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A TENTATIVE GRIND-LEACH PROCESS FOR ROVER FUELS

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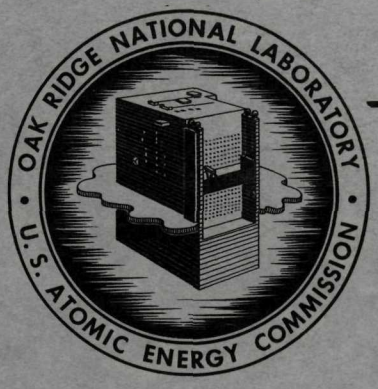

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

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ABSTRACT

A tentative flowsheet is presented for the recovery of uranium from prototype Rover fuel by leaching with boiling 15.8 M HNO_3. The effects of uranium content of the fuel, nitric acid concentration, and particle size on the efficiency of leaching were partially determined. For fuel containing more than 100 mg U per cc (5 wt %), 99.3% of the uranium was leached in 6 hr with 8 M HNO_3 when the fuel was ground to -16 mesh. However, only 98.6% of the uranium was leached from fuel containing 35 mg U per cc (1.8 wt %) in 6 hr with 15.8 M HNO_3 when the fuel was ground to -16 mesh. The use of 8 M HNO_3 on fuel of the latter composition resulted in even lower uranium recoveries.

CONTENTS

1.0 INTRODUCTION

The purpose of this report is to present recently obtained information on a "grind-leach" method of recovering uranium from prototype U-graphite fuel elements fabricated at Los Alamos for the Rover program. Preliminary results were published in previous progress reports.[1,2]

The fuel elements for the first Rover engine will be graphite plates impregnated with UC_2.[3] The uranium concentration in the fuel will vary from 25 to 250 mg/cc; i.e., from about 1 to 12 wt %. About 0.2 to 0.7 wt % iron will also be present in the fuel. It is assumed that the fuel will not be separated according to uranium content before delivery to a reprocessing plant. Therefore, the objective of this study was to determine optimum conditions for removing uranium over the entire loading range.

This report contains data on the recovery, by leaching with nitric acid, of uranium from fuel containing 35, 100, and 200 mg U per cc. The effects of particle size, acid concentration and leaching time on the uranium recovery were partially evaluated.

The authors wish to acknowledge J. F. Land for his aid in performing some of the experiments. Chemical and x-ray analyses were provided by the groups of G. R. Wilson, W. R. Laing and R. L. Sherman of the ORNL Analytical Chemical Division.

2.0 TENTATIVE FLOWSHEET

A tentative flowsheet, based on the grind-leach technique as the primary method for uranium recovery, is given in Fig. 1. The flowsheet conditions were calculated for a fuel charge containing 25 kg of uranium present at an average composition of 6 wt % before burnup. If the average iron concentration is taken as 0.3 wt %, the U/Fe mole ratio is about 4.7. The appropriate particle size and acid concentration required for efficient recovery of uranium from the lowest loading (35 mg/cc or 1.85 wt %) were taken as the limiting conditions for the entire fuel charge. Thus, about 99.3% of the uranium is recovered by using 15.8 M HNO_3 to leach fuel particles having a maximum diameter of about 1.1 mm (-16 mesh). The amounts of nitric acid consumed and gases produced were calculated from the following assumed stoichiometry:

$$UC_2 + Fe + 8\ HNO_3 \longrightarrow Fe(NO_3)_3 + UO_2(NO_3)_2 + C_2H_2 + 3H_2O + 2NO + NO_2 \quad (1)$$

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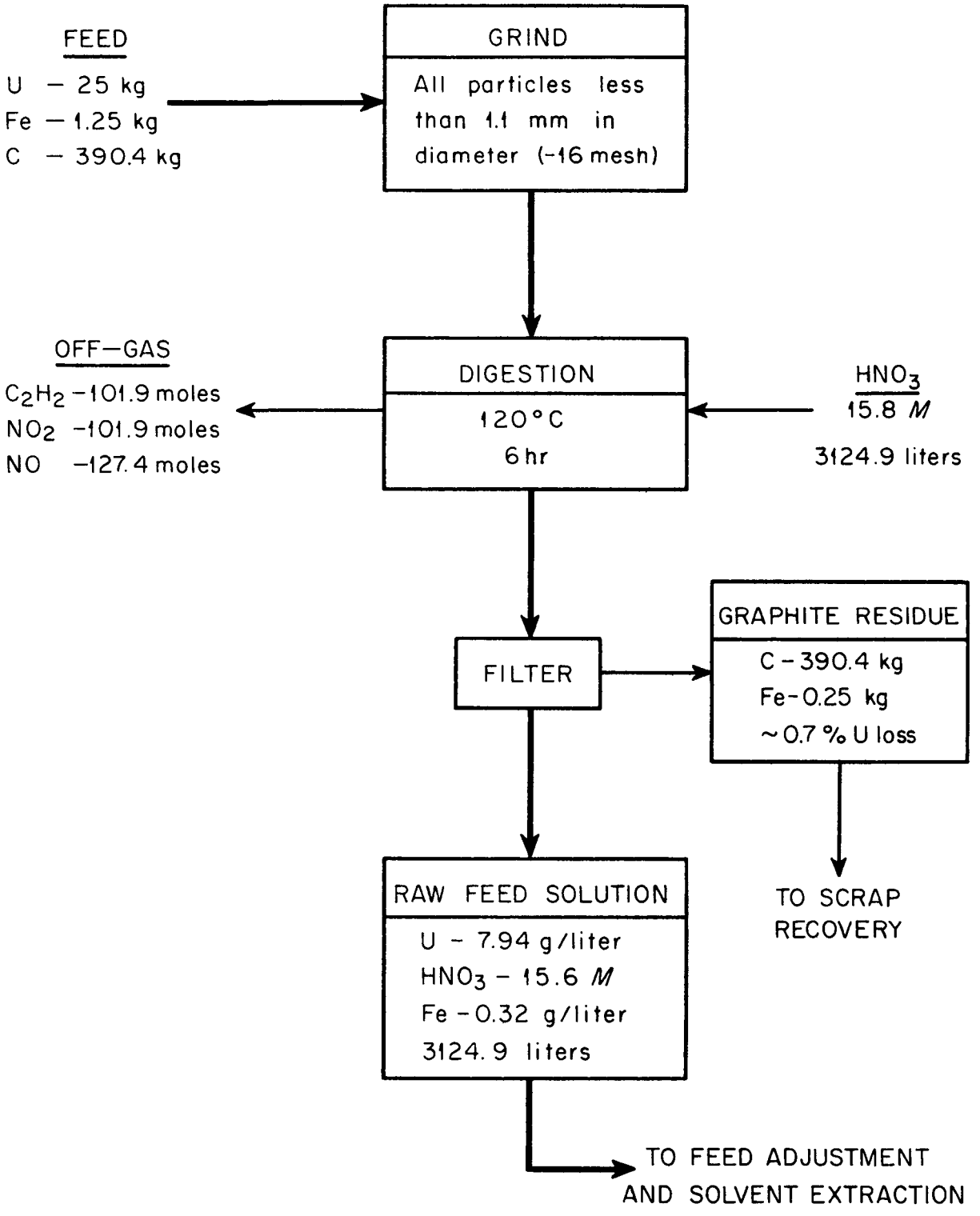

Fig. 1. Tentative Flowsheet for the Recovery of Uranium from Rover Fuel by a Grind-Leach Method.

In the first step of the flowsheet, the fuel is ground, perhaps using a wet-grinding technique, until the maximum particle size is about 1.1 mm (-16 mesh). The ground material is digested with boiling 15.8 M nitric acid for 6 hr using a volume of acid to weight of fuel ratio of 7.5 liters/kg. The raw solvent extraction feed solution, containing about 8 g U per liter, is removed from the dissolver vessel by filtration. A suitable solvent extraction feed solution may be obtained by evaporation of excess nitric acid and appropriate dilution with water. Since the nitric acid concentration in the raw feed solution, 15.6 M, is close to the azeotropic concentration, 15.8 M, the distillate may be recycled to the dissolver after only slight adjustment of the concentration.

Total uranium recovery may be achieved by conversion of the uranium in the graphitic residue to U_3O_8 by combustion,[2] and the subsequent dissolution of this compound in nitric acid.

3.0 RESULTS

Several series of experiments were performed to determine the effect of nitric acid concentration and time on the removal of uranium from U-graphite fuel specimens containing 35, 100 and 200 mg U per cc (1.85, 5.3, and 10.8 wt %), and ranging in size from -16 mesh particles to 4 x 2 x 0.64 cm plates. From these experiments, it was concluded that grinding is mandatory if 99% of the uranium is to be leached in 24 hr. Also, about 99.3% of the uranium can be leached with boiling 8 or 15.8 M nitric acid in 6 hr from -10 mesh particles containing 100 and 200 mg U per cc. The maximum uranium recovery in 6 hr from -16 mesh material containing 35 mg/cc was 98.6% using boiling 15.8 M HNO_3.

3.1 Stoichiometry of the Reaction

A brief examination was made of the apparent stoichiometry of the reaction of UC_2 and iron with nitric acid since this information is necessary for the calculation of the acid consumption and the amount of gases evolved during the leaching process. A stoichiometry which is consistent with the experimental data is:

$$UC_2 + Fe + 8HNO_3 \longrightarrow Fe(NO_3)_3 + UO_2(NO_3)_2 + C_2H_2 + 3H_2O + 2NO + NO_2. \quad (1)$$

The number of moles of nitric acid consumed per mole of metal dissolved was about 4 (Table 3.1.1). It was established from several experiments that about 80% of the iron present in the fuel specimen was converted to a soluble species. On this basis, the iron was assumed to be initially in the metallic state, since the oxides and carbides are essentially insoluble in nitric acid.

The stoichiometry, as described by Eq. 1, is definitely not exact since hydrocarbons other than acetylene are expected from the reaction with UC_2.[4] Also, oxides of nitrogen other than NO undoubtedly are formed in the reaction of iron and nitric acid. A more elaborate study of the reaction is therefore planned.

Table 3.1.1 Reaction of UC_2-Fe-Graphite Mixtures with Nitric Acid

Leaching conditions: 75 ml of boiling HNO_3 per 10-g sample.

Initial HNO_3 Conc. (M)	Initial HNO_3 (Moles)	HNO_3 Consumed (Moles)	U Leached (Moles)	Fe Leached (Moles)	Total Metal Leached (Moles)	Moles HNO_3 / Mole metal
4.0	0.3	0.0375	0.0044	0.00104	0.00544	6.9
4.0	0.3	0.0125	0.00432	0.00104	0.00536	2.33
4.0	0.3	0.0250	0.00445	0.00104	0.00549	4.55
4.0	0.3	0.0250	0.00439	0.00104	0.00543	4.60
4.0	0.3	0.0375	0.00458	0.00104	0.00562	6.67
8.0	0.6	0.025	0.00446	0.00104	0.00550	4.54
15.8	1.185	0.010	0.00446	0.00104	0.00550	1.82
						Avg. 4.5

3.2 Direct Leaching of Fuel Plates

Data in an earlier report[2] suggest that 99% of the uranium may be leached from the original fuel plates without grinding. However, a maximum of 98.5% of the uranium was leached in 24 hr from 2 x 4 x 0.64-cm sections of a fuel plate using 15.8 M HNO_3 (Fig. 2). Complete data are given in Table 3.2.1. The point representing 94.5% recovery at 24 hr in Fig. 2 is an average of the three separate runs listed in Table 3.2.1. The wide deviation in these three points cannot be explained. However, it was

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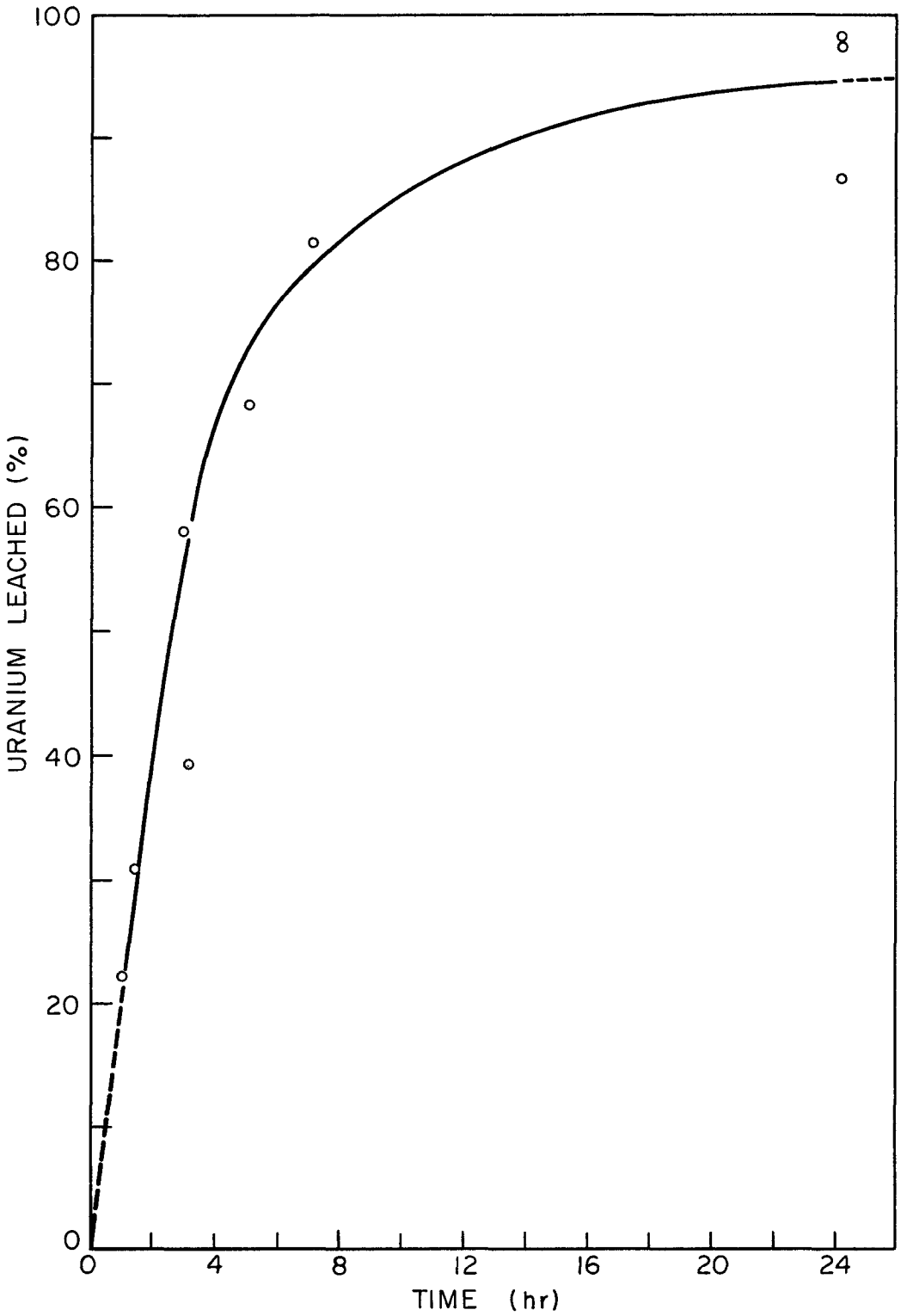

Fig. 2. Leaching, with Boiling 15.8*M* HNO_3, of 2x4x0.64-cm U-graphite Plates Containing 200 mg U per cc.

observed during these runs that the plates from which the greatest amount of uranium was leached exhibited a laminated structure. Low recovery was experienced from a plate which had a solid, more homogeneous physical structure. In view of the fact that most of the prototype plates exhibited this laminated appearance, it is possible that the inconsistancies in the results can be attributed to the difference in physical characteristics of the plates. However, since the uranium recovery achieved was not acceptable, the effect of plate lamination was not investigated further.

3.3 Effect of Particle Size, Nitric Acid Concentration and Uranium Loading on Uranium Recovery

Optimum conditions have not yet been established for recovery of more than 99% of the uranium at all fuel loadings. However, an estimate based on the available data suggests that leaching for 6 hr with 15.8 M HNO_3 of fuel which has been ground to -30 mesh may result in 99% recovery at all uranium loadings. The data show uranium loading to be the limiting variable when it is low. For example, uranium recovery was about 99.3% when-16-mesh fuel containing 100 and 200 mg U per cc was leached with 8 and 15.8 M HNO_3 for 1 to 2 hr, but only 98.6% in 6 hr with fuel containing 35 mg U per cc. Fuels of lower uranium loading (35 mg U per cc or less) must be ground finer and leached longer to achieve 99% uranium recovery.

Table 3.2.1 Leaching of 200 mg U/cc Graphite Plates With Boiling 15.8 M HNO_3

Size of specimens: 2 x 4 x 0.64 cm

Run No.	Sample Weight (g)	Weight of Residue (g)	U in Filtrate (g)	Total U (g)	U Recovered (%)	Leaching Time (hr)
18	9.9825	0.2373	0.8308	1.0681	22.22	1.0
19	9.9769	0.3225	0.7300	1.0525	30.64	1.5
20	9.9234	0.6050	0.4311	1.0361	58.39	3.0
21	9.9350	0.7575	0.3547	1.1122	68.10	5.0
22	9.9846	0.8900	0.2060	1.0960	81.20	7.0
23	9.9958	0.9275	0.1406	1.0681	86.83	24.0
24	9.9966	1.1000	0.0162	1.1162	98.54	24.0
25	9.9958	1.1000	0.0203	1.1203	98.18	24.0

3.3 1 Leaching of Fuel Containing 100 and 200 mg U per cc. It was determined previously[2] that an average of 99.3% of the uranium, in fuel containing 100 mg U per cc, could be recovered by leaching for 1 hr with 15.8 M HNO_3 if all the fuel particles were smaller than 16 mesh. Further experiments using larger particles (-8+10 mesh) revealed that 2 hr were required for 99.1% uranium recovery. For even larger particles, (-4+8 mesh) only 98.5% uranium recovery was achieved in 4 hr. It is obvious that the time required to leach 99% of the uranium increases with increasing particle size.

With the larger particles (-4+8 mesh), 17 hr were required for 99% uranium recovery (Fig. 3). The data used in plotting Fig. 3 are found in Table 3.3.1, and were obtained with fuel containing 200 mg U per cc. However, in all cases, the behavior of samples containing 100 and 200 mg U per cc was nearly identical under comparable conditions of particle size and acid concentration.

Table 3.3 1 Results of Leaching -4+8 Mesh 200 mg U/cc Graphite Particles with Boiling 15.8 M HNO_3

Weight of Sample (g)	U in Filtrate (g)	U in Residue (g)	Total U (g)	U Removed (g)	Leaching Time (hr)
10.0004	0.5225	0.5730	1.0955	47.69	0.083
9.9997	0.8100	0.3634	1.1743	68.98	0.25
10.0009	0.8300	0.2942	1.1242	73.83	0.50
10.0007	0.9950	0.1459	1.1409	87.20	1.0
10.0012	1.030	0.0762	1.1062	93.11	1.5
10.0010	1.0775	0.0600	1.1375	94.73	2.0
10.0004	1.0325	0.0680	1.1005	93.82	2.0
9.9993	1.0600	0.0439	1.1039	96.02	2.0
10.0001	1.0800	0.0243	1.1043	97.80	3.0
9.9990	1.0775	0.0176	1.0951	98.39	3.0
9.9997	1.0925	0.0263	1.1188	97.65	3.0
10.0015	1.0875	0.0090	1.0965	99.18	24
10.0004	1.0925	0.0070	1.0995	99.36	24
9.9997	1.1500	0.0050	1.1550	99.57	24

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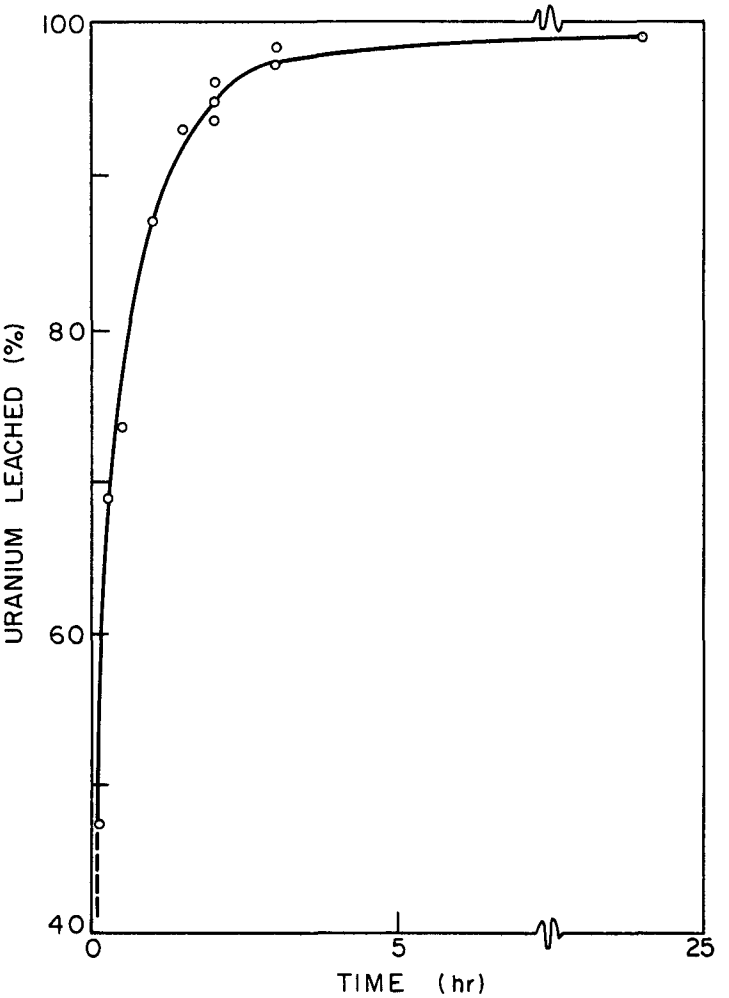

Fig. 3. Leaching, with Boiling 15.8 *M* HNO_3, of -4+8-Mesh Particles Containing 200 mg U per cc.

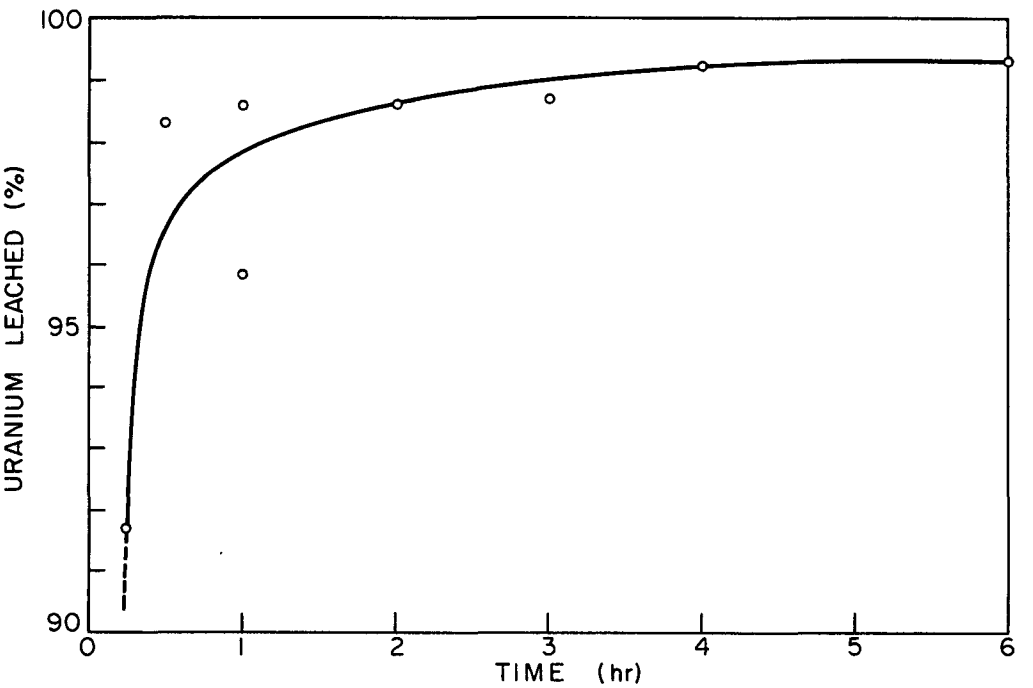

Fig. 4. Leaching, with Boiling 8 *M* HNO_3, of -10-Mesh Particles Containing 200 mg U per cc.

From the data presented above, it is seen that in order to recover more than 99% of the uranium with 15.8 M HNO_3 in less than 6 hr, fuel containing 100 mg U per cc must be ground to less than 8 mesh. If a longer leaching period can be tolerated, 99% of the uranium may be recovered from larger particles (-4 mesh) in 17-20 hr.

Eight-molar HNO_3 was as effective as 15.8 M HNO_3 in leaching fuel containing 100 and 200 mg U per cc. For fuel ground to -10 mesh, approximately 99.2% of the uranium is leached in 4-6 hr (Fig. 4 and Table 3.3.2). As with 15.8 M HNO_3, more than 99% may be recovered from larger particles (-4 mesh) if the leaching period is extended to about 24 hr.

Recovery of more than 99% of the uranium from -10-mesh particles in 4-6 hr with 4 M HNO_3 could not be achieved. With this mesh size, about 20 hr were required to recover 99% of the uranium (Fig. 5 and Table 3.3.3). For -4 mesh particles, only 98.9% of the uranium was leached in 24 hr.

Table 3.3.2 Results of Leaching -10 Mesh 200 mg per cc Graphite Particles with Boiling 8 M HNO_3

Weight of Sample (g)	U in Filtrate (g)	U in Residue (g)	Total U (g)	Uranium Removed (%)	Leaching Time (hr)
5.0000	0.4975	0.0451	0.5426	91.69	0.25
	0.5275	0.0092	0.5367	98.29	0.5
	0.5350	0.0078	0.5428	98.56	1.0
	0.5350	0.0234	0.5584	95.81	1.0
	0.5350	0.0076	0.5426	98.59	2.0
	0.5325	0.0068	0.5393	98.74	3.0
	0.5450	0.0041	0.5491	99.25	4.0
10.0000	1.0625	0.0069	1.0694	99.35	6.0

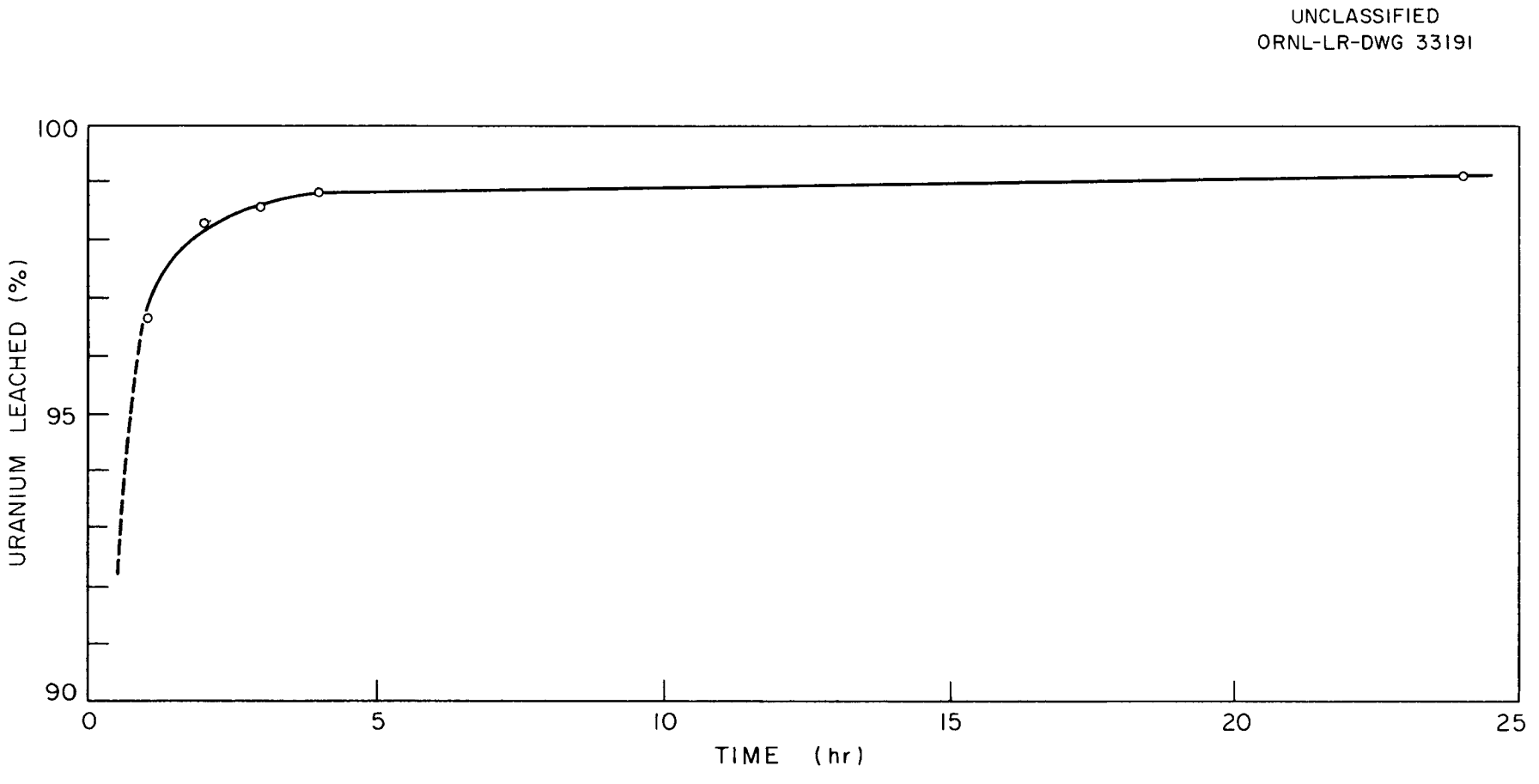

Fig. 5. Leaching, with Boiling 4 *M* HNO_3, of −10-Mesh Particles Containing 200 mg U per cc.

Table 3.3.3 Results of Leaching -10-Mesh 200 mg U per cc Graphite Particles with Boiling 4 M HNO_3

Weight of Sample (g)	U in Filtrate (g)	U in Residue (g)	Total U (g)	U Removed (%)	Leaching Time (hr)
10.0000	1.0275	0.0358	1.0633	96.63	1.0
	1.0475	0.0183	1.0658	98.28	2.0
	1.0600	0.0151	1.0751	98.6	3.0
	1.045	0.0127	1.0577	98.8	4.0
	1.0900	0.009	1.0990	99.18	24.0

3.3.2 Leaching of Fuel Containing 35 mg U per cc

Since more than 99% of the uranium was recovered with the 100 and 200 mg U per cc loadings in 6 hr with 8 and 15.8 M HNO_3 after grinding to 8-10 mesh, a single leaching of the 35 mg U per cc material (-10 mesh) with 15.8 M HNO_3 was performed. After 6 hr, only 97.6% of the uranium was recovered. The recovery, in 6 hr, was increased to 98.6% when the fuel was ground to -16 mesh.

With this low-loaded material, use of 8 M HNO_3 was not nearly as effective as 15.8 M HNO_3, since only 93.6 and 94.4% of the uranium was leached in 4 and 5 hr, respectively, from -16-mesh particles.

For greater than 99% recovery from the 35 mg U per cc material, a maximum particle size far below 1 mm (16 mesh) will be required, and, almost certainly, the use of 15.8 M HNO_3.

4.0 CONCLUSIONS AND SUGGESTED FUTURE WORK

The data imply that the factors which most greatly affect uranium recovery are the particle size and the uranium content of the fuel. It is also indicated that, if the fuel is ground fine enough, essentially quantitative recovery may be achieved in 6 hr at any uranium loading with 15.8 M nitric acid. There is also the possiblity that effective leaching of extremely fine material can be achieved with more dilute nitric acid solutions.

It this proves to be the case, little or no feed adjustment will be required; i.e., the leachate will either constitute a suitable solvent extraction feed solution or can easily be converted to one merely by the addition of a salting agent. For these reasons, the effect of leaching finely ground fuel of low uranium content with 2-4 M HNO_3 will be determined in future experiments. The efficiency of the leaching process at various volume of acid to mass of fuel ratios will also be determined.

Further work will also be required to determine more exactly the stoichiometry of the reaction. A clearer understanding of the mechanism of the leaching process might also prove useful. The rate at which uranium is leached is initially quite rapid. However, even after a long contact time, some uranium remains in the solid graphitic residue. One explanation of this behavior is that diffusion of uranyl nitrate out of the pores of the solid is extremely slow during the later stages of the leaching process. An alternative explanation is that some uranium is physically occluded by the graphite, precluding its reaction with nitric acid. In either case, the amount of uranium retained by the solids should decrease with decreasing particle size.

Other future work will include studies of the combustion of both the fuel and the solids which remain after leaching. In the event that the graphite becomes sufficiently radioactive, suitable means for storing the solid waste will be required. Ultimately, testing, on a laboratory scale, of the most attractive flowsheet with radioactive fuel is planned.

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