Acid Leaching and Anode Dissolution of Graphite-moderated Fuels

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Results of nitric acid leaching and anodic disintegration processing studies of two types of homogeneous graphite moderated fuels are reported. 2N nitric acid leaching at 90-100°C appears suitable as the primary processing method, whereby uranium and thorium are obtained in solution suitable for solvent extraction. Anodic disintegration in 2N nitric acid is a satisfactory wet method of breaking down the graphite fuel assemblies, but the disintegration process does not give the required uranium and thorium recoveries. It has not been possible to assign any electrochemical action to the anodic solution of uranium and thorium carbides.

INTRODUCTION

Graphite-moderated high temperature gas-cooled reactors

One type of advanced reactor under study at the Atomic Energy Research Establishment, Harwell, is the high-temperature gas-cooled graphite-moderated thermal breeder system based on the uranium 233-thorium 232 cycle. (Cockcroft 1957, 1957 a, 1957 b; U.K.A.E.A. Third Annual Report 1956-1957). Fuel temperatures of the order of 800°C may be achieved (Cockcroft 1957 b) and the heat developed is transferred by high pressure gas (Fortescue 1957, Kay 1957, Moore 1957).

In a typical design the fuel rods could consist of three separate units, a graphite container can, and a fissile-fertile U235-Th232 sleeve enclosing a central graphite rod. The fuel and fertile material would be incorporated as carbides in a graphite binder in sleeves an inch or so in diameter and a fraction of an inch thick (Times Scientific Review, 1957).

The results described in this paper have been obtained from processing studies of two types of fuel proposed for a 10MW experimental reactor.

Processing aspects

The processing studies have been based on the assumption that a mechanical separation of the fissile-fertile sleeves from the fuel elements cannot be achieved. Processing has therefore been considered to fall into two parts, namely the initial separation of the uranium and thorium from the large bulk of graphite in the system, and the subsequent separation and decontamination of fertile material in a solvent extraction plant of conventional design. The latter is not considered in this paper.

The initial separation methods which have been investigated include:

(i) oxidation of the graphite in a stream of air or oxygen,
(ii) extraction of the uranium and thorium from the fuel by acid, and pressure leaching,
(iii) anodic disintegration (the fuel element is made the anode in an electrolytic cell), and,
(iv) fluorination and bromination treatments.

Only the acid leaching and anodic disintegration studies are reported in this paper.

MATERIALS AND ANALYSIS

Materials

Two possible types of fuel have been examined.

COMPACTED FUEL

Cold compacted fuel was prepared in the Metallurgy Division, A.E.R.E., from mixed powders of graphite, uranium and thorium, milled dry in glass bottles charged with glass beads. The mixture was cold compacted in hardened steel dies at 8000lb. lb./sq. in., and fired in argon at 1,400°C. The non-irradiated compacted fuels were very brittle, had poor mechanical strength, could be easily ground, and were readily hydrolysed to a fine powder in contact with air, with evolution of hydrocarbon gases. These samples had the approximate composition C: Th: U:: 70:27:3 (w/w). In some cases graphite and uranium powders only were compacted, and then fired in argon.

GRAPHITISED FUEL

In this fuel, prepared in the Chemical Engineering Division, A.E.R.E., the fertile material was incorporated as thoria into a coke-pitch mixture which was extruded and then baked at 800-1,000°C to form a carbon artefact. The required uranium concentration was then obtained by impregnation with uranyl nitrate solution, and the element graphitised at 2,500°C to produce uranium and thorium carbides. The fuel was prepared in the form of rods, ½" diam., 3" long, and normally contained approximately 10 per cent. thorium and 1 per cent. uranium (w/w). In contrast to the compacted fuels, these samples were similar to pile-grade graphite in physical properties, i.e. they possessed good mechanical strength, and were not brittle. After sawing into small pieces, they could be readily ground. On standing in air, hydrolysis was not as rapid as with the compacted fuels, and these samples retained their mechanical strength on standing in air for several months.

In addition, experiments were performed on 6ft. lengths of graphite tube which had been proposed as a fuel element can for a 10 MW reactor experiment.

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Analysis

Solid samples were ignited at 1,000°C to remove carbon, and then fused with potassium bisulphate to render the uranium and thorium soluble in hydrochloric acid. Analyses for these elements were then carried out on separate aliquots of a sample solution. After separation from sulphate by an ammonia precipitation, thorium was determined colorimetrically as the thoronol complex on solution containing 0.1 mgm/ml and volumetrically using EDTA on the more concentrated thorium solutions. Uranium was estimated spectrophotometrically, using dibenzoyl methane. Solution analyses for uranium and thorium were performed in nitric acid solution directly as above.

In all cases where a mass balance of uranium and thorium between sample, solution and residue was required, the uranium and thorium contents of solution and residue were determined, and the additive figures normalised to 100 per cent. with respect to the original sample. The appropriate percentages leached into solution and retained in the residue were then calculated (see tables). In all cases the additive uranium and thorium contents of solution and residue were ± 1 per cent. of the respective contents of the original sample. All uranium and thorium analyses were performed in duplicate.

Analytical data on the exact carbide composition of the compacted and graphitised fuels are not available. Uranium mono-carbide can be obtained by reaction of U_3O_8 with carbon at 1,800°C, while a reaction temperature of 2,400°C produces uranium dicarbide. Reaction of UO_2 with graphite in near stoichiometric proportions at 2,400°C also produces the dicarbide (see Schwarzkopf and Kieffer 1953, Katz and Rabinowitch 1951, Katz and Seaborg 1957). Wylie (personal communication) has found that a minimum temperature of approximately 2,000°C is required to produce thorium dicarbide (yield >80 per cent.) by reaction between thoria and graphite. No evidence for monocarbide formation was found under these conditions. Prescott and Hincke (1927) quote a temperature of 1,800°C for dicarbide formation from thoria and graphite.

On this basis the temperature at which the compacted fuels were prepared (1,400°C) was probably insufficient to give a high conversion to uranium and thorium carbides. However, the odour of evolved hydrocarbon gases produced by hydrolysis on standing in air indicated that some carbide formation had occurred. It would appear that ignition at 2,500°C produced both uranium and thorium dicarbides in the case of the graphitised samples.

ACID LEACHING

It was thought that an initial separation of the uranium and thorium from the graphite might be obtained by acid leaching. If nitric acid was used as the leach liquor, the resultant solution after suitable head-end treatment could be fed into a solvent extraction plant. It is desirable to know to what extent the uranium, thorium, protactinium and fission products are leached into solution, are re-adsorbed on the graphite, or remain incorporated in the graphite.

Non-irradiated samples

Nitric acid leachings were performed under reflux and at 20, 60, 200, and 300°C on samples lightly crushed to pass a 22-mesh sieve. The 20° and 60°C experiments were carried out by shaking in a flask immersed in a thermostatically-controlled water bath and fitted with an air condenser. About 2-4gm. of sample was used in the initial experiments, but the subsequent experiments contained sufficient sample to give a nominal thorium concentration of M/10 and a uranium concentration of M/100 if quantitative leaching was achieved with the primary aliquot of acid. The selection of these concentrations

TABLE 1.—U AND Th RECOVERIES. HNO_3 LEACHING UNDER REFLUX.

EFFECT OF HNO_3 CONCENTRATION AND REFLUX TIME.

Sample	Acid normality	% leached into solution after refluxing for							
		1 hr.		2 hr.		3 hr.		4 hr.	
		U	Th	U	Th	U	Th	U	Th
Compacted	1	91	71	99.6	83	99.8	85	99.9	86
	4	90	89	99.7	93	99.9	94	99.9	94
	8	97.8	84	99.6	86	99.9	87	99.9	87
	16	99.0	82	99.5	83	99.9	84	99.9	85
Graphitised	1	77	71	83	75	85	77	87	79
	2	90	83	92	86	92	86	92	86
	4	87	73	88	75	88	75	88	75
	8	88	81	91	84	91	85	92	86
	16	95.4	81	96.2	83	96.4	83	96.5	83

TABLE 2.—U AND Th RECOVERIES. 4N HNO_3 LEACHING, EFFECT OF TEMPERATURE.

Sample	Temperature (°C)	Leaching time (hr.)	% leached into solution	
			U	Th
Compacted	20*	1	18	25
		2	51	29
		3	61	31
		4	91	42
	60*	1	98	57
		2	99.6	73
	Reflux	1	90	89
		2	99	93
		4	99.9	94
	200	8†	99.8	84
Graphitised	20*	1	44	38
		2	50	44
		3	54	47
		4	73	65
	60*	1	90	77
		2	91	78
	Reflux	1	87	73
		2	88	75
		4	88	75
	200	8†	97.9	85

* With shaking.

† Total contact time between fuel and HNO_3 = 16 hr.

was arbitrary. In all cases where repetitive leachings were done, the leached sample was filtered, washed, and then fresh acid added. A 4in. diameter stainless steel autoclave was used for the pressure leachings at 200°C and 300°C. Approximately 1gm. of sample was heated with nitric acid in a sealed silica ampoule immersed in water. The ampoule was not agitated and no gas overpressure was used.

Preliminary leaching experiments were performed on graphite impregnated with uranyl nitrate and fired at 400°C in argon to U308. These samples contained approximately 1-5 per cent. uranium (w/w) and were leached under reflux with 16N nitric acid. Uranium recoveries of > 98 per cent. were usually obtained for leaching times of three hours.

Results for nitric acid leaching of both the non-irradiated compacted and graphitised fuel samples are shown in Tables 1, 2, and 3. Duplicate experiments were not carried out, because each leaching was one of a series. The main conclusions are as follows:

EFFECT OF HNO_3 CONCENTRATION FOR LEACHING UNDER REFLUX (TABLE 1).

Generally, the higher the nitric acid concentration used as leach solution, the higher are the uranium and thorium recoveries. For the compacted samples, uranium recoveries > 99.5 per cent. are consistently obtained for leaching times of 2 hours, but the thorium recoveries are lower by up to 17 per cent. The graphitised samples give uranium and thorium recoveries up to 17 per cent. lower than do the compacted samples. 2 to 4N nitric acid appears suitable for use as leach solution. No advantage is gained in using nitric acid concentrations > 4N.

EFFECT OF LEACH TIME FOR LEACHING UNDER REFLUX (TABLE 1).

Most of the extractable uranium (> approximately 85 per cent.) and thorium (> approximately 70 per cent.) is removed by leaching for 1 hour. For longer leaching times, the uranium and thorium recoveries are increased, but only slightly. A sample of mixed residues (containing 9.5 mgm. Th/gm.) was digested with 4N nitric acid for 24 hr. under reflux, and a further thorium recovery of 65 per cent. of the thorium content of these residues was obtained. This indicated that the low thorium recoveries obtained with the graphitised samples were not due to acid inextractible thorium.

EFFECT OF LEACH TEMPERATURE (TABLE 2)

As expected, an increase in temperature from 20°C to approximately 100°C increases the uranium and thorium recoveries for the same leach time. This applies for both types of samples. For the compacted samples, pressure leaching at 200°C did not significantly change the uranium and thorium recoveries from those obtained under reflux.

EFFECT OF ADDED HF (TABLE 3)

Fluoride ion is known to catalyse the nitric acid dissolution of thorium metal and thoria (Moore, Goodall, Hepworth, and Watts, 1957). For the compacted samples, the use of both 0.01 and 0.05 M.HF does not alter the uranium recoveries for leach times >2hr. However, the thorium recoveries are significantly increased,

TABLE 3.—U AND Th RECOVERIES. 4N HNO_3 LEACHING UNDER REFLUX. EFFECT OF ADDED HF AND Th $(NO_3)_4$.

Sample	Added reagent (M)	Leaching time (hr.)	% leached into solution	
			U	Th
Compacted	HF 0.01	1	99	89
		2	99.9	98.4
	0.05	1	99	99
		2	99.9	99.3
Graphitised	0.05	1	93	93
		2	94	94
Compacted	Th $(NO_3)_4$ 0.2	1	99	81
		2	99.8	82
Graphitised	0.2	1	89	82
		2	93	82

and with 4N nitric acid and 0.05 M hydrofluoric acid, approximately 99 per cent. thorium can be extracted into solution. In the case of the graphitised samples, addition of 0.05 M hydrofluoric acid increases both the uranium and thorium recoveries, the latter significantly.

EFFECT OF ADDED Th^{4+} (TABLE 3)

The nitric acid leach solutions were made 0.2M in thorium nitrate. After digestion for 1 hour, the resulting thorium nitrate concentration was approximately 0.3M. The results indicate that the uranium and thorium recoveries were not significantly changed. An experiment was performed in which a compacted fuel sample was digested under reflux with 4N nitric acid for 4 hours to give a final solution 0.6 M in thorium. The overall recoveries of uranium and thorium were lowered to 87 and 71 per cent. respectively (c.f. Table 1).

Irradiated samples

The fate of fission products, protactinium, and the efficiency of uranium and thorium recoveries from irradiated compacted samples were investigated by 2N nitric acid reflux leaching of the following samples:

SAMPLE 1: Equal weights of uranium 235 and graphite powders were compacted at 10 ton/sq. in., irradiated in BEPO for 85 days at a flux of 1.4 x 10^{12} n/sq. cm./sec., and an irradiation temperature of 600°C. The sample was then cooled for 218 days, and refluxed in 2N nitric acid for 4 hours. The leach solution was filtered, and fission product and uranium analyses carried out on this solution, and on the control sample and residue after wet oxidation of the graphite with conc. perchloric/nitric acids.

SAMPLE 2: Equal weights of uranium 235, thorium and graphite powders, were compacted as above, fired in argon at 1,400°C, and irradiated in BEPO for 18 days at the same flux. After 42 days' cooling 1gm. of sample was leached with 2N nitric acid under reflux for periods of 1, 2, 4, and 28 hours. It was noticed that during irradiation the five individual sleeves comprising the specimen had adhered to one another, and could not easily be separated. As in the case of the non-irradiated samples, the solution was filtered and fresh acid used for each leach. Uranium, thorium, and protactinium analyses were performed on the leach solution, and on the control sample and residue after wet oxidation of the graphite. Protactinium 233 was determined by γ spectrometry using the 0.32 MeV peak (Fudge and Woodhead, 1955).

TABLE 4.—PERCENTAGE OF U AND FISSION PRODUCTS LEACHED FROM IRRADIATED GRAPHITE/URANIUM COMPACT (SAMPLE 1).

Element	% leached into soln. after refluxing in 2N HNO_3 for 4 hr.
Uranium	99.9
Fission product Sr	49
Zr	51
Nb	70
Cs	57
Ce	59
Gross γ	59

TABLE 5.—U, Th, Pa^{233} AND GROSS α, β AND γ RECOVERIES FROM IRRADIATED GRAPHITE/URANIUM/THORIUM COMPACT (SAMPLE 2). 2N HNO_3 LEACHING UNDER REFLUX. EFFECT OF REFLUX TIME.

	% leached into soln. after refluxing for			
	1 hr.	2 hr.	4 hr.	28 hr.
$U^{(Total)}$	25	47	72	99.3
Th	22	40	60	82
Pa^{233}*	17	30	47	70
Gross α	26	47	70	99.4
Gross β	20	36	54	76
Gross γ	13	27	44	69

* Mass balance incomplete due to adsorption. These percentages represent per cent. of Pa^{233} actually found in solution.

URANIUM AND THORIUM RECOVERIES

A uranium recovery of 99.9 per cent. was obtained from sample 1 after 4 hours' refluxing in 2N nitric acid (Table 4). For sample 2, the uranium recoveries are higher than those of thorium and increase with leaching time (Table 5). Tables 4 and 5 confirm that uranium recoveries $>$ 99 per cent. can be reproducibly obtained from the compacted samples.

FATE OF FISSION PRODUCTS

The distribution of typical fission products from sample 1 is shown in Table 4. Approximately 50-70 per cent. of the fission products strontium, zirconium, niobium, caesium, and cerium were leached into solution. Ruthenium was also leached into solution by the nitric acid, but it was not possible to obtain a complete mass balance because analysis indicated that ruthenium was lost in the wet oxidation stage of the sample, presumably as volatile ruthenium tetroxide. A gamma-spectrum analysis of the volatile product from the wet oxidation showed the characteristic gamma-energy of rhodium 106, in equilibrium with the parent ruthenium 106. Table 5 shows that the beta and gamma activities were leached from sample 2 with an overall recovery similar to that shown for individual fission products in Table 4.

FATE OF PROTACTINIUM 233

The apparent protactinium 233 recoveries are lower than those for thorium (Table 5), approximately 5 per cent. after 1 hour and ca. 10 per cent. after 2, 4, and 28 hours leaching. The protactinium bred in the thorium appears to be extracted with the bulk thorium, but because some 5-10 per cent. was lost due to adsorption on the graphite and/or on the walls of the leach vessel, the mass balance is incomplete.

ANODIC DISINTEGRATION OF GRAPHITE

Introduction

Because of its layer structure, graphite has different physical properties along and across the sheets of regular hexagons of carbon atoms which constitute the two dimensional molecule (Wells, 1950); e.g., it is possible to expand the lattice, in the direction perpendicular to the layers, by the insertion of layers of atoms or molecules between the sheets. Many natural graphites expand greatly along one axis and "puff-up" if moistened with nitric or sulphuric acids (Boersch and Meyer 1935). The composition of these graphite derivatives and the degree of expansion of the lattice are variable. However, pile-grade graphite is remarkably stable to oxidising agents such as boiling concentrated nitric acid.

Thiele (1938) has reported that when natural graphite was made the anode of an electrolytic cell containing sulphuric, nitric, perchloric, or hydrofluoric acid and a suitable voltage applied, the graphite swelled and decrepitated. No destruction was observed in the case of alkalis or orthophosphoric, hydrochloric, hydrobromic, hydriodic, chloracetic and chromic acids. However, with these acids, the anode was covered with an easily removable dull-black deposit. Thiele considered that oxygen did not penetrate between the graphite layers and force these apart mechanically, but that destruction of the anode was due to formation of various oxidation states of graphite. During the present investigations it was thought that if the graphite fuels could be disintegrated electrolytically to a fine powder, the uranium and thorium would be more readily available for acid leaching. Accordingly, experiments were performed on pile-grade graphite and on both types of fuel to test this hypothesis.

Experimental and results

Several types of electrolytic cell were used during these studies. For the pile-grade graphite and fuel samples which were available as solid rod, the graphite and fuel were made the anode in a 250 ml squat beaker. The cathode was usually a ⅜in. diameter rod of 18/8/1 stainless steel, but other materials, e.g., platinum and graphite were also used. Owing to hydrolysis in contact with air and water, the compacted carbide samples fell to powder. For powdered samples a cell was used, in which the sample was contained in, and formed the anode of, a platinum mesh basket.

Alternatively, the powder was placed on the bottom of a platinum dish which was the anode of an electrolytic cell, or floated on a mercury anode. Powdered carbide samples have also been anodically electrolysed in a streaming cell in which the sample was positioned between two sinter discs and solution streamed through the plug packing as current was passed. For the powdered samples both platinum and stainless steel cathodes were used.

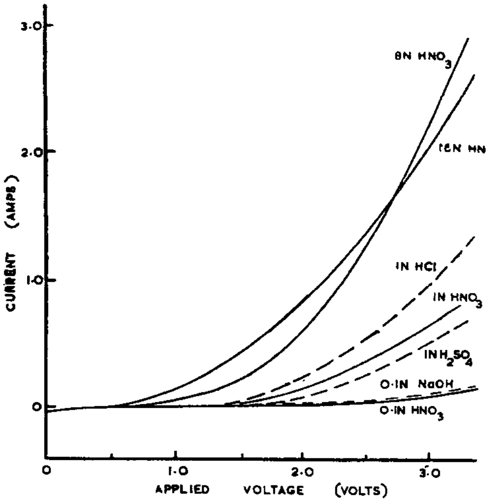

FIGURE 1: Current-voltage curves for graphite anode and stainless steel cathode in HNO_3, HCl, H_2SO_4, and NaOH solution.

The current was supplied from a bank of 24-volt batteries, and a 100-ohm rheostat placed in parallel with the cell controlled the applied voltage and current. These were measured on a "Unipivot" Versatile galvanometer coupled with a D.C. range box. After disintegration, the graphite was filtered, washed with water and acetone, dried under an infra-red lamp, and weighed.

CURRENT-VOLTAGE CURVES

Using a rod of pile-grade graphite (3in. long x 1in. diam.) as anode and a stainless steel rod cathode, current-voltage curves were obtained for a series of electrolytes. Figure 1 shows the current-voltage curves obtained with various concentrations of nitric, hydrochloric and sulphuric acids and caustic soda. For similar concentrations of acid or alkali, the curves were of similar shape. For the 1N acids the observed decomposition voltages were all in the region of 1.5-1.8 volts, which indicated that the same electrode processes were most probably occurring in each case. Similar results were obtained using cathodes of pile-grade graphite and platinum.

It was observed that decrepitation of the reactor-grade graphite anode occurred only when nitric acid was used as the electrolyte, and when the decomposition potential (+1.7 volt 1N for nitric acid) had been exceeded. No decrepitation took place with hydrochloric acid, sulphuric acid (c.f. Thiele, 1938) and caustic soda, even though there was copious evolution of oxygen at the anode. The range of electrolytes was therefore extended to include 2M solutions of sodium nitrate, calcium nitrate, lanthanum nitrate, thorium nitrate, perchloric acid, orthophosphoric acid, sodium selenate and sodium acetate. For these electrolytes it was only with sodium nitrate and the strong oxidising agent perchloric acid that breakaway of the graphite anode took place, and then only with anode potentials > approximately 6 volts. With both the 2M sodium nitrate and perchloric acid solutions, the weight of graphite removed per ampere-hour was approximately one-tenth of that with 2N nitric acid.

Stainless steel, platinum, and graphite were satisfactory as cathodes, remaining unattacked at low current densities. For these materials, the efficiency of disintegration was approximately constant (1.2 gm./ampere hour).

For mixed nitric acid/hydrochloric acid solutions the current-voltage curves were of similar shape to those for the pure acids, and the decomposition potentials were approximately +1.7 to +1.8 volts. The respective weights of graphite decrepitated per ampere hour in 4N acid solutions, using a 1in. diam. graphite anode and a ⅛in. diam. stainless steel cathode, were:

HNO_3, 1.26gm.; HNO_3/HCl (10:1), 0.76gm.; HNO_3/HCl (1:1), 0.03gm.; HCl, 0gm.

The joint presence of both hydrogen and nitrate ions appears essential for the rapid disintegration of pile-grade graphite. Because no disintegration was observed in solutions of hydrochloric or sulphuric acids, it seems reasonable to assume that nitrate ion is the controlling factor. In an attempt to elucidate the mechanism of the disintegration process, samples of graphite have been analysed (private communication, E. Wait) by X-ray powder diffraction before and after disintegration in nitric acid, using the Debye-Scherrer technique and a Guinier type focusing camera. Differences in the structure have been observed with the wet disintegrated graphite, and the results suggest that the disintegration process cannot be simply explained in terms of an increase in interlayer spacing. Disintegrated graphite powder, after removal of the nitric acid by drying under an infra-red lamp, was found to be identical in cell size and cell structure with the sample before disintegration.

ANODIC DISINTEGRATION OF FUEL SAMPLES

Table 6 shows the uranium recoveries obtained by anodic disintegration in nitric acid of graphite rods impregnated with uranyl nitrate solution, and also the uranium and thorium recoveries from graphitised fuels. Table 7 gives examples of uranium and thorium recoveries from compacted fuels, using various cell assemblies. Several interesting results appear from inspection of these tables.

The uranium recoveries are invariably higher than those for thorium (c.f. nitric acid leaching). In some experiments, e.g., using a platinum dish or basket anode, uranium recoveries > 98 per cent. have been obtained, but these are not reproducible. Increase in the number of ampere-hours passed generally gives an increase in both the uranium and thorium recoveries. When mercury was used as the anode, appreciable solution of mercury in nitric acid occurred. Increase of nitric acid concentration from 4-8N does not generally affect the uranium and thorium recoveries.

TABLE 6.—ANODIC DISINTEGRATION OF IMPREGNATED AND GRAPHITISED FUELS. U AND Th RECOVERIES.

Sample	Electrolyte	Cathode	Current (ampere)	Voltage	Disintegration time (hr.)	% found in soln.	
						U	Th
Graphite impregnated with $UO_2(NO_3)_2$ fired at 1000°C	8N HNO_3	Stainless steel	3.0	Decomposition potential	5	91	Sample contained no thorium
	8N HNO_3	Stainless steel	2.9	Decomposition potential	5.5	>98	Sample contained no thorium
	8N HNO_3	Stainless steel	2.6	Decomposition potential	8	>98	Sample contained no thorium
	8N HNO_3	Stainless steel	2.6	Decomposition potential	1	75	Sample contained no thorium
Graphitised	4N HNO_3	Pt gauze	3.0	Decomposition potential	4	96	Sample contained no thorium
	4N HNO_3	Pt gauze	1.5	Decomposition potential	1	89	88
	4N HNO_3	Pt gauze	1.5	Decomposition potential	7	89	82
	4N HNO_3	Pt gauze	1.5	Decomposition potential	10	96	84

TABLE 7.—ANODIC DISINTEGRATION OF COMPACTED FUELS.
U AND Th RECOVERIES. DIFFERENT ELECTROLYTE ASSEMBLIES.

Sample	Cell assembly	HNO_3 normality	Disintegration time (hr)	Current (amp)	% found in soln.	
					U	Th
Graphite/uranium/thorium	Pt dish anode, Pt cathode	4	7	1	75	61
Graphite/uranium/thorium	Pt dish anode, Pt cathode	4	7	1.5	76	64
Graphite/uranium/thorium	Pt dish anode, Pt cathode	4	7	2	99.4	78
Graphite/uranium/thorium	Pt dish anode, Pt cathode	4	22	1.5	96.4	71
Graphite/uranium/thorium	Pt dish anode, Pt cathode	4	1	1.5	36	26
Graphite/uranium/thorium	Pt dish anode, SS cathode	8	0.75	2.3	80	36
			1.5	2.3	86	48
			2.25	2.3	83	53
			4.5	2.3	83	54
Graphite/uranium/thorium	Pt dish anode, SS cathode	8	3.0	2.5	> 98	74
Graphite/uranium/thorium	Pt basket anode, SS cathode	8	4	3	> 98	78
Graphite/uranium/thorium	Pt plate anode at bottom of cell	8	3	0.7	68	42
Graphite/uranium	Pt dish anode, SS cathode	8	3	2.3	> 98	—
Graphite/uranium	Pt basket anode, SS cathode	4	2	2.6	—	56
Graphite/uranium/thorium	Hg anode* Pt cathode	4	4	3	28	7
Graphite/uranium/thorium	Streaming cell	4	2	0.2	79	79
Graphite/uranium/thorium	Streaming cell	4	2	0.4	79	83
Graphite/uranium/thorium	Streaming cell	4	4	0.4	98	63

* Dissolution of Hg in HNO_3 occurred (224 mgm. Hg/ml.).

In addition, the anodic disintegration process gives uranium and thorium recoveries no higher than those obtained by direct nitric acid leaching of the fuel (Tables 1-3). The results suggest that anodic disintegration is effective in breaking down the graphite fuel into small particles which are more amenable to nitric acid leaching. It has not been possible to assign any electrochemical action to the anodic solution of uranium and thorium carbides. It was also observed that, due to the passage of current, the electrolyte temperature increased (up to approximately 55°C), and, with the exception of the streaming cell experiments, agitation of the fuel particles took place.

ANODIC DISINTEGRATION OF FUEL ELEMENT GRAPHITE CANS

Although quantitative recovery of the uranium and thorium was not obtained by anodic disintegration, the graphite was broken down in such a way that a subsequent acid leaching was facilitated. Anodic disintegration offers a possible alternative to crushing and grinding for powdering a fuel element, with the advantages that partial dissolution of the uranium and thorium is obtained, and no dust hazard is created. Direct acid leaching of the disintegrated fuel may then be used to extract > 99 per cent. uranium and > 95 per cent. thorium. Accordingly, experiments were performed on a 6ft. length of graphite can proposed for a 10MW reactor experiment.

The cathode, which was used as the container vessel for the electrolyte solution, was a 7in. diam. stainless steel beaker of 10 litre capacity. The current (maximum output 60 amps at 24 volts) was supplied from a rectifier unit fitted with a "Variac" control on the primary winding.

TABLE 8.—DISINTEGRATION OF GRAPHITE FROM FUEL ELEMENT CAN IN 2N HNO_3

Run Number	Current (amp.)	Time (hr)	Initial Current Density (amp./cm²)	Maximum Temperature (°C)	Wt. of graphite deposited (gm.)	Efficiency gm. amp-hr)
1	10	7	.055	31	50.2	.71
2	20	7	.111	42	102.8	.73
3	30	7	.166	52	138.4	.66
4	40	7	.221	61	137.6	.49
5	50	7	.277	69	114.0	.33
6	30	2	.166	—	55.7	.93
7	30	4	.166	—	93.5	.78

In operation a known length of the graphite can (usually 4 inches) was immersed vertically in the nitric acid solution and the current, at a constant amperage, passed for the desired time. The disintegrated graphite was filtered, washed with water and acetone, dried under an infra-red lamp and weighed. It was then graded by sieving. The lower six inches of the can were then removed by cutting, and the same can used in subsequent experiments. The relative weights of graphite disintegrated under conditions of varying current density in 2N nitric acid are shown in Table 8. The particle size distributions of graphite from five of these experiments are recorded in Table 9. Experiments with 4N nitric acid gave similar results to those listed in Table 9.

Under the experimental conditions used, the efficiency of the disintegration (weight of graphite disintegrated/ampere hour) was a function of the current density, and above a current density of ca. 0.2 ampere/sq. cm. decreased with increase of current density. The weight of graphite disintegrated is approximately proportional to the number of ampere hours passed at any given current density. The particle size of the graphite varies considerably, with a general tendency as shown in Table 9 to decrease with an increase in current density.

When the current density was less than 0.2 ampere/sq. cm. filtration of the graphite from the electrolyte was rapid and a clear filtrate resulted. For current densities greater than this figure, filtration was slow, and the filtrate was brown and slightly opaque. The smaller particle size of graphite produced at the higher current densities may be partly due to the increased temperature leading to an accelerated rate of reaction between the nitric acid and the graphite. At current densities greater than approximately 0.15 ampere/sq. cm., cathodic dissolution of the stainless steel container vessel occurred and, after filtration, a violet solution due to soluble chromium was produced. An initial current density of 0.17 ampere/sq. cm. for 210 ampere-hour gave a solution which analysed as follows: iron 1.8 mgm./ml. and chromium 0.4 mgm./ml.

Experiments were also carried out in a 4in. diam. 4ft. long glass tube fitted with a ½in. deep annular stainless steel cathode held in position by two ¼in. diam. stainless steel rods (Figure 2). These rods were insulated by P.V.C. tubing and welded to the ring to make electrical connection. Using this apparatus, a higher current density (1.5 ampere/sq. cm.) over a small length of the graphite was obtained.

With the stainless steel annulus the graphite can was disintegrated and severed over a length

TABLE 9.—PARTICLE SIZE OF GRAPHITE DISINTEGRATED FROM FUEL ELEMENT CAN IN 2N HNO_3

Run Number	Particle size (microns), expressed as % falling within given range.						
	> 700	700-300	300-200	200-150	150-76	76-53	< 53
1	1.2	11.0	13.0	26.8	33.6	6.4	7.8
2	1.3	30.7	19.7	18.2	19.4	4.3	6.3
3	0.9	24.3	19.9	23.4	19.6	4.9	7.0
4	0.6	9.4	19.0	27.5	27.9	6.2	9.4
5	0.1	1.5	9.0	21.2	41.8	10.8	15.5

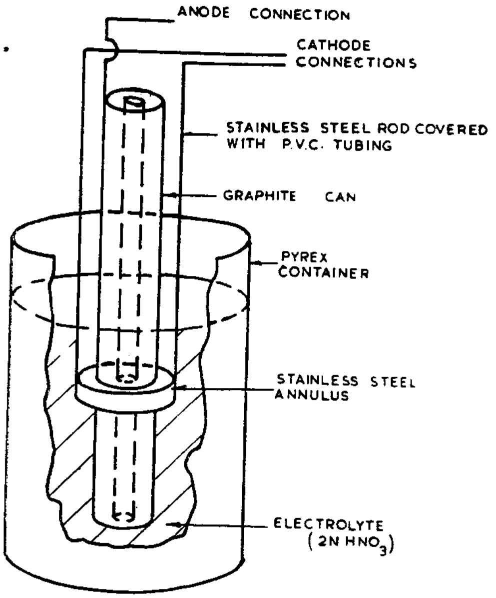

FIGURE 2: Arrangement for cutting graphite fuel can by anodic disintegration.

less than 1in. This suggests that the anodic disintegration process might be useful in separating the fissile fertile content of a graphite-moderated fuel from pure moderator which is used as a structural support. It should be possible to effect such a method without appreciable disintegration of the graphite support.

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