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A STUDY OF THREE METHODS
FOR REPROCESSING GRAPHITE FUELS:
MIXED ACID OXIDATION, GRIND-LEACH,
AND ELECTROLYTIC DISINTEGRATION

L. A. Decker and R. R. Hammer

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ABSTRACT

Two processes, mixed nitric-sulfuric acid oxidation and grind-leach, were found to be chemically feasible for reprocessing nuclear rocket fuels; with further work, these processes should be suitable also for reprocessing other graphite fuels such as those using uranium carbide particles coated with refractory materials.

A third process, electrolytic disintegration, was found to be unsatisfactory.

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I. SUMMARY

The results of limited laboratory tests show that the recovery of uranium from graphite fuels is chemically feasible with two processes which are alternates to the presently favored approach, combustion. These processes are mixed nitric-sulfuric acid oxidation and grind-leach. Both give essentially quantitative recovery of the uranium in the graphite fuels, appear to overcome the unique technical problems associated with those fuels, and appear to be suitable for installation at the Idaho Chemical Processing Plant (ICPP). Presumably, future fuels, which have been modified by coating the uranium carbide particles with silicon carbide, aluminum oxide or other refractory material, could be handled with either of these processes after further development. No obvious advantages over the combustion process were found in these limited studies, however.

A third process, electrolytic disintegration, was found to be ineffective in quantitatively recovering the uranium from graphite fuels. The method was successful in disintegrating solid pieces of fuel but did not penetrate the more resistant coatings on the fuel particles.

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II. INTRODUCTION

At present, no full scale reprocessing plant is capable of re-covering the unused uranium from irradiated nuclear fuels containing graphite as the principal component. The fuels which are generally called graphite fuels are being used in the various reactors of the nuclear rocket program ⁽¹⁾ and for High Temperature Gas-cooled Reactors (HTGR) such as the reactor in operation at Peach Bottom, Pa., and the one proposed for installation at Fort St. Vrain, Colorado. In both types of reactors the uranium is present as the carbide; the HTGR fuel contains thorium carbide in addition to the uranium. The early nuclear rocket fuels consist of uranium carbide dispersed in a graphite matrix; the later types have a pyrolytic carbide coating placed on the uranium carbide particles before dispersion, and the coolant channels are lined with niobium carbide. The HTGR fuel particles are also coated before dispersion in the graphite matrix. ^(2,3,4)

Much development work has been done on combustion processes for this fuel, because they accomplish the desirable effect of removing the bulk component (graphite) by burning it in a headend operation. The uranium (and thorium where present) are thereby converted to the oxides from which the uranium can be recovered by leaching and conventional solvent extraction methods or by a halide volatility process. The process presently considered as a leading contender for installation at ICPP burns the carbon continuously in a bed of inert alumina particles fluidized by a stream of oxygen-air. ^(5,6,7) The uranium is recovered by continuous leaching followed by solvent extraction.

Other approaches, (1) mixed nitric-sulfuric acid oxidation, (2) grind-leach, and (3) electrolytic decomposition, were considered in the event that unforeseen problems arose to make the combustion methods undesirable. Limited testing in the laboratory to determine the technical feasibility of applying each of these processes at ICPP was undertaken. These scoping studies were not intended to be an exhaustive development of the details of the alternate processes. The incentive to do this was lacking, because the combustion process had already advanced essentially to the point of practical application.

A group of fuel elements with pyrolytic-graphite-coated uranium dicarbide particles dispersed in a graphite matrix and having niobium carbide liners in the coolant channels was chosen for this study as being representative of the graphite fuels and representing one of the more difficult types to process. These elements were fabricated for the Kiwi reactor of the nuclear rocket program and had been tested in a hot hydrogen stream, the reactor coolant fluid. Hot hydrogen tested elements were chosen since there is evidence that migration of the uranium occurs at high temperatures allowing the formation of a solid solution with other metallic elements. ⁽⁸⁾ Although actual results from only one type of fuel were obtained from this study, inferences as to the utility of these processes for other fuel types can be drawn.

The three unique problems which any successful process for treating graphite fuels must overcome are as follows: (1) separation of the uranium from a large amount of relatively inert material, (2) penetration of the coating of the uranium containing particles where these are encountered, and (3) recovery of the uranium, some of which may exist as a solid solution with other metallic elements.

Each of the proposed or alternate processes differs from the others mainly in the manner in which the penetration of the coating of the uranium particles occurs. The burn-leach process accomplishes this by oxidation at high temperature, the grind-leach process uses mechanical grinding to rupture the coating, and the mixed acid oxidation penetrates the coating as a result of chemical oxidation. The electrolytic decomposition attempts to break the protection of the coating electrochemically.

Each of the alternate processes achieves the separation of the uranium from the large amount of graphite matrix by dissolving the uranium in aqueous solutions from which it can then be recovered by solvent extraction techniques.

Although the results of the laboratory work performed in connection with these other approaches are of general application, the processes are discussed as applying to the ICPP, specifically. No attempt has been made here to compare these other processes point by point with the combustion process, but rather to evaluate which of the three alternates might represent the best backup for the combustion processes.

III. MIXED ACID OXIDATION PROCESS

Uranium dicarbide is readily soluble in nitric acid, but the pyrolytic carbon coating on the uranium dicarbide particle prevents it from being contacted by the acid. An oxidizing solution which will penetrate the dense carbon coating is needed, therefore, to solubilize the uranium.

1. DESCRIPTION OF PROCESS

The test fuel (see page 3) disintegrates in a few seconds when immersed in a solution which is 44.5 mole percent H_2SO_4 , 12.5 mole percent HNO_3 , and 43.0 mole percent H_2O at temperatures slightly above $100^\circ C$. If the reaction is allowed to continue for several hours at a temperature near the initial boiling point of this acid mixture ($118^\circ C$ at 650 mm Hg), the coated particles are penetrated and the uranium dissolves. Separation of the solids followed by washing yields a solution which can be adjusted to permit extraction of the uranium with tributyl phosphate (TBP).

2. CORROSION EFFECTS

The potentially corrosive nature of the acid mixture limits the possible materials of construction of the dissolver to special-service materials. It should be noted that many materials will withstand mixed nitric-sulfuric acid mixtures at room temperature and/or very low water content. The severe conditions required to decompose the graphite structure of the fuel, however, eliminate most of these materials from consideration. A literature search indicated that tantalum would resist attack of a wide range of sulfuric-nitric acid mixtures. These results were confirmed in a laboratory corrosion test which duplicated expected plant dissolver service conditions. A corrosion rate of less than 0.02 mils per month was observed for a tantalum specimen which was exposed to the mixed nitric-sulfuric acid mixture at $120^\circ C$ for three consecutive 24-hour periods. A high silicon cast iron, Duriron, showed no corrosion after one 24-hour period. However, after one continuous 30 day test at $120^\circ C$ in the acid mixture with no fresh acid added, the corrosion rate was determined to be 14 mils per month. This result may be higher than would occur in plant service because of the loss of nitric acid and water from the solution during the 30-day test despite the presence of a reflux condenser.

These experimental results are shown in Table I and are compared with literature comments on these two materials and two other possible candidates, titanium, and Hasteloy C. A plastic coating material, Kynar (Pennsalt Chemicals polyvinylidene fluoride), was tested simultaneously with the Duriron and was found to withstand the 24 hour test with no weight change but was severely decomposed during the 30 day exposure. Carpenter 20 was shown to be unsatisfactory having a corrosion rate of 100 mils per month during one 10 hour test.

Table I
CORROSION OF VARIOUS MATERIALS BY MIXED NITRIC-SULFURIC ACID SOLUTIONS

Material	Corrosion Rate mils/mo	Temp. °C	Conditions	Test Period	Reference
			Composition of Solution Mole % H_2SO_4 - HNO_3 - H_2O		
Tantalum	< 0.02	120	44.5 - 12.5 - 43	72 hr	This study
	0.2	150	85 - 15 - 0	--	(9, 10)
Duriron	nil ^(a)	120	44.5 - 12.5 - 43	24 hr	This study
	14	120	44.5 - 12.5 - 43	30 days	This study
	0.2	150	85 - 15 - 0	--	(9, 10)
Titanium	< 2	25	22 - 78 - 0	--	(11)
Hasteloy C	< 2	25	Complete range	--	(12)
Carpenter 20	100	120	44.5 - 12.5 - 43	10 hr	This study
Kynar	nil ^(a)	120	44.5 - 12.5 - 43	24 hr	This study
	disintegrated	120	44.5 - 12.5 - 43	30 days	This study

(a) Nil in short term tests, high in long term (see text p. 5)

The results of this study show that tantalum would make a suitable container for the hot mixed acid. The extremely low corrosion rate indicates that there is no need for a corrosion allowance in the vessel design. A vessel clad with a tantalum lining of 5 mils would be acceptable and could be obtained for approximately 30 dollars per square foot of surface.

3. DISCUSSION

Figure 1 shows the principal operations involved in reprocessing the graphite fuels using the mixed acid oxidation headend treatment. The unbroken fuel rods are fed into a dissolver filled with the acid mixture where they disintegrate within a few minutes as the solution is heated. If the graphite rods were stored in aluminum cans they could probably be dropped into the dissolver unopened, because the aluminum would dissolve and add salting strength for the solvent extraction process.

The acid mixture dissolves the uranium as well as some of the niobium carbide, which hydrolyzes and precipitates upon dilution; however, this precipitate can be removed along with the undissolved niobium and graphite by filtering or centrifuging to produce a clarified feed for

Figure 1 Mixed Acid Oxidation Flowsheet for Graphite Fuel

the extraction column. A dilution factor of up to 27 is necessary to lower the sulfate concentration to about 0.5 molar for extraction of the uranium with TBP. Presumably, this dilution will provide sufficient wash volume for separation of the dissolved uranium from the solid residue.

Thorium-bearing fuels such as the Peach Bottom reactor fuel very likely can also be processed by this method since the sulfate concentration is low enough for complete solubility of the thorium sulfate in the nitric acid-aluminum nitrate solution. ⁽¹³⁾

The percentage recovery of the uranium depends on the liquid volume to solids ratio, the time of reaction, and the temperature of reaction. A reaction time of about 10 hours is sufficient to give greater than 99 percent recovery at a reaction temperature of 118°C (Table II).

Table II

EFFECTS OF TEMPERATURE AND REACTION TIME ON THE CHEMICAL DISSOLUTION OF URANIUM IN NUCLEAR ROCKET FUEL IN MIXED ACID ^(a)

Percent uranium dissolved at:				
<u>Temperature:</u>	<u>84°C</u>	<u>97°C</u>	<u>118°C</u>	<u>152°C</u> ^(b)
<u>Reaction Time</u>				
1 hour	23	--	67	70
8 hours	60	93	99 ± 1	99 ± 1
16 hours			99.9 ± 0.1 ^(c)	
24 hours	93	--	99.97 ± 0.03 ^(c)	99 ± 1

(a) 44.5 mole percent H₂SO₄, 12.5 mole percent HNO₃ and 43 mole percent H₂O.

(b) The initial boiling point of the solution is 118°C (at 650 mm) but after several minutes of reaction the boiling point rises as oxides of nitrogen are driven off.

(c) Determined from material balance which included analysis of the residue. The other results are based on assumed input, known to about ± 1%.

Solutions of sulfuric and nitric acid of certain compositions rapidly disintegrated solid specimens of fuel. Table III shows the effects of varying the ratios of acids and water. The solution composed of 44.5 mole percent H_2SO_4 , 12.5 mole percent HNO_3 , and 43 mole percent water disintegrated the fuel rapidly and resulted in greater than 99 percent recovery of the uranium. A solution of 90 mole percent sulfuric acid with no nitric acid present (regular 98 wt/o H_2SO_4) showed no reaction on the graphite after several minutes.

Table III
EFFECT OF COMPOSITION OF ACID SOLUTION ON THE CHEMICAL DISSOLUTION
OF URANIUM IN NUCLEAR ROCKET FUEL

Composition of Acid Solution (mole percent)			Uranium ^(c) Recovery (Percent)	Observations
H_2SO_4	HNO_3	H_2O		
90.0	0.0	10.0	0	No disintegration
85.2	14.8	0.0	99	Rapid disintegration
66.9	6.5	26.6	(b)	Rapid disintegration
44.5 ^(a)	12.5	43.0	99.9	Rapid disintegration
34.5	26.6	38.9	38	Rapid disintegration
29.5	16.9	53.6	55	Rapid disintegration
22.1	18.9	59.0	27	Rapid disintegration
11.0	22.2	66.8	0	No disintegration

(a) Obtained by combining 3 volumes 98 percent H_2SO_4 and 1 volume 70 percent HNO_3 .

(b) Analysis not made.

(c) For 16 hr. reaction time.

The uranium can be extracted with 10% TBP from a solution having the following composition: 0.5 g/l uranium, 1.2M acid, 3M nitrate, 0.5M sulfate and 1.0M aluminum. The aluminum concentration in the feed solution is controlled by the dilution required to lower the sulfate

Figure 2 Equilibrium diagram for uranium extraction in mixed acid oxidation flowsheet

concentration to a value (0.5M) which will allow quantitative removal of uranium by solvent extraction. Higher sulfate concentrations (2.0M) prevented adequate extraction because of the stability of the uranyl sulfate complexes.⁽¹⁴⁾ Solvent extraction of the adjusted solution with 10 percent TBP in kerosene resulted in total losses of less than 0.1 percent for three stages each of extraction and stripping. Extraction coefficients (E^o/a) for three stages for a typical feed composition were determined in the laboratory (batch contacting with an organic-to-aqueous volume ratio of 1:1) to be 15, 6.2, and 5.5, respectively (see Figure 2). The soluble organic compounds formed by the oxidation of graphite did not interfere in the extraction of uranium. Stripping the uranium from the organic phase proceeded with no difficulty; distribution coefficients (E^a/o) of 4.8, 200, and > 30 were obtained for three stripping stages.

IV GRIND-LEACH PROCESS

Uranium dicarbide is readily soluble in nitric acid, but the protective coatings on the uranium dicarbide particles prevent contact between the nitric acid dissolvent and the uranium particles unless they are first ruptured.^(15,16,17) The feasibility of quantitatively leaching the uranium from the fuel after grinding was investigated.

1. DESCRIPTION OF PROCESS

Figure 3 is an outline of the principal operations involved in the grind-leach process for processing graphite fuel. The fuel would be pulverized after being broken into pieces small enough to be suitable as feed material for a pulverizer. The pulverizer must be capable of reducing all of the fuel to particles which are smaller than the smallest coated uranium carbide particles. Solvent extraction with TBP in kerosene will separate the uranium from the nitric acid solution containing the fission products.

2. DISCUSSION

2.1 Leaching

A nitric acid concentration of 15.7M (70 percent) leached greater than 99 percent of the uranium from material which had been pulverized such that all coated particles were broken. A leach period of three hours was arbitrarily used in these studies since longer periods were not effective in increasing recovery to 100.0 percent.

One of the variables investigated was the effect of different exposure periods for the fuel in prior tests with hot hydrogen (see introduction). There appeared to be no non-leachable uranium combined as a solid solution with the niobium carbide resulting from such exposure. This conclusion is based on the observation that at least 99.8 percent of the uranium was leached from the pulverized fuel regardless of the length of time the fuel specimen had been maintained at the elevated temperature necessary for the formation of solid solutions. Included in the test specimens was a portion of an element which had been irradiated in the Kiwi B⁴D reactor test.

2.2 Solvent Extraction

The uranium can be recovered from the leach solution by solvent extraction with or without a solids separation step. Solids-containing solutions have been used as feed to the TBP extraction equipment at ICPP in the past, with some success. In general, solids produce a surfactancy effect which has been overcome by additives which modify the behavior of the surfactant. Even though it is possible to use the solutions with a solids content as high as would result from a grind-leach headend operation, it is generally desirable to process a clarified feed.

Figure 3 Block Diagram of Grind-Leach Flowsheet for Graphite Fuel

A concentration of 20 percent TBP in kerosene extracted the uranium from the slurry containing 8.9 g/l uranium and an acid concentration of 14.8M resulting from leaching a sample of irradiated fuel from the Kiwi B4D reactor test with 15.7M HNO_3 . Extraction coefficients (E^o/a) of 7.4, 18.1, and 21.5 were obtained for each of three stages, respectively, using an organic-to-aqueous solution ratio of 1:1 and direct contact between the organic phase and the slurry. Larger distribution coefficients would be attained by diluting the acid and adding salting agents.

Pilot plant work also demonstrated the feasibility of extraction column operation with a graphite slurry (8 g/l U, 30 g/l graphite, 8M HNO_3). Accumulation of the graphite at the interface of the disengaging section was prevented by adding gelatin (200 ppm) to the aqueous feed slurry.

V. ELECTROLYTIC DISINTEGRATION

Concentrated (70 percent) nitric acid disintegrates pieces of graphite fuel when a potential is applied between an anode in contact with the fuel piece and a cathode immersed in the solution. The disintegration proceeds rapidly until the coated uranium carbide particles are exposed. Reaction with the coating is very slow and leaves the coating essentially intact on a large number of particles. The process is not suitable, therefore, for recovering the uranium quantitatively in a reasonable length of time. (17), (18), (19)

Figure 4 Apparatus for electrolytic disintegration of graphite fuel.

The best conditions tested for disintegration of the graphite and dissolution of the uranium were a temperature of about 80°C, 70 percent nitric acid, a potential of about 8 volts and a current density of $\frac{1}{2}$ amp/cm² with the anode contacting the fuel. Tables IV, V, and VI show the effects of potential, temperature, and additives on uranium recovery.

2.1 Effect of Temperature.

Increasing the temperature toward the boiling point caused fluctuation in the flow rate of the acid and in the current flowing through the circuit. At 92°C the current fluctuated widely about the $4\frac{1}{2}$

1. EXPERIMENTAL PROCEDURE

Figure 4 shows the important features of the device used in the laboratory to investigate the electrolytic decomposition of graphite fuel. The platinum anode was a circular disk 25 mm in diameter, which was kept in contact with the fuel piece by pressure from above. The fritted disk supported the fuel and permitted electrical contact with the cathode through the solution. The nitric acid solution flowed through the cell at a rate of about 30 ml/min.

2. EXPERIMENTAL RESULTS

Uranium recoveries up to only 24 percent were obtained in several 8 hour experiments using varied concentrations of nitric acid and varied potentials. Addition of 0.4M $K_2Cr_2O_7$ increased the recovery to 39 percent.

Table IV

EFFECT OF POTENTIAL ON THE AMOUNT OF URANIUM DISSOLVED

(92-98°C, 70% HNO ₃ , 8 hrs)		
<u>Potential</u> (volts)	<u>Current</u> (amps)	<u>U Dissolved</u> (percent)
0	0	0.2
7.5	1.8-4.6	11
16	2-11	11
24	3-15	7.5
33	2-20	0.9

Table V

EFFECT OF TEMPERATURE ON THE AMOUNT OF URANIUM DISSOLVED

(70% HNO ₃ , ~ 5-8 volts, 8 hrs)		
<u>Temperature °C</u>	<u>Average Current</u> (amps)	<u>U Dissolved</u> (percent)
92	4½	11
82	4	24
47	2	15

Table VI

EFFECT OF ADDITIVES ON THE RATE OF DISSOLUTION

(10 volts, 3-7 amps, 70% HNO ₃ , 8 hrs, 92°C)	
<u>Additive</u>	<u>U Dissolved</u> (percent)
H ₂ O ₂ (2.0M)	4
NaNO ₂ (0.9M)	0.2
K ₂ Cr ₂ O ₇ (0.4M)	39

ampere nominal value shown in Table V because of the increased volume of gases surrounding the fuel and the electrodes. The reason for the slower rate of disintegration at the higher temperature shown in Table V was probably the great amount of boiling of the liquid in the vicinity of the graphite, which resulted in less contact of the solution with the graphite.

2.2 Effect of Solution Composition.

The higher the concentration of nitric acid the more rapidly the graphite pellets disintegrate. This would be the case if nitric acid or some nitrate species were responsible for the disintegration. The disintegration is probably caused by an oxidation product of nitric acid because the rate was greatly enhanced by applying an electric field and disintegration occurred only at the anode.

Of the additives sodium nitrate, potassium dichromate, and hydrogen peroxide, only the dichromate enhanced the rate of dissolution. This beneficial behavior is probably due to the powerful oxidizing nature of the reagent.

Another possible mechanism which could cause disintegration of the graphite matrix is the formation of graphitic nitrates which may undergo anodic oxidation to produce the gases NO_2 and O_2 within the graphite matrix. The influence of the pressure alone from these gases could disintegrate the graphite matrix.

3. PROCESS IMPLICATIONS

Disintegration of the graphite pieces occurs in a few minutes at the optimum conditions described in section 2.1. This effect could be useful in cases in which it is desired to pulverize the fuel only or in which the uranium is available for leaching in an uncoated form.

The pyrolytic carbon coatings on the uranium dicarbide particles remained resistant to the nitric acid even in the presence of the electric field used during the electrolytic decomposition of the fuel. The electrolytic decomposition process is, therefore, of no value for practical application for fuels containing coated particles.

VI CONCLUSIONS

The evaluation of alternate processes to combustion processes for nuclear rocket and HTGR fuels did not produce any convincing reason to abandon the already well advanced development of the combustion methods of recovering the uranium. Limited laboratory testing showed the chemical feasibility of two of the alternate processes: mixed nitric-sulfuric acid oxidation, and grind-leach, each followed by conventional solvent extraction. Recoveries of greater than 99.9 percent were obtained with these two processes from samples of Kiwi fuel from the nuclear rocket program. Either process could serve as a backup for the combustion processes if required. The problems which deserve more attention in the mixed acid oxidation process include corrosion of the container and the separation of the solid graphite residue from the uranium containing solution. The grind-leach process poses the same solids-liquid separation problem and also presents the problem of containment of radioactive fines during grinding.

The electrolytic decomposition process was shown to be of little value in recovering the uranium from these fuels. Complete disintegration of solid fuel pieces into finely divided material was easily accomplished, but the uranium recovery was too low to be of practical value due to the resistance of the pyrolytic carbon coating.

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