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HOT-CELL STUDIES OF AQUEOUS DISSOLUTION
PROCESSES FOR IRRADIATED CARBIDE

REACTOR FUELS

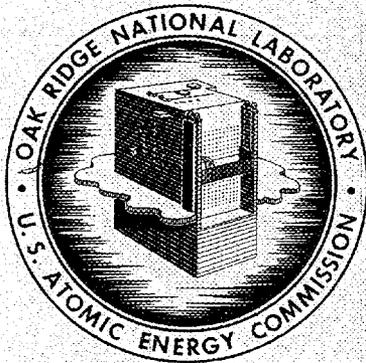
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ORNL-3660

Contract No. W-7405-eng-26
Chemical Development Section B
CHEMICAL TECHNOLOGY DIVISION

HOT-CELL STUDIES OF AQUEOUS DISSOLUTION PROCESSES FOR
IRRADIATED CARBIDE REACTOR FUELS

By

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SEPTEMBER 1964

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ABSTRACT

Three head-end processes for recovering uranium and plutonium from uranium and plutonium carbide reactor fuels were investigated using specimens irradiated to burnups of up to 20,000 Mwd/metric ton. Solvent extraction behavior of the fuel solutions produced was examined in batch shake-out tests. Reaction with steam (pyrohydrolysis) at 750°C was the best method tested, although direct dissolution in boiling 13 M (60%) HNO₃ followed by oxidation of residual organic impurities in the resulting solution is also potentially useful. Hydrolysis with liquid water at 80 to 100°C is not feasible since the irradiated carbides of uranium and plutonium are passive.

During pyrohydrolysis at 750°C (air excluded), the uranium monocarbide was converted to UO₂, containing only about 0.03% C. The gaseous reaction products were H₂, CO₂, and CO. Cesium was the principal fission product volatilized, but the amount was very low (0.5%). This cesium was trapped when the excess steam was condensed. The UO₂ product readily dissolved in 6.5 M HNO₃ to yield a solution suitable as a feed for Purex solvent extraction. Batch solvent extraction tests showed that greater than 99.9% of the uranium and plutonium could be recovered and separated from gross fission products by a factor of 10⁴. The pyrohydrolysis process was also successfully demonstrated with irradiated 20% PuC--80% UC specimens.

Irradiated uranium monocarbide or the mixed uranium-plutonium carbide could be dissolved directly in 60% HNO₃, but about 44% of the carbide carbon remained in solution, primarily as organic acids that interfered with solvent extraction. The organic impurities were largely eliminated by oxidative degradation. In solvent extraction tests of the treated solutions, recovery was nearly quantitative, but up to 0.4% of the plutonium was retained by the solvent after stripping. The plutonium retention was attributed to residual organic impurities. Uranium and plutonium were separated from gross fission products by a factor of 3.4×10^4 .

1. INTRODUCTION

The carbides of uranium, thorium, and plutonium are attractive fuel materials for power reactors. For example, the Consumer's Public Power Reactor at Hallam, Nebraska, will use uranium monocarbide. The fuel, with sodium as a bonding agent, will be sealed in stainless steel tubes 15-ft long and 0.952 in. in outer diameter.¹ The monocarbide used in these fuel elements will be slightly less than stoichiometric (slight excess of uranium) in order to prevent reaction with the stainless steel cladding. Since carbides represent a new class of fuels, it is necessary to develop methods for recovering the fuel values from spent elements, and some of that work is being done at Oak Ridge National Laboratory.

This report is concerned with the study of methods for providing nitric acid solutions of fuel values that can be sent directly to solvent extraction for the recovery of purified fuel. Aqueous systems were investigated—pyrohydrolysis, hydrolysis, and dissolution in nitric acid. Irradiated uranium monocarbide and mixtures of uranium and plutonium monocarbides were used, and the work was done with prototype fuel specimens in order to test the variables under actual conditions. Much of the work grew out of basic studies of unirradiated uranium carbides, whose reactions with water, nitric acid, and sodium hydroxide are reported elsewhere.²⁻⁶

These laboratory studies (1- to 200-g samples per batch) were done in Pyrex equipment. Only one process is recommended—the one based on the use of flowing steam at 750°C and atmospheric pressure to produce UO_2 (or oxides of other fuel values) which can subsequently be dissolved in nitric acid.

The processes will be discussed in their order of preference: pyrohydrolysis, direct dissolution of the carbide in nitric acid, and hydrolysis at 80 to 100°C. Also, since the objective was to develop a satisfactory head-end process for producing a feed solution suitable for Purex solvent extraction, data and evaluations on solvent extraction performance are included.

2. PYROHYDROLYSIS PROCESS

2.1 Process Flowsheet

Initial hot-cell evaluation of the hydrolysis-dissolution process (Sec 4.2) revealed that high-purity neutron-irradiated uranium monocarbide is nearly inert to water at 80 to 100°C.^{5,6} The "passivity" of irradiated uranium monocarbide prompted the development of the pyrohydrolysis process to convert the monocarbide to uranium dioxide. The process is designed to eliminate the carbon as volatile carbon oxides before dissolution of the uranium dioxide residue. The alternative process of direct dissolution of uranium monocarbide in nitric acid generates soluble organic acids, deleterious to solvent extraction, that are extremely difficult to destroy or remove (Sec 3.).

The proposed pyrohydrolysis process, as applied to the Consumers Public Power reactor fuel, is shown in Fig. 1. This reactor is fueled with bundles of stainless steel-clad, sodium-bonded hypostoichiometric uranium monocarbide rods 15-ft long and 0.952 in. in outer diameter (Table 1). After disassembly of structural hardware, eight-rod bundles of spent fuel would be fed through a hydraulic shear⁷ and chopped into 1-in. sections. Since uranium monocarbide is quite brittle, considerable shattering and powdering is expected. The chopped fuel is then transferred to the pyrohydrolysis unit and steamed at low temperature first to convert sodium to a dilute caustic solution which is discarded to waste.

The reactor is then purged with an inert gas (nitrogen) to eliminate air since the pyrohydrolysis reactions generate hydrogen and a hydrogen-oxygen explosion must be avoided. With the reactor temperature at 750°C, steam is fed downflow into the reactor at a rate of 20 kg/min for 4 hr to convert the uranium monocarbide to uranium dioxide (0.03% C), with attendant volatilization of hydrogen, carbon dioxide, and carbon monoxide. About 3.7 moles of hydrogen are discharged to off-gas per mole of uranium monocarbide consumed.

Dissolution of the oxide product proceeds rapidly in 6.5 M HNO_3 at 105°C; however, 4 hr is allowed for complete dissolution since the oxide must be leached from the stainless steel shells. Sufficient dissolvent

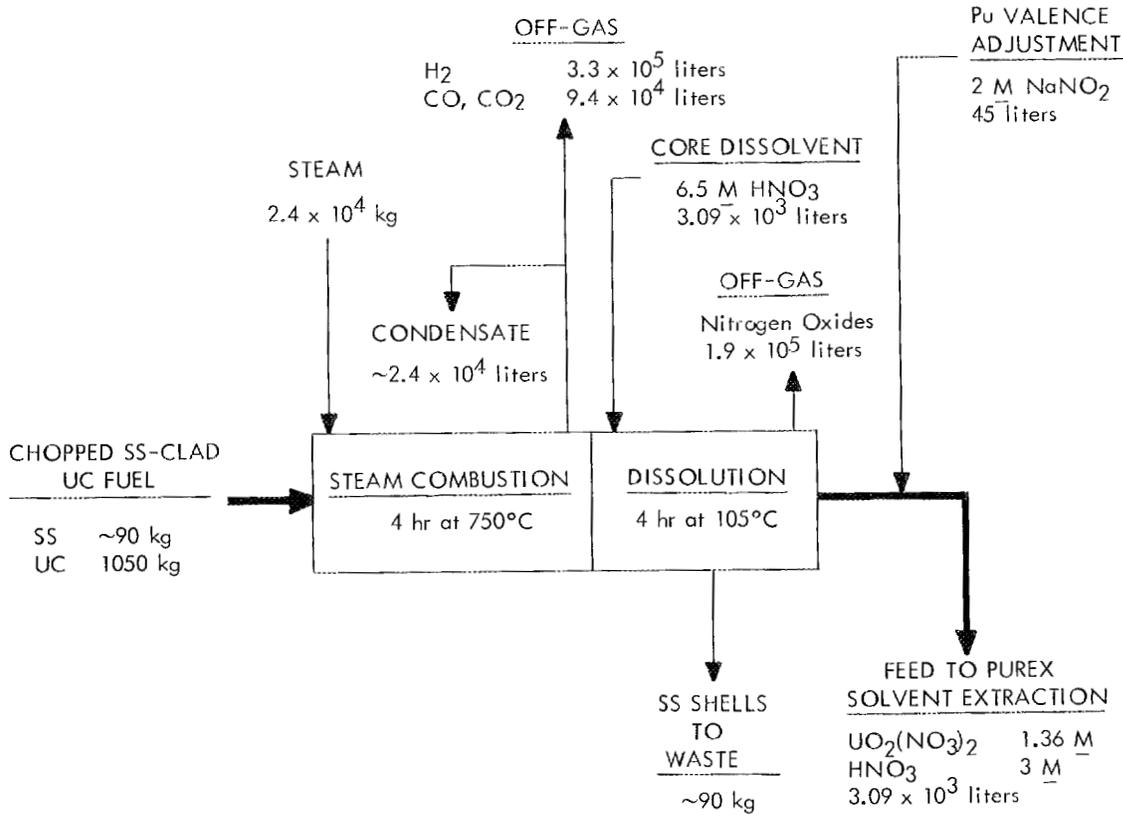


Fig. 1. Pyrohydrolysis Process for Uranium Carbide Reactor Fuel.

Table 1. Consumers Public Power Reactor (Hallam): Core I^a

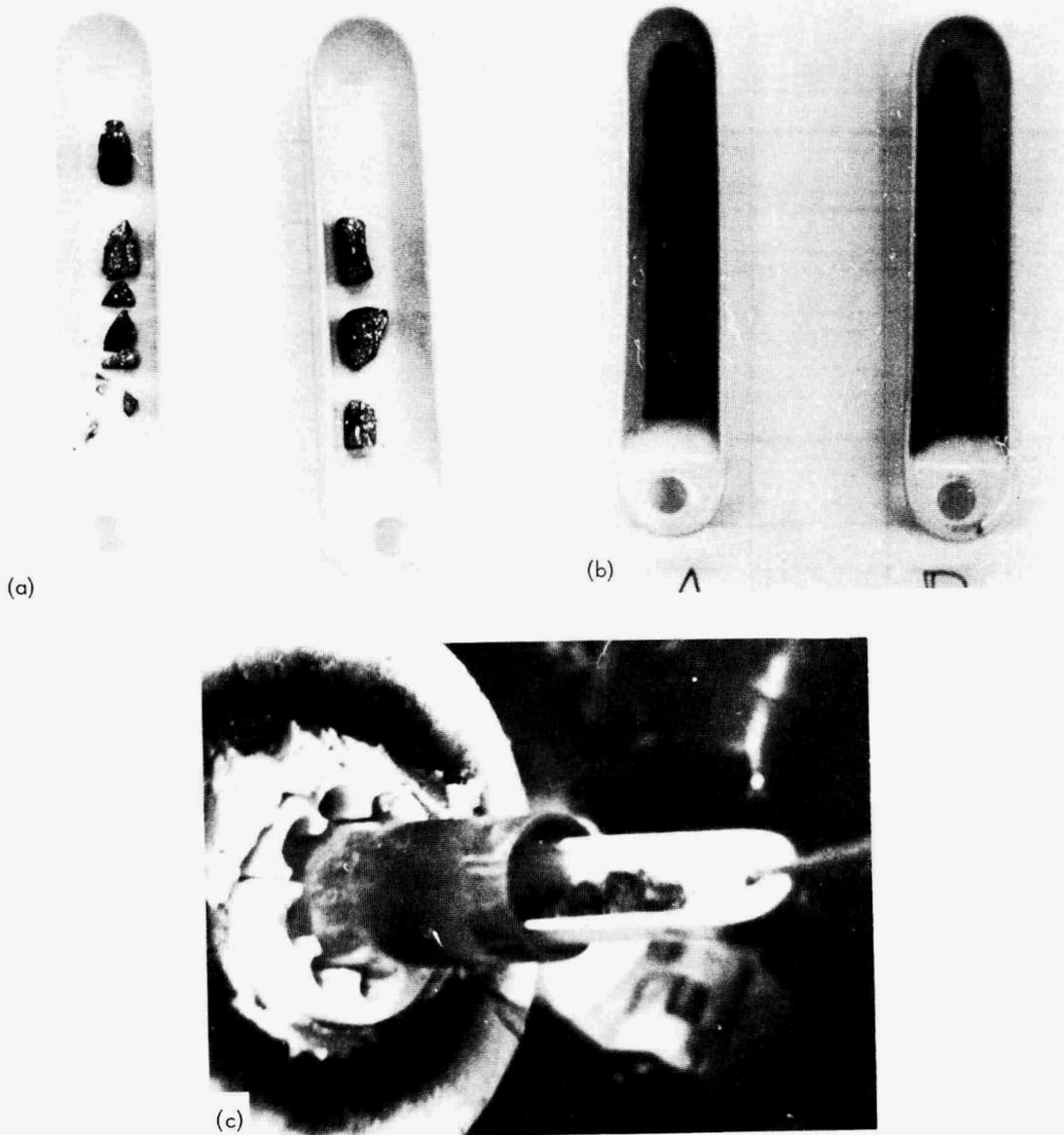
Reactor loading:	137 assemblies; 10 containing UC and 127 containing U--10% Mo	
UC assemblies:	8 rods in circular array about a central structural tube	
UC elements:	15-ft overall length by 0.952-in. OD	
	Active section: 13.25-ft by 0.872-in.-diam rod of hypostoichiometric UC (4.4 - 4.8% C)	
	30-mil radial annulus filled with Na, plus 2-in. layer of Na above upper end of active section.	
	304 stainless steel cladding, 10 mils thick	
	20 kg UC per element	
Fuel element composition:	Total U (before burnup)	19.12 kg
	U ²³⁵ enrichment	3.7 to 4.9%
	Carbon	0.88 kg
	Sodium	47.95 g
	Stainless steel	0.73 kg

^aPersonal communication with Keith Magnus, Atomics International.

is used to produce a Purex feed solution, 1.36 M $\text{UO}_2(\text{NO}_3)_2$ and 3 M HNO_3 , containing a trace of residual carbon. This solution, after plutonium valence adjustment to the (IV) state with nitrite, may be sent through a conventional Purex plant⁸ for recovery and separation of the fuel values from fission products by solvent extraction with tributyl phosphate.

2.2 Process Demonstration with Irradiated Carbide Fuels

Five hot-cell experiments on pyrohydrolysis were conducted with 4- to 7-g single pieces of stoichiometric uranium monocarbide (4.8% C) irradiated from 7500 to 16,000 Mwd/metric ton (Fig. 2a). The specimens were placed in a porcelain boat positioned horizontally in a Vycor tube enclosed by an electric furnace (Fig. 2c) and exposed to steam at atmospheric pressure at 700 to 800°C for up to 5 hr. Air could not be excluded from the reactor in this series of experiments; consequently, greater than 98% of the sample was converted to the higher oxide, U_3O_8 . The condensed steam



- (a) Unirradiated Uranium Carbide Before Treatment with High Temperature Steam. Irradiated uranium carbide appears the same after boiling in water.
- (b) Unirradiated uranium carbide after conversion to uranium dioxide by 750°C steam.
- (c) Irradiated uranium carbide (16,000 Mwd/tonne) after conversion by high temperature steam.

Fig. 2. Pyrohydrolysis of Uranium Monocarbide.

from the off-gas contained from 1.1% (700°C) to 42% (800°C) of the total cesium activity and 5.7% and 0.36% of the ruthenium and zirconium, respectively. Cesium was the principal fission product volatilized.

The oxide product was dissolved in nitric acid in 30 min producing a solution, 1.36 \underline{M} $\text{UO}_2(\text{NO}_3)_2$ and 3 \underline{M} HNO_3 , containing a small (unweighable) carbonaceous residue. The residual carbon content of the oxide could not be determined due to lack of special analytical facilities. Purex solvent extraction performance was highly satisfactory with this solution. In standard batch extraction and stripping tests (Sec 2.3.2), 99.99% of the uranium and plutonium was recovered. Phase coalescence times of 20 to 30 sec were observed which are normal for the Purex system.⁸

The pyrohydrolysis process was further evaluated in a series of hot-cell runs in small-scale equipment in which air was excluded (Fig. 3). This equipment duplicated that used in laboratory studies (Sec 2.3). The irradiated uranium monocarbide (4.8% C) reacted with steam at 700 to 750°C to produce a free-flowing uranium oxide residue and a dry off-gas of nearly identical volume and composition to that obtained with unirradiated uranium monocarbide. Apparently, the reaction of irradiated uranium monocarbide with high temperature steam proceeds stepwise, as postulated for unirradiated monocarbide (Sec 2.3). Stoichiometric uranium monocarbide, irradiated to 7500 Mwd/metric ton, was reacted with steam at atmospheric pressure at 700 to 750°C for 2 to 3 hr. Before each run, the system was purged with helium to eliminate air. At 750°C, the overall reaction was complete in one hour, which agrees closely with the overall rate obtained with unirradiated monocarbide (Fig. 4). At 720° and 750°C, the initial rate of reaction was the same; however, at the lower temperature the rate diminished slightly as the reaction approached completion. After condensation of the steam, the dry off-gas contained hydrogen, 83 vol %, carbon dioxide, 11%, and carbon monoxide, 6%, compared with 80% hydrogen, 16% carbon dioxide, and 4% carbon monoxide found in the off-gas from 750°C pyrohydrolysis of the unirradiated monocarbide.

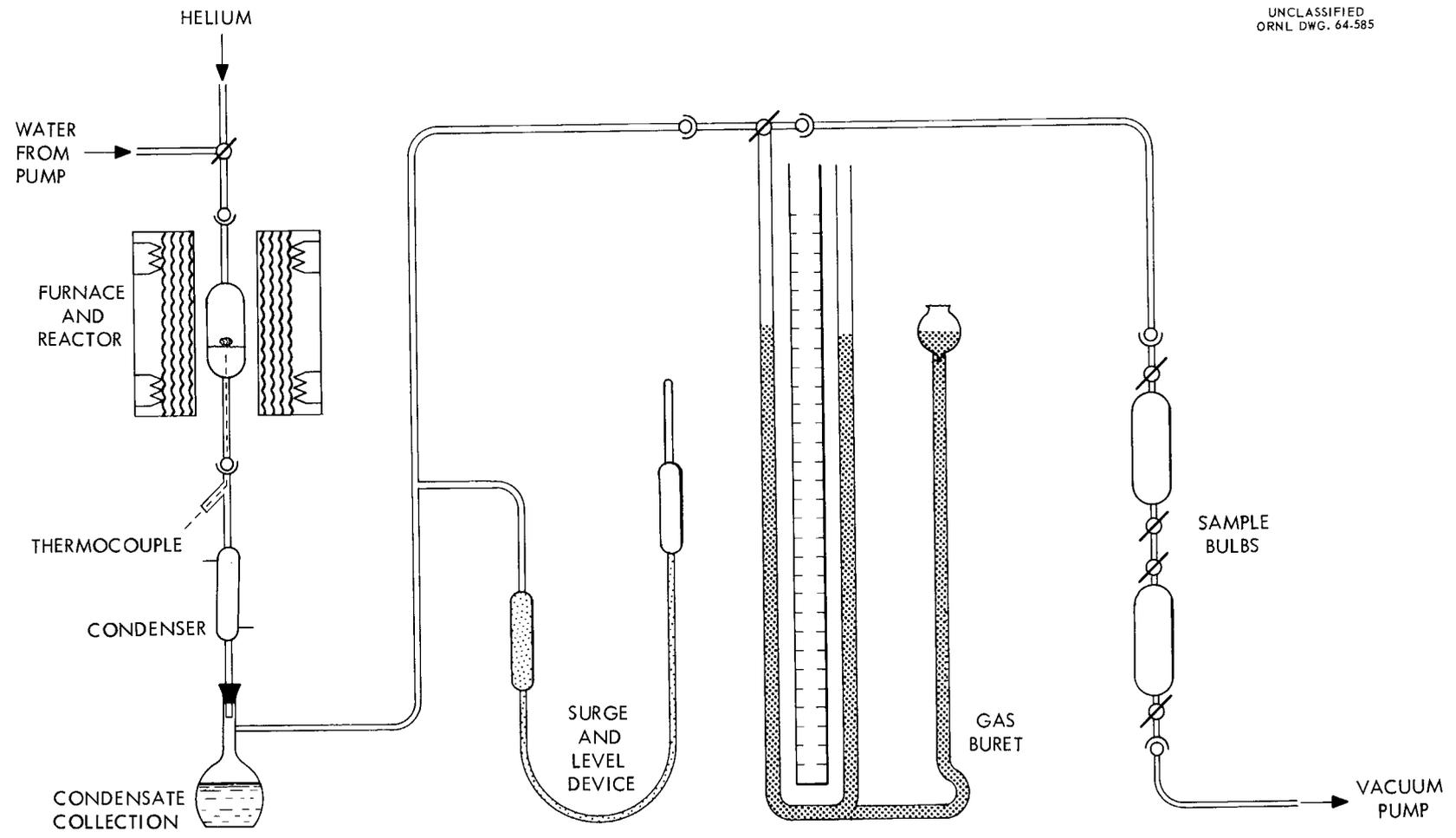


Fig. 3. Pyrohydrolysis Apparatus.

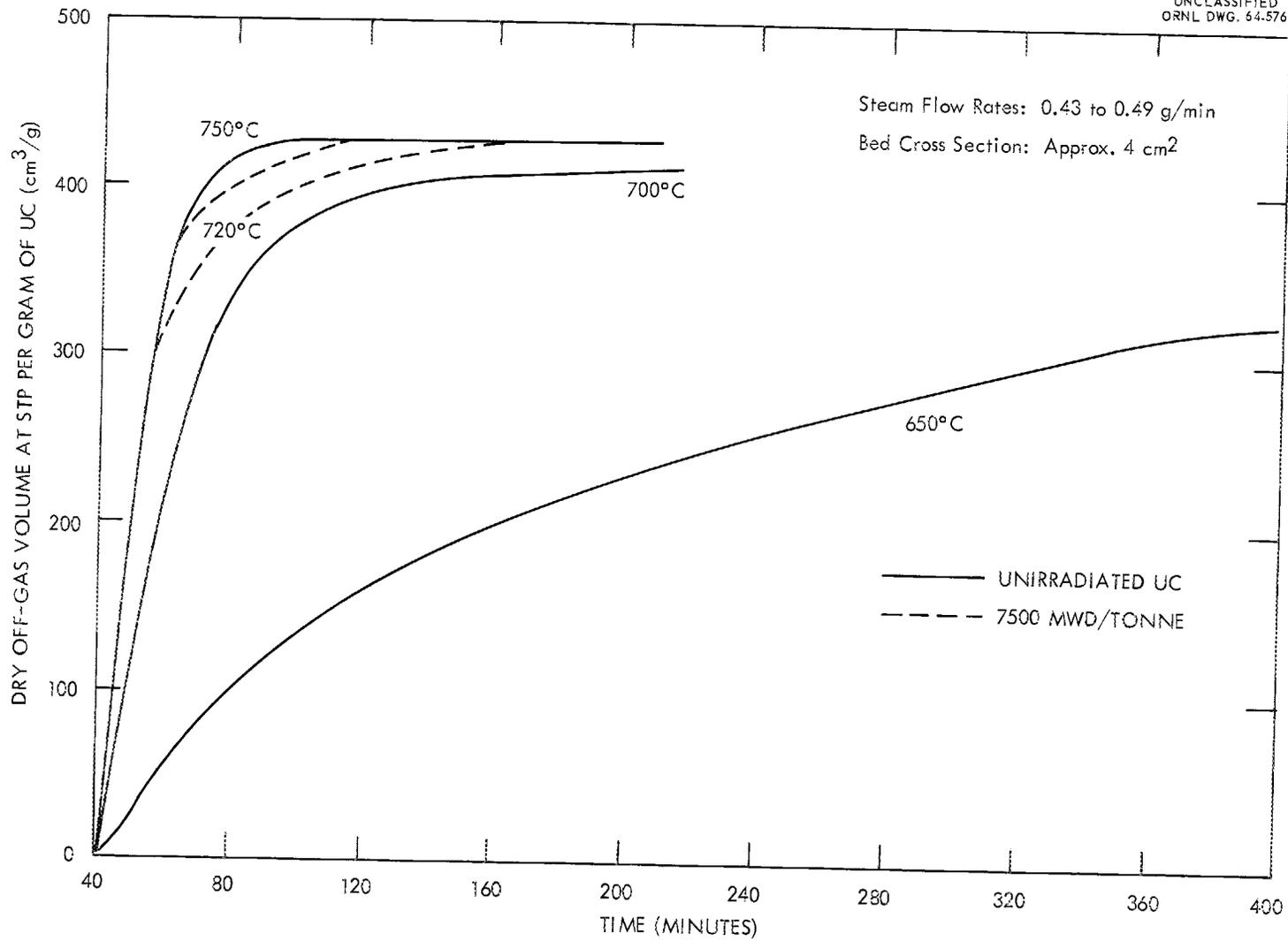


Fig. 4. Reactivity of Uranium Monocarbide with Steam at 650 to 750°C.

The uranium dioxide composited from seven experiments contained 0.25% residual carbon (3 mg C per gram of UO_2), compared with 0.03% carbon found in the oxide from laboratory studies with the unirradiated monocarbide (Sec 2.3). The determination of residual carbon in the highly radioactive oxide samples may be inaccurate since only gram amounts of oxide were available for analysis.* The composite steam condensate contained 0.48% of the cesium, 0.04% of the ruthenium, and 0.06% of the zirconium in the irradiated specimens, considerably less than the amounts volatilized in the experiments containing air. The activity in the dry off-gas samples was at the background level.

The pyrohydrolysis process was also successfully demonstrated with 20% PuC--80% UC specimens irradiated up to 20,000 Mwd/metric ton. In these runs, a paper filter was inserted immediately downstream from the steam condenser. One-gram samples of the mixed carbide fuel were reacted with steam at 750°C for 2 hr. About 0.74% of the cesium in the fuel sample appeared in the steam condensate and 0.07% was trapped on the filter. Again, the activity in the filtered off-gas was at the background level. In a run with a 900-Mwd/metric ton sample, 0.1% of the cesium was found on the filter.

A sample of the mixed carbide (20,000 Mwd/metric ton) was burned in a stream of oxygen for 2 hr at 800°C. In this case, the filter trapped 36% of the cesium and 2% of the ruthenium. Thus, the noncondensable off-gas from pyrohydrolysis contains much less radioactivity (background level) than that produced by direct oxidation at about the same temperature.

The mixed oxides when dissolved in nitric acid produced solutions that performed adequately in batch solvent extraction. Recovery of 99.98% of the uranium and 99.93% of the plutonium was obtained. Decontamination from fission product gamma activity was about 10^4 .

*By combustion- CO_2 absorption.

2.3 Flowsheet Development Studies

In development of the pyrohydrolysis process, primary objectives were (1) to establish the conditions for quantitative conversion of uranium monocarbide to uranium oxide at a reasonable temperature and reaction rate, and (2) to determine the volume and composition of the gaseous products.

Experiments were conducted in small Pyrex equipment using a vertically mounted quartz tube reactor enclosed by a resistance heater furnace (Fig. 3). Water was pumped at a controlled rate into the top of the reactor and vaporized before it contacted the approximate 5-g charge of uranium monocarbide. Excess water vapor was condensed from the off-gas, and the dry gas volume was metered and sampled for analysis. Before each run, the system was swept with helium.

Scouting experiments showed that arc-melted and cast uranium monocarbide reacted very slowly with steam at 400°C and atmospheric pressure, but, at 700°C, the monocarbide was completely converted to oxide in 3 to 5 hr. Air was not excluded from the reactor, and the product was U_3O_8 containing from 0.012 to 0.016% residual carbon. Further experiments were conducted at 650 to 750°C with air excluded from the reactor and attendant off-gas system. Since the off-gas from the pyrohydrolysis reaction is rich in hydrogen, the possibility of a hydrogen-oxygen explosion must be avoided.

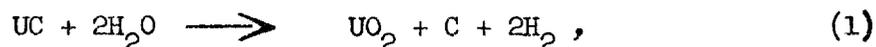
2.3.1 Conversion of UC to UO_2 with Steam at 650 to 750°C

Reaction rates of uranium monocarbide with superheated steam as a function of temperature are shown as the plots of dry off-gas volume vs time (Fig. 4). The reaction is practically complete in an hour at 750°C, or about 3 hr at 700°C. At 650°C, the reaction is still incomplete after 6 hr. Nominal 5-g batches of fragmented uranium monocarbide were used to simulate the fuel after chopping and to provide a uniform bed of material in the reactor to avoid channeling. The high-purity uranium monocarbide (4.68% carbon by analysis) was prepared by Atomics International by arc-melting and casting in graphite molds.

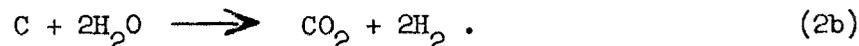
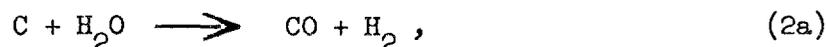
With air excluded, the oxide product from the reaction is a granular, free-flowing dark-brown powder (Fig. 2b), with an oxygen-to-uranium ratio of 2.03 and containing 0.03% residual carbon. This product was identified by x-ray diffraction as UO_2 , with a trace of U_3O_8 .

About 425 cc of noncondensable (dry) off-gas is evolved at STP per gram of uranium monocarbide consumed, compared with 93 cc of off-gas evolved per gram of the monocarbide hydrolyzed at 80°C. Using the analysis of the gaseous products from a run at 750°C (Table 2), the overall reaction of one mole of uranium monocarbide (4.68% C) with 3.7 moles of water yields uranium dioxide plus 3.7 moles of hydrogen, 0.68 moles of carbon dioxide, and 0.1 mole of carbon monoxide.

During the first half of the reaction at 750°C (Table 2) the gas is rich in hydrogen (86 vol %). As the reaction proceeds, the proportion of hydrogen decreases to 73.1 vol %. Also, as the reaction proceeds, carbon dioxide increases from 2.4 to 25.5 vol %, and carbon monoxide diminishes from 6 vol % to none. This suggests that the reaction proceeds in two stages. A relatively fast reaction occurs first:



and then the free carbon is converted to oxides at slower rates:



This theory is supported by the results of a run at 750°C which was stopped when only a third of the total yield of off-gas had been evolved. The product from this run contained 1.05 wt % of free carbon and 0.93 wt % of combined carbon (carbide).

At 650°C, the gas composition was constant throughout the reaction, indicating that at this temperature, reaction (1) proceeds at about the same rate as reactions (2a) and (2b).

Table 2. Gaseous Products from Reaction of Steam and UC at 750°C

Sample No. ^a	Volume of Dry Gas at STP per gram of UC (cm ³ /g)	Percentage by Volume			
		H ₂	CO ₂	CO	He plus Unidentified Gases
1st	52.9	75.8	2.4	1.6	19.2
2nd	52.9	86.0	6.2	6.0	1.8
3rd	52.9	85.0	10.7	3.4	0.8
4th	52.9	84.9	12.4	2.4	0.3
5th	52.9	79.6	17.3	1.3	1.8
6th	52.9	78.4	19.8	1.0	0.8
7th	52.9	75.0	24.0	0.4	0.6
8th	38.8	73.1	25.5	0.0	1.4
Left in Apparatus ^b	5.4	73.1	25.5	0.0	1.4

^aConsecutive samples taken; all the gas was collected and analyzed.

^bEstimated.

2.3.2 Uranium Recovery by Solvent Extraction

The uranium dioxide from a pyrohydrolysis run at 750°C was dissolved in excess 6.5 M HNO₃ at 105°C in 30 min to produce a solution of nominal Purex concentration, 1.36 M UO₂(NO₃)₂ and 3 M HNO₃. Dissolution was complete except for finely divided carbon, 0.03 wt % in the oxide product. About 2.5 moles of nitric acid are consumed per mole of uranium dioxide dissolved.

The solution (containing carbon) and a control solution of the same uranyl nitrate-nitric acid concentration prepared from laboratory reagents were both tested by solvent extraction with tributyl phosphate (Table 3). The uranyl nitrate was extracted from each solution using six aliquots of 30% TBP in Adakane, then stripped from the solvent from the first extraction with five aliquots of 0.01 M HNO₃. Uranium recovery was nearly quantitative (better than 99.99%) in both experiments. During extraction of the solution derived by pyrohydrolysis, phase-coalescence time averaged

Table 3. Typical Batch Solvent-Extraction Test Conditions
Simulating the Purex Process

Stream	Composition	Relative Volume
Feed stage aqueous (Feed plus Scrub)	1.05 M $UO_2(NO_3)_2$, 2.6 M HNO_3	5
Scrub	3 M HNO_3	2
Solvent	30 vol % tributyl phosphate in Adakane, pre-equilibrated with 2.6 M HNO_3	10
Strip	0.01 M HNO_3	20

Extraction: Six 2-min equilibrations of "feed stage aqueous" with fresh aliquots of solvent at 25°C.

Scrubbing: Six to eight 2-min equilibrations of "1st-stage solvent" from extraction with fresh aliquots of scrub at 25°C.

Stripping: Five 2-min equilibrations of "1st-stage solvent" with fresh aliquots of strip at 25°C.

50 sec, about twice that of the control; however, no significant difference between the settling times was observed during stripping. The increased settling time is attributed to the trace of finely divided carbon suspended in the solution derived from pyrohydrolysis. During the extraction, distribution of the carbon was random, and, upon settling, it accumulated at the interface. Further study is required using continuous countercurrent extraction equipment (mixer-settlers or pulsed columns) to establish whether the residual carbon may pose an engineering problem. Plutonium can also be extracted from these solutions (Sec 2.2).

2.4 Evaluation of the Pyrohydrolysis Process

A promising new dissolution process (pyrohydrolysis) was developed and was successfully applied to uranium monocarbide, plutonium carbide, and 20% plutonium carbide--80% uranium carbide prototype fuels. Highly irradiated, reactor-grade uranium monocarbide reacts with excess steam at a practical, controlled rate at 750°C and atmospheric pressure (air excluded) producing free-flowing uranium dioxide (0.03% residual carbon),

with the evolution of hydrogen and the carbon oxides. The uranyl nitrate-nitric acid solution obtained by dissolving the uranium dioxide in nitric acid is processed directly by conventional solvent extraction.

The stoichiometry of the stepwise reaction of uranium monocarbide with high temperature steam was established. The reaction rates and percentage composition of the off-gas were shown to be temperature dependent. With nonoxidizing conditions prevailing during pyrohydrolysis, cesium (0.5%) was the principal fission product entrained by the steam-off-gas stream, and it was effectively trapped in the excess steam condensate. The dry off-gas was free of radioactive contaminants (to background levels), indicating that elaborate off-gas treatment may not be required for this process. The results of hot-cell runs with irradiated carbide samples paralleled those from laboratory studies with unirradiated uranium monocarbide, indicating that adverse irradiation-induced effects are absent. The process performed equally well with highly irradiated specimens of plutonium carbide and 20% plutonium carbide--80% uranium carbide.

The residual sodium in the sheared, stainless steel-clad, sodium-bonded fuel rods should be easily removed by steaming at low temperature. Experimental work is planned to determine whether residual sodium influences the pyrohydrolysis reaction. A corrosion study is needed to find a suitable material for fabrication of the pyrohydrolysis-dissolution unit where conditions are alternately reducing and mildly oxidizing. Further laboratory and hot-cell experiments are required to determine potential application of this process to other carbide fuels and possibly the graphite-based fuels.

3.0 DIRECT NITRIC ACID DISSOLUTION PROCESS

3.1 Process Flowsheet

An alternative process was developed based on direct dissolution of uranium monocarbide in nitric acid (Fig. 5). Uranium monocarbide dissolves rapidly and completely in strong nitric acid, producing carbon dioxide (56% of the carbide carbon) and soluble organic acids. These organic impurities seriously interfere with the recovery of uranium and plutonium by solvent

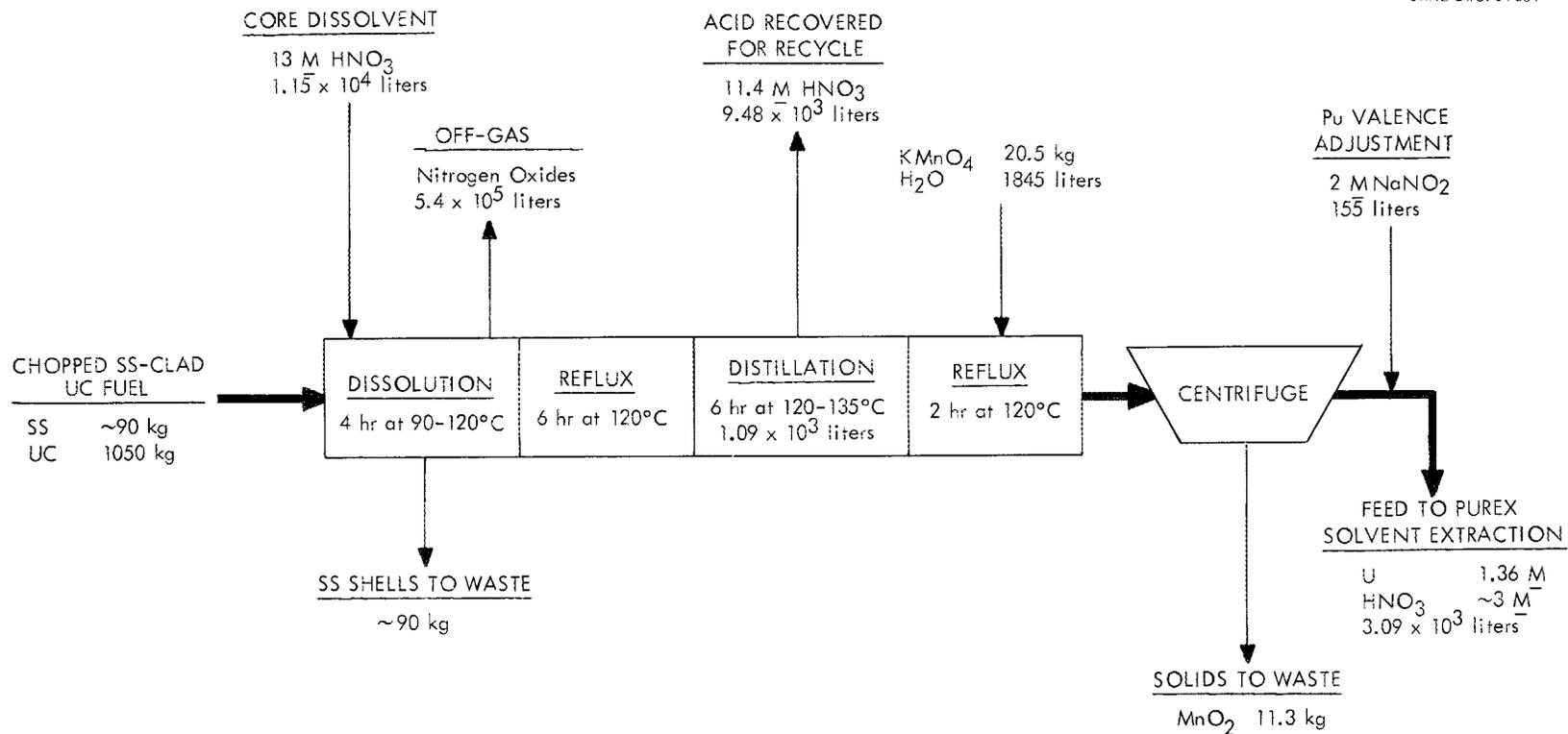


Fig. 5. Direct Nitric Acid Dissolution Process for Uranium Carbide Reactor Fuel.

extraction. No single method or combination of techniques has been found to completely degrade the mixture of organic impurities to carbon dioxide. The process relies on strong oxidizing conditions to degrade the bulk of these impurities and thereby minimize their effects.

The uranium monocarbide core can be dissolved in 4 hr at 90 to 120°C with a 320% excess of 60% HNO_3 . The resulting solution, 0.47 M in $\text{UO}_2(\text{NO}_3)_2$ and 11 M in HNO_3 , is refluxed 6 hr to degrade the organic impurities. The excess nitric acid is recovered by distillation and recycled as dissolvent. Little degradation occurs during distillation, and the organic impurities remain with the pot residue. The residue is diluted to provide a solution 1.36 M in $\text{UO}_2(\text{NO}_3)_2$ and 3 M in HNO_3 and refluxed 2 hr with 0.2 M KMnO_4 to promote further degradation.¹¹ At least 5% of the original carbon remains in the product after the oxidation step but the products which are deleterious to solvent extraction have been mostly eliminated. After feed clarification and plutonium-valence adjustment to the (IV) state with nitrite, the solution would be sent through the standard Purex process for recovery of the fuel values.

3.2 Process Demonstration with Irradiated Carbide Fuels

Hot-cell tests of the proposed process were conducted with uranium monocarbide (4.8 to 5.0% C) irradiated to 6000 Mwd/metric ton. Dissolution of 50-g samples in a 300% excess of 15.8 M HNO_3 and 6 hr of reflux produced solids-free, dark-red solutions. (In one run, however, a small (unweighable) amount of black solids was detected after 20 hr of refluxing. The black solids retained less than 0.01% of the uranium and plutonium in the fuel sample.)

The excess acid was removed by distillation. The condensate (13 M HNO_3) contained about 17% of the ruthenium in the fuel sample. The pot residue was adjusted to provide a solution 1.36 M in $\text{UO}_2(\text{NO}_3)_2$, 3 M in HNO_3 , and 0.2 M in KMnO_4 and refluxed for 2 hr. After filtering off the manganese dioxide, the solution had the characteristic yellow color of uranyl nitrate. The solution was treated with 0.1 M NaNO_2 for 1 hr to stabilize plutonium in the (IV) state, then subjected to extraction, scrubbing, and stripping under simulated Purex conditions (Table 3).

After extraction, only 0.004% of the uranium and 0.01% of the plutonium remained in the aqueous phase, which indicates that oxalic acid, a known organic impurity and aqueous-soluble complexer of plutonium (IV) (Sec 3.3), had been destroyed. Upon stripping, 99.99% of the uranium was recovered. Plutonium recovery was not so complete; 0.15% was held by the solvent. Phase-separation time (20 to 30 sec) appeared normal for the Purex system, as did the separation factor (uranium and plutonium from gross gamma activity) of 3.4×10^4 .

Samples of irradiated plutonium carbide (1000 Mwd/metric ton) and 80% uranium carbide--20% plutonium carbide (20,000 Mwd/metric ton) were successfully processed according to the proposed flowsheet. Dissolution of the samples in an excess of 13.2 M HNO_3 and 6 hr of refluxing produced solids-free, green-black solutions. During distillation, from 0.08 to 0.56% of the ruthenium was volatilized and was collected in the 11 M HNO_3 condensate. Ruthenium was the principal fission product volatilized.

After treatment with permanganate, the feed solution contained from 25 to 32% of the carbon originally present in the carbide specimens. This residual carbon had no adverse effects on extraction of the feed solutions. For example, batch extraction of a feed solution, 0.13 M $\text{Pu}(\text{NO}_3)_4$ --4.5 M HNO_3 , reduced the plutonium loss to 0.004%. However, after stripping, 0.4% of the plutonium was retained in the solvent. Thus, some of the organic products may be extracted into the solvent where they complex and retain plutonium.

3.3 Flowsheet Development Studies

Samples of the monocarbide (4.8% C) were dissolved in a 320% excess of 13 M HNO_3 in 4 hr; the vigorous reaction was regulated by controlled acid addition. A red-brown, solids-free solution was produced, and it was 0.47 M in $\text{UO}_2(\text{NO}_3)_2$ and 11 M in HNO_3 . Nitric acid consumption was 8.5 moles per mole of uranium monocarbide dissolved. During dissolution, 56% of the carbide was converted to carbon dioxide, and the remainder to nitric acid-soluble, high-molecular-weight organic compounds containing carboxyl and nitro groups, which impart a red-brown coloration to the

uranyl nitrate. About 5% of the carbide carbon is converted to oxalic acid, 10% to mellitic acid, and 29% to organic compounds as yet unidentified.¹²

The organic impurities were partially degraded by 6 hr of refluxing in the excess 11 M HNO_3 . After reflux, the solution was orange-yellow, and the content of organic impurities had been reduced from 44 to 25% of the original carbide carbon, as indicated by carbon analysis. During distillation, no further degradation was detected.

After treatment of the diluted pot residue with 0.2 M KMnO_4 and 2 hr of refluxing, followed by removal of the manganese dioxide, the solution retained only 5% of the original carbon as organic impurities. This solution performed adequately in the standard Purex extraction-stripping test (Table 3). Uranium recovery was greater than 99.99% and phase-coalescence times averaged 40 sec during extraction and 15 sec during stripping.

Simpson and Heath at Downreay¹³ have investigated the dissolution of uranium monocarbide in nitric acid and proposed that concentrated uranyl nitrate in 6 M HNO_3 may be extracted directly with tributyl phosphate, leaving most of the organic impurities in the acid fission product waste. Tests were conducted here to examine the feasibility of this procedure modified to include extended reflux in 6.7 M HNO_3 to destroy oxalic acid.

The uranium monocarbide (4.8% C) was dissolved in 13 M HNO_3 , producing stable solutions that were 1.05 M in $\text{UO}_2(\text{NO}_3)_2$ and 6.7 to 8.1 M in HNO_3 . Other solutions more dilute in uranyl nitrate and 5.7 M in HNO_3 (or less) were metastable; precipitation of uranyl oxalate occurred at 25°C within 24 hr, occasionally accompanied by uranyl nitrate crystals. All solutions received 4 hr of refluxing before storage.

The stable solution, 1.05 M in $\text{UO}_2(\text{NO}_3)_2$ and 6.7 M in HNO_3 , containing plutonium (IV), was refluxed for 27 hr and periodically tested by batch extraction and stripping (Table 4). The results suggest that the oxalate formed during dissolution limits the extraction of plutonium (IV) but has no significant effect on uranium extraction. A constant plutonium extraction loss of 0.35% was experienced with solution previously refluxed up to 27 hr. Although phase-coalescence time was satisfactory during

Table 4. Effects of Organic Impurities in UC-Derived Feed Solutions on the Extraction and Stripping of Uranyl Nitrate and Plutonium Nitrate Under Modified Purex Conditions

Conditions: Feed Solution: 1.05 M $\text{UO}_2(\text{NO}_3)_2$, 6.7 M HNO_3 , 1.18×10^7 Pu(IV) counts $\text{min}^{-1}\text{ml}^{-1}$; solution treated as indicated.

Solvent: 30 vol % tributyl phosphate in Adakane, pre-equilibrated with 6.7 M HNO_3 .

Aqueous Strip: 0.01 M HNO_3 .

Extractant: Seven (2 min) equilibrations at 25°C; solvent/feed volume: 2/1

Strip: Seven (2 min) equilibrations at 25°C; strip/solvent volume: 2/1

	Feed Solution Refluxed:			
	0 hr	4 hr	16 hr	27 hr
EXTRACTION				
Conc. of uranium in aqueous, mg/ml				
Ext. 5	0.038	0.235	0.005	0.003
6	0.013	0.002	0.003	0.002
7	0.003	0.0001	0.002	0.001
Plutonium in aqueous, counts $\text{min}^{-1}\text{ml}^{-1}$				
Ext. 5	5.9×10^4	5.3×10^4	4.3×10^4	4.4×10^4
6	6.5×10^4	4.5×10^4	4.1×10^4	4.0×10^4
7	4.7×10^4	4.7×10^4	4.2×10^4	4.0×10^4
Coalescence time, sec	ave. 30	ave. 35	ave. 20	ave. 20
Observations	---	---	---	---
STRIP				
Uranium in solvent, mg/ml				
Strip 5	0.053	0.019	0.004	0.018
6	0.003	0.005	0.007	0.001
7	0.003	0.004	0.004	0.001
Plutonium in solvent, counts $\text{min}^{-1}\text{ml}^{-1}$				
Strip 5	8.3×10^3	6.9×10^4	6.3×10^4	1.4×10^3
6	5.5×10^3	---	6.2×10^4	1.7×10^3
7	3.9×10^3	2.5×10^4	5.9×10^4	1.3×10^3
Coalescence time, sec	30 to 70	40 to 120	40 to 75	40 to 60
Observations	Solvent retains yellow color	Semistable emulsions	Solvent colored	Solvent colored

extraction, it increased as the stripping progressed. Plutonium stripping loss was erratic, ranging from 0.02% for solution refluxed 16 hr to 1% for solution refluxed 27 hr. In all tests, the originally water-white solvent retained a faint yellow color after stripping.

In this processing scheme, the distribution of carbon compounds was estimated by carbon analysis. After dissolution, 43% of the monocarbide carbon remains in the solution, mostly as highly colored organic impurities. After 24 hr of refluxing in 6.7 M HNO_3 , 28% remains as partially degraded organic impurities. Finally, 1.3% is extracted and largely remains in the solvent after stripping. The balance, 26.7%, is discarded with the aqueous waste from extraction.

The results suggest that, without substantial degradation of organic impurities, plutonium recovery may be limited in solvent extraction, and troublesome emulsions may build up, particularly in the stripping contactor. Also, the organic impurities, about 3 to 5 g/liter, will eventually pass on to the acid fission product waste evaporators and may pose special problems in waste management.

3.3.1 Oxidative Degradation of Organic Impurities

Oxidative degradation of the organic compounds is exceedingly difficult using treatments and chemical reagents considered safe for radiochemical processes. Extended refluxing in strong nitric acid slowly promotes degradation; however, extra equipment is needed for distilling the excess acid and backcycle to dissolution. Degradation was attempted by treating the dissolved fuel solution with various oxidizing agents. Permanganate was the best of those tested.

The superiority of permanganate over ceric ion as an oxidant for destroying the organic impurities is shown in Table 5. Aliquots of the diluted still residue, 1.54 M in $\text{UO}_2(\text{NO}_3)_2$, 3.3 M in HNO_3 , and 4.9 mg of carbon per ml, were treated with 0.02 to 0.2 M $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$, and other aliquots with 0.02 to 0.2 M KMnO_4 , refluxed 2 hr, and analyzed for total carbon. With 0.2 M KMnO_4 a fivefold reduction in carbon compounds was achieved; with 0.2 M ceric ion only one-fifth of the organic impurities was eliminated.

Table 5. Oxidative Degradation of Residual Organic Impurities in UC-Derived Feed Solution Using Permanganate and Ceric Ion

Conditions: Aliquots of the diluted still residue, 1.54 M $\text{UO}_2(\text{NO}_3)_2$, 3.3 M HNO_3 , and residual organic impurities, treated with KMnO_4 or $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ as indicated, and refluxed 2 hr.

Residual organic impurities determined by total carbon analysis

Molarity of Ce(IV)	Carbon (mg/ml)	KMnO_4 (M)	Carbon (mg/ml)
0.02	4.89	0.0	4.89
0.02	4.14	0.02	4.80
0.05	4.02	0.05	3.18
0.1	4.02	0.1	2.22
0.2	3.81	0.2	1.02

3.4 Evaluation of the Direct Nitric Acid Dissolution Process

Uranium monocarbide and other metallic carbide reactor fuels may be dissolved in nitric acid to yield aqueous solutions for subsequent processing by conventional solvent extraction with tributyl phosphate. A chemical flowsheet (Sec 3.1) was developed and tested with irradiated samples of UC, PuC, and 20% PuC--80% UC. Upon dissolution of uranium monocarbide in strong nitric acid, about 44% of the carbide carbon is converted to soluble organic acids and the remainder to carbon dioxide. The mixture of organic acids, deleterious to solvent extraction, is eliminated by gradual oxidative degradation (extended reflux of the fuel solution in strong nitric acid, distillation of the excess acid, and treatment with permanganate). Nearly quantitative recovery of uranium and plutonium, and normal decontamination from fission products, was demonstrated by solvent extraction of feed solutions thus produced from uranium monocarbide irradiated to 6000 Mwd/metric ton. Similar results were realized with other carbide fuel types irradiated up to 20,000 Mwd/metric ton.

The major disadvantage of the direct nitric acid dissolution process is the generation of complex organic acids. Oxidative degradation of the organic acid mixture is slow and incomplete when oxidation techniques com-

patible with radiochemical processing are used. Further study might well be devoted to other physical or chemical methods to reject the organic acids from the fuel solution or to prevent their formation during dissolution.

4. HYDROLYSIS-DISSOLUTION PROCESS

4.1 Process Flowsheet

Previous investigation of the hydrolysis reactions of uranium carbides provided the basis for development of the hydrolysis-dissolution process for uranium monocarbide²⁻⁵ (Fig. 6). Although the passivity of irradiated uranium monocarbide to water at 80 to 100°C precludes the use of this process on spent reactor fuel, it has potential application in recovery of uranium from unirradiated uranium carbide scrap. The process is attractive because hydrolysis proceeds at low temperatures with nearly quantitative conversion of the carbide carbon to volatile hydrocarbons.

If unirradiated, stainless-steel-clad, sodium-bonded uranium monocarbide is processed, the fuel rods must be sectioned to expose the core. Size reduction of the fuel has little effect on the hydrolysis rate since massive uranium monocarbide disintegrates as hydrolysis proceeds. It has been proposed⁹ that the sodium reservoir at the end of each fuel rod (Hallam reactor) be punctured and that most of the 48 g of sodium be drained out before shearing. Assuming 90% removal of sodium by this procedure, the probability of a violent sodium-water reaction is greatly reduced. With 20 moles of water supplied per mole of monocarbide hydrolyzed, the small amount of caustic formed, a 0.007 M solution of NaOH, would not affect the hydrolysis reaction.

Massive, unirradiated uranium monocarbide is hydrolyzed in about 8 hr in a twentyfold excess of water at 90°C, forming a slurry of hydrous uranium dioxide. The gaseous products from the reaction include: 86 vol % methane, 11 vol % hydrogen, plus small quantities of the higher hydrocarbons. If dicarbide impurity is present in the fuel, nonvolatile carbon compounds are also formed.

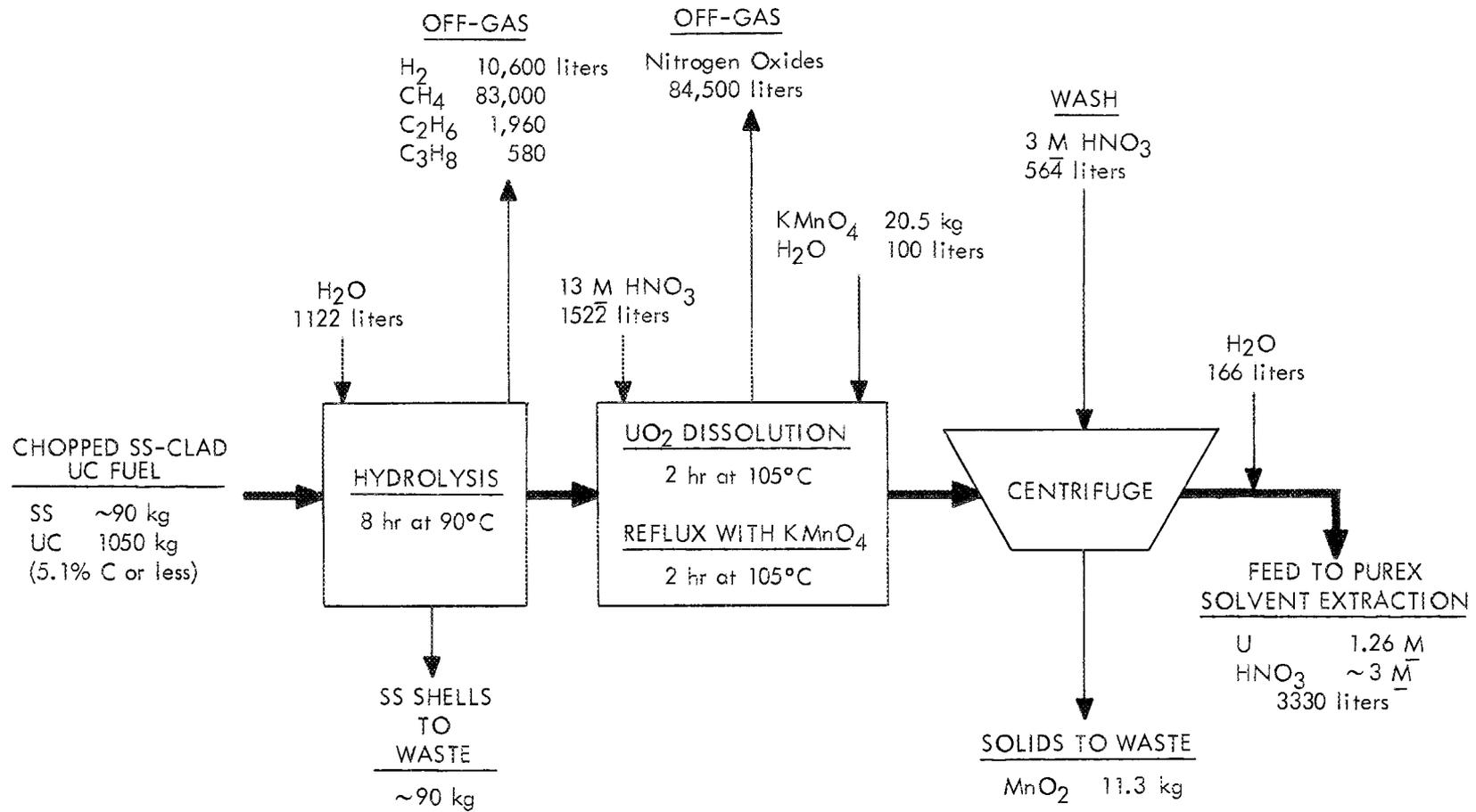


Fig. 6. Hydrolysis-Dissolution Process for Unirradiated Uranium Monocarbide.

Dissolution of the hydrous uranium dioxide is accomplished in 2 hr at 105°C with 60% HNO₃. The nonvolatile carbon compounds, stemming from the hydrolysis of dicarbide (when present), are partially dissolved in nitric acid, leaving a residue of wax-like solids. The nitric acid-soluble and insoluble organic residues, unless removed or destroyed, promote severe emulsification in the subsequent solvent extraction step. They are oxidatively degraded to innocuous forms by a 2-hr refluxing of the uranyl nitrate-nitric acid solution with 0.04 M KMnO₄, followed by centrifugation to remove the manganese dioxide precipitate that forms. The feed solution may then be processed to reclaim uranium by solvent extraction with tributyl phosphate.

4.2 Process Evaluation with Irradiated Carbide Fuels

In hot-cell tests of the proposed process, uranium monocarbide specimens irradiated from 600 to 16,000 Mwd/metric ton were subjected to hydrolysis with water at 80°C.⁶ The reaction of neutron-irradiated uranium monocarbide with water at 80°C was unlike that of unirradiated monocarbide (Table 6). Stoichiometric uranium monocarbide irradiated to 600 Mwd/metric ton required 22 hr for complete hydrolysis, in contrast to the 6 hr required for unirradiated samples. Also, a small increase in total off-gas volume was observed, with increased hydrogen and diminished methane production. Only 86% of the original carbide carbon was found in the gaseous products.

At irradiation levels of 5700 Mwd/metric ton and greater, uranium carbide was virtually "passive" in water at 80 to 100°C. For example, hyperstoichiometric uranium monocarbide irradiated to 6500 Mwd/metric ton was about 60% hydrolyzed after two weeks of contact with water at 80°C. Stoichiometric uranium carbide prepared and irradiated to 5700 Mwd/metric ton at Oak Ridge National Laboratory¹⁰ was less than 1% hydrolyzed in 23 hr. Four intact pellets of this same material were refluxed in water for 19 hr without any apparent physical change (Fig. 2a).

Table 6. Effect of Neutron-Irradiation Level on the Hydrolysis of Uranium Monocarbide in Water at 80°C

UC Specimen Mwd/metric ton of Uranium	Carbon (%)	Source	Reaction Time (hr)	Off-gas (cc/g UC at STP)	Off-gas Composition (%)		
					H ₂	CH ₄	C ₂ H ₆
0	4.8	ORNL	6	90	8.5	88	2.3
600	4.8	ORNL	22	96	28	67	3.0
5,700	4.8	ORNL	23 ^a	< 1	Insufficient volume for analysis		
6,500	4.8	AI	336 ^a	61			
7,500	4.5	AI	23 ^a	40			
16,000	4.3	NDA	21 ^a	< 1			

^aExperiment halted because of slow reaction.

Samples of irradiated 80% uranium carbide--20% plutonium carbide were exposed to water at 80°C. After 26 hr of contact, 69% of the cesium, 0.4% of the ruthenium, and 0.005% of the plutonium were leached from a specimen irradiated to 800 Mwd/metric ton. Limited hydrolysis produced 44 cc (STP) of off-gas per gram of mixed carbide, as compared to 74.4 cc of off-gas per gram of mixed carbide estimated if all of the uranium monocarbide had hydrolyzed. Another specimen irradiated to 20,000 Mwd/metric ton produced about 14 cc of off-gas per gram during 6 hr of contact with water at 80°C; 6% of the cesium was found in the water.

4.3 Flowsheet Development Studies

Unirradiated stoichiometric uranium monocarbide (nominal 4.8% C) when hydrolyzed with water at 25 to 99°C produced hydrous uranium dioxide and 93 cc (STP) of off-gas per gram of uranium monocarbide. The gas consisted of 86 vol % methane, 11% hydrogen plus small quantities of the higher hydrocarbons. All of the carbide carbon was found in the gaseous products.²⁻⁴ Uranium metal as an impurity in uranium monocarbide also hydrolyzes to produce two moles of hydrogen per mole of metal, while uranium dicarbide impurity yields C₂- to C₈-hydrocarbons and some nonvolatile waxes.⁴ When the hydrous uranium dioxide is dissolved in nitric acid, these waxes yield

both soluble and insoluble organic species which cause emulsions in subsequent solvent extraction.

4.3.1 Hydrolysis-Dissolution of Impure Uranium Carbide

Samples, 20 to 60 g, of unirradiated uranium monocarbide containing dicarbide impurity (5.1% C, compared with the stoichiometric 4.8%) were hydrolyzed in water in 2 to 4 hr at 90°C, forming a black slurry of uranium dioxide. About 92% of the carbon was converted to volatile hydrocarbons. The uranium dioxide was dissolved in boiling 4 M HNO_3 in 30 min, producing an orange-red solution. After 1.5 hr of refluxing, the solution, 0.5 M in $\text{UO}_2(\text{NO}_3)_2$ and 3 M in HNO_3 , contained free-settling yellow-brown solids, equivalent to 0.3 wt % of the uranium monocarbide. The solids, a mixture of high-molecular-weight organic compounds, dissolved readily in acetone though not in *n*-dodecane. They retained only 0.003% of the uranium in the fuel specimen. Infrared spectrographic examination indicated an unidentified complex mixture of organic acids and esters.

4.3.2 Extraction and Stripping Tests with Tributyl Phosphate

Portions of the filtered and unfiltered solutions were tested by batch solvent extraction; 15 vol % tributyl phosphate in Adakane was used as solvent with a dilute feed solution, 0.5 M in $\text{UO}_2(\text{NO}_3)_2$ and 3 M in HNO_3 (Table 7). After extraction, the unfiltered solution retained 0.077 mg of uranium per ml, compared with the 0.001 mg of uranium per ml retained in a control solution prepared from pure uranyl nitrate. Semi-stable emulsions persisted throughout the extraction, and phase separation time increased from 30 to 45 sec as extraction progressed. The filtered feed retained 0.025 mg of uranium per ml after extraction; however, phase settling time decreased from 35 to 10 sec during extraction. Stripping was characterized by absence of emulsions, average settling times of 10 sec, and negligible retention of uranium by the solvent. Apparently, removal of the organic solids is beneficial; and further improved solvent extraction may be gained by eliminating the soluble organic impurities.

Table 7. Solvent Extraction of Uranyl Nitrate-Nitric Acid Solutions Derived From Hydrolysis--Nitric Acid Dissolution of Uranium Monocarbide

Conditions: Aqueous Feed: 120 mg U/ml, 3 M HNO₃
 Solvent: 15 vol % tributyl phosphate in Adakane
 Aqueous Strip: 0.01 M HNO₃
 Extraction: Six (2 min) equilibrations at 25°C; solvent/ feed volume: 2/1
 Strip: Five (2 min) equilibrations at 25°C; strip/ solvent volume: 2/1

	Control ^a	Feed Solution, Unfiltered	Clarified Feed	Feed Solution 0.04 M in KMnO ₄ ; 2-hr Reflux, Filtered
Extraction				
Uranium in aqueous, mg/ml				
Ext. 6	0.001	0.077	0.025	0.004
Coalescence time, sec	ave. 15	ave. 45	ave. 25	ave. 20
Emulsions	No	Semistable	Slight	No
Strip				
Uranium in solvent, mg/ml				
Strip 5	0.0001	0.012	0.0001	0.001
Coalescence time, sec	ave. 10	ave. 15	ave. 12	ave. 12
Emulsions	No	No	No	No

^aFeed solution of identical composition prepared from laboratory reagents.

4.3.3 Oxidative Degradation of Organic Impurities

Since organic compounds will be formed in proportion to the dicarbide impurity in uranium monocarbide, a suitable method for their removal was sought. Oxidative degradation by refluxing in 3 M HNO₃ was too slow. However, making the unfiltered solution 0.04 M in KMnO₄ (2 hr of refluxing) and filtering to remove manganese dioxide effectively eliminated the interference from organic impurities. A reddish tinge to the yellow uranyl

nitrate solution indicated the presence of trace impurities. Extraction and stripping tests were free of emulsions, and coalescence time averaged 15 sec. Uranium extraction and stripping losses were 0.004 and 0.002%, respectively (Table 7).

The manganese dioxide was washed with water and methanol to remove uranyl nitrate and organic residue. The washed precipitate retained 0.05% of the uranium in the fuel sample. Infrared spectra of the precipitate, the methanol leach, and the filtered solution indicated that the organic residue was a mixture of partly nitrated, saturated aliphatics and unsaturated olefins. The presence of carboxyl groups was not detected.

The solutions derived from uranium carbide (4.8 to 5.0% C) contained no organic solids; however, the presence of soluble organic compounds was indicated by the reddish color of the solution. Making the solution 0.05 M in $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ and refluxing for 2 hr also produced acceptable feed solution.

4.3.4 Optimum Conditions for Hydrolysis-Dissolution to Produce Purex Feed

To produce a Purex feed solution, 1.26 M in $\text{UO}_2(\text{NO}_3)_2$ and 3 M in HNO_3 , from uranium carbide, hydrolysis was conducted with a minimum excess of water sufficient to cover the chopped fuel load. Uranium monocarbide (4.8 to 5.2% C) was hydrolyzed with $\text{H}_2\text{O}/\text{UC}$ mole ratios from 11 to 20. Dissolution of the uranium dioxide slurries in boiling nitric acid produced Purex feed solutions that were up to 1.68 M in $\text{UO}_2(\text{NO}_3)_2$ and 3 M in HNO_3 , which, after permanganate treatment, remained stable during storage for 2 months at 25°C. Nitric acid consumption was 2.89 moles per mole of uranium dioxide dissolved.

4.3.5 Process Demonstration with Plutonium Tracer

The proposed hydrolysis-dissolution process (Fig. 5) was successfully tested batchwise with unirradiated uranium carbide (5.2% C) and plutonium(IV) tracer. The dark-red solution containing yellow solids was treated with 0.04 M KMnO_4 and refluxed for 2 hr. The manganese dioxide was separated and washed with 3 M HNO_3 . Before washing, the precipitate retained 0.03

and 0.65% of the uranium and plutonium originally in the fuel sample. Repeated washing reduced these losses to 0.028 and 0.13%, respectively.

The clarified solution was treated with 0.1 M NaNO_2 to stabilize plutonium in the tetravalent state, and the solution was processed batch countercurrently through the Purex first cycle of solvent extraction (Table 8). Solvent extraction performance was satisfactory across the first cycle, and no emulsions were observed. Uranium recovery was nearly quantitative, more than 99.9% with four extraction stages, four back-extraction stages, and seven strip stages. Plutonium loss was 0.05% at the seventh extraction stage. A simulated eighth stage reduced this loss to 0.026%. After seven partition stages, no plutonium was lost to the uranium product stream.

Table 8. Conditions Employed in Batch Countercurrent Simulation of Standard Purex Process

	Stream	Relative	Composition
	in	Volume	
	out		
Extraction-Scrub:	AF	3	3.1 <u>M</u> HNO_3 , 280 mg U/ml, 3.8×10^6 Pu counts $\text{min}^{-1}\text{ml}^{-1}$, 0.1 <u>M</u> NaNO_2
7 ext. stages			
4 scrub stages	AS	2	3 <u>M</u> HNO_3
4 throughputs	AX	9 ^a	30% TBP in Adakane (<u>n</u> -dodecane)
Partition:	AP	9.5	30% TBP, 0.18 <u>M</u> HNO_3 , 86 mg U/ml, 1.1×10^6 Pu counts $\text{min}^{-1}\text{ml}^{-1}$
7 part. stages			
4 back ext. stages	BS	2.5	30% TBP
4 throughputs	BX	1.25	0.1 <u>M</u> HNO_3 , 0.02 <u>M</u> $\text{Fe}(\text{NH}_2\text{SO}_3)_2$
Strip:	BU	12	0.02 <u>M</u> HNO_3 , 69 mg U/ml
7 stages	CX	18	0.01 <u>M</u> HNO_3
4 throughputs			

^aSolvent relative volume reduced 10% to compensate for below-standard uranium concentration of feed.

The results indicate that impure uranium monocarbide (up to 5.2% C) can be processed in a Purex plant if permanganate is used to eliminate soluble and insoluble organic impurities. A similar permanganate head-end treatment has been used in Purex plants to secure extra decontamination of uranium and plutonium from the fission products (ruthenium, zirconium, and niobium) and provide feed clarification before solvent extraction.

4.4 Evaluation of the Hydrolysis-Dissolution Process

Laboratory-scale development studies established that the hydrolysis-dissolution process may be effectively employed to convert unirradiated uranium carbide to uranyl nitrate-nitric acid solution from which the uranium can be recovered by established extraction technology. Hyperstoichiometric uranium monocarbide is completely hydrolyzed with water at 80 to 100°C to hydrous uranium dioxide, with nearly quantitative conversion of the carbide to gaseous hydrocarbons. Dissolution of the oxide residue in nitric acid produces a feed solution requiring only minor treatment before solvent extraction. Hydrolysis-dissolution can be conducted in a single stainless steel reaction vessel without fear of excessive corrosion.

If a technique were discovered to eliminate the passivity of irradiated uranium and plutonium carbides to hydrolysis in water at 80°C, hydrolysis-dissolution would be the preferred aqueous head-end process for carbide fuel. The many attractive features of this process should stimulate further hot-cell investigation of the passivity phenomenon. This study should have as objectives the understanding of the mechanism of passivity and the development of methods to activate the hydrolysis of irradiated carbide fuels.

5. CONCLUSIONS

Three aqueous dissolution processes were developed for fuels containing uranium and plutonium monocarbide using both unirradiated and irradiated (up to 20,000 Mwd/metric ton) fuel samples. It was concluded that:

1. Pyrohydrolysis is an effective, practical head-end process for converting irradiated uranium and plutonium monocarbide to aqueous solutions

from which the fuel values may be recovered by established (solvent extraction) technology. The process is insensitive to irradiation-induced effects. With further development effort, it may have potential application to the graphite-based fuels, for example, pyrolytic carbon-coated uranium-thorium carbides.

2. The otherwise promising hydrolysis-dissolution process cannot be applied to the highly irradiated carbide fuels owing to irradiation-induced "passivity" of the metallic carbides toward hydrolysis in water at 80 to 100°C. Although the "passivity" phenomenon was well established by tests with samples of irradiated carbide fuels, the mechanism of irradiation-induced nonreactivity is not understood. If a means were discovered to promote the low temperature hydrolysis of the irradiated carbides, this process would be considered superior since it minimizes radiochemical engineering problems.

3. Irradiated carbide fuels can be converted to aqueous solutions by dissolution in nitric acid. However, before the fuel values can be recovered and decontaminated with negligible loss and without emulsion difficulties by conventional (TBP) solvent extraction, the solutions must first be freed of soluble organic acids generated during dissolution. Since a completely effective method of eliminating the organic acid impurities remains to be developed for the direct nitric acid dissolution process, it is considered a less desirable alternative to pyrohydrolysis.

6. ACKNOWLEDGEMENT

The authors wish to acknowledge the assistance of Mr. J. H. Kittel of Argonne National Laboratory, Mr. A. Strasser of the United Nuclear Corporation, and Mr. R. C. Westphal, Mr. D. K. Magnus, and Mr. J. F. Leirich of Atomics International, for the procurement of highly irradiated specimens from their experiments on uranium and plutonium monocarbide reactor fuels. Experimental work at this Laboratory was conducted by Technicians L. A. Byrd, R. C. Shipwash, A. V. Wilder, and G. E. Woodall. Analyses were performed by the groups of W. R. Laing, C. E. Lamb, R. L. Sherman, and E. I. Wyatt of the ORNL Analytical Chemistry Division.

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