

805  
2/19/55  
2/18/55  
OER  
7-18-55

CENTRAL RESEARCH LIBRARY  
DOCUMENT COLLECTION

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES  
  
3 4456 0349837 4

Inv  
56

ORNL 1859  
Metallurgy-Raw Materials 5A

DECLASSIFIED

Classification Changed To:

Authority Of:

AEC 2-7-57  
H. H. K. R.

THE USE OF AMINES AS EXTRACTANTS FOR  
THORIUM (AND URANIUM) FROM SULFURIC  
ACID DIGESTS OF MONAZITE SANDS

D. J. Crouse  
J. O. Denis

Inv  
55

**CENTRAL RESEARCH LIBRARY  
DOCUMENT COLLECTION**

**LIBRARY LOAN COPY**

**DO NOT TRANSFER TO ANOTHER PERSON**

If you wish someone else to see this document,  
send in name with document and the library will  
arrange a loan.



OAK RIDGE NATIONAL LABORATORY  
OPERATED BY  
CARBIDE AND CARBON CHEMICALS COMPANY  
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION



POST OFFICE BOX P  
OAK RIDGE, TENNESSEE

~~RESTRICTED DATA~~  
~~This document contains Restricted Data as defined in the Atomic Energy Act of 1954. Its transmission or disclosure is prohibited by law.~~

~~SECRET~~

ORNL 1859

This document consists of 34 pages.  
This is copy 5 of 121, Series A.

Subject Category: Metallurgy-  
Raw Materials

THE USE OF AMINES AS EXTRACTANTS FOR  
THORIUM (AND URANIUM) FROM  
SULFURIC ACID DIGESTS OF MONAZITE SANDS

D. J. Crouse  
J. O. Denis

February 1, 1955

Date Issued

FEB 16 1955

URANIUM CHEMISTRY OF RAW MATERIALS SECTION  
K. B. Brown, Supervisor

MATERIALS CHEMISTRY DIVISION  
G. H. Clewett, Division Head

OAK RIDGE NATIONAL LABORATORY  
Operated by  
CARBIDE AND CARBON CHEMICALS COMPANY  
A Division of Union Carbide and Carbon Corporation  
Oak Ridge, Tennessee

Contract No. W-7405-eng-26

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES



3 4456 0349837 4

INTERNAL DISTRIBUTION

- |  |                                |
|--|--------------------------------|
| 1. C. E. Center                                | 39. R. S. Livingston           |
| 2. Biology Library                             | 40. T. A. Lincoln              |
| 3. Health Physics Library                      | 41. A. S. Householder          |
| 4-5. Central Research Library                  | 42. C. S. Harrill              |
| 6. Reactor Experimental<br>Engineering Library | 43. C. E. Winters              |
| 7-18. Laboratory Records Department            | 44. D. W. Cardwell             |
| 19. Laboratory Records, ORNL R.C.              | 45. E. M. King                 |
| 20. C. E. Larson                               | 46. A. J. Miller               |
| 21. L. B. Emlet (K-25)                         | 47. D. D. Cowen                |
| 22. J. P. Murray (Y-12)                        | 48. R. A. Charpie              |
| 23. A. M. Weinberg                             | 49. M. J. Skinner              |
| 24. E. H. Taylor                               | 50. S. J. Cromer               |
| 25. E. D. Shipley                              | 51. G. E. Boyd                 |
| 26. G. H. Clewett                              | 52. K. B. Brown                |
| 27. W. H. Jordan                               | 53. D. J. Crouse               |
| 28. F. C. VonderLage                           | 54. C. F. Baes                 |
| 29. J. A. Swartout                             | 55. J. G. Moore                |
| 30. S. C. Lind                                 | 56. C. A. Blake                |
| 31. F. L. Culler                               | 57. J. O. Denis                |
| 32. A. Hollaender                              | 58. H. M. McLeod               |
| 33. A. H. Snell                                | 59. R. W. Dodson (consultant)  |
| 34. M. T. Kelley                               | 60. H. Eyring (consultant)     |
| 35. J. A. Lane                                 | 61. J. W. Kennedy (consultant) |
| 36. K. Z. Morgan                               | 62. G. T. Seaborg (consultant) |
| 37. J. H. Frye, Jr.                            | 63. J. H. Rushton (consultant) |
| 38. C. P. Keim                                 | 64. J. Bigeleisen (consultant) |

EXTERNAL DISTRIBUTION

- 65. Allied Chemical & Dye Corporation
- 66-67. Argonne National Laboratory
- 68. Arthur D. Little, Inc.
- 69-70. Atomic Energy Commission, Washington
- 71. Battelle Memorial Institute
- 72. Bureau of Mines, Salt Lake City
- 73. Carbide and Carbon Chemicals Company (K-25 Plant)
- 74. Chicago Patent Group
- 75-76. Columbia University (Hassialis)
- 77-83. Division of Raw Materials, Washington
- 84. Dow Chemical Company, Pittsburgh
- 85-88. General Electric Company, Richland
- 89-92. Grand Junction Operations Office
- 93. Hanford Operations Office
- 94. International Minerals and Chemical Corporation

- 95. Iowa State College
- 96. Los Alamos Scientific Laboratory
- 97. Mallinckrodt Chemical Works
- 98-99. National Lead Company, Inc. (Winchester)
- 100. National Lead Company of Ohio
- 101. New Brunswick Laboratory
- 102. New York Operations Office
- 103. Patent Branch, Washington
- 104. Rohm and Haas Company
- 105. Tennessee Valley Authority (Walthall)
- 106. Texas City Chemicals, Inc.
- 107-108. U. S. Geological Survey
- 109. University of California Radiation Laboratory, Berkeley
- 110. Virginia-Carolina Chemicals, Inc.
- 111-120. Technical Information Service, Oak Ridge
- 121. Division of Research and Medicine, AEC, ORO

TABLE OF CONTENTS

	Page
I. INTRODUCTION. . . . .	1
II. DESCRIPTION OF COMPOUNDS. . . . .	3
III. EXPERIMENTAL. . . . .	5
A. Preparation Of The Leach Liquor. . . . .	5
B. Extraction Of Thorium. . . . .	6
C. Extraction Of Rare Earths. . . . .	10
D. Extraction Of Uranium. . . . .	12
E. Extraction Of Phosphate. . . . .	14
F. Thorium Loading. . . . .	14
G. Stripping The Organic Phase. . . . .	14
IV. PROPOSED FLOWSHEETS . . . . .	19
A. The Extraction System. . . . .	19
B. The Stripping System . . . . .	22
V. SUMMARY . . . . .	28
VI. ACKNOWLEDGEMENTS. . . . .	29
VII. REFERENCES. . . . .	30

## INTRODUCTION

Studies of methods for treating monazite sand to recover thorium as an extremely pure product and to recover the uranium and rare earths in a usable form were initiated several years ago at Ames Laboratory and at the Battelle Memorial Institute.<sup>(1)</sup> As an outcome of this work, two process schemes have been proposed.

The process developed by Ames Laboratory<sup>(1,2)</sup> consists of the following main steps:

- 1) Digestion of the ground monazite sand in 93% H<sub>2</sub>SO<sub>4</sub> at elevated temperature.
- 2) Dissolution of the solid reaction products in water and clarification of the leach solution.
- 3) Fractional precipitation by dilution and addition of NH<sub>4</sub>OH to give a thorium-rich fraction, a rare earths-rich fraction, and a uranium-rich fraction.
- 4) Dissolution of the thorium-rich fraction in HNO<sub>3</sub> and purification by solvent extraction with TBP.
- 5) Dissolution of the uranium-rich fraction in HNO<sub>3</sub> and purification by solvent extraction with TBP.

The above process has been demonstrated on a pilot plant scale, producing a thorium nitrate product which contained less than 4 ppm total rare earths.<sup>(2)</sup> The thorium-rich fraction used as feed to the TBP extraction system contained 24.3% ThO<sub>2</sub>, 22.0% total rare earth oxides, 20.6% P<sub>2</sub>O<sub>5</sub>, and 16.7% SO<sub>4</sub>. Thorium recovery in the extraction operation was 92%. Only 53-54% of the total uranium reported in the uranium-rich fraction obtained in the precipitation step.

In the Battelle process,<sup>(4)</sup> the monazite sand is first reacted with hot concentrated NaOH solution to dissolve the phosphate. The residue, consisting mainly of the hydrous oxides of Th, U, and the rare earths is then dissolved in HCl and the Th and U are separated from the bulk of the rare earths by selective hydroxide precipitations. Final separation and purification of the Th and U is made by dissolution of the Th-U fraction in HNO<sub>3</sub> and solvent extraction with TBP.

The New Brunswick Laboratory has investigated a number of variables in the Ames and Battelle processes and has suggested several modifications.<sup>(5,6)</sup>

Sometime ago, at this laboratory, interest was developed in the possibility of recovering thorium (and uranium) from sulfate liquors, as obtained in the Ames process, by solvent extraction methods. Initial tests were made with certain organophosphorus compounds as the extractants<sup>(7,8)</sup> and some of these gave successful extractions but difficulties were encountered in the stripping cycle. Studies of these compounds are continuing. More recently, however, the major interest has centered upon the use of long chain amines as the active extractant. Report ORNL-1734<sup>(9)</sup> describes studies by this laboratory on the use of amines as extractants for uranium from acidic sulfate liquors. In the course of this investigation, the extraction by 0.1M amine solutions of numerous other metal ions from 1.0M sulfate solutions was examined briefly. It was found that the primary amines extracted thorium very efficiently at pH 0.3, 0.9, and 1.7. Extraction of thorium by secondary amines was dependent on the structure of the alkyl chains. The straight chain secondary (dilauryl) had a low coefficient ( $\sim 3$ ) at pH 0.3 but a somewhat higher coefficient at pH 0.9\*. On the other hand, the highly branched secondary amine (C&C 15F53) extracted scarcely any thorium at pH 0.3 and 0.9 ( $E_{\text{ex}}^0 = 0.1$  or less) but showed some extraction at pH 1.7. The tertiary amines were very weak extractants ( $E_{\text{ex}}^0 = 0.2$  or less) for thorium at all pH levels tested.

The demonstrated ability of certain amines to extract thorium efficiently from sulfate solutions suggested the possibility of their use in a solvent extraction process for recovery of thorium from monazite liquors, such as those obtained in the Ames process. Therefore, a study was made of the apparent feasibility of such a process. The examination was of a preliminary nature, designed not to give complete evaluation of any specific process, but rather to determine whether more detailed development studies were justified. The general interest has been the separation of thorium from most of the rare earths, phosphate, and possibly uranium by simple solvent extraction operations. It was assumed that the thorium product would require further purification in a TBP solvent extraction system, although the possibility of achieving a metal grade thorium product by an amine extraction process has not been entirely eliminated from consideration.

In the data reported below, coefficients are shown for the extraction of thorium from the monazite sulfate liquor by several amines of representative types. Also the distribution of rare earths between the organic and aqueous phase, the separation of thorium from rare earths, uranium and phosphate, and the rate of rare earth-thorium exchange in the organic are reported for certain of the extractants. In

---

\*Erratum. Because of an analytical error, the coefficient at pH 0.9 is reported to be  $>300$  whereas rechecks at a later date indicate that the coefficient is approximately 10.

addition, several methods for stripping the thorium from the organic phase have been given a preliminary evaluation. All of the measurements were made by batch equilibration. Some postulated extraction-stripping flowsheets are presented even though sufficient data is not available for choosing the optimum process.

## II. DESCRIPTION OF COMPOUNDS

The amines discussed in this report were obtained from Rohm and Haas, Armour Chemical Division of Armour and Company, and Carbide and Carbon Chemicals Company. A list of the compounds and the suppliers is presented in Table 1. Of the reagents tested, only Primene JM-R\* is currently available in commercial quantities. Rohm and Haas Amine EB-765-2, Armeen 2-12, and tri(n-octyl)amine were supplied in relatively large lots (50-150 lb). The others were obtained as small samples. Even though all of the amines listed are, at present, not commercially available, it is believed that most of them could be made available at reasonable cost if a demand for them was demonstrated.

Each of the reagents tested, except Armeen 2-12, was used directly as received from the supplier. Of the group, tri(n-octyl)amine was the only reagent examined thoroughly as to compound purity. Indications of purity level are given for some of the other amines by the equivalent weight determinations shown in Table 1 but such measurements are of limited value in cases where the reagents are homologous mixtures, e.g., Primene JM-R, Compound 123, Armeen 2S, 2T, and probably R&H EB-765-2. From manufacturers' information and from measurements made here, the most probable composition of the reagents may be described briefly as follows:

Primene JM-R: A mixture of branched primary amines with an average of about 20 carbons per chain. The nitrogen is attached to a tertiary carbon. Average eq. wt. specified by manufacturer = 301; av. eq. wt. by titration = 313.

C&C Amine 21F81: A 17 carbon branched chain primary amine apparently containing some inert impurities. Eq. wt. from formula = 255; eq. wt. from titration = 288.

---

\*Price of Primene JM-R in quantity is approximately 70¢/lb; a less pure form (not redistilled) Primene JM-T sells for 50¢/lb.

Table 1

AMINE COMPOUNDS

<u>Amine</u>	<u>Type</u>	<u>Equivalent Weight*</u>	<u>Structure</u>	<u>Manufacturer</u>
Primene JM-R	Primary	313	Branched, saturated	Rohm & Haas
C&C Amine 21F81	"	288	" "	Carbide
Compound 123	Secondary	360	Straight chain, saturated	Armour
Armeen 2S	"	560	" " unsaturated	"
Armeen 2T	"	550	" " "	"
Amine EB-765-2	"	378	Branched, unsaturated	Rohm & Haas
Di(2-butyloctyl)	"	364	Branched, saturated	Carbide
Amine 15F53	"	274	Branched, saturated	"
Tri(n-octyl)	Tertiary	354	Straight chain, saturated	"

\*Equivalent weight determined by non-aqueous titration.

Compound 123: Center portion of the major fraction obtained by distilling Armeen 2-12\*. Probably contains mostly dilaurylamine together with mixed secondary amines of about the same molecular weight and boiling points as dilauryl. Eq. wt. for dilaurylamine by formula = 354; eq. wt. for Compound 123 by titration = 360.

Armeen 2S: A mixture of unsaturated, straight chain secondary amines containing a small amount of primary amines (85% secondary and 5% primary according to manufacturer's data). Average eq. wt. specified by manufacturer = 520-540; average eq. wt. by titration = 560. (Alkyls are derived from soy bean oil.)

Armeen 2T: A mixture of unsaturated, straight chain secondary amines containing a small amount of primary amines (85% secondary and 5% primary according to manufacturer's data). Average eq. wt. specified by manufacturer = 520-540; average eq. wt. by titration = 550. (Alkyls are derived from tallow.)

R&H Amine EB-765-2: A mixture of secondary amines with one highly branched alkyl chain in which a tertiary carbon is attached to the amine group; the other hydrocarbon chain is highly branched and unsaturated. Average eq. wt. specified by manufacturer = 375; average eq. wt. by titration = 378.

Di(2-butyloctyl)amine: Eq. wt. from formula = 354; eq. wt. by titration = 364.

C&C Amine 15F53: Secondary amine with branched alkyl chains of 9 carbon atoms each. Some branching occurs on the carbons adjacent to the nitrogen. Eq. wt. from formula = 270; eq. wt. by titration = 274.

Tri(n-octyl)amine: Greater than 99% tertiary amine by differential titration.<sup>(10)</sup> Eq. wt. from formula = 354; eq. wt. by titration = 354.

### III. EXPERIMENTAL

#### A. Preparation Of The Leach Liquor

The monazite liquor used in these experiments was prepared from Indian monazite sands\*\* in a manner approximating

---

\*Armeen 2-12 is a mixture of straight chain secondary amines supplied by Armour, estimated to contain 85% secondary and 3% primary amines. (Alkyl chains derived from coconut oil.)

\*\*Purchased from Foote Mineral Company in November 1947.

that recommended by Ames Laboratory.<sup>(1)</sup> The procedure was as follows:

300 gms of the sand was added slowly to 462 gms 93%  $H_2SO_4$  in a 4 liter beaker heated to  $150^{\circ}C$  with a Glas-Col heating mantle. The reaction mixture was agitated by a glass stirrer driven by a Ful-Tork Lab Motor. After addition of the sands the temperature was raised to  $200^{\circ}C$  and the digestion continued for two hours. The stirrer was employed until the digest mixture became too viscous for further agitation. After digestion the mixture was cooled to room temperature and ~~added~~ slowly with three liters of water. As soon as sufficient water was added to soften the mixture, stirring was started and continued for one hour. After an 18 hour ageing period, the slurry was filtered. Celite was used to increase the filtration rate and improve the clarity of the filtrate.

The above procedure was performed six times to give a combined volume of 18 liters of liquor. Analysis of the liquor is listed in Table 2.

#### B. Extraction Of Thorium

Table 3 presents results for the extraction of thorium from monazite liquor by several different amines\* in hydrocarbon diluents. In each test the aqueous and organic phases were shaken together in a separatory funnel for two minutes and allowed to separate. The thorium concentration in each phase was then determined by chemical and spectrographic methods.

The long chain primary amines proved to be extremely efficient extractants for thorium from the monazite liquor, i.e., 0.1M solutions of these amines gave extraction coefficients greater than 70. Little, if any, difference was noted in the performance of the two particular primary amines tested. Except for C&C Amine 15F53 (a highly branched secondary amine with branching close to the nitrogen) some extraction was also achieved with the secondary amines although the extraction coefficients at identical reagent concentrations were much lower than those with the primaries. As expected, practically no thorium was extracted with tri(n-octyl)amine.

---

\*Except as otherwise indicated, the amine was converted to the sulfate salt form before use in the extraction tests, by prior contact with an acidic sulfate solution (0.5M  $Na_2SO_4$ , 0.5M  $H_2SO_4$ ). This was done to avoid the rise in  $\bar{p}H$  and possible precipitation of metal salts which would result from contact of the acidic liquor with basic free amine in experimental tests where the organic to aqueous ratios were extreme. It is not anticipated that such pretreatment would be necessary in a process operation.

Table 2  
ANALYSIS OF MONAZITE LEACH LIQUOR

	Analysis (g/l)	
	<u>Chemical</u>	<u>Spectrographic</u>
ThO <sub>2</sub>	7.2	6.8
Total rare earth oxides (including Ce <sub>2</sub> O <sub>3</sub> )	44.2	---
Ce <sub>2</sub> O <sub>3</sub>	21.9	19
La <sub>2</sub> O <sub>3</sub>	----	10
Pr <sub>2</sub> O <sub>3</sub>	----	2
Nd <sub>2</sub> O <sub>3</sub>	----	8
Sm <sub>2</sub> O <sub>3</sub>	----	1.5
U <sub>3</sub> O <sub>8</sub>	0.2	---
SO <sub>4</sub>	129	---
PO <sub>4</sub>	28	---

---

The liquor had a pH of 0.05 and a specific gravity of 1.145 at 25°C.

Table 3

## EXTRACTION OF THORIUM FROM MONAZITE LIQUOR WITH AMINES

Amine	Amine Type	Amine Conc.	Diluent	Liquor pH	Phase Sep'n. Time (sec)	Th Extraction Coeff., $E_a^O$
C&C Amine 21F81	Primary	0.1M	Amsco D-95	0.05	45	>70
" " "	"	0.2	" "	"	35	>140
Primene JM-R	"	0.1	" "	"	50	>70
" "	"	0.2	" "	"	50	>140
" "	"	"	Kerosene	"	120	>140
" "	"	"	95% kerosene - 5% capryl alcohol	"	90	>140
" "	"	"	Amsco G	"	120	>140
Armeen 2T***	Secondary	0.1	" "	0.05	135	0.5
" "	"	"	" "	0.2*	135	1.9
Armeen 2S***	"	"	" "	0.05	120	0.9
" "	"	"	" "	0.2*	120	2.4
Compound 123***	"	"	Amsco D-95	0.05	35	0.7**
" "	"	"	" "	0.2*	35	2.1**
R&H Amine EB-765-2	"	"	Kerosene	0.05	55	0.16
" " "	"	0.2	"	"	75	0.3
Di(2-butyl-octyl)	"	"	95% kerosene - 5% capryl alcohol	"	60	1.8
C&C Amine 15F53	"	0.1	Amsco D-95	"	25	<0.05
Tri(n-octyl)	Tertiary	0.2	95% kerosene - 5% capryl alcohol	"	75	<0.05

!  
∞  
!

Table 3 (Cont'd.)

EXTRACTION OF THORIUM FROM MONAZITE LIQUOR WITH AMINES

Extraction Conditions:

Phase ratio: 3<sup>o</sup>:1<sup>a</sup> for extractions with 0.1M amine solutions.  
1.5<sup>o</sup>:1<sup>a</sup> for extractions with 0.2M amine solutions.

Temperature: R. T.

Contact time: 2 minutes.

\*Extraction from a leach liquor which had been raised to pH 0.2 with NH<sub>4</sub>OH and filtered to remove the precipitated thorium. The thorium concentration in the liquor was then 4.3 g/l.

\*\*Extractions performed at 45°C to avoid precipitation of the amine salt from the organic phase due to solubility limitations of this particular amine in the hydrocarbon diluents.

\*\*\*Amine solution was not pre-treated with an acidic sulfate solution.

Since the extractive power of the secondary amines for thorium had, in previous tests<sup>(9)</sup> proved to be dependent on pH, some studies were made with these reagents on a monazite liquor which had been partially neutralized prior to extraction. In these tests, the pH of the liquor was raised with  $\text{NH}_4\text{OH}$  from its original value of 0.05 up to 0.2 at which point approximately 25% of the thorium precipitated and was filtered off. Extraction coefficients for thorium from the filtrate by three different secondary amines are shown in Table 3. The coefficients were improved by the increase in pH but were still fairly low, i.e.,  $E_a^0 = \sim 2$  for 0.1M reagent.

Several different commercial solvents were employed as diluents in the experiments described above. (In some instances the choice of diluent was dictated by the structure of the amine being tested. A more detailed discussion of the problem of diluent choice is presented in report ORNL-1734.) In the case of Primene JM-R, where one-to-one comparisons were possible, the extraction coefficients were the same with Amsco D-95\*, Amsco G\*, or kerosene as the diluent. Addition of 5% by volume of capryl alcohol to the kerosene diluent improved the phase separation rate and the clarity of the organic extract.

### C. Extraction Of Rare Earths

Rare earth extractions from the monazite sulfate liquor were measured with two primary amines and one secondary amine, 0.2M in kerosene diluent. In order to eliminate competition by Thorium, the extractions were performed with liquor from which all the thorium had been removed by prior extraction with Primene JM-R. Test results are listed in Table 4. With primary amines, it may be noted, the rare earth extractions were appreciable; extraction coefficients were not calculated since, under the conditions of the test, the extraction values were probably severely limited by loading of the organic amine reagent. With the secondary amine, the extractions were extremely low, e.g., a 0.2M solution of di(2-butyloctyl)amine extracted <0.2 g/l total rare earth oxide. In this case, extraction coefficients were also not calculated since the quantities of rare earths extracted were below the limits of detection by the chemical analyses. Extractions of rare earths with tri(n-octyl)amine (not shown in table) were also negligible.

Although true coefficients for extraction of rare earths by primary amines were not obtained from the above tests, it is obvious from Table 3 that these coefficients are relatively low when compared to those for thorium; otherwise, the very

---

\*Petroleum products of high aromaticity.

Table 4

EXTRACTION OF RARE EARTHS FROM MONAZITE LIQUOR RAFFINATE\*

		Analysis - g/l											
		Aqueous					Organic						
		Chemical	Spectrographic				Chemical	Spectrographic					
Amine	Diluent**	Total Rare Earth Oxides	La <sub>2</sub> O <sub>3</sub>	Ce <sub>2</sub> O <sub>3</sub>	Pr <sub>2</sub> O <sub>3</sub>	Nd <sub>2</sub> O <sub>3</sub>	Sm <sub>2</sub> O <sub>3</sub>	Total Rare Earth Oxides	La <sub>2</sub> O <sub>3</sub>	Ce <sub>2</sub> O <sub>3</sub>	Pr <sub>2</sub> O <sub>3</sub>	Nd <sub>2</sub> O <sub>3</sub>	Sm <sub>2</sub> O <sub>3</sub>
Primene JM-R	Kerosene	30.5	6.3	12.2	0.9	4.0	0.6	8.6	1.3	3.4	0.3	0.9	0.07
" "	95% Kerosene - 5% capryl alcohol	34.0	7.1	12.6	0.9	4.0	0.6	4.5	0.7	2.1	0.2	0.5	0.05
C&C Amine 21F81	Kerosene	32.4	7.0	13.7	1.4	4.4	0.7	4.4	1.1	2.6	0.2	0.7	0.07
" " "	95% Kerosene - 5% capryl alcohol	34.1	6.1	11.9	0.7	3.4	0.6	4.7	0.7	2.1	0.2	0.5	0.05
Di(2-butyloctyl)	Kerosene	41.6	7.6	15.3	1.2	4.2	0.9	<0.2	---	---	---	---	----
" " "	95% Kerosene - 5% capryl alcohol	40.1	7.8	15.6	1.4	4.9	0.9	<0.2	---	---	---	---	----

-11-

\*Prepared by extraction of monazite liquor with 0.2M Primene JM-R in Amsco G to give a raffinate containing <0.03 g/l Th. Total rare earth oxides in the raffinate were 40.8 g/l (By chemical analysis).

Extraction Conditions:

Amine concentration: 0.2M  
Phase ratio: 1.5<sup>o</sup>:1<sup>a</sup>  
Temperature: R.T.  
Contact time: 2 minutes

efficient extraction of thorium by these amines could not have been realized from a liquor in which the mole ratio of total rare earths to thorium is approximately 10. Hence, even though the primary amines extract appreciable amounts of rare earths when thorium is not present, it is possible to take advantage of the large difference in coefficients (i.e., limit the rare earth contamination of the extract) by loading the organic phase with thorium to a concentration near its saturation value. This is illustrated in Table 5 for Primene JM-R and C&C Amine 21F81. For example, in tests with the latter reagent, the total concentration of Ce and La in the organic extract was decreased from 1.8 g/l to <0.18 g/l as the thorium concentration in the extract was increased from 3.1 to 6.0 g/l.

In considering the use of primary amines in a counter-current extraction process, it is evident then that, in the lower stages of the system (regions of negligible thorium concentration), the organic phase will become loaded with rare earths, the loading level being dependent upon operational conditions. As it passes to regions of higher thorium concentration, the rare earths will be removed from the organic phase by replacement with the more readily extracted thorium. The required holdup time in the extraction system, and thus the relative success of the operation, will be largely determined by the rate of the rare earths and thorium exchange. For this reason, tests were made in which rare earths were first extracted from a thorium free liquor raffinate into a 0.2M solution of Primene JM-R in kerosene. Subsequently, samples of this extract, containing 6.2 g/l total rare earth oxides (chemical analysis), were shaken in a separatory funnel with an equal volume of the monazite liquor for 2, 5, and 10 minute periods. Spectrographic analysis of the organic phases showed that, in each case, the Ce and La concentrations in the extract were below the limit of spectrographic analyses (<150 ppm Ce, <100 ppm La) and that the thorium extraction coefficients were essentially the same after each time interval. The replacement of the rare earths in the extract by thorium was, then, essentially complete within two minutes time, and control of selectivity by high thorium loading of the organic phase is feasible in a countercurrent extraction system.

Scrubbing with  $H_2SO_4$  could be utilized to further purify the organic extract although a study of the efficiency of this operation has not as yet been made. Also, it may be noted from Table 4 that the addition of capryl alcohol to the diluent appeared to depress the rare earth extractions.

#### D. Extraction of Uranium

Because of analytical uncertainties, accurate uranium extraction coefficients were not determined. However, rough

Table 5

EFFECT OF Th LOADING ON SELECTIVITY OF AMINES

Amine	Amine Conc.	Phase Ratio org/aq	Raffinate	Organic Phase			Decontamination Factor***
			(g/l) Th*	Th	Ce**	La**	
C&C Amine 21F81	0.1M	3	<0.03	2.1	0.46	0.14	14
" " "	"	2	0.43	3.1	<0.12	<0.06	>70
" " "	0.2M	2	<0.03	3.1	1.40	0.44	7
" " "	"	1.5	<0.03	4.2	0.82	0.26	16
" " "	"	1	0.33	6.0	<0.12	<0.06	>130
Primene JM-R	0.2M	2	<0.03	3.1	1.28	0.34	8
" " "	"	1.5	<0.03	4.4	0.48	0.15	30
" " "	"	1	1.05	5.8	<0.4	<0.2	>40

\*Chemical and spectrographic analysis.

\*\*Spectrographic analysis (as metal).

$\frac{[(Ce + La)/Th]}{[(Ce + La)/Th]}$  in head liquor

\*\*\*  $\frac{[(Ce + La)/Th]}{[(Ce + La)/Th]}$  in extract

Extraction conditions: Diluent - Amsco D-95  
 Temperature - R. T.  
 Contact time - 2 minutes.

estimates of the coefficients were obtained and these are presented in Table 6. Rohm and Haas Amine EB-765-2 and tri(n-octyl)amine, which were very weak extractants for thorium, showed moderately high extraction coefficients for uranium. Extraction of uranium by the primary amine, Primene JM-R, was essentially nil, undoubtedly due to competition from thorium (and rare earths) which were present in much higher concentration than the uranium.

Extraction of uranium with tri(n-octyl)amine was found to be valuable for analytical purposes in determining the uranium content of monazite head liquors or raffinates.

#### E. Extraction of Phosphate

An effective separation of thorium from phosphate was achieved in the amine extractions. A 0.2M solution of Primene JM-R in Amsco G, after contact with an equal volume of the monazite liquor, contained 5.8 g/l Th and only 0.04 g/l  $PO_4$ .

#### F. Thorium Loading

The thorium loading characteristics of Primene JM-R in kerosene were studied by contacting 0.1M and 0.2M solutions of this amine with successive volumes of monazite liquor until the thorium analysis of the raffinate became essentially equal to that of the head solution. With the particular liquor studied (Table 2), the maximum loadings were  $\sim 2.9$  g/l Th in the 0.1M amine solution and  $\sim 5.8$  g/l Th in the 0.2M solutions. This corresponds to an amine to thorium mole ratio in the organic phase of approximately 8.

#### G. Stripping The Organic Phase

Thorium was stripped effectively by treatment of the pregnant organic phase with nitric acid, nitric acid plus nitrate salt, or solutions of basic reagents such as  $Na_2CO_3$ , NaOH, or  $NH_4OH$ . Results of the stripping tests are presented in Tables 7 and 8.

Use of hydroxides results in direct precipitation of the thorium. Simultaneously, the amine sulfate and bisulfate salts are converted to free amine which can then be directly recycled to the extraction system. Treatment with  $Na_2CO_3$  solutions also results in the formation of free amine but the thorium, in this case, is taken into the aqueous phase as the soluble carbonate complex and most of any rare earths present are precipitated as their insoluble carbonate salts. In some of the tests in Table 7, the solubilities of thorium in the carbonate solutions were exceeded and considerable precipitation occurred.

Table 6

EXTRACTION OF URANIUM FROM MONAZITE LIQUOR

<u>Amine</u>	<u>Amine Type</u>	<u>Amine Conc. (M)</u>	<u>Diluent</u>	<u>Phase Ratio org/aq</u>	<u>Approximate Uranium Extraction Coefficient</u>
Primene JM-R	Primary	0.2	Kerosene	1.5	<0.1
" "	"	"	"	1	<0.1
R&H Amine EB-765-2	Secondary	0.1	"	3	4
Tri(n-octyl)	Tertiary	0.2	95% Kerosene - 5% capryl alcohol	3	7
" "	"	"	" " "	3	9*
" "	"	"	" " "	3	7**

\*Monazite head liquor spiked with U to 0.3 g U/l.

\*\* " " " " " " " " 0.5 g U/l.

Extraction Conditions: Aqueous: Monazite liquor, U = 0.18 g/l.  
 Temperature: R.T.  
 Contact time: 2 minutes.

Table 7

STRIPPING THORIUM FROM PRIMENE JM-R

Stripping Solution	Pregnant Organic Solution	Phase Ratio Org/Aq	Thorium Analysis (g/l)		Th Stripping Coeff., $S_{\text{O}}^a$	Remarks
			Aq.	Org.		
1.0M HNO <sub>3</sub>	A	1	5.5	<0.03	>150	Rapid phase separation
" "	"	3	14.0	0.7	20	" " "
" "	"	5	15.0	2.0	7	" " "
" "	"	8	15.3	2.9	5	" " "
2.0M "	"	5	----	0.05	>99% Stripped	Th ppt'n. from solution on standing
3.0M "	"	5	----	<0.03	"	" " " " " "
50% NaOH***	"	35	----	<0.03	"	(1)
10% NaOH	"	7	----	<0.03	"	(2)
2% NaOH	"	1.4	Emulsion		---	Phase separation difficult
8% Na <sub>2</sub> CO <sub>3</sub>	B	2	8.5*	<0.03	>99% Stripped	3% of the total Th precipitated**
" "	"	5	13.9*	1.9	57% Stripped	39% " " " " "
12% "	"	3	12.5*	<0.03	>99% Stripped	5% " " " " "
" "	"	7.5	19.0*	1.8	59% Stripped	32% " " " " "
16% "	"	4	17.6*	<0.03	>99% Stripped	0% " " " " "
" "	"	10	17.9*	2.1	52% Stripped	11% " " " " "

Table 7 (Cont'd.)

STRIPPING THORIUM FROM PRIMENE JM-R

\*Analysis of the aqueous after filtration to remove precipitate. The precipitate did not collect at the interface but settled rapidly in the aqueous phase.

\*\*Based on analysis of the head organic. The % thorium precipitated is included in the % thorium stripped.

\*\*\*Concentrations expressed in % are on a weight-volume basis.

- (1) Wet precipitate settled into  $\sim 1/4$  of the organic volume in 3 minutes leaving a clear supernatant organic. No distinct aqueous phase was visible.
- (2) The precipitate was dispersed in both the organic and aqueous phases.

Extraction Conditions:

Pregnant organic Solution A: 0.2M Primene JM-R in Amsco D-95 loaded to  $\sim 4.8$  g/l Th by extraction from monazite liquor.

Pregnant organic Solution B: 0.2M Primene JM-R in Amsco G loaded to  $\sim 4.4$  g/l Th by extraction from monazite liquor.

Temperature: R.T.

Contact time: 2 minutes.

Table 8

STRIPPING OF THORIUM FROM PRIMENE JM-R WITH ACIDIC NITRATE SOLUTIONS

<u>Stripping Solution</u>	<u>Phase Ratio Org/Aq</u>	<u>Final pH of Aqueous</u>	<u>Analysis (g/l)</u>						<u>Thorium Stripping Coefficient S<sub>0</sub></u>
			<u>Aqueous</u>			<u>Organic</u>			
			<u>Th</u>	<u>SO<sub>4</sub></u>	<u>NO<sub>3</sub></u>	<u>Th</u>	<u>SO<sub>4</sub></u>	<u>NO<sub>3</sub></u>	
0.2M HNO <sub>3</sub> - 0.8M NH <sub>4</sub> NO <sub>3</sub>	4	0.85	11.7	29.4	35	2.6	6.9	5.6	4.5
" " " "	5	0.86	12.8	31.5	29	2.8	7.6	4.8	4.5
0.2M HNO <sub>3</sub> - 1.8M NH <sub>4</sub> NO <sub>3</sub>	8	0.90	28.8	71.7	55	1.9	5.0	6.6	15
" " " "	10	0.92	31.1	78.2	52	2.4	6.4	6.0	13
0.2M HNO <sub>3</sub> - 2.8M NH <sub>4</sub> NO <sub>3</sub>	12	0.92	46.7	122	70	1.2	4.0	7.3	39
" " " "	15	0.99	51.2	126	58	1.6	5.3	6.2	32

Stripping Conditions: Head organic: 0.2M Primene JM-R in kerosene loaded to 5.4 g/l Th and 13.4 g/l SO<sub>4</sub>.  
 Temperature: R.T.  
 Contact time: 2 minutes.

When nitric acid or acidic nitrate solutions are employed for stripping, the amine nitrate salt is formed. Direct recycle of the reagent in this form would introduce nitrate ions into the extraction system causing a severe loss of extraction efficiency. Hence, it would be necessary to regenerate the free amine before recycling by treatment with a base. The nitrate salt formed in the regeneration step could then be utilized for further stripping.\* Table 8 shows the distribution of thorium, sulfate, and nitrate between the aqueous and organic phases when acidic nitrate solutions were employed for stripping. Solutions reasonably concentrated in thorium (50 g/l) were obtained by this stripping method. The organic extract used in this test contained six moles of sulfate per mole of thorium. It is interesting to note that the sulfate and thorium reporting to the stripping solutions is close to this same ratio even in cases where only partial stripping was achieved.

#### IV. PROPOSED FLOWSHEETS

Based on the data presented above, and other data accumulated in previous amine studies, a number of flowsheets have been postulated for the recovery of thorium (and uranium) from monazite liquors. A diagram of a general overall extraction-stripping process is presented in Figure A. The other figures (B, C, and D) show some possible variations in the method used to recover thorium from the organic extract. It must be remembered that the suggested flowsheets have not been examined in detail and, therefore, should not be considered as established processes but rather as process proposals which appear chemically sound and operationally feasible based on experimental data obtained thus far. No choice has been made between the various stripping methods suggested. Each alternative seems to possess at least one advantage not common to the others, and the proper choice could be made only after a more critical examination of reagent consumption and operational characteristics of each process.

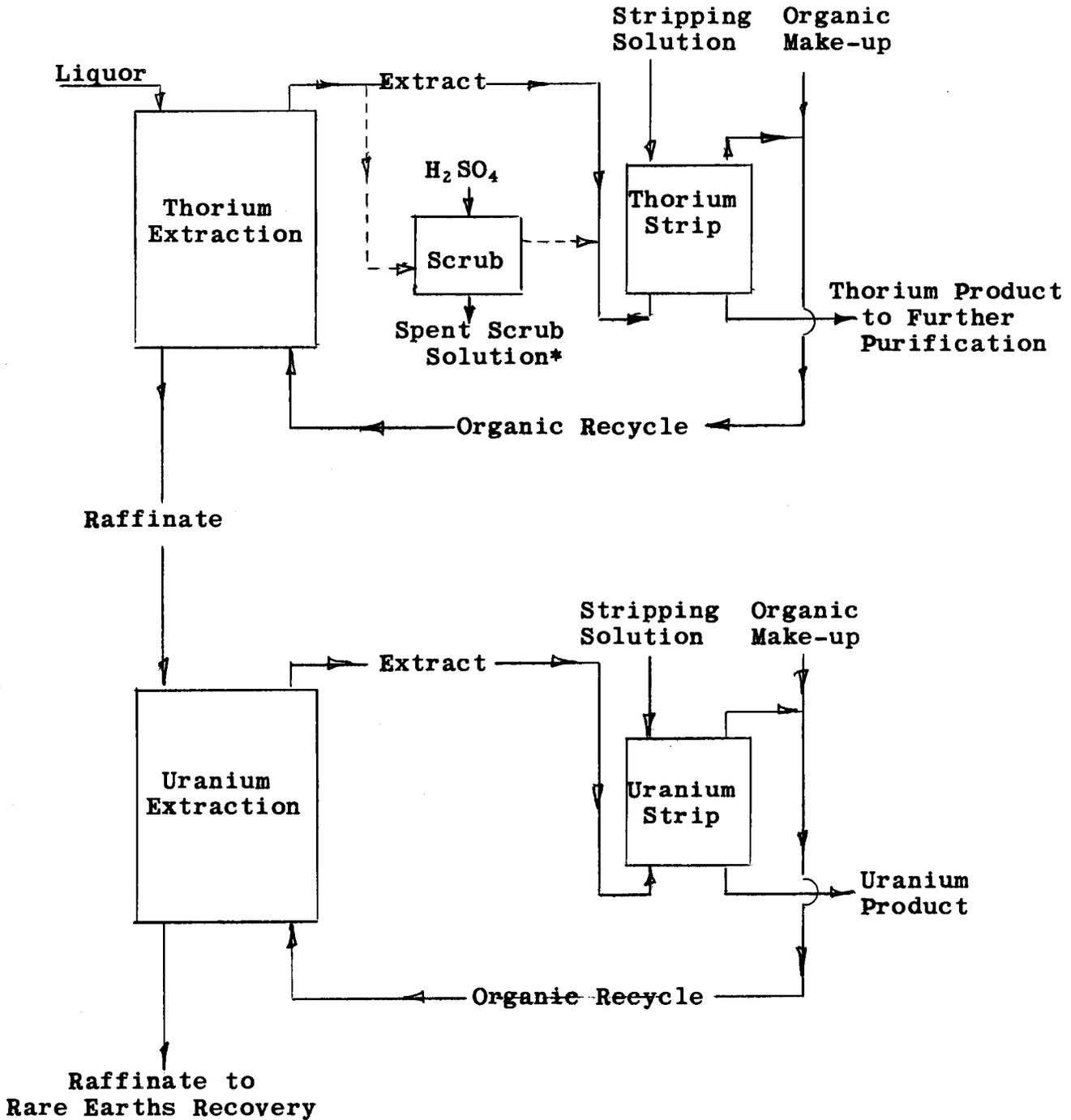
##### A. The Extraction System

It is assumed that the liquor available for processing would have approximately the same composition as the one used for these studies (see Table 1).

In the flow diagram shown in Figure A, an appropriate amine in hydrocarbon diluent is contacted countercurrently with

---

\*A more detailed discussion of the stripping mechanisms (in this case for uranium stripping) is presented in report ORNL-1734.



\* Recycle to the sand dissolution operation.

FIGURE A: RECOVERY OF THORIUM AND URANIUM FROM MONAZITE SULFATE LIQUOR WITH AMINES

the monazite liquor. Primary amines, due to their high extraction coefficients for thorium, appear to be the preferred extractants although some of the secondary amines might also be useful if sufficiently high reagent concentrations or a sufficient number of extraction stages were used. Thorium is recovered from the extract as a high grade product by one of several stripping methods (Figures B, C, or D) and is then sent to final purification, probably by TBP extraction. If desired, the extract is scrubbed, prior to stripping, with a solution of sulfuric acid to improve the purity of the thorium product. The stripped organic phase is recycled to the extraction system. At intervals, organic make-up is added to the organic recycle streams in quantity sufficient to compensate for amine and diluent losses suffered in the extraction and stripping operations. These losses, comprising entrainment losses of the organic phase in the aqueous solutions plus solubility of the amine in the raffinate\*, and evaporation losses of the diluent, would be small under normal operating conditions.

Although the extraction of uranium from the monazite liquor has not been studied extensively, several possibilities are suggested by the data.

1) If a primary amine is used as the extractant only a small amount of uranium is removed from the liquor (Table 6) due to competition by thorium for the reagent. In this case, the uranium could be removed from the raffinate by solvent extraction with a secondary or tertiary amine, both classes of compounds being selective for uranium over rare earths. It also would be possible to recover the uranium and rare earths from the raffinate by the Ames precipitation procedure.

2) Uranium recovery prior to the thorium extraction could apparently be accomplished by those reagents which do not extract appreciable thorium, e.g., symmetrical tertiary amines, possibly other tertiary amines, and secondary amines with sufficient branching on carbon atoms adjacent to the nitrogen.

---

\*Primene JM-R showed an initial solubility loss of about 25% to a solution of approximately the same salt content and acidity (1.2M SO<sub>4</sub>, 0.3M PO<sub>4</sub>, pH = 0.1) as the monazite liquor and, after this point, the "steady-state" loss was about 60 ppm. The latter figure corresponds to a utilization of <0.01 lbs of amine/lb of thorium oxide removed. C&C Amine 15F53 used in the above experiments also has appreciable steady-state distribution to the acid liquors, (9) but a higher molecular weight compound with similar branching, C&C Amine 16F27, has shown a low loss. The other amines used in these studies, C&C Amine 21F81, Armeen 2S and 2T, Compound 123, R&H Amine EB-765-2, di(2-butyloctyl)amine and tri(n-octyl)amine, all showed unimportant losses to the aqueous phase.

3) If the secondary amines were found useful as thorium extractants from the monazite liquor, a simultaneous extraction of uranium could also be obtained. In this case, the separation of uranium from thorium must be accomplished in subsequent operations, e.g., in the stripping section of the TBP process.

The economy of a uranium extraction process with amines would depend mainly upon the loading level since reagent costs for stripping would be approximately proportional to the degree of loading. The maximum loadings obtainable from the monazite liquor have not yet been determined.

## B. The Stripping System

Although all of the stripping data described above was obtained with the primary amine, Primene JM-R, the same general stripping methods would be applicable to other amines, with some variation in efficiency, particularly in the nitrate strip method, depending upon the particular reagent used.

### Nitrate Stripping

In the flowsheet shown in Figure B, an acidic nitrate solution is used to strip the thorium from the organic extract in a countercurrent system. The amine reagent after stripping is in the form of the nitrate salt, and before recycling back to the extraction step, is regenerated to the free amine by contacting with a slight excess of sodium or ammonium hydroxide. The sodium or ammonium nitrate salt solution formed in the regeneration step is used for further stripping after acidification with  $\text{HNO}_3$ . The only nitrate consumed in the stripping operation is that which passes out with the thorium in the pregnant strip solution. The  $\text{NO}_3/\text{Th}$  ratio in this solution can be kept to a minimum by increasing the number of stripping stages. By proper adjustment of nitrate concentration in the strip solution and flow ratios of the organic and strip solutions, it is possible to obtain relatively high concentrations of thorium in the pregnant strip solutions.

Two alternatives are presented for handling the pregnant strip solution. In the first, it is sent directly to the TBP extraction system after fortification with  $\text{HNO}_3$ . In this case, it would not be necessary to strive for nitrate economy in the amine stripping operation since high concentrations of nitric acid are required for salting the TBP extraction. The maximum suitable concentration would presumably be limited below that value where nitrate complexes of thorium may be formed which can be extracted by the amine (see case for

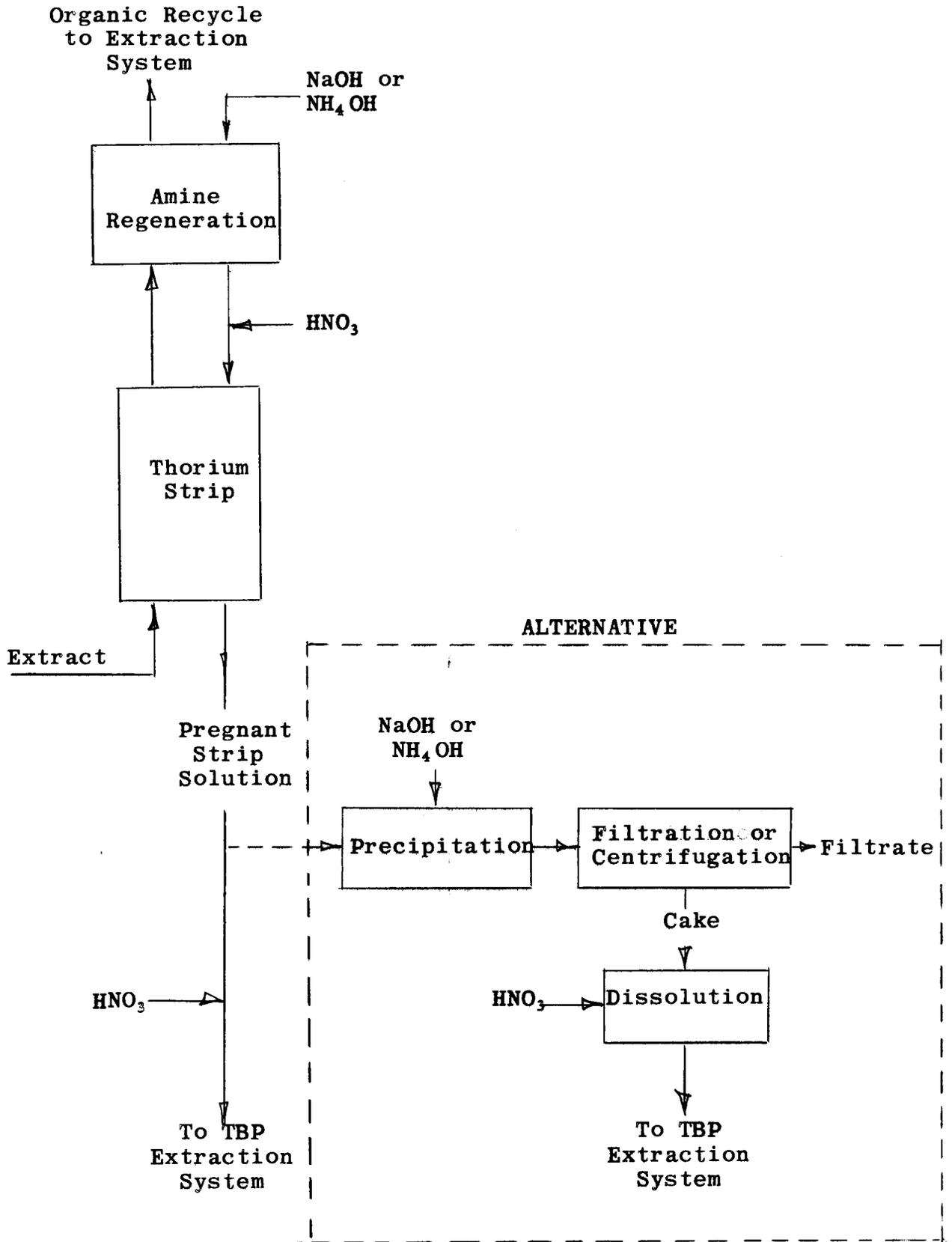


FIGURE B: NITRATE STRIPPING METHOD

uranium, p. 92, ORNL-1734). A disadvantage in sending the strip solution directly to the TBP extraction system would arise due to the presence of sulfate. In the tests with Primene JM-R the mole ratio of sulfate to thorium in the extract was approximately 6, and this same ratio would exist in the strip solution. Ames Laboratory has reported<sup>(2,3)</sup> that thorium extraction coefficients from a solution containing 9.8 g ThO<sub>2</sub>/l and 8 g P<sub>2</sub>O<sub>5</sub>/l were lowered by about a factor of two as the sulfate concentration of the feed was increased from 0 to 40 g/l. This was true for solutions that had a nitric acid concentration of 3.0M, 5.0M, and 8.0M.

In the second alternative, the thorium is precipitated from the pregnant strip solution with a base. The precipitate is recovered by filtration or centrifugation, possibly coupled with decantation, and is then dissolved in HNO<sub>3</sub> as feed for the TBP extraction system. This procedure would allow rejection of almost all of the sulfate from the system, preparation of feed solutions more concentrated in thorium, and a decrease in the total nitrate salting requirements. In a qualitative test thorium was precipitated with concentrated NH<sub>4</sub>OH from a nitrate strip solution containing 11.7 g Th/l. The precipitate settled within half an hour into approximately half of the aqueous volume leaving a very clear supernatant. The thickened slurry filtered very readily and the filter cake dissolved rapidly in 2.0M HNO<sub>3</sub>.

### Hydroxide Stripping

In the hydroxide stripping method shown in Figure C, the thorium precipitate is obtained directly by contacting the organic phase with a solution of sodium or ammonium hydroxide. From the chemical standpoint, either dilute or concentrated solutions of base can be used as long as a sufficient quantity of the base is supplied in excess to convert the amine salt to free amine and to precipitate the thorium. However, when dilute solutions are used, the thorium precipitate tends to distribute between both liquid phases, concentrating mainly at the interface. This makes separation of the three phases difficult. With concentrated solutions of a base, such a small volume is required that essentially only two distinct phases result, i.e., a wet precipitate dispersed in the organic phase. The wet precipitate settles fairly rapidly in the organic phase and can probably be recovered easily by centrifugation coupled with decantation. The economy of such a stripping process depends mainly upon efficient recovery of the amine and diluent occluded by the precipitate. To determine the purity of product that might be obtained by flowsheet C, a test was run in which 0.2M Primene JM-R in Amsco G was contacted with the monazite liquor at a 1:1 phase ratio. The thorium was precipitated from the organic extract

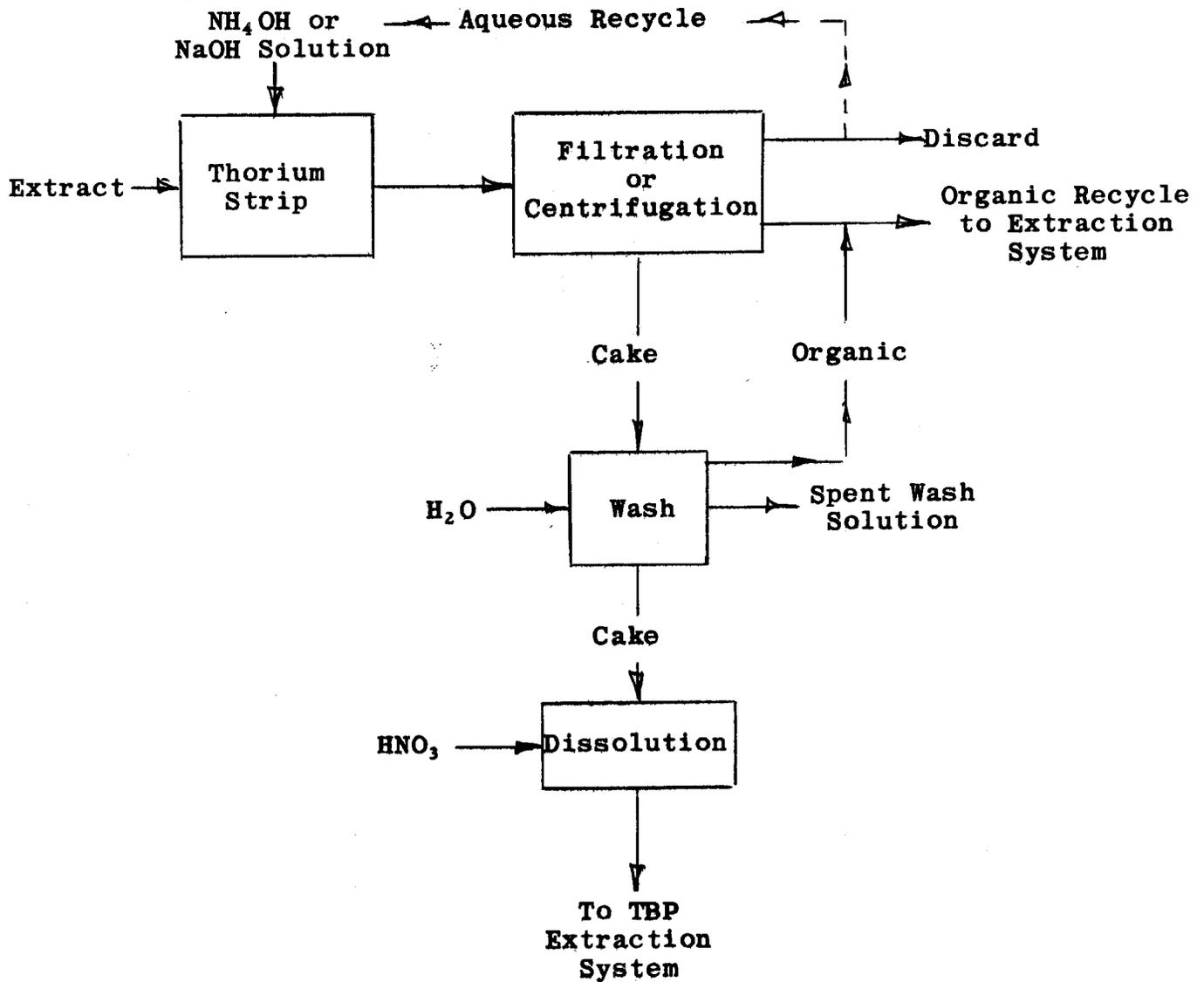


FIGURE C: HYDROXIDE STRIPPING METHOD

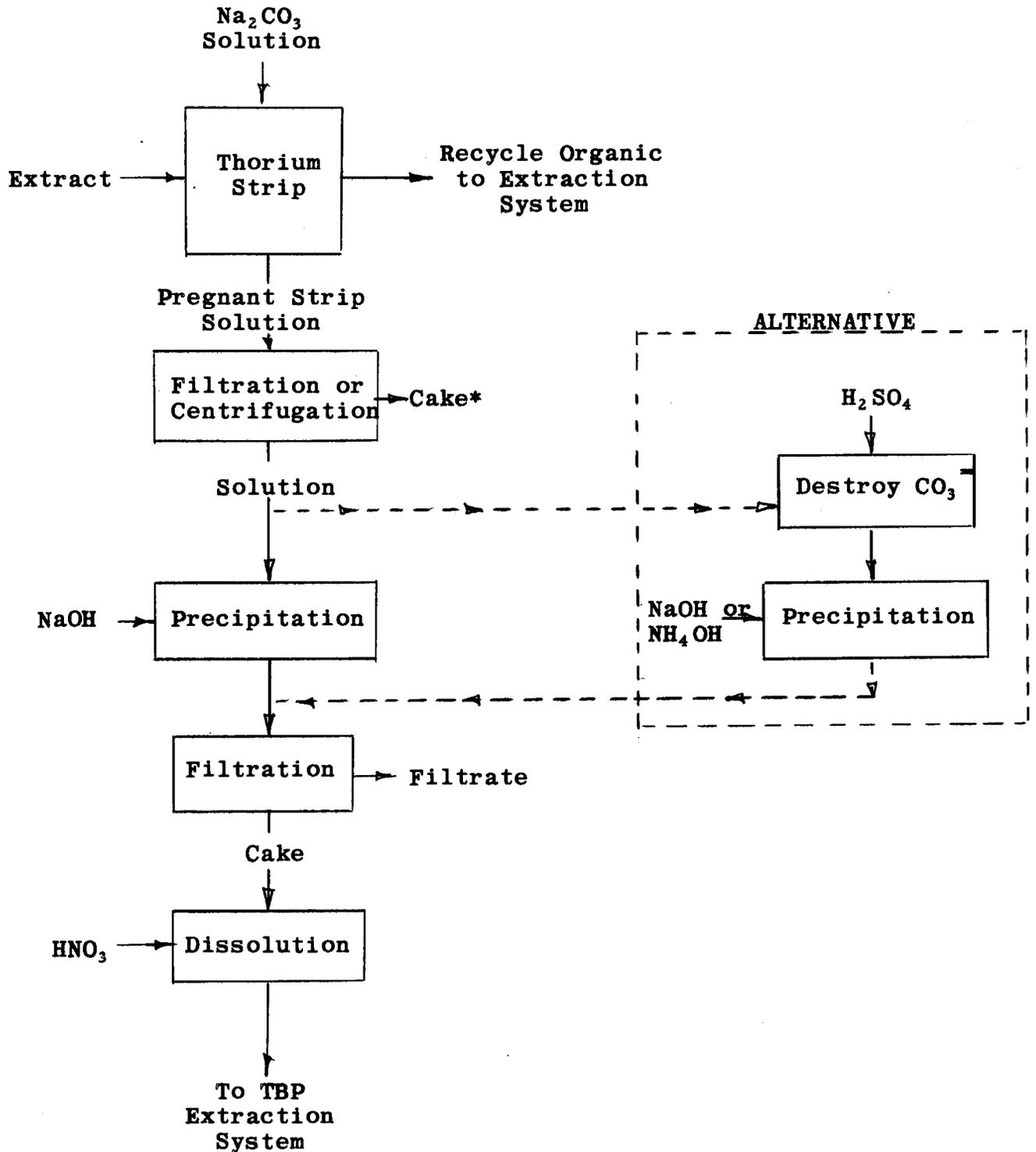
with concentrated  $\text{NH}_4\text{OH}$ , filtered, washed with hot water, and dried at  $110^\circ\text{C}$ . The product analyzed 44.8%  $\text{ThO}_2$ , 0.9% total rare earth oxides, 0.24%  $\text{PO}_4$ , and 52.4% L.O.I. at  $1000^\circ\text{C}$ . On a calcined basis, this corresponds to 94%  $\text{ThO}_2$ , 1.8% total rare earth oxides and 0.5%  $\text{PO}_4$ . Better products should be obtainable in a countercurrent operation where greater loadings of the organic phase with thorium would be obtained.

### Carbonate Stripping

In the carbonate stripping process shown in Figure D, a 10-15% solution of sodium carbonate is contacted with the organic extract. The thorium is liberated to the aqueous phase as the soluble carbonate complex. Most of any rare earths present in the extract are precipitated at this point and can be separated from the pregnant strip solution, thereby giving a further purification of the thorium. If a significant quantity of thorium was inadvertently carried by the rare earth precipitate, it could be recovered by re-dissolving the precipitate in  $\text{H}_2\text{SO}_4$  and recycling to the extraction system. The thorium is removed from the carbonate strip solution by adding  $\text{NaOH}$  and digesting at elevated temperatures. Since the tendency of thorium to hydrolyze is strong, the concentration of  $\text{NaOH}$  required to effect the precipitation should not be very high, although the optimum conditions for the precipitation have not yet been determined. In the alternative method of recovering thorium from the pregnant strip solution,  $\text{H}_2\text{SO}_4$  is added to a pH of  $\sim 1$  and the solution heated to drive off  $\text{CO}_2$ . The thorium is then precipitated by addition of base. A test of the latter flowsheet using Primene JM-R as extractant gave a thorium product which had the following concentrations of rare earths in ppm: Y,  $< 80$ ; La, 80; Ce, 1600; Pr,  $< 200$ ; Nd,  $< 800$ ; Sm,  $< 200$ ; Gd,  $< 80$ . The rare earth precipitate filtered from the pregnant carbonate strip solution analyzed 54.5% rare earth oxides and 6.2%  $\text{ThO}_2$ . The thorium in the precipitate represented about 0.2% of the total thorium stripped from the extract.

### Chloride

Chloride solutions ( $\text{NaCl}$ ,  $\text{HCl}$ , etc.) should also be useable for stripping thorium in a manner similar to that for uranium. In this case,  $\text{NaCl}$  would be an acceptable and low priced stripping reagent, operating in a manner generally analogous to but less efficient than nitrate salt solutions. Danger of chloride contamination in the TBP cycle must be considered.



\* Recycle to sand dissolution operation if thorium content is high enough to warrant it.

FIGURE D: SODIUM CARBONATE STRIPPING METHOD

## V. SUMMARY

A brief study has been made of the use of long chain amines as extractants for thorium (and uranium) from liquors obtained by digestion of monazite sand with sulfuric acid. Coefficients for extraction of thorium were measured for several amines of representative types and certain of these were also examined with respect to their extractive power for uranium, rare earths, and phosphate. In addition, a brief evaluation was made of several methods for recovering thorium from the extract. All tests were of the batch equilibrium type. The principal conclusions to be drawn from the tests may be listed as follows:

1) Solutions of the primary amines (0.1 - 0.2M in hydrocarbon diluents) exhibited very high thorium extraction coefficients from the monazite liquor. Little uranium was extracted by these reagents when the organic phase was appreciably loaded with thorium.

2) The extraction power of the secondary amines for thorium was dependent upon the structure of the hydrocarbon chains but in all cases was greatly inferior to that of the primaries at identical reagent concentration levels.

3) Insignificant quantities of thorium were extracted by the symmetrical tertiary (tri-n-octyl) amine tested.

4) Primary amines were found to extract considerable quantities of rare earths from the liquor when thorium was not present. It was possible, however, to decrease rare earth contamination of the extract to a low level by saturating the organic phase with thorium. The thorium-rare earth exchange rate proved to be rapid, indicating that control of selectivity by this method would be practical in a countercurrent extraction system.

5) Appreciable coefficients for extraction of uranium were observed for a secondary amine, Rohm and Haas Amine EB-765-2, and the symmetrical tertiary amine, tri(n-octyl)-amine. Extractions of rare earths by these compounds were very low.

6) Efficient separation of the thorium from phosphate was achieved in the amine extractions.

7) Solutions of nitric acid, nitric acid plus nitrate salt, sodium carbonate, and sodium and ammonium hydroxide stripped thorium very effectively from the extract. Other stripping methods analogous to those worked out for uranium could also be used. With hydroxide reagents, the thorium was precipitated directly from the organic phase.

Several possible extraction-stripping flowsheets are presented for consideration although insufficient experimental data was available for choosing the optimum of these processes. It appears probable, however, that, by proper choice of amine reagents and sequence of operations, essentially complete recovery of both thorium and uranium could be achieved from the monazite sulfate liquors by solvent extraction methods. The thorium product, essentially free of uranium, and containing only small amounts of rare earths and phosphate, should be much more amenable to final purification by TBP extraction than the thorium concentrate obtained by fractional precipitation methods. After recovery of thorium and uranium, the raffinate would be available for recovery of rare earths. In view of the success of the initial tests, a larger scale evaluation of the proposed processes would appear to be justified.

## VI. ACKNOWLEDGEMENTS

The authors wish to acknowledge the contributions of R. S. Lowrie, who made the initial literature survey and aided in preparation of leach liquors.

Amine distribution determinations were made by John G. Moore and Donald E. Horner.

Spectrographic analyses were made by the ORNL Isotope Analysis Methods Laboratory under the supervision of J. A. Norris.

Chemical analyses were obtained from the Y-12 Section of the ORNL Analytical Division under the direction of C. D. Susano.

VII. REFERENCES

- 1) Kernal Glenn Shaw, Morton Smutz, and G. L. Bridger, "A Process for Separating Thorium Compounds from Monazite Sands," Ames Laboratory, ISC-407, January 1954.
- 2) M. E. Whatley, Morton Smutz, and G. L. Bridger, "Purification of Thorium by Solvent Extraction," Ames Laboratory, ISC-415, July 1953.
- 3) J. Bochinski, K. G. Shaw, M. E. Whatley, and M. Smutz, "Progress Report on Ames Monazite Process," Ames Laboratory, ISC-302, November 1, 1952.
- 4) G. D. Calkins, R. B. Filbert, Jr., A. E. Bearse, and J. W. Clegg, "Recovery of Thorium and Uranium from Monazite Sand," Battelle Memorial Institute, BMI-243 and BMI-243A, September 15, 1950.
- 5) "Quarterly Progress Report for the Period Ending September 30, 1952," New Brunswick Laboratory, NYO-2032.
- 6) "Quarterly Progress Report for the Period Ending March 31, 1953," New Brunswick Laboratory, NYO-2041.
- 7) "Progress Report, Uranium Chemistry of Raw Materials Section, January 1, 1952 to March 31, 1952," Oak Ridge National Laboratory, ORNL-1308.
- 8) "Progress Report, Uranium Chemistry of Raw Materials Section, April 1, 1952 to June 30, 1952," Oak Ridge National Laboratory, ORNL-1384.
- 9) K. B. Brown, C. F. Coleman, D. J. Crouse, J. O. Denis, and J. G. Moore, "The Use of Amines as Extractants for Uranium from Acidic Sulfate Liquors," Oak Ridge National Laboratory, ORNL-1734, May 27, 1954.
- 10) James S. Fritz, Iowa State College, Acid-Base Titrations in Non-Aqueous Solvents, The G. Frederick Smith Chemical Company, Columbus, Ohio, 1952.