66 4019 29

DP-1016

AEC RESEARCH AND DEVELOPMENT REPORT

CURIUM PROCESS DEVELOPMENT

III-2. IDENTIFICATION OF SOLVENT DEGRADATION PRODUCTS

D. L. WEST and R. NARVAEZ

DU PONT
REG. U. S. PAT. OFF.

Savannah River Laboratory

Aiken, South Carolina

Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U. S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy $3.00; Microfiche $0.65

664019

DP-1016

Chemistry
(TID-4500)

CURIUM PROCESS DEVELOPMENT

III-2. IDENTIFICATION OF SOLVENT DEGRADATION PRODUCTS

by

David L. West and Richard Narvaez

Approved by

E. L. Albenesius, Research Manager
Analytical Chemistry Division

November 1966

E. I. DU PONT DE NEMOURS & COMPANY
SAVANNAH RIVER LABORATORY
AIKEN, S. C. 29801

CONTRACT AT(07-2)-1 WITH THE
UNITED STATES ATOMIC ENERGY COMMISSION

ABSTRACT

The principal products of solvent degradation during two of the solvent extraction steps of the curium process were identified as primary and secondary amines (from the tertiary amine extractant) and aromatic alcohols and ketones (from the diethylbenzene diluent). In batch tests, the principal causes of solvent degradation were radiolysis in the extraction banks of the nitrate-to-chloride conversion step and chemical oxidation during solvent washing in the lanthanide removal step. Hydrazine was shown to inhibit solvent degradation in the conversion step.

FOREWORD

This report is one in a series that describes the development of separations processes for purifying ^{244}Cm produced in Savannah River reactors. The series is being issued under the general title Curium Process Development. Following the general title, a roman numeral designates the subject area of the report, and an arabic numeral designates the series report number in that subject area. A subtitle describes the content of each report. Subject areas foreseen for this series are:

I. General Process Description
II. Chemical Processing Steps
III. Analytical Chemistry Support

Reports issued in this series include:

I. General Process Description by I. D. Eubanks and G. A. Burney (USAEC Report DP-1009).

III-1. Analytical Techniques for Characterizing Solvent by R. Narvaez (USAEC Report DP-1010).

III-3. Analytical Control by E. K. Dukes (USAEC Report DP-1039).

CONTENTS

Page

LIST OF TABLES AND FIGURES 6

INTRODUCTION 7

SUMMARY 7

DISCUSSION 8

  Degradation in the Nitrate-to-Chloride Conversion Step . 10

    Test Conditions 10
    Identification of Degradation Products 10
    Degradation Rates 15

  Degradation in the Lanthanide Removal Step 15

    Test Conditions 15
    Identification of Degradation Products 16
    Degradation Rates 16

  Effect of Hydrazine as a Degradation Inhibitor 17

BIBLIOGRAPHY 18

LIST OF TABLES AND FIGURES

Page

Table

I Characteristics of Degradation Products of Diethylbenzene 13

II Degradation in Simulated Conversion Step 15

III Degradation in the Lanthanide Removal Step . . . 17

Figure

1 Nitrate-to-Chloride Conversion Step 8

2 Lanthanide Removal Step 9

3 Gas Chromatograms of Curium Process Solvent . . 11

4 Gas Chromatogram of Irradiated Diethylbenzene . 13

5 Infrared Spectra of Degraded Solvent 14

6 Radiolysis of Diethylbenzene in Presence of Hydrazine 17

INTRODUCTION

The Savannah River program for producing ^{244}Cm includes the development of separations processes for purification of the ^{244}Cm produced in Savannah River reactors.(1) This report summarizes a study of solvent degradation during two solvent extraction steps:

- Nitrate-to-chloride conversion step, for conversion of a nitrate solution of curium, americium, and lanthanides to a suitable feed for the subsequent lanthanide removal step.
- Lanthanide removal step, in which the trivalent actinides are preferentially extracted from the trivalent lanthanides.

The objectives of this study were to determine the major degradation products, their sources, and their rates of production and to investigate means of inhibiting degradation. The scope of the work was limited to batch exposures of solvent components to environments that simulated those in the processing steps.

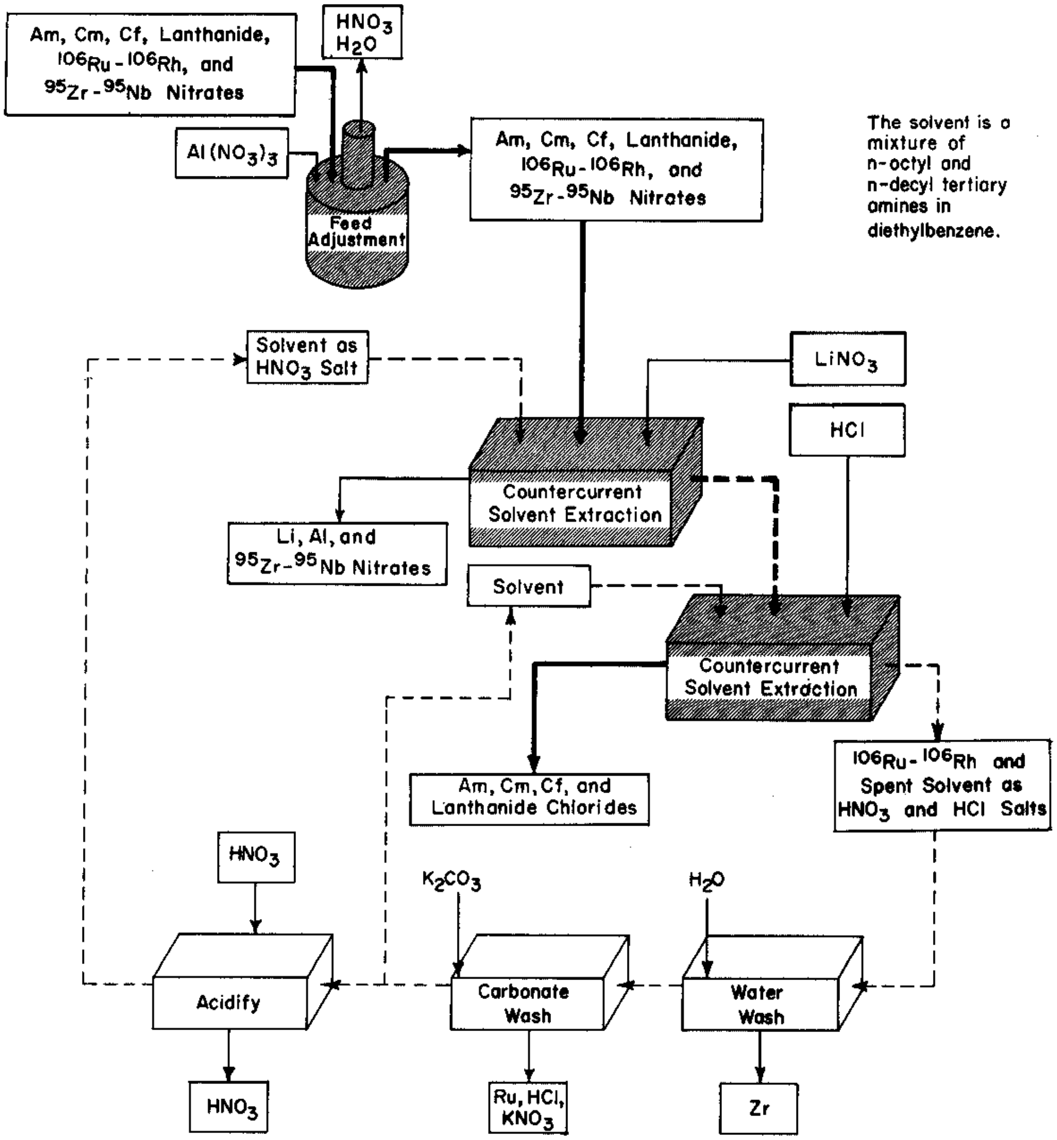
SUMMARY

The major products of solvent degradation were identified in two solvent extraction steps that simulated conditions of the curium process. Primary and secondary amines, from the tertiary amine extractant, and aromatic alcohols and ketones, from the diethylbenzene diluent, were the principal products detected in degraded solvent from the nitrate-to-chloride conversion and the lanthanide steps. Gas chromatography, infrared spectrometry with a multiple-reflectance cell, and thin-layer chromatography were the analytical methods used.

Rates of degradation, derived from batch tests that simulated processing steps, revealed that radiolysis in the extraction banks in the conversion step and chemical oxidation during solvent washing in the lanthanide removal step were the principal causes of solvent degradation. Hydrazine was shown to inhibit solvent degradation in the conversion step.

DISCUSSION

Batches of solvent were exposed to chemicals and radiation that simulated those in the two solvent extraction steps. The major degradation products were determined by analytical techniques described in a previous report in this series.(2) Flowsheets for both steps of the process, including solvent recycle, are shown in Figures 1 and 2.



The solvent is a mixture of n-octyl and n-decyl tertiary amines in diethylbenzene.

FIG. 1 NITRATE-TO-CHLORIDE CONVERSION STEP

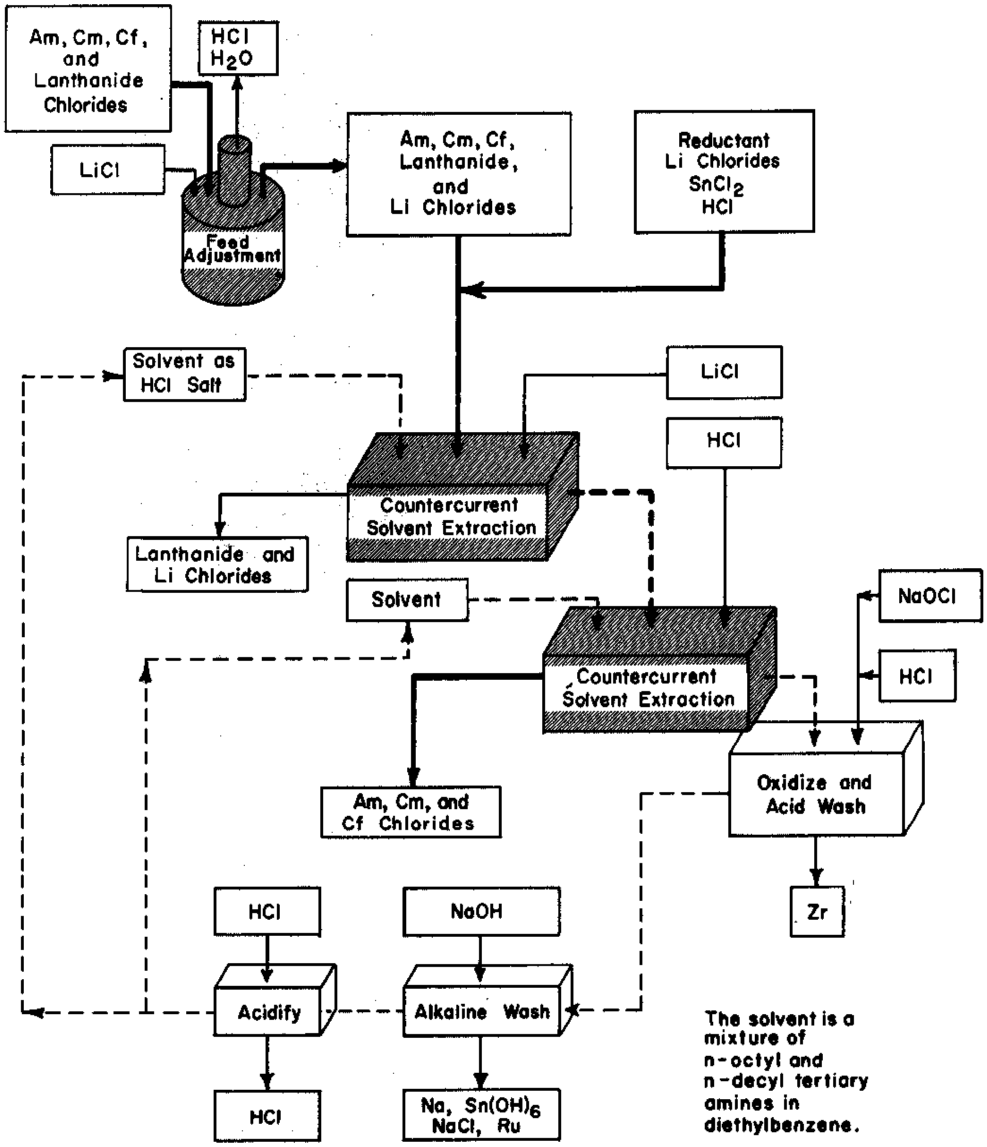


FIG. 2 LANTHANIDE REMOVAL STEP

DEGRADATION IN THE NITRATE-TO-CHLORIDE CONVERSION STEP

Test Conditions

Curium process solvent, 30 vol % tertiary amine in diethylbenzene (DEB), was mixed for 48 hours with an equal volume of an aqueous solution of the following composition to simulate the extraction banks of the nitrate-to-chloride conversion step:

$Al(NO_3)_3$	1.1M
$LiNO_3$	4.5M
HNO_3	0.2M
Cm	4.3×10^{10} dis/(min)(ml)
Ce	1.7×10^{9} dis/(min)(ml)

On the basis of the activity extracted into the organic phase and the exposure time, the solvent was calculated to have received a radiation dose of 26 watt-hr/liter. The actual radiation dose to solvent in the conversion step will be ~1 watt-hr/liter per cycle.

Identification of Degradation Products

Thin-layer chromatographic analysis of the solvent showed ~0.5 vol % each of primary and secondary amines. Thus, ~3% of the original tertiary amine mixture degraded under these conditions. The solvent was subsequently neutralized with dilute sodium hydroxide solution and analyzed by gas chromatography (GC).* Figure 3 shows two major components, labeled "A" and "B," that were not present in the original solvent. The concentrations of components A and B present were estimated at 2 and 12 vol %, respectively. In the following paragraphs, these components will be shown to be derived from DEB; thus, ~20% of the original DEB degraded under these conditions.

Component A was easily removed by washing the solvent with water, and its GC retention time was identical to that of ethanol. Therefore, component A was tentatively identified as ethanol from the alkaline hydrolysis of an ethyl ester. This identification was further supported by batch irradiation of DEB mixed with dilute nitric acid (112 watt-hr/l from ^{60}Co). Component A did not appear in GC analysis of the unwashed DEB, but did appear

---

* Direct GC analysis of the solvent in the nitrate form is complicated by reaction of the nitric acid with the amines in the gas chromatograph.

Conditions for Chromatograms

Column: 6 ft x ¼ in. OD, 5% silicone gum rubber (General Electric SE-30) on diatomaceous earth (120- to 140- mesh "Gas Chrom" Z from Applied Science Laboratories, Inc.)
Carrier Gas: Helium
Program: 9° C/min
Range: 100 to 235° C
Sample Aliquot: 1 μl

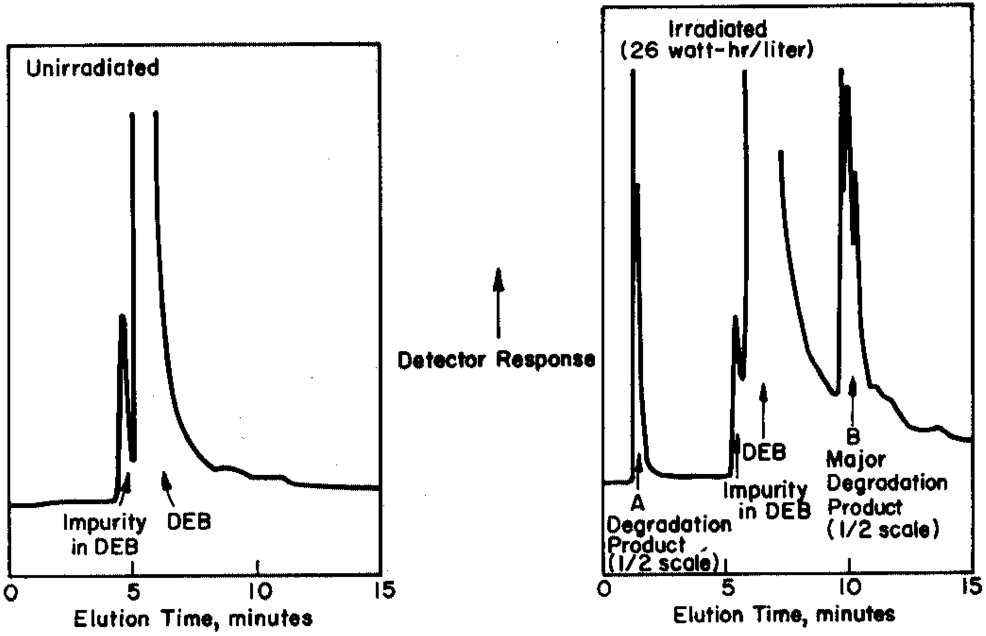


FIG. 3 GAS CHROMATOGRAMS OF CURIUM PROCESS SOLVENT

after washing with dilute NaOH. In addition, component A was detected in the NaOH solution that was used to wash the solvent.

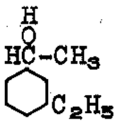
Component B was also produced on irradiation of the DEB-HNO$_3$ mixture with ^{60}Co. Subsequent analysis of the DEB on a column of "Apiezon" L* wax showed that component B was a mixture of at least three components. (The "Apiezon" L column has higher resolving power among alcohols, aldehydes, and ketones than does the SE-30 column used in Figure 3.) A typical gas chromatogram is shown in Figure 4. Comparison of the retention characteristics of the peaks on the SE-30 column with those on the "Apiezon" L column indicates that the peaks B$_A$, B$_B$, and B$_C$ were in the B region of the SE-30 chromatogram, whereas the peaks between DEB and B$_A$ probably were masked by the DEB peak on the SE-30 column and thus were not detected.

---

*"Apiezon" is a trademark of Metropolitan-Vickers Electrical Co., Ltd.

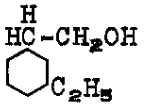
Because the B region represented the major degradation products, emphasis was placed on further identification of the B_A, B_B, and B_C peaks. The retention times of B_A, B_B, and B_C relative to that of DEB are shown in Table I. (The relative retention times of unknown compounds are customarily compared with those of known compounds to provide qualitative identification.) Although compounds I-IV below were not available, comparison of the relative retention times of similar compounds indicated that compounds I-IV would be expected to have relative retention times in the range covered by B_A, B_B, and B_C of Figure 4.*

I



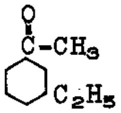
(Secondary Alcohol)

II



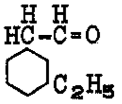
(Primary Alcohol)

III



(Ketone)

IV



(Aldehyde)

Additional identification of peaks B_A, B_B, and B_C was obtained by GC-IR analysis, in which each of these three fractions was collected separately from the gas chromatographic column into an internal-reflectance infrared cell, and the IR absorption spectra were measured. Each of the fractions showed IR absorption frequencies that were characteristic of an alkyl-substituted benzene compound. In addition, peaks B_B and B_C exhibited absorption frequencies (Table I) that are characteristic of aromatic carbonyls, probably ketones. The absence of functional group absorption in peak B_A does not preclude the presence of weakly absorbing groups, such as alcohols.

Chromatographic fractions also were collected directly on a thin-layer chromatographic (TLC) plate as separate spots, and their mobilities were compared with known compound types (GC-TLC analysis). On the basis of the relative mobilities (R_f) shown in Table I, B_A was identified as an aromatic alcohol, and B_B and

---

*Only the meta isomers are shown; the sample that was degraded was 90% meta-DEB. Concurrent work at ORNL with para-DEB showed that the para ketone corresponding to compound III was a principal degradation product.(3)

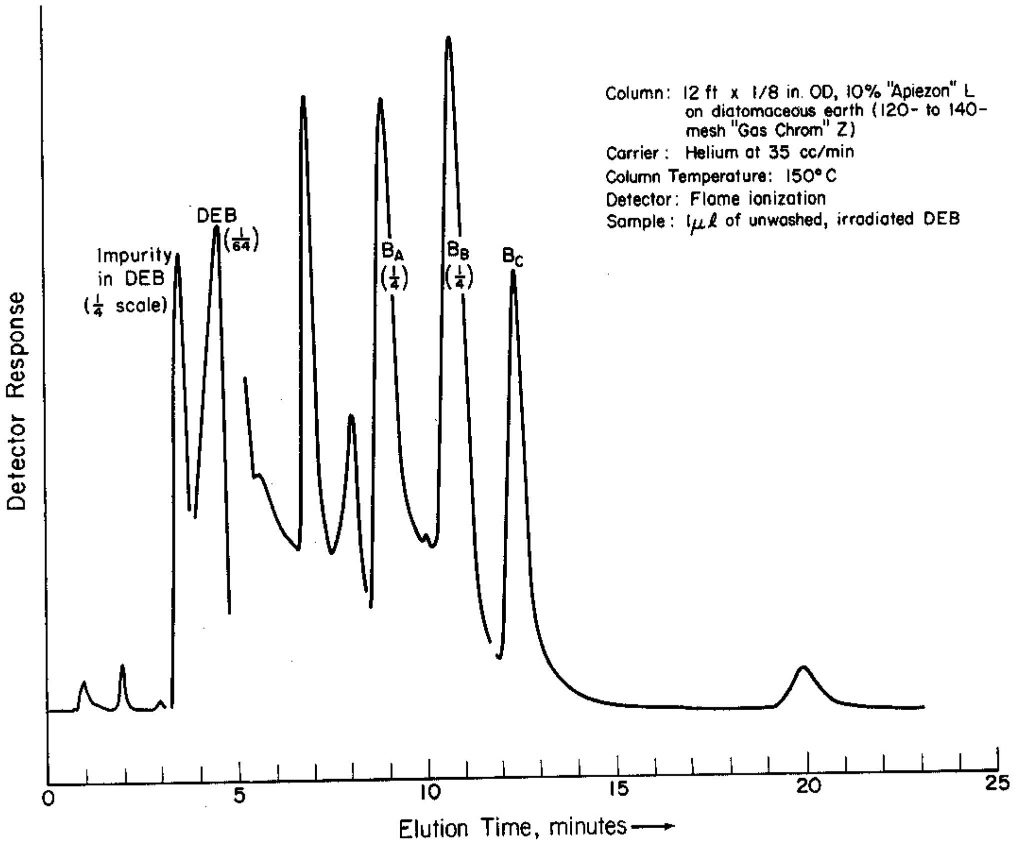


FIG. 4 GAS CHROMATOGRAM OF IRRADIATED DIETHYLBENZENE

TABLE I

Characteristics of Degradation Products of Diethylbenzene

Peak Designation (Figure 4)	GC Retention Ratio[(a)]	IR Absorption Frequency, cm^{-1}[(b)]	TLC Retention (R_f)[(c)]
B_A	2.0	None	0.35
B_B	2.4	1680, 1353, 1265	0.50
B_C	2.7	1680, 1353, 1265	0.42

(a) Ratio of retention time of peak over that of DEB on "Apiezon" L column at 150°C.

(b) In addition to those attributed to alkyl-substituted benzene skeletal frequencies.

(c) Component/benzene ratio of mobility on Eastman chromatogram sheet; type K301 silica gel with fluorescent indicator.

B_C as aromatic carbonyl compounds. The quantities of material were not large enough to permit removal of the TLC spot fractions for subsequent IR examinations.

Infrared analysis of specific fractions separated by the analytical separation scheme$^{(2)}$ revealed, in addition to aromatic carbonyl absorption bands, bands which were attributed to nitration products (Figure 5). These nitration products were present only in trace quantities.

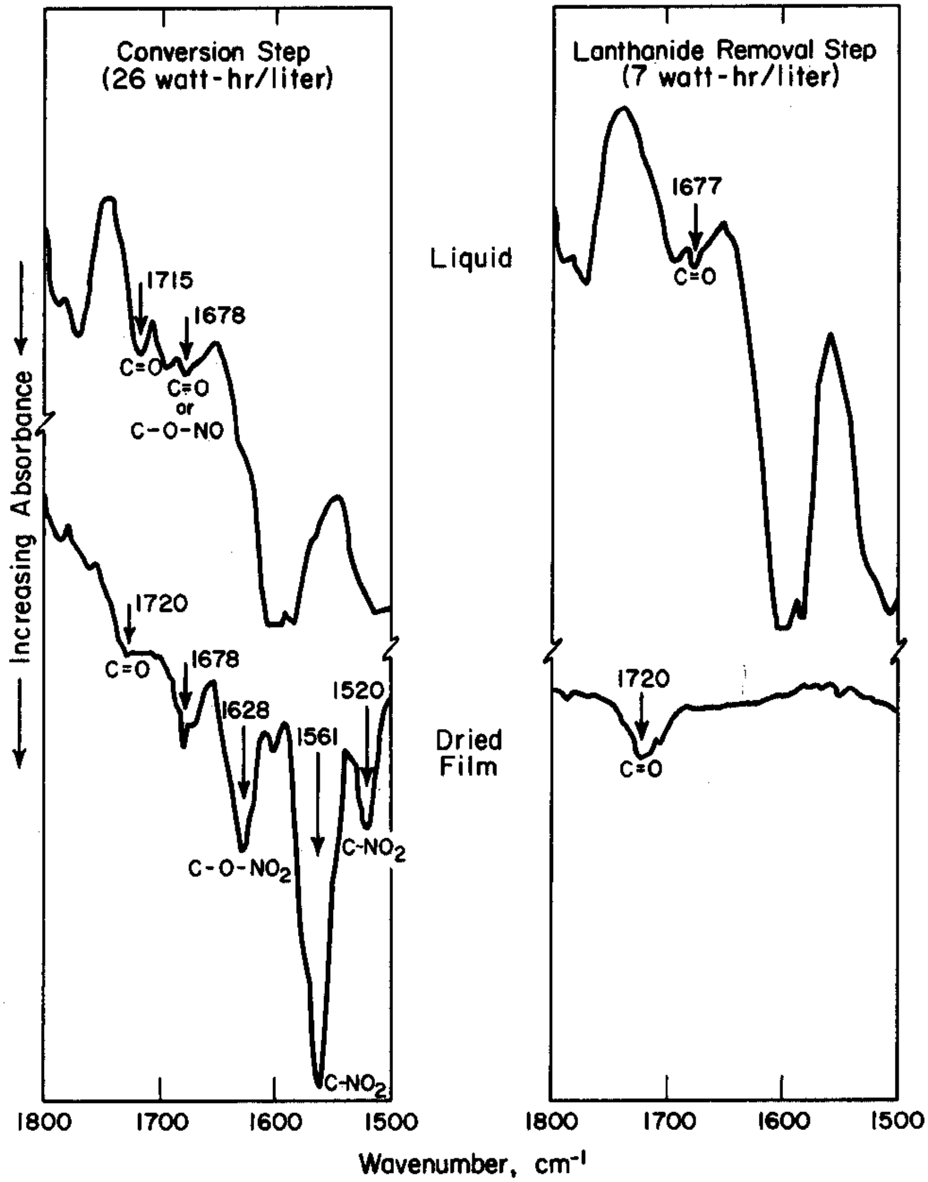


FIG. 5 INFRARED SPECTRA OF DEGRADED SOLVENT

In the absence of radiation, no degradation was detected when the solvent was exposed up to 17 hours to any of the chemical environments of the conversion cycle, including the wash steps.

Degradation Rates

The major degradation of solvent in the conversion step is radiation-induced oxidation. The degradation per unit exposure (watt-hr/l) is summarized in Table II. The rate of nitration was <0.01% nitration per watt-hr/l.

TABLE II

Degradation in Simulated Conversion Step

	% Degradation per watt-hr/l
Diethylbenzene	0.8
Tertiary amine	0.1

DEGRADATION IN THE LANTHANIDE REMOVAL STEP

Test Conditions

Curium process solvent was mixed with aqueous solutions that simulated the environment in the extraction banks during lanthanide removal. The solvent was mixed for 3 hours with an aqueous solution of the following composition:

LiCl	10.5M
HCl	0.07M
$SnCl_2$	0.05M
Cm	9.4×10^{10} dis/(min)(ml)

After the phases settled for 18 hours, the solvent was removed and mixed with 8M HCl for 3 hours. On the basis of the activity in the organic phase and the contact time, the solvent received a radiation dose of 7 watt-hr/l.

Identification of Degradation Products

GC and TLC analyses showed only aromatic oxidation products (components A and B) and primary and secondary amines. Infrared analysis showed only absorption bands which correspond to aromatic carbonyl compounds (Figure 5).

No significant degradation was detected on exposure of solvent to similar aqueous mixtures in the absence of radiation.

Extensive degradation of both the DEB and tertiary amines was observed when the solvent was contacted with a NaOCl-HCl mixture that simulated the wash step[1] employed in the lanthanide removal step. More than 10% of the tertiary amine degraded to secondary amines in a 24-hour period of contact. In addition, there was extensive (not measured) degradation of the DEB to produce oxidation products.

Degradation Rates

The rates of degradation in the lanthanide removal step (based on the primary and secondary amine products for tertiary amine degradation and oxidation products for DEB) are shown in Table III. The tertiary amines are more susceptible to degradation in the chloride matrix (lanthanide removal) than is the DEB; the opposite is true in the conversion step.

The relatively high degradation of the tertiary amines observed in the lanthanide removal step represents a maximum because the $SnCl_2$ was not replenished during the test and probably was depleted. In the presence of radiation, the hydrochloric acid is decomposed.

$$2HCl \xrightarrow{G \sim 2} H_2 + Cl_2$$

and

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

In addition, Sn^{2+} is oxidized in a radiation field; a G value of 1.25 was reported by Arnell[4] in a 0.8M HCl solution in the absence of oxygen. In the present test, the solution was stirred in the presence of air; therefore, the Sn^{2+} was probably depleted, leaving the solvent in an oxidizing medium. If a reducing medium were maintained by adding fresh Sn^{2+}, as it is under process conditions, solvent degradation should be negligible.

Although no rate measurements were made, extensive oxidative degradation was observed in the hypochlorite wash step. Because the NaOCl-HCl mixture is a strong oxidizing medium, it is probably a major cause of solvent degradation.

TABLE III

Degradation in the Lanthanide Removal Step

	% Degradation per watt-hr/l
Diethylbenzene	<0.07[(a)]
Tertiary amines	~1

(a) Value reported represents limit of analytical method; therefore, no aromatic degradation was detected.

EFFECT OF HYDRAZINE AS A DEGRADATION INHIBITOR

The major cause of solvent degradation in the conversion step is radiation-induced oxidation in the solvent extraction banks. Addition of 0.2M hydrazine reduced the DEB degradation from 0.8 to ~0.08% per watt-hr/l, as shown in Figure 6. No tertiary amine degradation was detected. On the basis of these experiments, the addition of hydrazine was included in the conversion step flowsheet. Demonstration of this modified flowsheet with miniature mixer-settlers will be described in a subsequent report in this series.

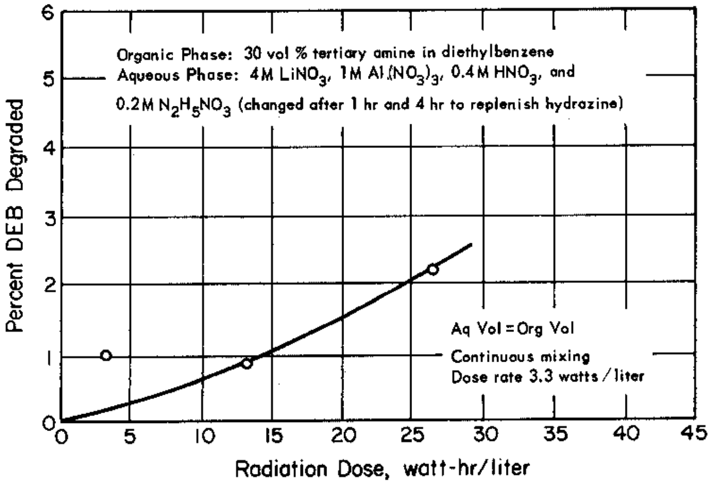


FIG. 6 RADIOLYSIS OF DIETHYLBENZENE IN PRESENCE OF HYDRAZINE