200	99.39	0.15	99.54	0.19	0.27	99.73
25	13.84	0.45	-4+8	98.30	0.59	98.89	0.95	0.16	99.84
19	14.12	0.42	-16+30	99.79	0.03	99.82	0.07	0.097	99.90
20	14.29	0.41	-16+30	99.37[c]	0.28[c]	99.65[c]	0.22[c]	0.105[c]	99.90[c]
22	14.15	0.41	-16+30	99.51	0.14	99.65	0.25	0.105	99.90
33	12.75	0.39	-100+200	99.70	0.09	99.79	0.13	0.075	99.92
28	15.19	0.47	-200	99.65	0.17	99.82	0.14	0.033	99.97

[a] Combustion analyses.

[b] 100% minus loss to graphite residue.

[c] 1st leach, 25 ml of acid per 10-g sample.

sample decreased the uranium recovery after the first leach by 0.1%, but the second leach recovery increased by a corresponding amount so that the over-all yields were the same (Table 2.1, runs 23, 13, 17, and 20). It is doubtful whether the volume of nitric acid can be decreased much below 25 ml per 10-g sample and still be sufficient to completely cover the graphite matrix.

Effect of Acid Concentration in Leaching 14% Uranium Fuel. Increasing the nitric acid concentration from 4 to 15.8 M increased the uranium recovery from -16 mesh fuel by 0.1% (Fig. 2.3, Table 2.2).

Table 2.2. Effect of Nitric Acid Concentration on Leaching of 13.9 wt % Uranium-Graphite Fuel, -16 Mesh

Leaching procedure: 10 g of sample digested 4 hr with 50 ml of boiling 15.8 M HNO_3 and filtered, and residue washed three times with water; digested again with 25 ml of boiling 15.8 M HNO_3 and washed once with water

		Reflux Time, hr		Uranium Recovered, %				
Run No.	HNO_3 Conc., M	1st Leach	2nd Leach	1st HNO_3 Leach + 2 Water Washes	3rd Water Wash	Total Solubilized 1st Leach + 3 Washes	2nd HNO_3 Leach + 1 Water Wash	Graphite Residue
1	16	3.5	4	99.47	-	99.47[a]	0.43	0.10
7	16	4	-	99.78	0.07	99.85	-	0.13
8	16	4	-	99.78	0.09	99.87	-	0.14
11	16	4	-	99.64[b]	0.18	99.82[b]	-	0.18[b]
12	16	4	-	99.69[b]	0.13	99.82[b]	-	0.18[b]
2	12	4	4	98.83	-	98.83[a]	1.03	0.14
4	12	5	-	99.71	0.12	99.83	-	0.15
5	12	5	-	99.20	0.51	99.71	-	0.26
6	12	6	-	99.50	0.13	99.63	-	0.35
3	4	4	3	98.96	-	98.96[a]	0.71	0.33
9	4	4	-	99.49	0.23	99.72	-	0.30
10	4	4	-	99.42	0.34	99.76	-	0.27

[a] Two water washes.

[b] 25 ml of acid per 10-g sample.

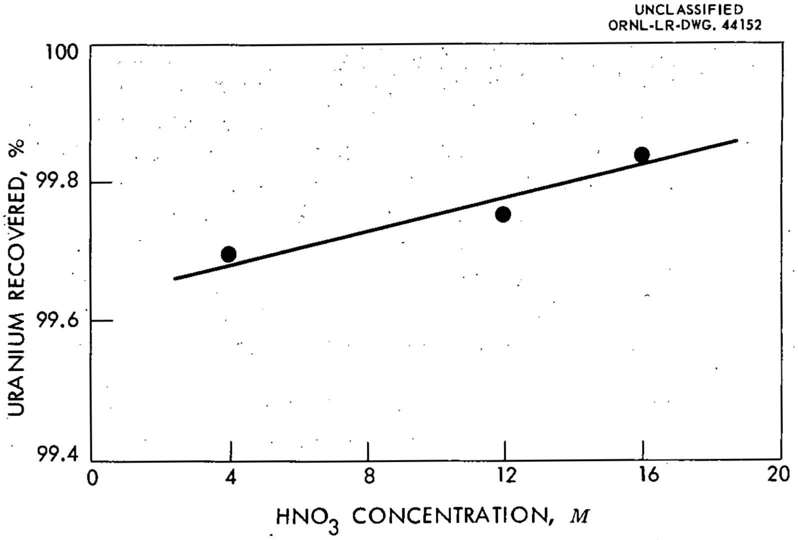

Fig. 2.3 Effect of nitric acid concentration on uranium recovery from 13.9 wt % uranium in graphite fuel. One 4-hr leach of -16 mesh particles with boiling nitric acid, 50 ml of acid per 10-g sample.

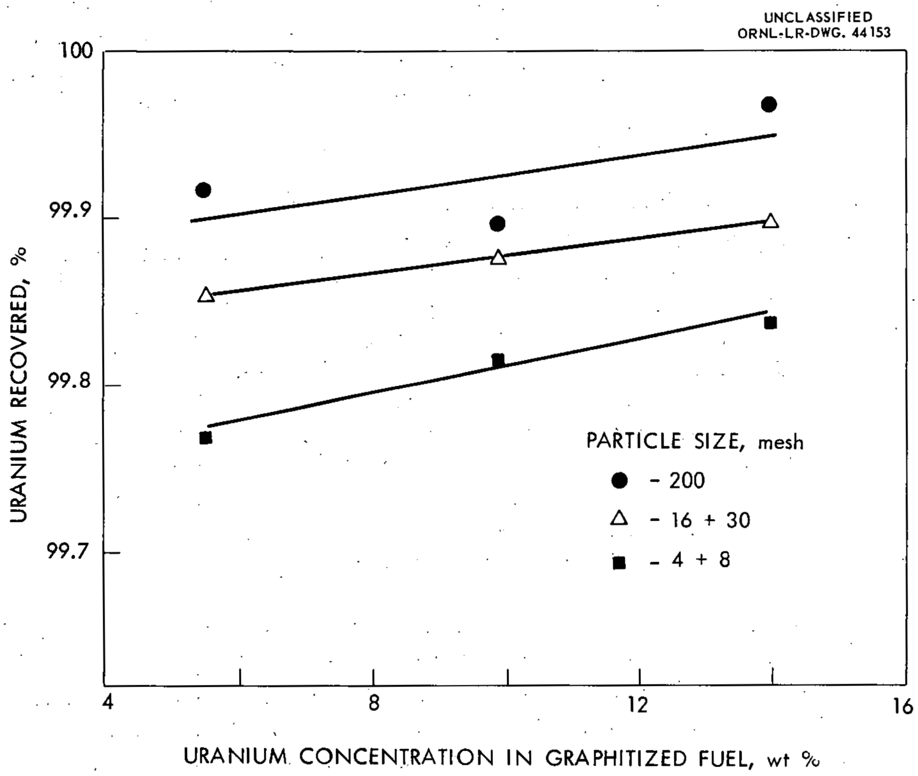

Fig. 2.4. Uranium recovery as a function of initial uranium concentration in admixture high-density-graphitized fuels after two 4-hr leaches with boiling 15.8 M HNO_3. Residue washed with cold water after each leach.

Effect of Uranium and Iron Concentrations. Uranium recovery from 5.5, 9.7, and 14.0 wt % uranium specimens increased slightly with increasing uranium concentration (Fig. 2.4), while uranium recovery from the 11.2 wt % sample was consistently lower by 0.2-0.3%. The exact history of each fuel specimen is not known, but the iron content of the 11.2 wt % specimen was 2-10 times higher than in the other specimens (Table 2.1). In general, the uranium concentration in the graphite residue increased with increasing iron content (Fig. 2.5). This effect may be caused by solid solution formation between uranium and iron and iron carbide (the last two are unreactive toward nitric acid), or variations in the iron impurity content may simply be an indication of variations in the porosity and density of the samples as manufacturing techniques were changed. Data are insufficient to draw a definite conclusion.

At low iron concentration, the uranium concentration in the graphite residue after leaching seems to approach a limiting value of 40-150 ppm by weight in the graphite, depending on the particle size but independent of the initial uranium concentration over the range 5.5-14 wt %. This view is consistent with that of Fromm,[4] who electrolytically disintegrated solution-impregnated graphite (14% uranium) in boiling concentrated nitric acid. The solution after electrolytic disintegration contained 99.91% of the original uranium.[4] After two leaches with boiling concentrated nitric acid, the uranium recovery was 99.95%; after three, 99.96%; four, five, or six, 99.97%. The limiting uranium concentration in the graphite (~70% passed a 35 mesh sieve) was 50 ppm.

b. Leaching of Fuel Containing <5% Uranium

Effect of Particle Size, Water Washes, Successive Nitric Leaches, and Reflux Time. Decreasing the particle size from -4 +8 mesh to -200 mesh increased the uranium recovery from 0.7, 2, and 4 wt % uranium-graphite fuels by 7, 3, and 0.6%, respectively (Table 2.3). Nothing was gained by grinding the 2% uranium fuel any finer than 200 mesh. Significant amounts of uranium were recovered in the water washes. With 2% uranium fuel that had been leached once with boiling 15.8 M HNO_3, 1 to 6% of the total uranium present was found in the second water wash, and as high as 1.3% in the third (Table 2.4). Variations in the filtration pressure account for some spread in the results. Boiling water offered no advantages over cold water. A fourth wash recovered very little uranium, ~0.01%, in the only case studied.

One 4-hr leach followed by a second 4-hr leach with fresh acid is recommended for optimum uranium recovery. The 2-, 4-, and 6-hr leaches of the 2% uranium-graphite fuel gave nearly the same metal recovery, being only slightly lower in 2 hr (Table 2.5). An additional 0.7-0.9% of the total uranium was obtained from -16 +30 mesh 2% uranium fuel with a second leach of 2-6 hr, and 2% with a 40-hr second leach. When the standard procedure of two 4-hr leaches was used with 0.7-4% uranium fuels, about 6% of the total uranium recovered from -4 +8 mesh samples appeared

Table 2.3. Recovery of Uranium from 0.7-4 wt % Uranium-Graphite Fuel Specimens by Leaching with Boiling 15.8 M HNO_3

Leaching procedure: 10 g of sample digested 4 hr with 50 ml of boiling 15.8 M HNO_3 and filtered, and residue washed three times with water; digested again with 25 ml of boiling 15.8 M HNO_3 and washed once with water

				Uranium Recovered, %					
Run No.	U in Fuel, %	Fe in Fuel, %	Particle Size, mesh	1st HNO_3 Leach + 2 Water Washes	3rd Water Wash	Total Solubilized 1st Leach + 3 Washes	2nd HNO_3 Leach + 1 Water Wash	Graphite Residue[a]	Total Solubilized[b]
B-8	0.694	0.129	-4+8	74.0	0.68	74.7	5.48	19.9	80.1
B-9	0.681	0.136	-16+30	79.3	0.73	80.0	3.23	16.7	83.3
B-10	0.740	0.232	-200	85.4	0.10	85.5	1.76	12.7	87.3
32	1.92	0.26	-4+8	85.4	4.58	90.0	5.83	4.21	95.8
6	1.93	0.25	-16+30	95.7	0.89	96.6	0.78	2.6	97.4
12	2.00	0.26	-16+30	95.4	0.21	95.6	0.89	3.5	96.5
1	1.97	0.26	-16+30	95.6[c]	0.86	96.4	0.68	3.0	97.0
2	1.95	0.27	-30+50	95.9[c]	1.09	96.9	0.59	2.5	97.5
14	1.92	-	-100+140	97.1[c]	0.09	97.2	0.42	2.4	97.6
13	2.00	-	-200	98.3[c]	0.14	98.4	0.55	0.98	99.0
16	2.06	-	-325	98.2[c]	0.05	98.2	0.6	1.2	98.8
B-11	4.26	0.38	-4+8	91.9	0.57	92.5	6.48	1.03	99.0
B-20	4.24	0.40	-4+8	90.8	0.41	91.2	7.21	1.54	98.5
B-12	4.05	0.37	-16+30	98.6	0.43	99.0	0.66	0.35	99.6
B-19	4.38	0.48	-200	99.4	0.02	99.4	0.23	0.37	99.6

[a] Combustion analyses.

[b] 100% minus loss to graphite.

[c] 6-hr first leach.

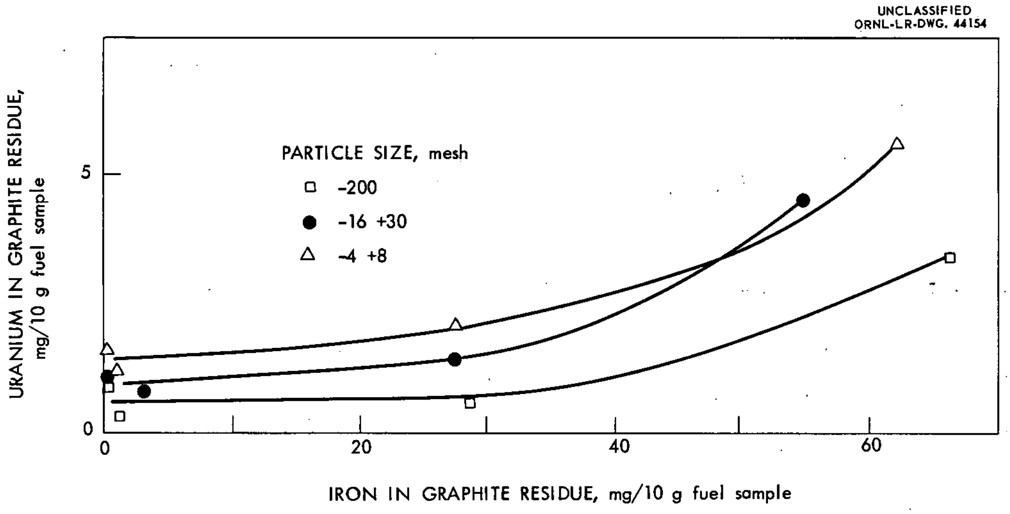

Fig. 2.5. Uranium present in graphite residue after two 4-hr leaches with boiling 15.8 *M* HNO_3 as a function of iron concentration. Uranium concentration before leaching 5.5-14 wt %; after leaching 0.004-0.06 wt %. Graphitized fuel.

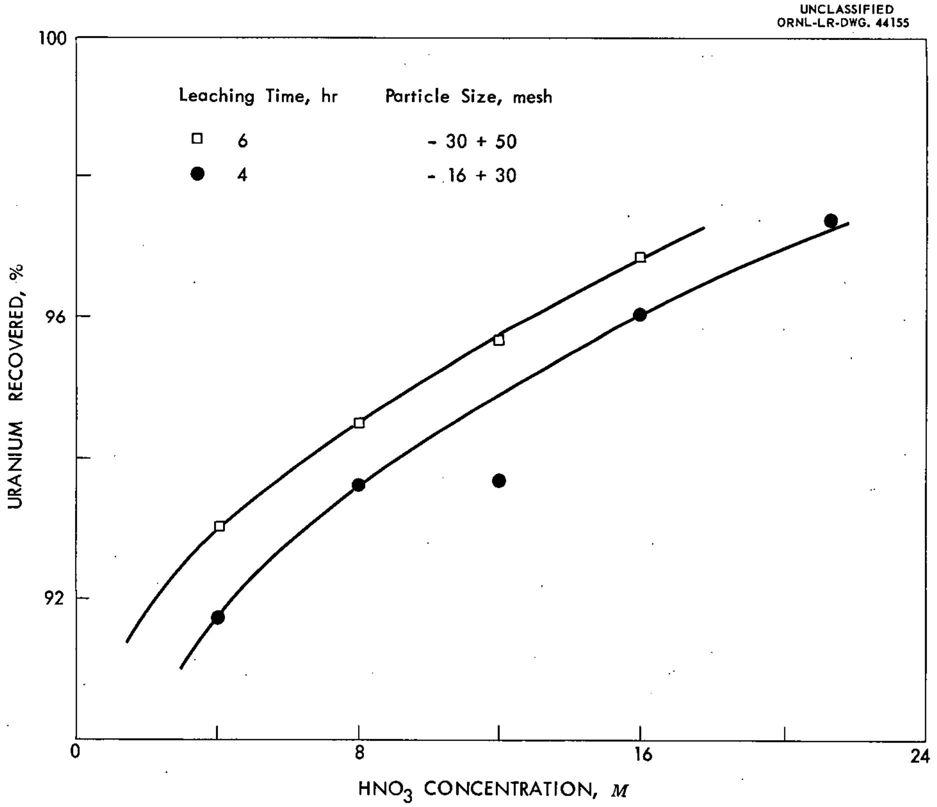

Fig. 2.6. Effect of nitric acid concentration on the recovery of uranium from 2% uranium-graphite fuel. Single 4-hr leach with 50 ml of boiling acid per 10-g fuel sample.

Table 2.4. Effect of Water Washes on Uranium Recovery from 2% Uranium-Graphite Fuel

Leaching procedure: as in Table 2.3

	Uranium Recovered, %		
Run No.	1st HNO_3 Leach + 1 Water Wash	2nd Water Wash	3rd Water Wash
1	91.1	4.48	0.86
2	91.7	4.15	1.09
3	88.4	5.99	1.34
4	90.4	3.31	0.79
5	91.9	3.41	0.81
6	91.9	3.78	0.89
7	87.4	5.18	1.06
8	89.2	4.96	0.95
12	94.0	1.35	0.21

in the second nitric acid leach (Table 2.3). With -200 mesh fuel samples, the amount dissolved in the second nitric acid leach decreased from 2% with the 0.7% uranium-graphite fuel to 0.2% with the 4% fuel. The second nitric acid leach was more effective than washing with water (Table 2.3). Because successive leaches increased the uranium recovery, the effect of Soxhlet extraction was investigated. Soxhlet extraction of -16 +30 mesh specimens of the 2% uranium-graphite fuel with azeotropic nitric acid (15.3 M) yielded uranium recoveries of 95.8% for 6- and 9-hr cycles and 98.4% for 22-hr cycles, as compared with 97.0% for the batch two-leach (6-hr) treatment. The lower yields from Soxhlet extraction are probably related to either the lower reaction temperature or absorption of atmospheric moisture by the nitric acid vapors, so that the cycling acid was less than 15.3 M.

Effect of Acid Concentration in Leaching 2% Uranium Fuel. Uranium recovery decreased with decreasing acid concentration (Fig. 2.6, Table 2.5). About 97% of the uranium was recovered with 21.2 M HNO_3 from -16 +30 mesh 2% uranium fuel, but only 93% with 4 M. A similar decrease was observed with -30 +50 fuel, i.e. 97.5% with 15.8 M to 94.2% with 4 M. With -200 mesh material only 96.2% of the uranium was recovered with 8 M acid as compared with 99.0% with 15.8 M acid.

Effect of Uranium Concentration. Uranium recovery decreased rapidly with decreasing initial uranium concentration, i.e. from 99.6% with 4% uranium-graphite fuel (-16 +30 mesh) to 83.3% with 0.7% uranium-graphite

Table 2.5. Effect of Acid Concentration and Leaching Time on Uranium Recovery from 2% Uranium-Graphite Fuel

Leaching procedure: 10 g of sample digested with 50 ml of boiling nitric acid and filtered, and residue washed three times with water; digested again with 25 ml of boiling nitric acid, and washed once with water

Run No.	HNO_3 Conc., M	Reflux Time, hr		Uranium Recovered, %					
		1st Leach	2nd Leach	1st HNO_3 Leach + 2 Water Washes	3rd Water Wash	Total Solubilized 1st Leach + 3 Washes	2nd HNO_3 Leach + 1 Water Wash	Graphite[a] Residue	Total Solubilized[b]
				Fuel Ground to -16 +30 Mesh					
55	21.2	4	4	97.4	0.2	97.6	1.2	1.2	98.8
1	15.8	6	6	95.6	0.86	96.4	0.68	3.0	97.0
6	15.8	4	4	95.7	0.89	96.6	0.78	2.6	97.4
12	15.8	4	4	95.4	0.21	95.6	0.89	3.5	96.5
5	15.8	4	40	95.3	0.81	96.1	2.12	1.8	98.2
8	15.8	2	2	94.2	0.95	95.1	0.89	4.0	96.0
7	12	4	4	92.6	1.06	93.6	0.94	5.4	94.6
9	8	4	4	92.3	1.33	93.6	1.40	5.0	95.0
10	4	4	4	90.7	0.99	91.7	1.64	6.7	93.3
				Fuel Ground to -30 +50 Mesh					
2	15.8	6	6	95.8	1.09	96.9	0.59	2.5	97.5
3	12	6	6	94.4	1.34	95.7	0.75	3.5	96.5
4	8	6	6	93.7	0.79	94.5	0.84	4.6	95.4
15	4	6	6	93.0	0.05	93.0	1.14	5.8	94.2

[a] Combustion analyses.

[b] 100% minus loss to graphite.

fuel (-16 +30 mesh) (Table 2.3). The limiting uranium concentration in the graphite residue, 40-150 ppm after leaching, observed with fuels containing more than 5% uranium, was not reached with two leaches of -200 or -325 mesh samples of fuel containing less than 5% uranium. The explanation is probably a matter of diffusion rates. As the uranium is dissolved from the higher uranium content fuels, a more porous graphite is left through which diffusion is more rapid than with the low uranium content fuels.

2.3 Stoichiometry

An investigation of the stoichiometry of the reaction of uranium-graphite fuel with nitric acid was started. This information will allow calculation of the acid consumption and the amount of gases evolved during the leaching process. An average of 3.2 moles of nitric acid was consumed per mole of metal when the leaching was done in a helium atmosphere. Pure UC_2 reacts vigorously with water to yield a complex mixture of hydrocarbons and hydrogen.[5] No reference to the reaction of uranium carbides with nitric acid could be found. The only product gases from the reaction of uranium-graphite fuel with nitric acid that could be detected by infrared and gas chromatographic analyses were nitrogen oxides. No carbon-containing gas was found. The preliminary data on the relative amounts of the nitrogen oxides produced, nitric acid consumption, and the amount of nitrous acid formed suggest that the uranium was present in the fuel samples as UO_2 rather than UC_2.

Fuel containing 14 wt % uranium was selected for this study to obtain maximum acid consumption and gaseous products at a ratio of 5 ml of acid to 1 g of sample.

a. Acid Consumption

An average of 3.2 moles of HNO_3 (either 12 $\underline{M}$ or 15.8 $\underline{M}$) was consumed per mole of metal when the leaching was done in a helium atmosphere (Table 2.6). Errors other than in pipetting (± 0.05 ml, i.e. ± 0.8 mmole of total acid) will result in loss of nitric acid from the system, so that the amount of acid consumed, as determined by difference, will tend to be slightly larger than the true value.

In some solutions an acid weaker than nitric was found. This acid could be differentially titrated in acetone after removal of the uranium by ion exchange. Indications are that it was nitrous acid, although positive identification was not made. The equilibria

$$HNO_3 + HNO_2 \rightleftharpoons N_2O_4 + H_2O \rightleftharpoons 2NO_2 + H_2O$$

are known.[6] The nitrous acid concentration is thus directly dependent on the concentration of the gases N_2O_4 and NO_2 and inversely dependent on the nitric acid concentration. Vacuum filtration, which removes the N_2O_4

and NO_2 from the system, will shift this equilibrium, removing nitrous acid from the solution. Variations in filtration technique would cause variations in the nitrous acid concentration such as were observed experimentally.

b. Gaseous Products

In a series of experiments covering the nitric acid range 4-15.8 M, the only gases detected by infrared and gas chromatographic analyses were the nitrogen oxides NO_2, NO, and N_2O. No peaks were observed for hydrocarbons, CO, or CO_2, and there were no unidentified peaks by either method. Infrared analysis is quite sensitive to the C-H bond in organic materials, and the gas chromatograph is moderately sensitive for CO and CO_2. Duplicate runs with a given acid concentration gave identical infrared spectra. The infrared spectra of the gases evolved when 15.8 and 12 M HNO_3 were used in leaching were almost identical, but with 4 M HNO_3 the spectra showed more NO and less NO_2, as would be expected. It seems safe to conclude that the gaseous products of the reaction were only a mixture of nitrogen oxides and that there was no volatile carbon compound in the gas phase.

Table 2.6. Acid Consumed in Leaching 13.9 wt % Uranium-Graphite Fuel, -16 Mesh, with Nitric Acid in a Helium Atmosphere

Run No.	HNO_3 Conc., M	Acid, mmoles				Metal Solubilized, mmoles		Moles HNO_3 Used per Mole Metal
		HNO_3 Added	Left After Reaction	Weaker Acid	HNO_3 Used	U	Fe	
7	15.8	777.8	759.7	3.40	21.5	5.82	0.338	3.49
8	15.8	777.8	759.7	2.80	20.9	5.78	0.346	3.41
11	15.8	395.2	373.0	0	22.2	5.75	0.340	3.64
12	15.8	397.7	381.5	0	16.2	5.83	0.324	2.63
4	12	602.4	590.4	2.20	14.2	5.76	0.372	2.31
5	12	602.4	584.9	2.25	19.7	5.79	0.394	3.18
6	12	602.4	583.1	2.27	21.6	5.81	0.397	3.49
							avg	3.2

Gas Chromatograph—Visible Spectra. The gas chromatograph is a recent development which has been very useful for the quantitative analysis of gas mixtures, but has not been applied specifically to nitrogen oxide mixtures of this type. Fair calibration curves were obtained with standard amounts of NO and N_2O, but with the present experimental arrangement NO_2 peaks tended to smear and were not reproducible. Since the amount of helium diluent is unknown, NO_2 cannot be determined by difference. The NO/N_2O volume ratio varied from 1.2 with 12 M or 15.8 M acid to 1.8 with 4 M (Table 2.7).

Table 2.7 Gas Chromatographic Analyses for NO and N_2O

Sample size: 10.8 ml

Run No.	HNO_3 Conc., M	NO, ml	N_2O, ml	NO/N_2O
12	16	2.0	1.7	1.17
6	12	1.9	1.5	1.27
9	4	2.3	1.4	1.64
10	4	3.2	1.8	1.78

Two independent determinations of NO_2 in the gas by visible spectra gave an approximate value of 10.4 vol % when 15.8 M HNO_3 was used. The equilibrium amount of the dimer, N_2O_4, present at this temperature and partial pressure of NO_2 is 5.5% (based on $K_{dissociation} = 0.1426 - 9.7588C$, where C = moles of N_2O_4 per liter if N_2O_4 did not dissociate).[7] A rough estimate of the relative proportions of the nitrogen oxides in the gaseous product at 25°C, a total pressure of 1 atm, and a NO_2 partial pressure of 0.10 atm is 1.9 NO_2/3.4 NO/2.9 N_2O/1.0 N_2O_4. If it is assumed that the N_2O_4 is completely dissociated for purposes of considering the relative mole quantities of gases in the various oxidation states, the ratios are 1.4 NO_2/1.2 NO/1.0 N_2O.

For the experiments 10 g of sample was placed in the 250-ml flask and the flask attached to the apparatus shown in Fig. 2.7. The entire system was flushed with helium for 1 hr to remove oxygen, which would react with any NO that might be formed in the reaction. After the system was thoroughly flushed, nitric acid was introduced through the separatory funnel and the mixture refluxed. Two 10.8-ml gas samples were collected for gas chromatographic analysis on a silica gel column and one 250-ml sample for either infrared or visible spectrum analysis.

Chemical Absorption. It has been reported that NO_2 and NO may be determined chemically by selective absorption.[8,9] The NO_2 is adsorbed in a 0.1 N NaOH solution while NO and N_2O pass through.[8] The NO is then removed by a 0.1 N ceric (or permanganate)—1 M H_2SO_4 solution. Nitrous oxide is not absorbed chemically by any of the standard techniques.[9] The reactions in the first scrubber would thus be

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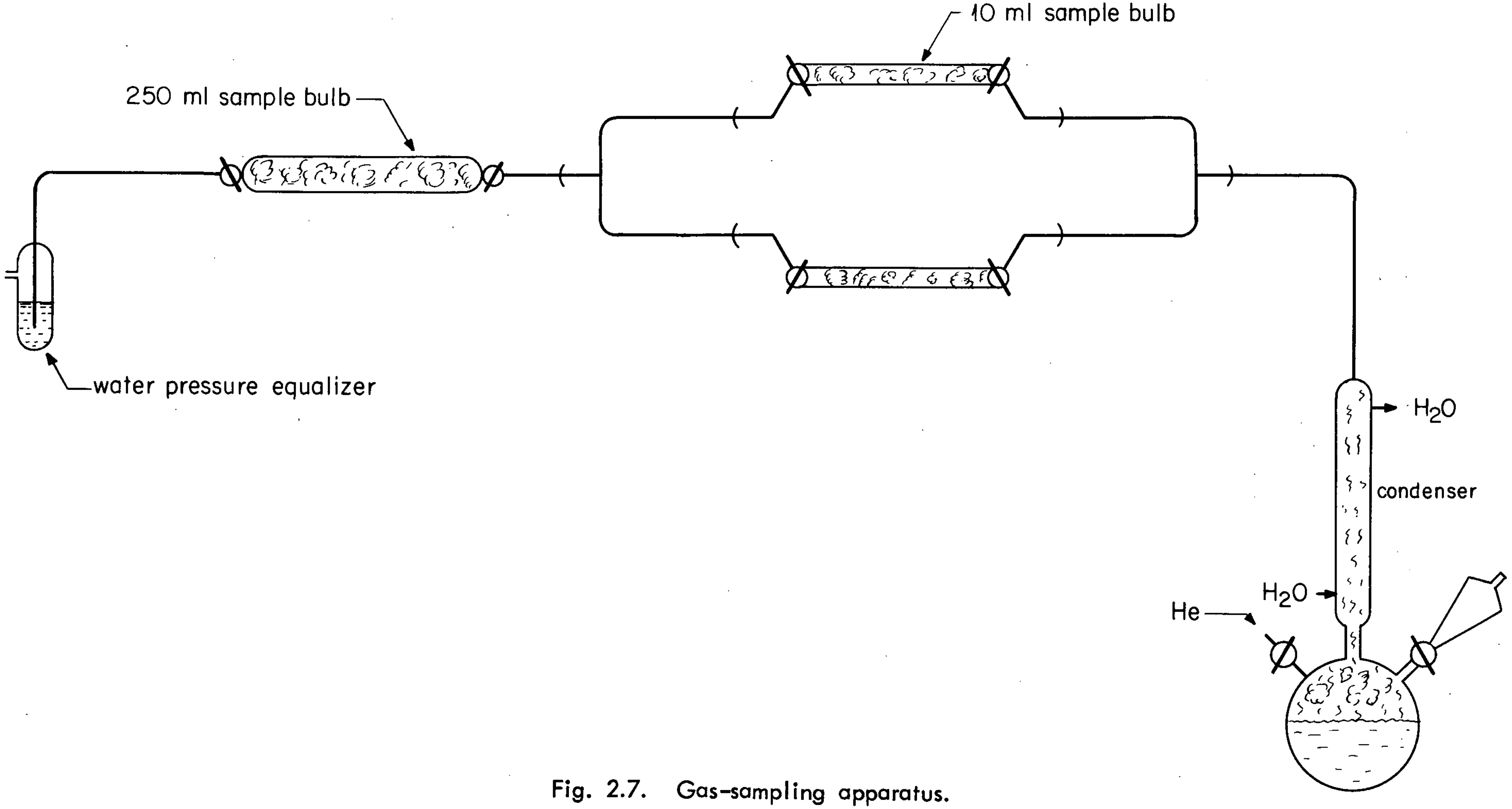

Fig. 2.7. Gas-sampling apparatus.

$$2\ NO_2 + 2\ NaOH \longrightarrow NaNO_3 + NaNO_2 + H_2O$$

$$HNO_3 + NaOH \longrightarrow NaNO_3 + H_2O$$

The nitric acid is carried over by evaporation from the solution. The excess base is back-titrated with standard acid to determine the total acid in the scrubber, and nitrite is determined by oxidation to nitrate with standard 0.1 N Ce^{4+}—1 M H_2SO_4 solution. In the second scrubber, nitric oxide is oxidized to nitrate upon absorption, and the excess ceric ion back-titrated with standard ferrous sulfate for the quantitative determination.

Two preliminary experiments were made before it was discovered* in connection with gas chromatography studies that although nitric oxide is not absorbed by 0.1 N NaOH, as is NO_2, the N_2O_3 formed by interaction between NO and NO_2 in mixtures of the gases is partially absorbed. The percentage absorbed at any given ratio of NO to NO_2 is a constant, but no simple relation between the amount absorbed and the gas composition was found which could be used as a calibration curve. Therefore, chemical absorption data can give only the total number of milliequivalents of NO, N_2O_3, NO_2, and N_2O_4. In the two preliminary experiments, 5.9 mmoles of uranium and 0.2 mmoles of iron reduced 9.4 and 12.2 meq of the combined NO, N_2O_3, NO_2, and N_2O_4.

c. Reaction Equations

Oxidation-reduction reactions involving nitric acid are among the most complicated known because of the large number of nitrogen oxides that may be produced and the various equilibria among these gases, water, HNO_3, HNO_2, and atmospheric oxygen. Experiments were performed in a helium atmosphere to eliminate one of the many variables. An additional complexity is introduced in that the chemical form of the uranium and iron in the fuel specimens was not certain. The fuel, as originally prepared, was UC_2 in graphite; however, it had been allowed to stand in moist air for a year before chemical studies were begun. Graphite dispersions of UC_2 are converted to the oxide in a few days.[10] No data on the reaction of pure UC_2 or UC with nitric acid are available for comparison.

It was established experimentally that UO_2^{2+} and Fe^{3+} are the metal ion products of the reaction. The gas phase consists entirely of nitrogen oxides. The original uranium compound is probably an oxide rather than a carbide, since no carbon compound appeared in the gas phase and nonvolatile carbon compounds such as acetic acid, which are stable in refluxing 15.8 M HNO_3, if present in the solution at all were in such low concentration that they could not be identified. Further work will be required to study the gases evolved from UC_2 since the presence of acetylene, CO, or similar gases could be dangerous in the dissolver system.

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*By A. D. Horton of the ORNL Analytical Chemistry Division, August 1959.

A very rough check of this speculation may be made with the preliminary data now available (Table 2.6). If the half reactions

	meq oxidized/10-g sample of 13.9 wt % uranium fuel
$UO_2 \longrightarrow UO_2^{2+}$	11.6
$Fe \longrightarrow Fe^{3+}$	1.0

are the correct ones, a total of 12.6 meq of metal would be oxidized. This oxidizing power is supplied by a series of nitric acid half-reactions (Table 2.8).

Table 2.8. Oxidation-Reduction Half-reactions of Nitric Acid

HNO_3 Consumed, meq/mmole of nitrogen product	Reaction	Change in Oxidation No. per mole of nitrogen product	NO_3^- Reduced, meq/mmole of nitrogen product
2.8z	$2\ H^+ + NO_3^- \longrightarrow NO_2 + H_2O$	1	1.4z
3(mmoles HNO_2)	$3\ H^+ + NO_3^- \longrightarrow HNO_2 + H_2O$	2	2(mmoles HNO_2)
4.8z	$4\ H^+ + NO_3^- \longrightarrow NO + 2\ H_2O$	3	3.6z
10z	$10\ H^+ + 2NO_3^- \longrightarrow N_2O + 5\ H_2O$	8	8z
17.6z + 3(mmoles HNO_2)			13.0z + 2(mmoles HNO_2)

From the ratios of the amounts of the dissociated gases as determined by gas chromatographic and visible spectral analysis (1.4 NO_2/1.2 NO/1.0 N_2O), and the total amount of HNO_2 (assuming it was the weaker acid), it can be readily shown (Table 2.8) that the milliequivalents of nitrate reduced is equal to 13.0z + 2(mmoles HNO_2). The unknown z is the number of millimoles of N_2O produced in the reaction. Because the total volume of gas produced is not known, it is necessary to calculate z from the acid consumption. The millimoles of acid consumed is equal to 17.6z + 3(mmoles HNO_2). The results of these calculations are given in Table 2.9. An average of 14.0 meq of nitric acid was reduced as compared with the oxidation of 12.6 meq of metal for an error of 11%.

Table 2.9. Milliequivalents of Nitric Acid Reduced in Oxidation of 5.8 mmoles of Uranium in Graphite

$$z = \frac{(\text{mmoles } HNO_3 \text{ used}) - 3(\text{mmoles } HNO_2 \text{ produced})}{17.6}$$

$$\text{meq of } HNO_3 \text{ reduced} = 13.0z + 2(\text{mmoles } HNO_2 \text{ produced})$$

Run No.	HNO_3 Conc., M	HNO_3 Used, mmoles	HNO_2 Produced, mmoles	z, mmoles N_2O	HNO_3 Reduced, meq
7	15.8	21.5	3.40	0.642	15.2
8	15.8	20.9	2.80	0.710	14.8
11	15.8	22.2	0	1.26	16.4
12	15.8	16.2	0	0.920	12.0
4	12	14.2	2.20	0.432	10.0
5	12	19.7	2.26	0.739	14.0
6	12	21.6	2.27	0.841	15.5
				avg	14.0

Since these quantitative data on gas analysis are very preliminary, this discussion is of qualitative value only. Nevertheless, it may be concluded that the data accumulated thus far are reasonably consistent with the behavior expected from UO_2 in graphite. If UC_2 in graphite should be the starting material, 23.2 meq, or about twice that found, of oxidizing power would be required to oxidize 5.8 mmoles of $U^{2+} \longrightarrow UO_2^{2+}$. Additional quantitative studies are planned after the ORNL Analytical Chemistry Division has had an opportunity to further develop a gas chromatographic technique for the nitrogen oxides. The ratio of the gases will be determined by gas chromatography, and then, using either the total of NO and NO_2 as determined by chemical absorption or acid consumption, the total amount of each gas may be calculated.

3.0 URANIUM-THORIUM-GRAPHITE FUEL

Decladding of stainless steel—clad uranium-thorium-graphite fuel with 4 or 6 M H_2SO_4 appears feasible. No reagent was found, in the brief studies, which would leach more than 93% of the metals from -200 mesh fuel samples. Combustion of the graphite followed by dissolution of the residue in 13 M HNO_3—0.04 M NaF—0.04 M $Al(NO_3)_3$ gave quantitative metal recovery.

Uranium (1.5%)—thorium (7.2%)—graphite prototype samples of the General Atomics gas-cooled reactor were prepared by the National Carbon Company. The fuel elements proposed for the reactor are 1/2-in.-thick graphite tubes filled with right-cylinder fuel slugs, 3.25 in. dia by 3 in. long. In the first core a thin stainless steel cladding for the graphite tube is proposed. Prototypes for study were prepared from uranium and thorium dioxides mixed with calcined petroleum coke and pitch binder. They were molded, baked at 850°C, impregnated with pitch and rebaked to increase the density, graphitized at 2800°C in purified argon, cooled in an inert atmosphere, and machined to size. It is not known whether the original carbides were converted to the oxides before the chemical studies were made.

3.1 Chemical Decladding

The stainless steel cladding could be removed either chemically or mechanically. Two decladding reagents that have been shown to give satisfactory dissolution of stainless steel, sulfuric acid and dilute aqua regia, were investigated. Preliminary tests indicated the possibility of chemically decladding with sulfuric acid with sufficiently low uranium loss that recovery of uranium from the decladding solution is unnecessary. This does not appear to be the case with aqua regia.

When semicircular pieces (3-1/8 in. dia, 1/4 in. thick) of the unclad fuel cylinders were digested with refluxing 4 and 6 $\underline{M}$ H_2SO_4 for 6 hr, uranium and thorium losses to the solutions were of the order of 1% (Fig. 3.1). After 32 hr uranium losses to 4 and 6 $\underline{M}$ H_2SO_4 were 5 and 3%, respectively, with thorium losses even lower. For comparison, about 24% of the uranium was leached in 6 hr from fuel ground to -16 +30 mesh by 6 $\underline{M}$ H_2SO_4.

In a 6-hr digestion of 1/4-in.-thick pieces of the prototype fuel slugs with 5 $\underline{M}$ HNO_3—2 $\underline{M}$ HCl for 6 hr, 33% of the uranium dissolved (Fig. 3.2).

3.2 Grinding and Leaching

Leaching of the ground fuel with concentrated nitric acid and Thorex dissolvent was briefly investigated as a possible method for uranium recovery. The rate at which uranium and thorium were leached by boiling 15.8 $\underline{M}$ HNO_3 increased with decreasing particle size, but there appeared to be little gained by grinding finer than -4 +8 mesh (Figs. 3.3 and 3.4). In each case thorium dissolved more slowly than uranium in 15.8 $\underline{M}$ HNO_3. With fuel ground to -200 mesh, only about 93% of the uranium and 90% of the thorium could be recovered even after a second digestion with fresh acid (Table 3.1). In general the second digestion with fresh acid resulted in an increase in uranium and thorium recovery of only 1 to 2%.

When a -200 mesh sample of the fuel was digested with two successive portions of boiling 13 $\underline{M}$ HNO_3—0.04 $\underline{M}$ NaF—0.04 $\underline{M}$ $Al(NO_3)_3$, a good dissolvent for thorium and thorium oxide, 87.7% of the uranium and 87.3% of the thorium were recovered. A second leach increased the yield only 1%. When the nitric acid concentration was increased to 15.8 $\underline{M}$ with 0.04 $\underline{M}$ NaF

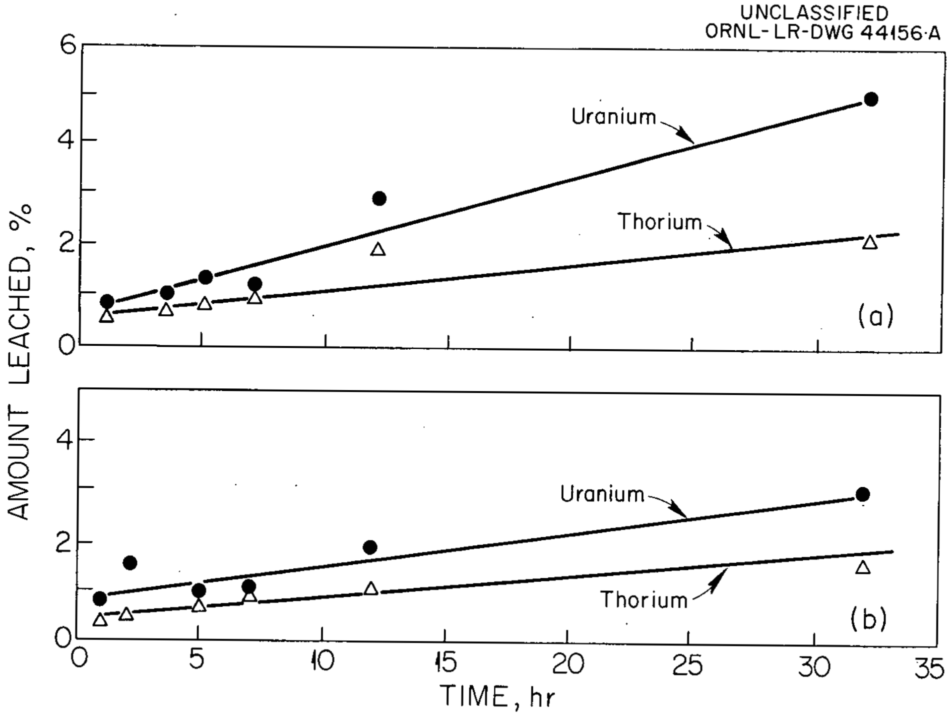

Fig. 3.1. Leaching of 3-1/8-in.-dia 1/4-in.-thick semicircular plates of General Atomics reactor fuel with boiling (a) 4 *M* H_2SO_4 ; (b) 6 *M* H_2SO_4 . Fuel composition: 1.54 % uranium, 7.18 % thorium in graphite.

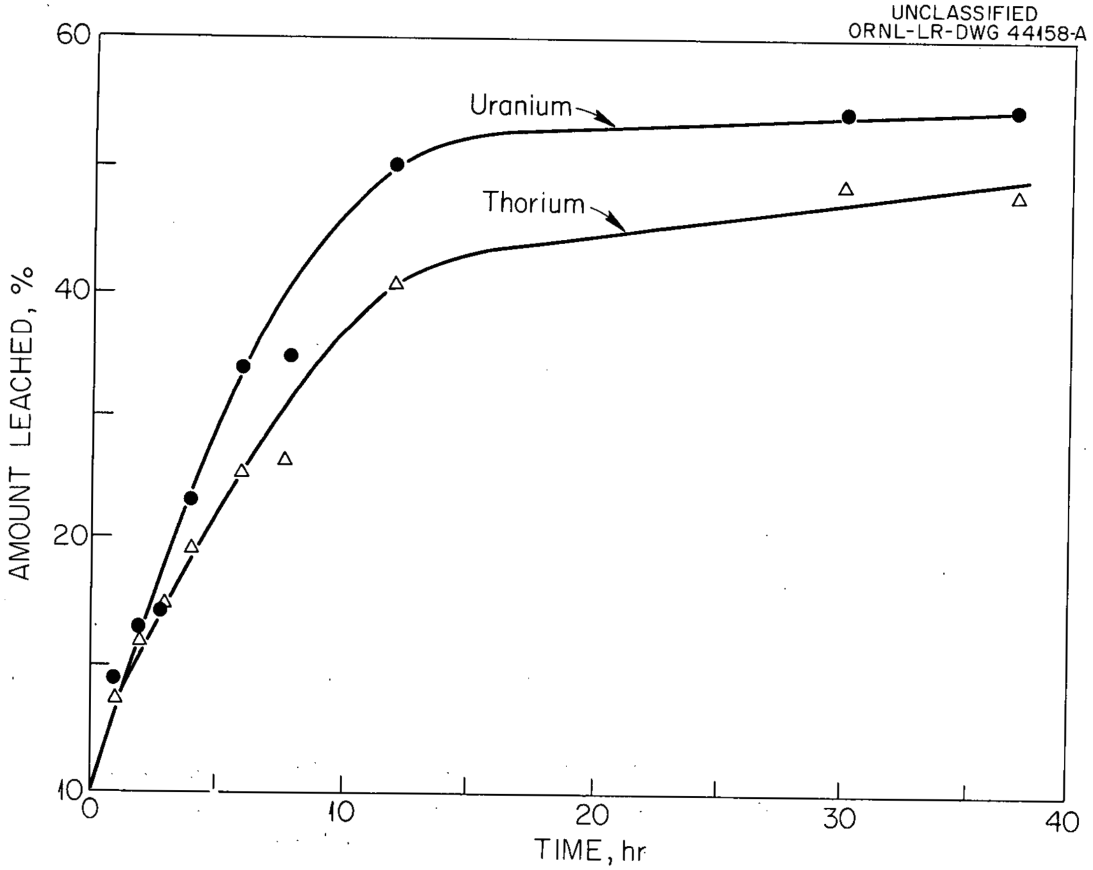

Fig. 3.2. Effect of time on leaching of 3-1/8-in.-dia, 1/4-in.-thick semicircular plates of General Atomics reactor fuel with boiling 5 *M* HNO_3- 2 *M* HCl (200 ml acid per 50-g sample). Fuel composition: 1.54 % uranium, 7.18 % thorium in graphite.

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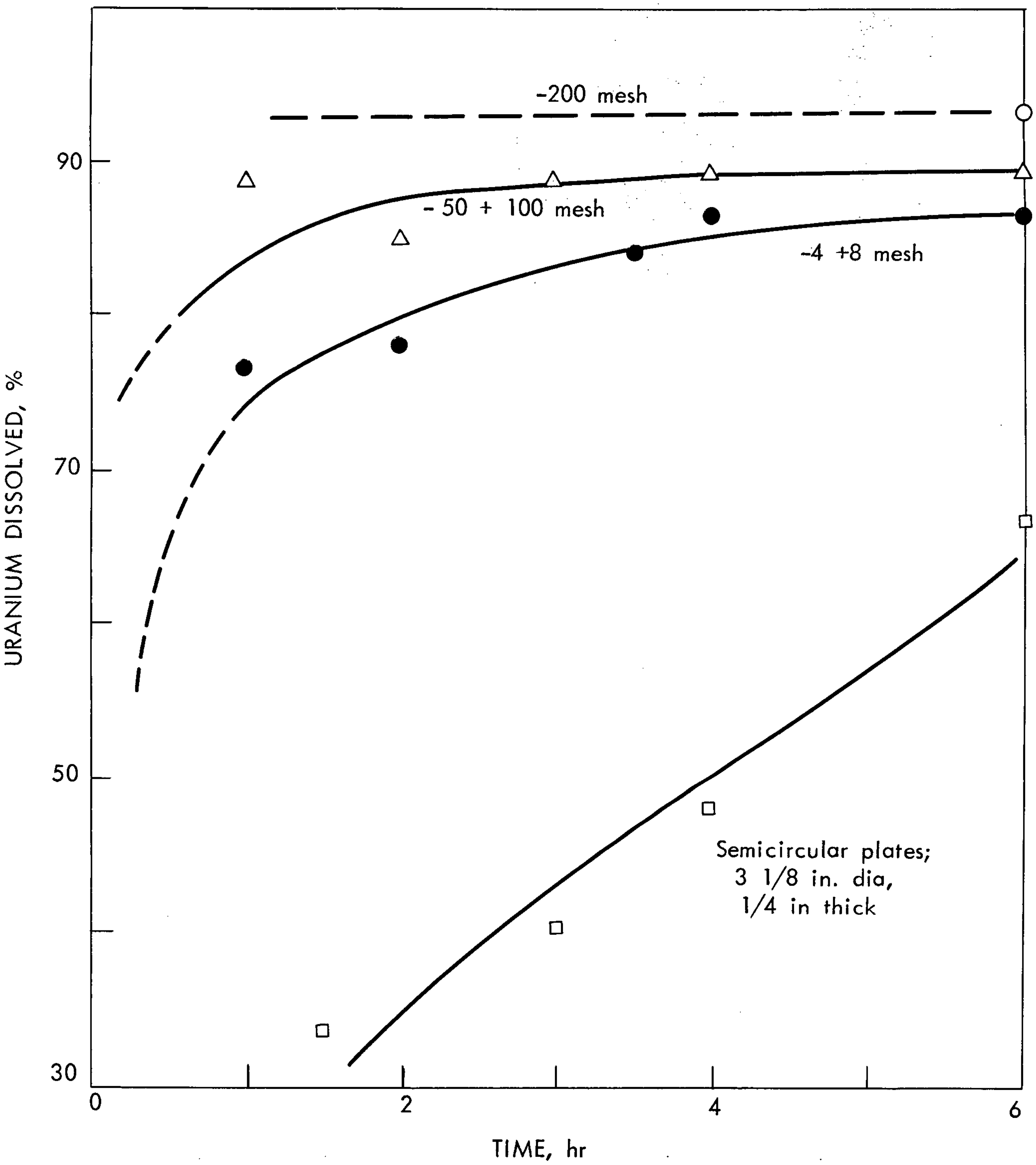

Fig. 3.3. Effect of particle size on the rate of leaching of uranium from prototype General Atomics reactor fuel with 50 ml of boiling 15.8 M HNO_3 per 10-g sample. Fuel composition: 1.54% uranium, 7.18% thorium in graphite.

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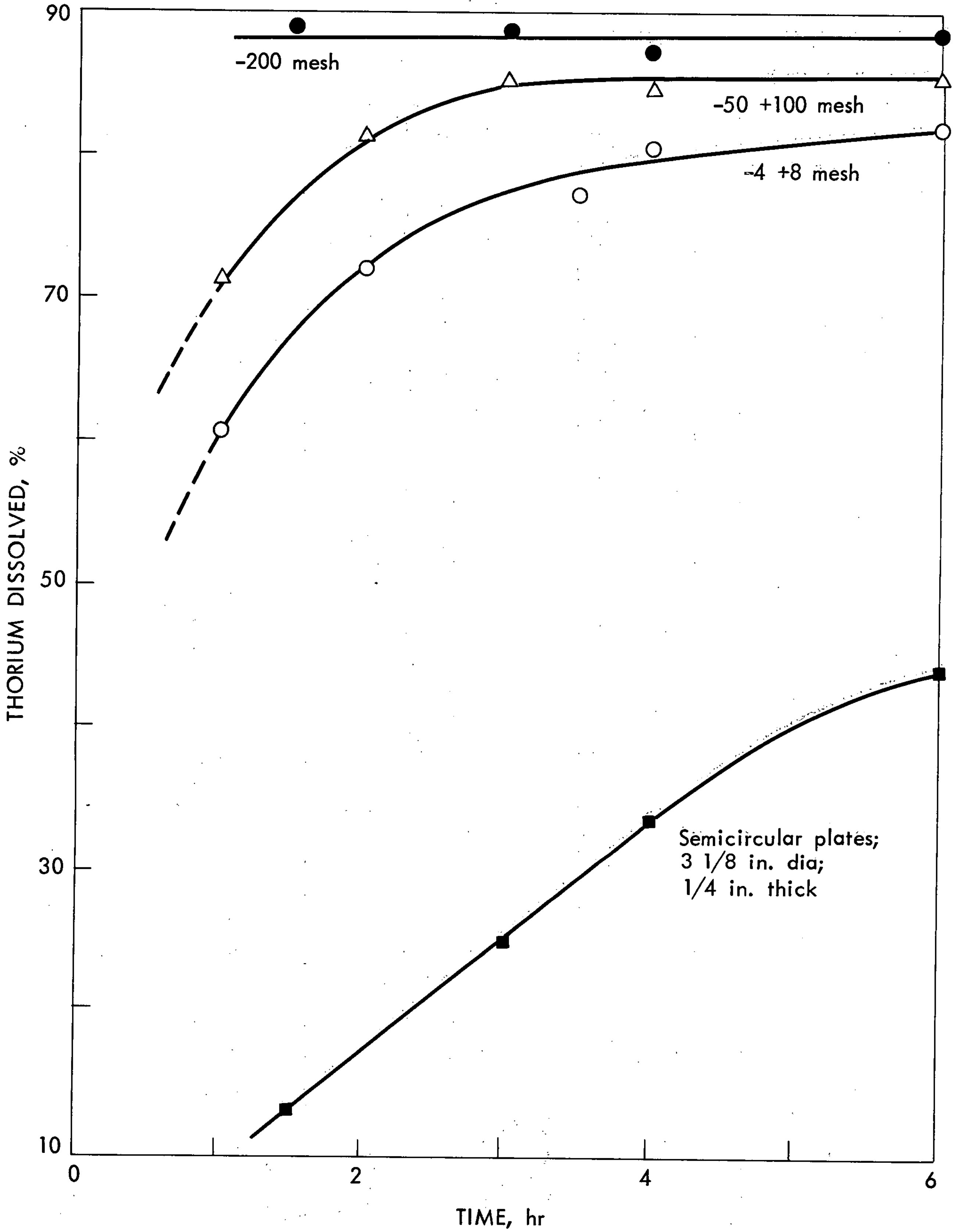

Fig. 3.4. Effect of particle size on the rate of leaching of thorium from prototype General Atomics reactor fuel with 50 ml of boiling 15.8 M HNO_3 per 10-g sample. Fuel composition: 1.54% uranium, 7.18% thorium in graphite.

Table 3.1. Effect of Particle Size on Leaching of 1.5% Uranium-7.2% Thorium-Graphite Fuel with Boiling 15.8 M HNO_3

Leaching procedure: 10 g of samples digested 4 hr with 50 ml of boiling 15.8 M HNO_3 and filtered, and residue washed three times with water; digested again with 25 ml of boiling 15.8 M HNO_3, and washed once with water

Particle Size, mesh	Metal Recovered, wt %											
	1st HNO_3 Leach + 2 Water Washes		3rd Water Wash		Total Solubilized 1st Leach + 3 Washes		2nd HNO_3 Leach + 1 Water Wash		Graphite[a] Residue		Total[b] Solubilized	
	U	Th	U	Th	U	Th	U	Th	U	Th	U	Th
semicircles 3-1/8 in. dia x 1/4 in. thick	78[c]	58[c]							22[c]	42[c]	78[c]	58[c]
-4 +8	86.3	82.1	0.4	1.9	86.7	84.0	2.6	5.7	10.8	10.3	89.2	89.7
-16 +30	83.9	81.6	0.1	1.2	84.0	81.8	6.1	4.1	9.9	14.2	90.1	85.8
-50 +100	89.4	85.1	0.1	0.1	89.5	85.2	0.9	1.9	9.5	12.9	90.5	87.1
-200	92.5	88.6	0.3	0.1	92.8	88.7	0.6	1.4	6.8	9.9	93.2	90.1

[a] Combustion analyses.

[b] 100% minus loss to graphite residue.

[c] 50-g sample leached with 200 ml of acid for 10 hr.

and 0.04 M $Al(NO_3)_3$, the uranium recovery from -200 mesh material increased to 91% and thorium to 88%. A second leach with pure 15.8 M HNO_3 increased the yield 1%. Metal recovery with the fluoride-catalyzed 15.8 M HNO_3 was slightly lower than with pure 15.8 M HNO_3.

The low uranium recoveries from the General Atomics fuel by the grind-leach method was unexpected. With a total metal concentration of 8.7% in the fuel, the porous graphite left after 80-90% of the metal has been solubilized should allow diffusion of the sort found in the 5.5-14 wt % uranium fuels, where yields were much higher. If one supposes by analogy with the uranium-graphite fuels that the carbides have been converted to oxides (Sect. 2.3), the possibility of UO_2-ThO_2 solid solution exists. The 13 M HNO_3—0.04 M NaF—0.04 M $Al(NO_3)_3$ solution which dissolves sintered UO_2-ThO_2 offered no improvement over 15.8 M HNO_3.

3.3 Soxhlet Extraction

There was little gain in uranium or thorium recovery with Soxhlet extraction. Soxhlet extraction for 10 hr with azeotropic nitric acid (15.3 M) of 1/4-in.-thick plates recovered 79.8% of the uranium and 67.9% of the thorium. Leaching of a similar plate with boiling 15.8 M HNO_3 for 10 hr dissolved 78% of the uranium and 58% of the thorium. When 1/2-in. plates were subjected to Soxhlet extraction with azeotropic nitric acid for 10 hr only 35.6% of the uranium and 26.6% of the thorium were recovered.

3.4 Combustion-Digestion

An alternative method for recovering uranium from the fuel is combustion followed by dissolution of the resulting oxides. In one experiment 20 g of fuel was burned at a furnace temperature of 700°C with an oxygen flow rate of 190 cc/min. The oxygen utilization efficiency was estimated as 90%. The U_3O_8-ThO_2 residue dissolved completely in boiling 13 M HNO_3—0.04 M NaF—0.04 M $Al(NO_3)_3$. The actual temperature of the graphite during combustion was not known; however, in an earlier experiment the nickel boat melted, indicating a temperature rise to at least 1450°C.

4.0 LITERATURE SURVEY AND EVALUATION OF POTENTIAL PROCESSING METHODS

A literature survey indicated that only two methods for the recovery of uranium from graphite fuels warranted experimental study. Oxidation of the graphite followed by digestion of the ash leads to nearly quantitative uranium recovery. This would probably be the preferred technique if the engineering problems associated with the remote operation of a highly exothermic reaction at temperatures ranging from 800 to greater than 1500°C, with a construction material that is stable to oxidation and the acid leach solutions or else a method of transferring highly radioactive ash from the furnace to the dissolver, and a practical method of treating large volumes of radioactive exhaust gases could be solved. Graphite disintegration, either mechanically or chemically, followed by leaching of the powder with nitric acid offers the advantages of minimum off-gas, concentrated solid (graphite) and liquid wastes, a less corrosive system, and less explosion hazard. If mechanical grinding is selected, there will be major engineering problems in developing a remote grinder. There will always be some uranium loss to the graphite. Other processes that might be considered either result in lower uranium recoveries or involve even more complex engineering problems. Because the problems associated with graphite oxidation are primarily engineering rather than chemical, initial laboratory studies were confined to the grind-leach method (Sect. 2). The chemical problems of graphite oxidation such as volatilization of fission products will be studied in future work.

Clad or coated graphite fuels introduce an additional complexity. Metal cladding could be removed by either the standard dissolution techniques or mechanically. The declad graphite fuel would have to be transferred to either the burning facility or the grinder. Leaching of the declad fuel without first grinding would not give satisfactory uranium recovery. Research on coating of graphite fuels with such materials as SiC shows promise of producing fuel elements that are stable to oxidation at temperatures of 1000°C.[11] Before such fuel elements could be burned the coating would have to be removed mechanically or chemically to expose a reactive surface. If the uranium does not migrate into the coating, uranium recovery by grinding and leaching from coated shapes would probably be similar to recovery from uncoated.

4.1 Particle Size Reduction and Nitric Acid Leaching

A nitric acid leach coupled with particle size reduction of the fuel as necessary for satisfactory uranium recovery is one of the simpler chemical systems for recovering the uranium. This process minimizes the radioactive off-gas problem and waste storage since the graphite waste could be stored in a compact mass or, if of low activity, after the leach might be burned for essentially complete uranium recovery. No difficulties with explosions have been encountered at Y-12 in contacting uranium residues containing 2-5% colloidal carbon with nitric acid.[12] The major problem is handling of the solids, in particular, filtration and particle size reduction.

Mechanical Grinding. Tests at Johns Hopkins University indicated that a high-speed impact hammer mill would pulverize 0.2% uranium—electrode graphite on a plant scale with dust losses no greater than 0.1%.[13] About 94% of the resulting powder passed a 20 mesh sieve, 50% a 100 mesh sieve. It was felt that with suitable modification of the machine and discharging of the powder directly to the liquid leach solution, grinding losses would not exceed 0.02-0.04%.[13] Experience at Y-12 has shown that ball mills are too slow to be of much value in grinding large quantities of graphite.[12]

Electrolytic Disintegration. Solution-impregnated 14% uranium-graphite samples have been electrolytically disintegrated in boiling concentrated nitric acid.[4] About 70% of the disintegrated material passed a 35 mesh screen. Uranium recovery after disintegration was 99.91%. Three additional leaches with boiling concentrated nitric acid increased the recovery to

99.97%, but there was no advantage in further leaches. This method of particle size reduction was expensive and did not give any better uranium recovery than was obtained by grinding and leaching of a 14% uranium-graphite admixture fuel (Sect. 2.2). Electric power was consumed at the rate of 3 kwh per pound of graphite, although the power was not totally lost since it was dissipated as heat to boil the nitric acid in the electrolytic bath.

Ultrasonics. Ultrasonics would probably not be a very practical way to disintegrate graphite, but ultrasonic leaching of fission products from calcined clays increased the leaching rate by a factor of 20 over leaching without ultrasonics.[14] Preliminary ultrasonic leaching studies on graphite fuels seem justified.

Chemical Disintegration. It has been suggested that the property of interlamellar compound formation by graphite might be used as a chemical means for disintegrating graphite fuels. For example, Riley[15] states: "If a piece of graphite is placed on molten potassium in an evacuated tube, it swells and falls to pieces." Two other review papers state that graphite is readily wetted and penetrated by molten potassium, forming interlamellar compounds with physical swelling of the crystal in the direction perpendicular to the graphite sheets, but make no mention of physical disintegration.[16,17] Hennig[18] has prepared large pieces of potassium-graphite compounds by heating graphite in potassium at 400°C without physical destruction of the specimen. Rubidium and cesium behave in a manner analogous to potassium. Sodium and lithium diffuse less readily into the graphite. They do not react below 500°C and only slowly above that temperature. If the graphite fuels do not disintegrate when swelled by potassium, it may be possible to explode the crystal internally by rapidly contacting the interlamellar compound with water, steam, or nitric acid. Any process involving both alkali metals and nitric acid may lead to explosions, and the problem here is further complicated by the fact that the alkali metal—graphite compounds ignite in air and react explosively with water.[16]

Graphite is reported to disintegrate in liquid bromine;[10,15,23] however, Hennig has reported the reaction of graphite pieces with bromine vapor without crumbling.[19] Assuming that bromine would disintegrate graphite fuel elements, there is still the problem of high corrosion rates. Although the major portion of the bromine in the interlamellar compound may be removed by vacuum distillation, there is always a small residue left in the graphite,[19] which would be carried over into the nitric acid leach.

4.2 Graphite Oxidation and Digestion

Removal of the graphite by oxidation followed by dissolution of the uranium oxide will give nearly quantitative uranium recovery but poses a number of problems with highly radioactive materials. If the carbon is sufficiently radioactive that the CO and CO_2 cannot be vented to the atmosphere, 1900 liters (STP) of gas per kilogram of carbon must be stored, or adsorbed and stored. If the carbon may be vented to the atmosphere, there is still the problem of separating fission product particulate fines and gases such as xenon and krypon from the large volumes of carbon oxides. Provision must be made for trapping fission product oxides which are volatile at the high temperatures required (>800°C). If the equipment is designed to minimize uranium dust losses through the exhaust gases, this method will potentially yield nearly quantitative uranium recovery. Y-12 has had no difficulty with volatilization of the uranium during combustion.[12] The combustion residue, which contains 2-5% carbon, is leached with nitric acid (15.8 M gave the highest recovery[20]). The ash after the nitric acid leach may be fused with NaOH,[12] $NaHSO_4$, $K_2S_2O_7$, Na_2O_2, or Na_2CO_3, or treated with HF mixtures if the silica content of the ash is high,[21] followed by a second treatment with nitric acid to get essentially complete uranium recovery from the residue. Insoluble, high-fired iron oxides in the ash from fuels containing appreciable amounts of iron may or may not contain uranium. Graphite oxidation does not eliminate the solids-handling problem, although it does decrease the quantity of solid. Ash leach solutions must still be separated from insoluble residues, and the combustion ash must either be transferred from the furnace to a dissolver or the furnace must be of a material stable to oxidation at temperatures of at least 800°C, and, also, to the necessary acid leach solutions.

Carbon Burner. The most economical method of oxidizing graphite is the carbon burner, since the reaction is self-sustaining once it has been initiated. Y-12 has had considerable experience in small-scale burning of unirradiated scrap; however, major modifications of their processes would be required to handle irradiated material.[12] It is necessary to use oxygen rather than air to maintain a reasonable rate of burning. The reaction is highly exothermic after the ignition temperature has been reached, so that temperature limitations imposed by available materials of construction forces operation of carbon burners at temperatures where the oxidation rate is low. The oxygen flow rate must be controlled, not only to maintain the desired temperature but also to keep the concentration of carbon monoxide and oxygen in the exhaust gas stream below explosive limits. The graphite beds are not easy to ignite; soaking with kerosene seems to help.[12]

A cylindrical metal furnace containing a firebrick lining with a 15-in.-dia opening for the graphite has been used at Y-12.[12] Oxygen comes up through the bed, while the exhaust gases pass out through a caustic scrubber and filter to the stack. Uranium carry-over to the scrubber was quite low. When the furnace was operated at red heat with charges of 30-60 kg of carbon, the average rate of burning was 20 kg per 24 hr. Ash was removed from the furnace by a vacuum cleaner type of suction probe. Because some uranium is adsorbed in the firebrick, used brick must be ground and leached.

A small metal burner, 6 in. dia by 12 in. deep with a metal hearth, was used to burn 1-kg batches of carbon.[12] The walls were water-cooled to eliminate the firebrick which adsorbed uranium. Throughput was 1 kg of carbon in 6-8 hr.

Water-Gas Reaction. In laboratory-scale experiments 98% of the uranium in a 1.4% uranium-carbon material was recovered by oxidizing the carbon by the water-gas reaction and leaching the ash with 15.8 M HNO_3.[20] The carbon pellets were preheated in nitrogen to 1100-1150°C before the steam was introduced. At this temperature the reaction proceeded rapidly according to the equation $C + H_2O \longrightarrow CO + H_2$. The rate of reaction was readily controlled by the rate of addition of water to the steam generator. Prolonged times were required for complete reaction of the carbon, but 85-90% reaction was readily achieved. Over-all uranium recoveries by leaching, with 5 portions of boiling 30% HNO_3, of ashes containing up to 40% of the original carbon were essentially the same. The process is moderately expensive since external heat must be supplied, although some heat will come from burning the exhaust carbon monoxide and hydrogen. There is danger that the carbon monoxide and hydrogen in the exhaust gas may explode.

Muffling. Although uranium recovery from muffle ash was higher than from carbon burner ash, presumably because muffling at 1000°C completely oxidized the carbon whereas carbon burner ash contained 2-5% carbon, the cost of electric power and time of operation required were so high as to eliminate muffle treatment from consideration.[20]

Sodium Carbonate Fusion. Treatment of 1 part of 0.2% uranium-carbon with 5 parts of sodium carbonate by weight and heating the mixture to 750°C for 17 hr burned away the carbon without dusting and left a residue that was completely soluble in nitric acid.[21] For a 2 wt % uranium-carbon fuel there were 1000 atoms of sodium to each uranium atom. The uranium was satisfactorily recovered by solvent extraction, but the waste volume was very large. Fusions with Na_2O_2, $K_2S_2O_7$, or $NaHSO_4$ are equally impractical methods of processing large quantities of irradiated graphite-containing fuel, although they may be useful for analytical purposes.

4.3 Volatility

Fluorine. No data are available on the recovery of uranium from homogeneous uranium-graphite bodies by volatilization with fluorine. Surface deposits of uranium on carbon parts have been fluorinated at 300-350°C without great success.[22] Moisture in the carbon hindered the conversion of uranium tetrafluoride to the hexafluoride at 300-350°C, so that a predrying step was necessary. Above 350°C reaction between carbon and fluorine was rapid and difficult to control, so that careful temperature control was required. At best, results were not very reproducible. Between 500 and 700°C the carbon-fluorine reaction was usually explosive.[16] Any fluoride volatility process must be designed so that reaction in this temperature range is avoided. The catalytic effect of UC_2 on the fluorine-graphite explosive reaction has not been investigated (see below). The usual corrosion problems associated with fluorine at high temperatures (above 700°C) will be encountered in operating a fluoride volatility process.

Bromine Trifluoride. North American Aviation Company[23] has removed 99.8% of the uranium as UF_6 from graphite, which was impregnated from uranyl nitrate solution and heated to form uranium oxide or carbide (14% uranium). Their procedure was to saturate the material with liquid bromine and then treat with at least 0.5 mole of BrF_3 per mole of graphite.[23] They obtained no better uranium recovery than was obtained by grinding and leaching (Sect. 2). A temperature of 100°C was used and the gauge pressure was 15 psi or less. The greater portion of the graphite reacted to form a BrF_3-graphite interlamellar compound from which most of the BrF_3 could be removed by subsequent heating under vacuum. Another interlamellar compound, probably carbon monofluoride, was also formed which was subject to very rapid decomposition above 400°C and caused explosions if confined during the decomposition. In the presence of UC_2, a third and violent reaction occurred between BrF_3 and graphite, producing CF_4 and a large amount of heat. This reaction could be avoided by pretreatment with liquid bromine, but moist air pretreatment had no effect. Uranium recovery with BrF_3 is not recommended because of the explosion hazard.

Boron Trifluoride. A limited number of attempts to fluorinate uranium-graphite scrap at Y-12 with boron trifluoride all ended in explosions.[12]

Chlorination. Balcziak and Newnam[24] investigated the feasibility of recovering uranium by chlorinating 15% uranium-85% carbon powders which had been ground until 95% of the material passed an 80 mesh screen. Best results were obtained by chlorinating for 30 min at 1000°C, which resulted in 99.71% uranium recovery. During chlorination the carbon usually lost 50% in weight. Some carbon was lost as CO and CO_2. An attempt to chlorinate at 1100°C resulted in an explosion, indicating that at this high temperature either an explosive compound was formed or the reaction was too vigorous. Increasing the chlorination time at 1000°C resulted in no increase in uranium recovery. Yields decreased with decreasing temperature, dropping to about 99% after 1 hr at 800°C. The authors concluded that 0.3-0.5% of the uranium is held as a stable silicate or tungstate which withstands the action of hot chlorine.

Purdue Research Institute workers[25] found that -40 mesh carbon electrode material containing about 0.2% uranium was inert toward chlorine at temperatures up to 1000°C. There was no weight loss by the carbon and no water-soluble material in the carbon after chlorination.

Uranium recovery from graphite fuels by chlorination will involve temperatures of at least 1000°C and high corrosion rates. It is questionable whether recoveries will be satisfactory with low uranium concentrations. No data on chlorination of graphite pieces larger than 40 mesh powder are available.

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