13 c
14
D W 11-3-68
MASTER

ORNL-4618

UC-10 - Chemical Separations Processes
for Plutonium and Uranium

SOLVENT STABILITY IN NUCLEAR FUEL
PROCESSING. CYCLIC IRRADIATION
STUDIES OF 15 vol % TBP-n-DODECANE

J. G. Moore
D. J. Grouse

THIS DOCUMENT CONFIRMED AS
UNCLASSIFIED
DIVISION OF CLASSIFICATION
BY JH Kahn/amb
DATE 12/19/70

OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

FT775

BLANK PAGE

Printed in the United States of America. Available from
National Technical Information Service

U.S. Department of Commerce, Springfield, Virginia 22151

Price: Printed Copy \$0.50, Microfiche \$0.65

THIS REPORT HAS BEEN PREPARED AS AN ACCOUNT OF WORK SPONSORED BY THE UNITED STATES GOVERNMENT. NEITHER THE UNITED STATES NOR THE UNITED STATES Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

BLANK PAGE

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

OEAL-4613

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

SOLVENT STABILITY IN NUCLEAR FUEL PROCESSING:

CYCLIC IRRADIATION STUDIES OF 15 vol %

TBP-n-DODECANE

J. G. Moore

D. J. Crouse

NOVEMBER 1970

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

CONTENTS

	<u>Page</u>
ABSTRACT	1
1. INTRODUCTION	2
2. REAGENTS, IRRADIATION PROCEDURE, AND CHARACTERIZATION TESTS	3
2.1 Reagents	3
2.2 Irradiation Procedure	4
2.3 Zirconium Extraction and Retention Tests	4
2.4 Ruthenium Extraction and Retention Tests	7
2.5 Plutonium Extraction and Retention Tests	8
3. RESULTS	8
3.1 Retention of Uranium	8
3.2 Extraction and Retention of Zirconium	9
3.3 Extraction and Retention of Ruthenium	13
3.4 Extraction and Retention of Plutonium	13
3.5 Measurements of Surface Tension and Interfacial Tension	14
4. DISCUSSION	15
5. ACKNOWLEDGMENTS	17
6. REFERENCES	17

SOLVENT STABILITY IN NUCLEAR FUEL PROCESSING:

CYCLIC IRRADIATION STUDIES OF 15 vol %

TBP-n-DODECANE

J. G. Moore

D. J. Crouse

ABSTRACT

Cyclic irradiation tests were made in which 15 vol % TBP-n-dodecane in contact with 0.38 M $\text{UO}_2(\text{NO}_3)_2$ --3 M HNO_3 was irradiated by a ^{60}Co source for 20, 60, or 120 min (single-cycle radiation doses of 0.3, 1, or 2 whr/liter). The uranium was then stripped from the organic phase with dilute nitric acid, and the solvent was regenerated by washing with a 0.3 M Na_2CO_3 solution. This cycle was repeated until the solvent had received a total radiation dose of 6 to 10 whr/liter. Periodically, the solvent was sampled and its extraction and metal retention characteristics were determined. In each test, the phase separation was rapid and clearly defined; there was no evidence of the formation of solids. Exposures at a level of 0.3 whr liter⁻¹ cycle⁻¹ had no detectable effect on the solvent performance. At the higher exposures, there was slight retention of uranium by the stripped solvent and an increase in the ability of the solvent to extract zirconium. The zirconium extraction coefficients for solvents irradiated at 1 and 2 whr liter⁻¹ cycle⁻¹ were about two and three times, respectively, those obtained with unirradiated solvent. However, the coefficients did not increase with cycling, indicating that the degradation products formed during the irradiation were removed effectively from the solvent by the sodium carbonate wash.

Assessment of these results in terms of the solvent exposures that are expected during the processing of 30-day-cooled LMFBR fuels in pulsed columns indicates that process problems arising from irradiation of the solvent will be minimal.

BLANK PAGE

1. INTRODUCTION

Because LMFBR fuels will be irradiated to high burnups at high specific power and, for economic reasons, will be processed after relatively short decay (possibly as little as 30 days), the aqueous solutions prepared by the dissolution of these fuels will have high radiation power densities. For example, it is estimated¹ that a feed solution prepared by dissolving 30-day-cooled mixed-core-and-blanket materials from the Atomic International Reference Oxide Reactor² to a heavy-metal concentration of about 70 g/liter would have a power density of about 6 ($\beta + \gamma$) w/liter.* Dissolution of the core alone and/or preparation of more-concentrated feed solutions would increase the power density of the solution severalfold. One of the major questions of the applicability of tributyl phosphate (TBP) extraction (i.e., the Purex process) to the recovery of uranium and plutonium from highly radioactive feeds concerns the effects that irradiation will have on the solvent and its subsequent process performance. It is known that solvent degradation products (TBP decomposition products and nitration products of the hydrocarbon diluent) can decrease separations from fission products, increase plutonium retention by the solvent, and contribute to the formation of crud and emulsions. In the Purex process, the solvent is washed with an aqueous solution of Na_2CO_3 after each cycle to remove TBP decomposition products and thereby prevent their accumulation to a level that would cause severe process problems.

A recent review and assessment of past laboratory studies and production experience concerning solvent stability showed that, unfortunately, most of the available information is of little or no use for predicting solvent performance during the processing of short-cooled high-burnup fuels.³ In most of the solvent irradiation tests described in the literature, the solvent received a large radiation dose (in some cases, without nitric acid present), and then its extraction characteristics were tested. Thus, the

* This estimate assumes that all of the fission products would dissolve. Actually, dissolution tests with irradiated LMFBR fuels have shown that some of the more important fission products such as ^{106}Ru and $^{95}\text{Zr-Nb}$ are not dissolved completely by boiling 8 to 12 M HNO_3 .

results are not useful for predicting solvent performance in an actual processing system, in which the solvent receives a relatively small dose during each cycle and is washed between cycles to remove offending degradation products. In addition, kerosenes or "naphthas," which are now known to be much less stable in process use than the presently favored normal paraffin hydrocarbons such as n-dodecane, were used as the diluents in most of the earlier studies.

This report describes the results of a series of batch cyclic irradiation tests in which we used n-dodecane as the diluent and attempted to simulate processing conditions more closely. In these tests, (1) 15 vol % TBP in n-dodecane was mixed with 0.38 M $\text{UO}_2(\text{NO}_3)_2$ --3 M HNO_3 while being irradiated by a ^{60}Co source (i.e., a simulated extraction step), (2) the uranium was stripped from the extract with dilute nitric acid, and (3) the stripped solvent was washed with 0.3 M Na_2CO_3 solution and 0.1 M HNO_3 . This complete process cycle was then repeated until the desired total solvent radiation dose was obtained. Samples of the solvent were withdrawn periodically for characterization tests.

In general, the test results indicate that, even when short-cooled LMFBR fuels are processed, problems arising from solvent radiation damage should not seriously affect the efficiency of the Purex process. Similar batch cyclic tests are being made with fuel solutions derived from leaching irradiated LMFBR fuel specimens to confirm this preliminary conclusion.

2. REAGENTS, IRRADIATION PROCEDURE, AND CHARACTERIZATION TESTS

2.1 Reagents

Technical-grade TBP was purified by boiling with a dilute aqueous solution of sodium hydroxide.⁴ One volume of TBP was added to five volumes of 0.1 N NaOH, and the mixture was distilled at atmospheric pressure until two volumes of distillate had been collected. After the mixture remaining in the pot had cooled to room temperature, the TBP was separated from the aqueous phase, washed three times with water at a phase ratio of 1/1, and stored in the dark prior to use.

The n-dodecane, obtained from Union Carbide Corporation, was 99.75 mole % pure according to chromatographic analysis.

2.2 Irradiation Procedure

One volume (1500 to 2400 ml) of freshly prepared 15 vol % DBP in n-dodecane was added to 0.5 volume of 0.38 M $\text{UO}_2(\text{NO}_3)_2$ --3 M HNO_3 in a stainless steel reactor vessel (Fig. 1). As the phases were mixed, the ^{60}Co source capsule was lowered into the well of the vessel, and the mixture was irradiated for 20, 60, or 120 min. These periods were equivalent to solvent radiation doses of about 0.3, 1, and 2 whr/liter, respectively. After irradiation, the mixture was immediately transferred to a separatory funnel, the phases were allowed to separate, and the aqueous phase was removed. The organic phase (the organic extract) was stripped of its uranium content by five consecutive contacts with 0.5 volume of 0.01 M HNO_3 and was then washed twice with 0.5 volume of 0.3 M Na_2CO_3 and once with 0.2 volume of 0.1 M HNO_3 . The complete procedure was repeated until the solvent had received an integrated radiation dose of 6 to 10 whr/liter. Samples of the organic and aqueous phases were taken periodically after the irradiation, stripping, and solvent wash steps for uranium analyses and solvent characterization tests. Samples that could not be analyzed on the day of collection were refrigerated and stored in the dark until used. The organic samples taken after the carbonate--nitric acid wash treatment were reloaded with uranium before the ^{95}Zr and ^{106}Ru extraction and retention tests were begun. The testing procedure and sampling points are summarized in Fig. 2.

2.3 Zirconium Extraction and Retention Tests

Extraction of zirconium by the solvent was measured by contacting aliquots of uranium-containing solvent from the irradiation contact and of carbonate-washed solvent (after it had been reloaded with uranium) with a solution of the following composition for 5 min:

<u>Constituent</u>	<u>Concentration</u>
U	10 g/liter
HNO_3	3 M
Zr	0.9 g/liter
^{95}Zr -- ^{95}Nb	$\sim 8 \times 10^5$ counts min^{-1} ml^{-1}

ORNL-LR-DWG. 58049 R2

Fig. 1. Diagram Showing the Four-liter Reactor-Agitator in the ^{60}Co Source Cavity.

Fig. 2. Test Procedure for Cyclic Irradiation Experiments.

The phases were separated, the organic phase was centrifuged for 2 min, and a gross gamma count was made of the organic and aqueous phases. The organic phase was then stripped by five consecutive 2-min contacts with 0.01 N HNO_3 , each at a phase ratio of 1/1, and a gross gamma count was made of the stripped solvent. All tests were made in duplicate. Since niobium is only weakly extracted by TBP,⁵ the zirconium extraction coefficient was calculated by assuming that all gamma activity in the organic phase in excess of the activity arising from uranium was due to ^{95}Zr . In addition, the aqueous feed was assumed to be at equilibrium with respect to the ^{95}Zr - ^{95}Nb couple so that about 40% of the total activity in the original feed was due to ^{95}Zr .

The zirconium feed solution was prepared by adding ^{95}Zr - ^{95}Nb tracer to 0.63 *M* oxalic acid. The oxalate was destroyed by adding equal volumes of concentrated HNO_3 and 30% H_2O_2 to the tracer solution and heating almost to dryness. This procedure was repeated three times. After the last evaporation, sufficient uranium, nitric acid, and zirconium nitrate were added to give the desired concentrations in the feed solution.

2.4 Ruthenium Extraction and Retention Tests

Three molar nitric acid containing about 0.3 g of ruthenium per liter, ^{106}Ru tracer ($\sim 1 \times 10^6$ counts $\text{min}^{-1} \text{ ml}^{-1}$), and 10 g of uranium per liter was shaken for 5 min with a sample of uranium-bearing solvent from the irradiation-extraction step. The organic and aqueous phases were then separated, and the organic phase was centrifuged prior to determination of the ruthenium concentration by gross gamma counting. Ruthenium retention in the organic phase was measured after five consecutive 2-min contacts with 0.01 N HNO_3 . Similar extraction-stripping tests were made using samples of the carbonate--nitric acid--washed solvent after the solvent had been loaded with uranium. All tests were made in duplicate.

In order to obtain reproducible results, precautions were taken to ensure that the desired ruthenium species was present in the aqueous phase at the time of its contact with the solvent. A ruthenium stock solution was prepared by adding ^{106}Ru (as RuCl_3 in 2.3 N HCl) to 6 *M* HNO_3 having a ruthenium concentration (as RuCl_4) of 19 g/liter. The chloride was removed

by repeatedly distilling off 0.5 volume of the aqueous and adding 0.5 volume of 5 M HNO_3 to the residue until the distillate no longer contained chloride. The residue was dissolved and then diluted to 5 volumes with sufficient concentrated nitric acid to give a final nitric acid concentration of 10 M; the resulting solution was refluxed for 1 hr. One hour prior to determining the ruthenium extraction coefficient, 1 ml of this ruthenium stock solution was added to 10 ml of $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3$ solution to make up the aqueous feed for the extraction test.

2.5 Plutonium Extraction and Retention Tests

Plutonium extraction and retention tests were made with samples of the solvent extract obtained from the irradiation-extraction step and with the carbonate-washed solvent after it had been reloaded with uranium. The organic solutions, each having a uranium concentration of about 35 g/liter, were contacted for 2 min with equal volumes of 3 M HNO_3 having a plutonium concentration of about 0.6 g/liter and a uranium concentration of 15 g/liter. The plutonium concentration in each phase was measured using an alpha liquid scintillation counter. The organic phase was stripped by three consecutive contacts with 0.5 volume of 0.17 M HNO_3 --0.1 M $\text{Fe}(\text{SO}_3\text{NH}_2)_2$, and the residual alpha activity was measured.

3. RESULTS

The only observed changes that occurred in the solvent performance as the radiation dose per cycle was increased were: (1) an increase in the ^{96}Zr extraction coefficient, and (2) a slight retention of uranium by the stripped solvent. These effects did not build up with cycling, however, indicating that the solvent wash treatment was effective in removing the offending solvent degradation products.

3.1 Retention of Uranium

There was a small increase in the amount of uranium that was retained by the solvent after stripping as the radiation dose per cycle was increased from 0.3 to 2 whr liter⁻¹ cycle⁻¹ (Table 1). The quantity of uranium

Table 1. Effect of Irradiation on Uranium Extraction and Retention

Solvent Radiation Dose (whr liter ⁻¹ cycle ⁻¹)	Uranium in Stripped Solvent (mg/liter)	
	Range	Average
0.0 (unirradiated solvent)	0.7-1.3	1.0
0.3	0.2-1.0	0.6
1.0	1.2-5.5	3.3
2.0	12-15	14

retained by solvent receiving a dose of 0.3 whr liter⁻¹ cycle⁻¹ was 0.2 to 1 mg/liter, which is essentially the same range of values obtained in parallel tests for solvent that had not been irradiated during extraction. With radiation doses of 1 and 2 whr liter⁻¹ cycle⁻¹, 1 to 5 and 12 to 15 mg of uranium per liter, respectively, were retained. Presumably the observed retention was due to the presence of HDBP (a degradation product of TBP), which was formed to a greater extent at the higher irradiation levels. However, the quantity of retained uranium did not increase with cycling (Fig. 3), indicating that the carbonate wash treatment efficiently removed the HDBP.

3.2 Extraction and Retention of Zirconium

The most significant observation in these tests was the increased ability of solvent that had been irradiated to 1 or 2 whr liter⁻¹ cycle⁻¹ to extract ⁹⁵Zr (Table 2). The average ⁹⁵Zr extraction coefficient obtained with unirradiated solvent was 0.012. Irradiation to a level of 0.3 whr liter⁻¹ cycle⁻¹ caused no detectable increase in the extraction coefficient. However, solvent irradiated to 1 or 2 whr liter⁻¹ cycle⁻¹ gave ⁹⁵Zr coefficients of 0.027 and 0.036, respectively, or coefficients that were a factor of 2 to 3 higher than the coefficient obtained with unirradiated solvent. In addition, results showed (although the data are very scattered) that more zirconium was retained by the more highly irradiated solvents on stripping with dilute nitric acid.

ORNL DWG 70-11021

Fig. 3. Retention of Uranium by Irradiated 15% TBP--n-Dodecane After Stripping with 0.01 M HNO₃.

Table 2. Results of Zirconium Extraction and Retention Tests

Solvent Radiation Dose (whr liter ⁻¹ cycle ⁻¹)	⁹⁵ Zr Extraction Coefficients		% of Original ⁹⁵ Zr Retained	
	Range	Average	Range	Average
Organic Samples Taken After Irradiation Contact				
0.0	0.009-0.015	0.012	0.10 -1.23	0.57
0.3	0.006-0.018	0.011	0.047-0.57	0.20
1.0	0.022-0.029	0.027	0.40 -1.32	0.81
2.0	0.033-0.040	0.036	0.53 -1.28	0.70
Organic Samples Taken After Carbonate--Nitric Acid Wash				
0.0	0.009-0.017	0.012	0.21 -1.08	0.57
0.3	0.004-0.012	0.008	0.027-0.87	0.23
1.0	0.009-0.014	0.011	0.29 -0.76	0.48
2.0	0.009-0.014	0.012	0.29 -0.78	0.56

The zirconium extraction coefficients, although larger at the higher exposure levels, did not increase with cycling (Fig. 4). Irradiated solvent that had been washed with a sodium carbonate solution gave coefficients equal to, or less than, those obtained with unirradiated solvent (Table 2). These results indicate that the degradation products responsible for the increased zirconium extraction (presumably mostly HDBP) were effectively removed by the alkaline wash treatment. In fact, there is some indication that, at low dose rates (e.g., 0.3 whr liter⁻¹ cycle⁻¹), the extraction and retention of zirconium are diminished slightly. The data are too scattered and insufficient to confirm this; however, the effect has been observed by others.⁶

In these experiments, as described previously, the solvent was irradiated while it was in contact with UO₂(NO₃)₂--3 M HNO₃; no fission products were present. Samples of the irradiated solvent were then withdrawn for zirconium extraction tests. To ensure that the results would be the same

Fig. 4. Extraction of ^{95}Zr by Irradiated 15 vol % TBP--n-Dodecane.

with zirconium and ruthenium present during irradiation, as they would be in actual fuel processing, two additional experiments were made with 3 M HNO_3 --0.4 M $\text{UO}_2(\text{NO}_3)_2$ aqueous feeds that contained either (1) 0.9 g of zirconium per liter and ^{95}Zr - ^{95}Nb tracer or (2) 0.9 g of zirconium per liter, ^{95}Zr - ^{95}Nb tracer, and 0.3 g of ruthenium per liter. Each experiment consisted of three cycles at a radiation dose level of 0.3 whr liter $^{-1}$ cycle $^{-1}$. In addition, a parallel (control) three-cycle test was made with the first aqueous feed outside the radiation field. Results (not presented here) indicated that the presence of zirconium and ruthenium during irradiation had no effect. As before, the ^{95}Zr extraction coefficients were the same as, or slightly lower than, those for the unirradiated solvent, and any ^{95}Zr remaining in the organic phase after stripping with 0.01 M HNO_3 was removed by the carbonate wash.

3.3 Extraction and Retention of Ruthenium

Irradiation up to a dose of 2 whr liter $^{-1}$ cycle $^{-1}$ had no effect on the extraction and retention of ruthenium. Both the ^{106}Ru extraction coefficients obtained with unirradiated (control) solvent and those obtained with solvent that had been irradiated to about 0.3, 1, and 2 whr liter $^{-1}$ cycle $^{-1}$ were about 0.002 (Table 3). From 0.11 to 0.16% of the ^{106}Ru in the feed was retained by the stripped solvent; variations within this range showed no dependence on solvent radiation dose.

As in the tests with ^{95}Zr (see Sect. 3.2), additional tests, each consisting of three cycles of irradiation at 0.3 whr liter $^{-1}$ cycle $^{-1}$, were made in which ruthenium or ruthenium and zirconium were present during the irradiation-extraction step. Again, irradiation at this level appeared to have no effect on the ^{106}Ru extraction and stripping behavior.

3.4 Extraction and Retention of Plutonium

The quantities of plutonium that were extracted or retained by the solvent after stripping were the same for unirradiated solvent and for solvent that had been irradiated up to 2 whr liter $^{-1}$ cycle $^{-1}$. After extraction, each solvent had a plutonium concentration of about 0.4 g/liter. This concentration was reduced to less than 5×10^{-6} g/liter by stripping

Table 3. Results of Ruthenium Extraction and Retention Tests

Solvent Radiation Dose (whr liter ⁻¹ cycle ⁻¹)	¹⁰⁶ Ru Extraction Coefficients		% of Original ¹⁰⁶ Ru Retained	
	Range	Average	Range	Average
Organic Samples Taken After Irradiation Contact				
0.0	0.0019-0.0026	0.0022	0.13 -0.19	0.16
0.3	0.0014-0.0024	0.0020	0.076-0.14	0.11
1.0	0.0014-0.0028	0.0022	0.12 -0.18	0.15
2.0	0.0021-0.0026	0.0023	0.15 -0.17	0.16
Organic Samples Taken After Carbonate--Nitric Acid Wash				
0.0	0.0019-0.0026	0.0022	0.13 -0.19	0.16
0.3	0.0014-0.0024	0.0020	0.073-0.13	0.11
1.0	0.0016-0.0025	0.0020	0.12 -0.17	0.15
2.0	0.0016-0.0023	0.0019	0.13 -0.15	0.14

the organic phase with ferrous sulfamate solution. In the stripping contacts, the plutonium was reduced to Pu(III), simulating plutonium partitioning from uranium. At the higher irradiation levels (1 and 2 whr liter⁻¹ cycle⁻¹), where significant amounts of HDBP were undoubtedly formed, measurable retention of plutonium by the solvent might be expected if the plutonium were stripped with dilute nitric acid.

3.5 Measurements of Surface Tension and Interfacial Tension

The cyclic irradiation in the tests just described had essentially no effect on either the surface tension of the regenerated solvent or the interfacial tension between the solvent and the aqueous uranium feed solution. The measurements were made with a Kruss' du Nouy Tensiometer immediately after the solvent had been contacted for 2 min with 0.5 volume of a uranium feed solution of the same composition as that used during the irradiation-extraction step (see Sect. 2.2). There was less than 8%

variation in the surface tension values and less than 6% variation in the interfacial tension values (Table 4).

4. DISCUSSION

The effects of irradiation on solvent properties, as observed in the cyclic tests described in this report, are summarized in Table 5. Irradiation of 15% TBP--n-dodecane at 0.3 whr liter⁻¹ cycle⁻¹ to an integrated dose of about 6.5 whr liter⁻¹ had no apparent adverse effect on solvent performance. The quantities of uranium, plutonium, zirconium, and ruthenium that were extracted and retained were the same as those observed for unirradiated solvent. Increasing the dose level to 1 and 2 whr liter⁻¹ cycle⁻¹ increased the ⁹⁶Zr extraction coefficients by factors of 2 and 3, respectively, and caused only a slight retention of uranium. However, cycling caused no buildup of the effects; they were apparently caused by the presence of HDBP, which would be formed in significant amounts at these irradiation levels. The carbonate wash treatment, which removed HDBP effectively from the solvent, eliminated the irradiation effects; that is, the performance of the washed solvent was equivalent to that of unirradiated solvent. In each test, phase separation was rapid and well-defined. Even at the highest irradiation level (2 whr liter⁻¹ cycle⁻¹), there was no evidence of the formation of solids (e.g., precipitation of the zirconium salt of HDBP, which has a low solubility).

Recent estimates by Groenier⁷ indicate that, when 30-day-cooled mixed-core-and-blanket material (average burnup of 33,000 Mwd/metric ton) from the Atomics International Reference Oxide Reactor is processed in pulsed columns, the solvent doses will be about 0.12 and 0.26 whr liter⁻¹ cycle⁻¹, respectively, for 15% and 30% TBP solvents. The estimated solvent doses are almost insensitive to changes in the heavy-metal concentration of the feed in the range of 70 to 210 g/liter. The estimated exposures for processing core material (burnup of 80,000 Mwd/metric ton) alone are about 60% higher than for processing mixed-core-and-blanket material.

As discussed above, the solvent performance in the cyclic irradiation tests described in this report was not affected by radiation doses of 0.3 whr liter⁻¹ cycle⁻¹, which is higher than the dose expected to be received by the

Table 4. Effect of Irradiation on the Surface Tension of the Regenerated Solvent and the Interfacial Tension Between the Solvent and the Uranium Feed Solution

Solvent Radiation Dose (whr liter ⁻¹ cycle ⁻¹)	Surface Tension (dyne-cm)		Interfacial Tension (dyne-cm)	
	Range	Average	Range	Average
0.0	26.4-26.8	26.6	14.4-16.2	15.3
0.3	24.2-24.8	24.6	15.2-15.7	15.5
1.0	24.6-24.9	24.7	14.3-15.0	14.6
2.0	24.9-25.4	25.2	15.1-15.4	15.2

Table 5. Cyclic Irradiation Tests with 15% TBP--n-Dodecane

Test	Exposure per Cycle (whr/liter)	Number of Cycles	Total Exposure (whr/liter)	Effect on Extraction Properties
1	0.29-0.34	20	6.5	No change observed.
2	0.93-1.01	10	9.5	Quantity of zirconium extracted was twice that obtained for unirradiated solvent; stripped solvent retained 3 mg of U per liter
3	1.94-2.02	3	5.9	Quantity of zirconium extracted was three times that obtained for unirradiated solvent; stripped solvent retained 14 mg of U per liter

solvent when mixed-core-and-blanket materials are processed with either 15% or 30% TBP. For the most severe case considered by Groenier, that is, the processing of core material alone with 30% TBP, where the exposure would be 0.42 whr liter⁻¹ cycle⁻¹, some increase in ⁹⁵Zr extraction might conceivably occur. However, this effect should be small (much less than a factor of 2) if detectable at all. Of course, the use of fast contactors would decrease the solvent dose to a level far below that where effects on solvent performance have been observed. Our tests, therefore, lead to the preliminary conclusion that problems arising from solvent radiation damage sustained during the treatment of short-cooled LMFBR fuels will be minimal. This conclusion needs confirmation in tests with actual fuel solutions. Also, it must be remembered that these tests do not show the effects of extended use of solvent in a processing plant. This can lead to a slow accumulation of degradation products in the solvent phase that may impair solvent performance. These degradation products usually derive primarily from the reaction of nitric acid with the diluent, the reaction rate (and thus the accumulation of degradation products) increasing when the extraction process is conducted at elevated temperatures and/or in a high radiation field. The use of normal hydrocarbons (principally dodecane) as process diluent has greatly decreased the extent of problems arising from diluent degradation; but, if necessary, the solvent can be purified periodically by distillation to remove offending degradation products.

5. ACKNOWLEDGMENTS

The authors gratefully acknowledge W. B. Howerton for his assistance in performing the experiments; C. A. Blake for his helpful advice and discussions; W. Davis, Jr., and A. H. Kibbey for their aid in calibrating the ⁶⁰Co source; and the Analytical Chemistry Division group headed by W. R. Laing for chemical analyses.

6. REFERENCES

1. Aqueous Processing of LMFBR Fuels - Technical Assessment and Experimental Program Definition, ORNL-4436 (June 1970).

2. K. Buttrey et al., Liquid Metal Fast Breeder Reactor Task Force Fuel Cycle Study, NAA-SR-Memo-12604 (January 1968).
3. C. A. Blake, Jr., Solvent Stability in Nuclear Fuel Processing: Evaluation of the Literature, Calculation of Radiation Dose, and Effects of Iodine and Plutonium, ORNL-4212 (March 1968).
4. K. Alcock et al., "The Extraction of Nitrates by Tri-n-Butyl Phosphate (TBP). I. The System TBP + Diluent + H₂O + HNO₃," Trans. Faraday Soc. 52, 39-47 (1956).
5. C. J. Hardy and D. Scargill, "The Extraction of Niobium(V) from Nitric Acid Solution by Tri-n-Butyl Phosphate (TBP)," J. Inorg. Nucl. Chem. 13, 174 (1960).
6. L. Salomon, E. Vervecken, and E. Lopez-Menchero, Predictions on the Behavior of First Cycle Solvent During the Processing of Highly Irradiated Fuels, ETR-213 (June 1967).
7. Chem. Technol. Div. Ann. Progr. Rept. May 31, 1970, ORNL-4572, pp. 63-64.