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AEC Research and Development Report
Nuclear Reactors for Rocket Propulsion
M-3679 (39th Ed.)
November 1965

ICPP LABORATORY STUDIES ON A COMBUSTION-NITRIC ACID
LEACH PROCESS FOR ROVER FUEL
(Title Unclassified)

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DATE **AUG 28 1973**

For The Atomic Energy Commission

Bram C. Feldman

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Chief, Reactor, Space and Technology Branch
Division of Classification

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LEACH PROCESS FOR ROVER FUEL

by

L. A. Decker

A B S T R A C T

A process is needed to recover the uranium from the uranium carbide-graphite fuel elements such as are being tested for the Rover space reactor program. The process described in this report resulted from laboratory studies using actual specimens of Rover fuel including one irradiated specimen. The studies indicated that a burn-leach process using nitric acid only as the leach reagent would be feasible if combustion temperatures are maintained at or below 800°C. The specimens used in the study were burned in air or air diluted with nitrogen and then the ash was leached with 8M nitric acid. Uranium recoveries of up to 99.8 percent were obtained from fuel burned at 800°C.

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by

L. A. Decker

I. SUMMARY

Processes are being developed at the Idaho Chemical Processing Plant (ICPP) and elsewhere for the recovery of the uranium from the graphite fuels such as are being tested for use in the Rover space reactors. Laboratory studies carried out at ICPP on actual specimens of Rover fuel indicate that a burn-leach process using nitric acid alone as the leach reagent would be feasible if combustion temperatures are maintained at or below 800°C. The specimens were burned in air or air diluted with nitrogen and then the ash was leached with nitric acid. Uranium recoveries of up to 99.8 percent obtained from fuel burned at 800°C show the feasibility of the process. The fuel pieces had been tested in hydrogen at 2475°C for up to 10 minutes so that any migration of uranium to the niobium liner which could be expected should have taken place.

II. INTRODUCTION

A process is needed to recover the uranium from fuel used in the development of nuclear reactors for space such as those being developed in the Rover Program⁽¹⁾. Development work to determine the best type of process for this fuel has been carried out at Oak Ridge National Laboratory⁽²⁾ and at Brookhaven National Laboratory⁽³⁾. Supplementary studies to follow up on that development work have been carried out at ICPP.

The fuel elements for the Rover reactors are composed of uranium dicarbide dispersed in graphite which has been extruded into the shape of hexagonal rods. The fuel rods have coolant channel holes drilled lengthwise which are coated with vapor-deposited niobium carbide⁽⁴⁾. The uranium dicarbide particles are coated with pyrolytically deposited graphite to retain fission products before being dispersed in the bulk graphite. However, at high reactor temperatures the uranium migrates through the coating and comes in contact with the niobium carbide liner. If the high temperature is maintained for more than a few minutes, the uranium and niobium may form mixed carbides which, if burned at high temperatures, usually will produce an insoluble mixed oxide solid solution⁽²⁾.

[REDACTED]

A reasonable first step in processing the Rover fuel appears to be combustion at a temperature that removes the major constituent, graphite, as a gas but avoids the formation of a solid solution, leaving an ash consisting of niobium oxide, uranium oxide, and fission product oxides. The uranium oxide can then be dissolved in nitric acid and leached from the remainder of the ash if the formation of clinkers and solid solutions is avoided during the burning process. Clinkers would occlude uranium and prevent attack by the nitric acid. Solid solutions of uranium and niobium oxides would be insoluble in straight nitric acid because of their refractory nature. Both clinker formation and solid solutions can be avoided through proper temperature control. Clinker formations can be avoided if the temperature is kept below the fusion temperature of the ash and solid solutions can be avoided if the carbides are converted directly to oxides at less than 800°C without coming into contact with the other constituents. Thus the temperature must be high enough for complete combustion of the carbon but low enough to prevent undesirable chemical reactions such as the formation of a refractory solid solution.

The burn-leach process described in this report was designed to minimize the formation of solid solutions of uranium and niobium oxides by control of the combustion temperatures. This can be accomplished by using a fluidized bed reactor or controlling the oxygen content of the combustion gas, or both.

III. BURN-LEACH STUDIES

The burn-leach studies were conducted to determine the effect of thermal history of the fuel, temperature of combustion, and acid concentration during leaching on the recoverability of uranium from the graphite fuel. Fuel elements of the coated particle-niobium carbide lined configuration which had been subjected to hot hydrogen testing at 2475°C for one minute, five minutes, and ten minutes were used in the studies. Thus, if uranium migration at high temperatures did present severe problems in the subsequent recovery of uranium, the fuel element which received the longest exposure at the high temperature presumably would experience the most migration of uranium, resulting in the lowest recovery because more uranium would have contacted the niobium carbide liner.

1. Experimental Equipment and Procedures

Combustion temperatures of 800°C, 1000°C, and 1200°C were used to oxidize the carbon in a combustion tube furnace. An uncrushed length of fuel element was inserted and burned in a quartz tube with a one-inch inside diameter. The closure at each end was a ground glass joint which

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permitted the progress of the combustion to be observed. A chromel-alumel thermocouple immediately downstream of the burning sample recorded the temperature of combustion and controlled the input of electrical heat. The accuracy of the controlling thermocouple was verified by comparing its readings with those of a platinum thermocouple built into the tube furnace and also by means of an optical pyrometer for the higher temperatures.

The oxidizing gas mixture, either air or air diluted with nitrogen, was dried, filtered, preheated, and the carbon dioxide removed before it entered the combustion chamber. The rate of combustion was followed by determining the amount and rate of production of carbon dioxide. This was done initially by absorbing the carbon dioxide on Ascarite and weighing at intervals; however, when an infrared analyzer became available, this equipment with a strip chart recorder automatically recorded the carbon dioxide content of the exit gas.

The air or air mixed with nitrogen was controlled at about 10 psig and then throttled so that upon venting to atmospheric pressure the flow through the combustion tube was about 6270 cc/min (STP). The preheater furnace was maintained at about 1000°C so that the air passing through this furnace was heated to greater than 200°C in one straight pass. The combustion tube furnace was preheated to the desired temperature before inserting the fuel specimen. The time of starting for the rate determination was taken as the time of insertion of the fuel piece into the hot combustion tube with the combustion gas flowing through. Within about two minutes the reaction was visible as a blue flame surrounding the specimen. The rate of burning decreased gradually as the surface area of the fuel piece decreased during burning. The niobium carbide, which lined the coolant holes of the fuel, was converted to the oxide as the carbon was burning and remained as intact tubes of niobium oxide.

After cooling, the uranium oxide powder and the niobium oxide tubes were transferred to a flask fitted with a reflux condenser and leached with nitric acid at the boiling point for about one hour. The boiling action was the only agitation during the leaching. After filtering, the solution was analyzed for uranium and, in some cases, for niobium. In order to obtain a material balance on the system the residue was dissolved in 8M HF-2M HNO₃ and analyzed for niobium and uranium. No precipitation of niobium occurred when the latter solution was diluted with 8M HNO₃.

2. Results of Burn-Leach with Unirradiated Fuel

The recovery of uranium by leaching the ash resulting from burning Rover fuel was found to be independent of the time of exposure

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in the hot hydrogen test and to the percent of oxygen in the combustion gas. The controlling variable that did influence the recoverability was the temperature of combustion. The results of leaching 23 burned specimens of fuel are summarized in Table I.

Table I
URANIUM RECOVERY IN COMBUSTION-LEACH PROCESS

<u>Fuel Element</u>	<u>Time (min) Hot Hydrogen Test at 2475°C</u>	<u>Temperature of Combustion</u>	<u>% U Leached (Average of Individual Results)</u>
A	1	800	99
		1000	99.2
B	5	800	99.4
		1000	98.2
		1200	82.5
C	10	800	99.0
		1200	88
KIWI B4D	Used in reactor test	800	99.8
	1 min 1670°C		
	1 min 2400°C		

The temperature remained steady during combustion in air or air diluted with nitrogen; however, combustion in oxygen showed a temperature increase over the control point.

The rate of burning appeared to be proportional to the surface area of the burning specimen - starting at a high rate and gradually decreasing. The information in Table II gives an indication of the rate of burning under varying conditions. The time required to burn 60 percent of the carbon initially present in the specimen at different temperatures and in different combustion atmospheres is listed.

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Table II

TIME FOR SIXTY PERCENT COMBUSTION OF CARBON INITIALLY
PRESENT IN ROVER FUEL SPECIMENS

<u>No. of Samples</u>	<u>Combustion Atmosphere</u>	<u>Temperature of Combustion</u>	<u>Average Time for 60% Completion</u>
4	Air	800°C	21 minutes
3	Air	1000°C	17 minutes
1	Air	1200°C	13 minutes
3	10% oxygen, 90% nitrogen	800°C	33 minutes

3. Results of Burn-Leach of Irradiated Fuel

The recoverability of uranium from irradiated fuel was also determined by burning and leaching a specimen from a fuel element of KIWI B4D using the conditions that gave greater than 99 percent recovery of uranium with unirradiated fuel. The fuel specimen was burned at 800°C in an air flow of 6270 cc/min (STP). The combustion air was preheated by passing through a tube furnace held at 1000°C. A plot of the CO₂ analysis indicated that the carbon was 60 percent consumed in 24.5 minutes and that the 3.95-gram sample containing 3.25 grams of carbon was completely converted to the oxides within 123 minutes. The ash was leached with 50 ml of 16M nitric acid by boiling for 4 hours. The resulting solution had 6.39 g/l uranium or a total of 0.320 gram. After leaching, the residue was dissolved in 30 ml 8M HF-2M HNO₃ and by analysis found to contain 0.001 gram of uranium which represents about a 0.2 percent loss.

4. Flowsheet

Figure 1 shows a block diagram of a flowsheet for the burn-leach process. The furnace can be either fluidized bed or fixed bed using either oxygen or air to promote combustion; however, the temperature is more easily controlled by using air or air diluted with nitrogen. A leaching vessel separate from the furnace will require some means of transport of the ash. The niobium oxide will be in the form of tubes or parts of the walls of the tubes unless some violent action such as a jet grinder breaks them. These pieces of niobium oxide are dense so that it may be difficult to transfer them from the leach vessel to the filter.

Fig. 1 Burn-Leach Flowsheet

(a) Assuming 15 percent uranium, 10 percent niobium content

(b) Contains 9.34×10^4 liters of O₂, the stoichiometric amount to oxidize 50 kg of carbon to CO₂. This quantity of air passing through an opening 100 cm² during 8 hours represents a velocity of about 16 cm/sec which is below the fluidizing velocity of about 30 cm/sec.

(c) Fifty kg of carbon @ 8 kg cal/g represents 4.0×10^8 small cal which is an average of 5×10^7 cal/hr for the 8 hours. About 1/5th of this heat can be carried away by the nitrogen in the air for combustion.

(d) 20 percent TBP in kerosene will give 99.99 percent recovery of uranium from this feed under typical extraction column conditions⁽⁵⁾.

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On the other hand, the high density of the niobium oxide may be enough to just permit it to be separated from the solution by gravity. Eight-molar nitric acid is sufficiently concentrated to leach the uranium from the ash. After combining of the wash and leach solutions, the uranium concentration is about 20 g/l and the nitric acid concentration is about 4M. This solution is suitable as feed for an extraction column using 15 or 20 percent tributyl phosphate as the extractant⁽⁵⁾. The waste from such a flowsheet will include solid niobium oxide and the nitric acid solution of fission products which can be concentrated for storage or blended with other waste solutions for calcination.

IV. CONCLUSIONS

The uranium can be recovered from test fuel elements of the Rover reactors by burning in air and leaching the residue with nitric acid to dissolve the uranium. With proper control of the combustion temperature very little uranium will be lost in the leaching step, because insoluble mixed oxides will not form as they do when uranium carbide migrates during the conversion from carbide to oxide at too high a temperature. A recovery of greater than 99 percent was obtained in every case in which the temperature was maintained at 800°C or lower during combustion.

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