26

663772

DP-1215

AEC RESEARCH AND DEVELOPMENT REPORT

CURIUM PROCESS DEVELOPMENT

III-6. CHARACTERIZATION OF EMULSIONS FORMED IN CURIUM SOLVENT EXTRACTION

D.A. BROWN

A.L. MARSTON

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

663772

DP-1215

Chemistry
(TID-4500, UC-4)

CURIUM PROCESS DEVELOPMENT

III-6. CHARACTERIZATION OF EMULSIONS FORMED IN CURIUM SOLVENT EXTRACTION

by

D. A. Brown and A. L. Marston

Approved by

R. L. Folger, Research Manager
Analytical Chemistry Division

April 1970

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

Qualitative analysis of emulsions that formed in the mixer-settlers in the curium separations process causing poor hydraulic performance showed silica, aluminum, and lithium as inorganic impurities, and amides as organic impurities. Solids that might contribute to emulsion formation in feed solutions were also analyzed. Impurities, such as dodecylamine in the extractant or sodium silicate in the aqueous phase, increased disengaging times in laboratory tests. Efforts to form and classify emulsions in the laboratory as stable as those in the curium process were unsuccessful.

FOREWARD

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
IV. Equipment Development and Testing

Reports issued in this series include:

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

II-1. *Separation of Americium from Curium by Precipitation of* $K_3AmO_2(CO_3)_2$ by G. A. Burney (USAEC Report DP-1109).

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

III-2. *Identification of Solvent Degradation Products* by D. L. West and R. Narvaez (USAEC Report DP-1016).

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

III-4. *Evaluation of Potential Hazards from Chlorination of Amines and Ammonia* by D. L. West, M. L. Hyder, G. A. Burney, and W. E. Prout (USAEC Report DP-1142).

IV. *Equipment Development and Testing* by A. A. Kishbaugh, H. Bull, III, G. W. Gibson, Jr., and L. F. Landon (USAEC Report DP-1146).

CONTENTS

LIST OF TABLES

INTRODUCTION

The curium separations process with tertiary amine as the extractant was described previously.[1] In some curium processing campaigns, stable emulsions formed and caused poor hydraulic performance. No available published information was useful in avoiding this emulsion formation.

In a program to improve hydraulic performance:

- The process-formed emulsions were analyzed.
- The effect of impurities in used and unused extractant on disengaging time was determined.
- Attempts were made to form emulsions in the laboratory similar to those in the curium process and to classify these emulsions as organic dispersed in aqueous phase or water dispersed in organic phase.

SUMMARY

Properties of the emulsions formed in the curium separations process were determined by laboratory tests. Emission spectroscopy, thin-layer chromatography, and infrared analysis were used to qualitatively identify the components of the emulsions, but were not successful in defining their composition quantitatively. The emulsions contained silicon, aluminum, and lithium as major inorganic impurities and amides as organic impurities.

The effect on disengaging times of impurities in "Adogen" 364*-diethylbenzene (DEB) (the solvent) and of impurities in the aqueous phase contacted with the solvent was measured in laboratory tests. Silica and dodecylamine had a major effect on disengagement. A surfactant was found to shorten disengaging time.

Efforts to form emulsions in the laboratory as stable as those in the curium process were unsuccessful. The most stable laboratory emulsion (∿30 minutes lifetime) formed in 1% sodium silicate aqueous solutions contacted with solvent. This emulsion was classified as organic dispersed in aqueous phase. Other emulsions were too unstable to classify reliably.

---

* "Adogen" 364 is a mixture of n-octyl and n-decyltertiary amines.
"Adogen" is a trademark of Ashland Chemical Company, Columbus, Ohio.

DISCUSSION

ANALYSIS OF PROCESS EMULSIONS

The general properties of viscous emulsions formed in the mixer-settlers were determined in preliminary tests. Qualitative information about these emulsions is summarized in Table I, but their composition could not be defined.

TABLE I

Properties of Typical Emulsions and Solids from Curium Separations

	Formed During Feed Preparation	Formed During Mixer-Settler Operations
1st Cycle	5 vol % solids, SiO_2, in original feed. Removed by double filtration (between storage tank and evaporator, and between evaporator and feed tank).	Viscous, intractable emulsions. Probably caused by overconcentrated, acid-deficient feed. Cloudy viscous solvent followed contact with cold feed material.
2nd Cycle	Dark, flaky solid containing iron and zirconium (mostly corrosion products).	White, flocculent, interfacial emulsion flushed from 2A Bank (see Table II). Insoluble in diethylbenzene.
3rd Cycle	Gelatinous emulsion became granular on dilution. Insoluble in HCl. Contained silicon.	Silicon-containing emulsion that was dispersible or soluble in organic solvents such as diethylbenzene and $CHCl_3$.

During one period when emulsions and solids formed in the solvent extraction process, a representative sample was removed from the second cycle (2A Bank) and analyzed by emission spectroscopic, thin-layer chromatographic, and infrared spectroscopic techniques.

Emission Spectroscopy

A sample of the 2A emulsion was washed with water, diethylbenzene (DEB), and acid before analysis by emission spectroscopy (Table II). Silica was a major impurity. The 13M LiCl-4.5M LiOH solutions used in the process contained <0.05% silica. The silica apparently came from the curium feed because disengaging tests and analysis of cold feed were completely satisfactory. The curium feed was not analyzed. Neither the relative nor absolute amount of the major impurities was determined.

TABLE II

Emission Spectrographic Analyses of Curium Process Emulsions and Related Solutions

Source	Major	Minor	Trace
Emulsions			
Mixer-Settlers			
2A[a]	Si, Al, Fe, Li	Na, Am	Cr, Ni, Cm
2A-stage 9	Li		
2A-stage 11	Li	Si	
3A	Si, Li		
Feed Solutions			
3AF	Li, Na	Ta, Zr, Fe, Al	
3AF (unwashed)	Si, Li		
3AF (washed)[b]	Si		
Waste Evaporator	Si, Fe		Mn, Mg, Cr, Zr, Ta
Solutions			
2nd Cycle Cold Feed[c]			
4.5M LiOH	60 μg Si/ml		
13M LiCl	<6 μg Si/ml		

---

[a] This sample was also analyzed by TLC and IR spectroscopy.

[b] Before washing, the 3AF solid was gelatinous; after washing, it was granular.

[c] Analyzed to determine the source of silica in the 2nd cycle.

Thin-Layer Chromatography

Analysis of the emulsion in the 2A Bank by thin-layer chromatography (TLC) showed mostly tertiary amine and some amide. A chloroform extract of these emulsions showed a faint spot for tertiary amine and a much darker spot at the point of introduction. This dark spot was surrounded by a bleached, or undeveloped, area that is typical of acidic compounds. The spot may be caused by a highly polar compound or by one that cannot be dissolved and transported by the developing solution of $CHCl_3$, CH_3OH, and NH_3. It probably represents undissolved emulsion that was carried into the pipet with the $CHCl_3$ solution and then deposited on the TLC plate. Although $CHCl_3$ is one of the best TLC solvents, it did not completely dissolve the emulsion; therefore, only a partial analysis was possible.

Infrared Spectroscopy

An infrared (IR) spectrum of the process emulsion (dispersed in a KBr disk) indicated the presence of fatty amines and DEB, but water obscured the carbonyl region. Broad bands at 1050 cm^{-1} and 1500 cm^{-1} were not successfully assigned.

An IR spectrum of the emulsion dispersed in $CDCl_3$ showed an additional band at 1720 cm^{-1}, the carbonyl region. However, the remaining carbonyl region was obscured by $CDCl_3$ and DEB.

Dry nitrogen was bubbled through a vial of this solution to evaporate $CDCl_3$, volatile organic compounds, and water. After 3 days, small dry translucent solids appeared; these solids absorbed water rapidly when exposed to the air. Lithium, aluminum, and silicon salts are all hygroscopic.

The spectrum of this dry solid in KBr showed strong bands at 1730, 1350, and 1200 cm^{-1} and weak bands at 2900, 1430, and 1000 cm^{-1}. The weak C-H stretching bands at 2900 cm^{-1} indicated that little organic material was present. Assignment of other bands to complex inorganic ions was not completely satisfactory. The bands at 1730 and 1350 cm^{-1} might be oxalate, but the oxalate band at 800 cm^{-1} is missing. Furthermore, oxalate should not be in the process at this point. The broad band at 1000 cm^{-1} and that at 1200 cm^{-1} are not caused by $LiAlSiO_4$ or SiO_2 because other characteristic bands are missing.

X-ray powder analysis of the dry solid was unsuccessful because the high radiation of the sample blackened the film. A diffractometer scan on a tungsten planchet showed only tungsten background lines because the dry solid deliquesced rapidly.

ANALYSIS OF SOLVENT

Solvent Purity

Determination of Impurities

Impurities in solvents were investigated because they might cause slow phase disengagement or emulsion formation. One lot of "Adogen"-DEB contained more primary and secondary amines and carbonyl impurities than previous lots (Table III). These impurities did not inhibit phase disengagement in most cases. However, one drum of this solvent was in service during a major bank pluggage. The remainder of the drum contained 20 gal of solvent and 2 gal of emulsion, which was recovered by centrifugation. From 300 g of emulsion, 5.6 grams of dry white powder was recrystallized from ethanol, representing 0.15% of the solvent. IR and NMR spectra, CHN analysis, and Nitrox oxygen analysis indicate that the solid was a fatty secondary amide or imide.

TABLE III

Composition of Tertiary Amine Extractants

Extractant	Tertiary Amine Value[a]	% Primary Amines	% Secondary Amines	IR Absorbance (1750-1500 cm^{-1})[b]
Old "Adogen"				
When received	—[c]	<0.1	0.1-0.2	0.3
After >2 years storage	144	<0.1	<0.1	0.33
New "Adogen"	—[c]	0.1	0.3	0.7
"Alamine"*- 336	152	<0.1	<0.1	0.04

a. Inversely proportional to the molecular weight of the tertiary amine (mg KOH/g tertiary amine).

b. Indicative of carbonyl content.

c. Not determined.

* "Alamine," a registered trademark of General Mills for fatty amines, is an alternative extractant.

Effect of Impurities on Disengaging Times

Emulsions vary in color, viscosity, and behavior for minor changes in composition. The effect of impurities on emulsion properties was determined by simple disengaging tests with unused solvent and actual process feeds. Acceptable limits for disengaging times in actual process solutions are <30 sec for the first appearance of the aqueous layer and <90 sec for complete separation of the organic and aqueous phases. Disengaging times were measured in solvent from process solutions [with ditertiarybutylhydroquinone (DTBH), a reductant in the curium process] and in DTBH-free solvent from unused "Adogen." The presence of DTBH did not affect disengagement.

Impurities were added to unused solvent ("Adogen"-DEB) and the effect of these impurities on disengaging time was observed (Table IV). Inorganic impurities (0.15 g) were added to 5 ml of 10M LiCl-0.36M HCl aqueous solution before contact with the solvent. Organic impurities (0.15 g) were added to 15 ml of solvent acidified by equilibrating with 0.36M HCl. Disengaging tests showed that primary amine and sodium silicate impurities caused the longest disengaging times. To compare these disengaging times to those of process solvent, disengaging times for third cycle process solvent contacted with cold and radioactive third cycle aqueous feed solutions were measured (Table V). The process solvent first was acidified in the same manner as the impurity-containing laboratory solvent. No excessive disengaging times were observed even though both phases from the tests with radioactive feed (3AF tanks A and B) remained cloudy. No emulsions formed.

TABLE IV

Effect of Impurities on Disengaging Times of Unused "Adogen"-DEB Solutions and Aqueous Phases

Impurity Added	Disengaging Time, sec First Appearance of Aqueous	Complete Separation
None	10-15	45-60
Di-n-octylamine	15	60-70
Dodecylamine	>120	>120[a]
Octanoic acid	20	75
Nonamide	15	60-70
Amide mixture from "Adogen"	15	75
Sodium silicate solution	20	>120[b]
$ZrOCl_2 \cdot 8H_2O$	45	120
$SnCl_2 \cdot 2H_2O$	20	105

---

[a] Emulsion formed on stirring; 10-12 minutes for separation.

[b] Emulsion formed; ~8 minutes for complete separation, with slight additional stirring.

TABLE V

Disengaging Times for Third Cycle Process Solutions

Phases Contacted[a]		First Appearance of Aqueous, sec	Complete Separation, sec
Aqueous	Organic		
3AF (Cold)	3AX	33	88
3AF (Tank A)	3AX	24	66
3AF (Tank B)	3AX	8	32

a. In each test 5 ml of aqueous was mixed for 1 minute with 15 ml of organic.

In other laboratory tests, neutral solvent, when contacted with water or dilute HCl (∿0.4M), took longer to disengage and showed greater tendency to emulsify than acidified solvent contacted with acidified feeds. These tests indicate that emulsions in the mixer-settlers may be caused in part by acid deficiency. Finally, two immiscible organic phases formed when pure "Adogen" or an alternative extractant, "Alamine," as first equilibrated with 0.4M HCl. Infrared analyses and equilibration tests with acid showed that the phases were $R_3N{\cdot}HCl$ and R_3N. This two-phase effect was never observed during acidification of tertiary amine-DEB mixtures.

A surfactant to aid disengagement in tertiary amine extractants was recommended.[2] The surfactant FC-170* was tested with emulsion-forming impurities (Table VI). Addition of 50 ppm surfactant to the aqueous phase contacted with unused solvent shortened disengaging time and aided separation of the two phases for pure and impure solvent.

Disengagement of sodium silicate solutions was difficult to measure because a gel formed when 0.15 g of the Na_2SiO_3 solution was first added to 5 ml of the 11M LiCl-0.4M HCl solution. In most disengaging tests with these high levels of silica, emulsions formed regardless of the manner in which the impurity was added. In a few tests, the silica coagulated to form a gel, similar to that reported in 3AF tanks and the 3A bank.

---

* Product of Minnesota Mining & Manufacturing Co.

TABLE VI

Effect of Surfactant on Disengaging Times of "Adogen"-DEB Solutions and Aqueous Phases

		Disengaging Time, sec	
	Impurity Added	First Appearance of Aqueous	Complete Separation
No surfactant	None	10	60-75
	Dodecylamine	25	300-600[a]
	Amide mixture	15	65
	Sodium silicate solution	180	>600[a]
With surfactant[b]	None	10	45
	Dodecylamine	20-30	150
	Amide mixture	10	50
	Sodium silicate solution	120-180	>600

---

a. The difference between times shown for dodecylamine and sodium silicate in Tables IV and VI indicate the effect of stirring rate and impeller height when emulsification tendency is high.

b. 50 ppm FC-170 in aqueous phase.

Solvent Stability

Solvent stability was investigated because it might be a source of impurities in the extractant. A partially full drum of an old lot of "Adogen" was analyzed to test long-term storage stability under adverse conditions (Table III). This drum was probably stored in the open for two summers, with no blanket of nitrogen. This extractant still met specifications for tertiary amine, primary and secondary amine impurities, and IR-absorbing carbonyl impurities.

EXPERIMENTAL EMULSIONS

Preparation

Tests to form emulsions in the laboratory similar to those in the curium process and then to classify those emulsions were unsuccessful. The most stable laboratory emulsion (∿30 minutes lifetime) formed when ∿1% sodium silicate solution was contacted with solvent. Lower concentrations of sodium silicate solution (∿0.1%) gave even less stable emulsions (∿2 minutes lifetime).

Classification

One stable emulsion, prepared with excess sodium silicate, could be classified and was found to be organic-in-aqueous phase. All subsequent tests with lower concentrations of sodium silicate, or with dodecylamine or powdered graphite as additives, gave confusing results which indicated water-in-oil emulsions in all cases. None of these could be considered a stable emulsion.

Oil- and water-soluble dyes were used to classify the emulsions. The dyed phases were then inspected under a low power (10X) microscope.

A simple conductivity circuit could classify neutral water-in-oil emulsions, where no conductivity was observed, but could not classify water-in-oil emulsions when the organic phase contained acid salts, such as $R_3N \cdot HCl$.

REFERENCES

1. I. D. Eubanks and G. A. Burney. *Curium Process Development-I. General Process Description.* USAEC Report DP-1009, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1966).

2. R. D. Baybarz. Oak Ridge National Laboratory, personal communication (1969).