ORNL-2099
Chemistry

PROGRESS REPORT ON URANIUM EXTRACTION WITH ORGANONITROGEN COMPOUNDS

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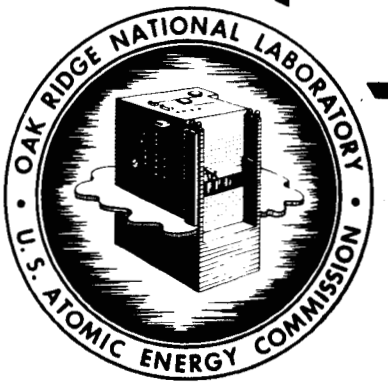

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I. INTRODUCTION

In ORNL-2002 a brief narrative account was given of the status of several research and development projects now under study in the Oak Ridge National Laboratory Raw Materials Section. It was also mentioned that a more detailed description of these studies, including experimental data, would be presented in subsequent progress reports.

The present report has been prepared in accordance with this plan and gives a reasonably full account of most of the recent studies that have been made on uranium extractions with long chain amines. Similar reports covering other projects listed in ORNL-2002 are being prepared and will be published later.

Previous studies on the long chain amines as solvent extraction agents have been described in topical reports ORNL-1734, ORNL-1922, and ORNL-1959.

II. EXPERIMENTAL DATA AND DISCUSSION

A. Comparisons of the Uranium Extraction Power of Several Different Amines

Previous reports have described extractions with several amines in which one of the alkyl groups carried an aromatic substituent. One of these compounds, N-Benzyl-1(3-ethylpentyl)-4-ethyloctylamine, in either kerosene or benzene, gave uranium extraction coefficients which were much higher than had been obtained with any other organonitrogen compound.

The observance of this unusual extraction performance suggested further evaluations of similar reagents. Recently several such reagents have been obtained and examined in screening tests using the same experimental procedures as described before (see ORNL-1922, page 4). The results from these screening tests, together with results previously reported for other compounds of related structures, are given in Table 1. Structures and indicated purity levels for the new reagents are shown in Appendix A. The more important observations and conclusions drawn from examination of these data are itemized below.

1) The di(α-methylbenzyl)amine, like dibenzylamine, is a poor uranium extractant. High losses to the aqueous liquor could be a contributing factor to the poor performance of these reagents.

2) Although the test data thus far are limited, it is indicated that generally improved extraction power (in benzene) is obtained with benzylalkyl (R') amines as compared to dialkyl (R'R") or (R'R') amines. For example, N-benzyl-lauryl > dilauryl; N-benzyl-n-tetradecyl>>di-n-tetradecyl; N-benzyl(7-ethyl-2-methylundecyl-4)>>>N-decyl(7-ethyl-2-methylundecyl-4). It is also interesting to note that the branched tetradecyl compound in this series was greatly superior to the straight chain compound, i.e., N-benzyl(7-ethyl-2-methylundecyl-3)>>N-benzyl-n-tetradecyl.

3) Placement of the aromatic substituent more distant from the nitrogen appears to decrease extraction power, i.e., N-n-tetradecyl(3-phenylpropyl)amine < N-benzyl-n-tetradecylamine. Again, however, final conclusions would be dangerous on the basis of such limited evidence.

4) With either kerosene or benzene as the diluent, the extremely high extraction power of N-benzyl-1(3-ethylpentyl)-4-ethyloctylamine was approached, or possibly equalled, by N-benzyl(7-ethyl-2-methylundecyl-4)amine. Unfortunately the distribution of this latter reagent from kerosene to acidic sulfate liquor is fairly high (see Table 15). Distribution losses from aromatic diluents have not been measured.

Table 1

PRELIMINARY TESTS OF URANIUM EXTRACTIONS FROM SULFATE SOLUTIONS

Secondary Amines	Conc. M	Init. Aq. pH	Kerosene Extn. %	Kerosene E_a^o	Chloroform Extn. %	Chloroform E_a^o	Benzene Extn. %	Benzene E_a^o	Benzene Prewashed Extn. %	Benzene Prewashed E_a^o	Phase Separation
Dibenzyl	0.1	1.0	-	-	76	3	-	-	nil	nil	Poor in $CHCl_3$
Di(α-methylbenzyl)	0.1	0.9	0	0	87	6.7	2	0.02	nil	nil	Good
Dilauryl	0.1	1.0	-	-	99	100	99	80	98	60	Good
N-Benzyllauryl	0.1	0.9	Third Phase		99	340	99	130	99	110	Good
Di-n-tetradecyl	0.05	1.0	-	-	95	20	96	20	95	20	Good
N-Benzyl-n-tetradecyl	0.1	0.9	Third Phase		>99	246	99	410	99	294	Good
N-n-Tetradecyl(3-phenylpropyl)	0.1	0.9	-	-	>99	250	99	75	99	77	Good
N-n-Decyl(7-ethyl-2-methylundecyl-4)	0.1	0.9	99	131	96	23	97	97	98	63	Good
N-Benzyl(7-ethyl-2-methylundecyl-4)	0.1	0.9	>99	>1000	>99	350	>99	>1000	99	>1000	Good

Table 1 (Cont'd.)

PRELIMINARY TESTS OF URANIUM EXTRACTIONS

FROM SULFATE SOLUTIONS

Secondary Amines	Conc. M	Init. Aq. pH	Kerosene Extn. %	Kerosene E_a^o	Chloroform Extn. %	Chloroform E_a^o	Benzene Extn. %	Benzene E_a^o	Benzene Prewashed Extn. %	Benzene Prewashed E_a^o	Phase Separation
N-Benzyl-1(3-ethyl-pentyl)-4-ethyl-octyl	0.1	0.9	>99	>1000	99	110	>99	>1000	>99	>1000	Good
N-(2-ethylhexyl)-α-methylbenzyl	0.2	1.0	-	-	99	185	99	70	99	90	Good
N-(2-ethylhexyl)-α-xylylbenzyl	0.15	1.0	-	-	56	1	86	6	85	6	Good
N-(1-isobutyl-3,5-dimethylhexyl)-α-methylbenzyl	0.1	0.9	Third Phase		17	0.2	-	-	31	0.4	Good
Di(2-ethylhexyl)	0.1	1.0	-	-	96	25	99	100	98	40	Good
*N-(p-sec.-amyl-benzyl)-1-iso-butyl-3,5-di-methylhexyl	0.14	0.9	97	30	97	40	>99	700	>99	700	Good
N-(2-naphthyl-methyl)-1-iso-butyl-3,5-di-methylhexyl	0.1	0.9	>99	500	>99	130	>99	>1000	>99	>1000	Good

Table 1 (Cont'd.)

PRELIMINARY TESTS OF URANIUM EXTRACTIONS

FROM SULFATE SOLUTIONS

*Questionable purity (see Appendix).

Extraction Conditions: Organic contacted with aqueous (1:1 ratio) containing 1 g U/l and 1 M SO_4 for 5 minutes. Phases were allowed to separate and analyzed for uranium.

5) Extraction power, considerably above average, was obtained with two other aromatic substituted compounds when benzene was used as the diluent, i.e., N-(p-sec.-amylbenzyl)-1-isobutyl-3,5-dimethylhexylamine and N-(2-naphthylmethyl)-1-isobutyl-3,5-dimethylhexylamine. The latter compound also showed somewhat better than average extraction power when kerosene was used as the diluent. Distribution losses from kerosene to aqueous sulfate liquors are reasonably low for the first compound but fairly high for the latter (Table 15). Again distributions have not yet been measured for either of these reagents from aromatic diluents.

6) N-(1-isobutyl-3,5-dimethylhexyl)-α-methylbenzyl and N-(2-ethylhexyl)-α-xylylbenzyl amines are poor extractants whereas reasonably good extraction was obtained with N-(2-ethylhexyl)-α-methylbenzylamine. The inferior performance by the first two compounds is similar to that noted previously with other highly branched (sterically hindered) amines - see ORNL-1734 and -1922.

7) Marked diluent effects from the three diluents tested were again noted in many of the extraction experiments and again the magnitude and direction of these effects were not necessarily the same with different amines. Such results offer a continued reminder that rigorous comparison of extraction properties must be based on comparison of several different amine-diluent combinations rather than the amine reagents in a single diluent.

In summary, from the results thus far, it must be concluded that when one of the radicals of a secondary amine is a benzyl or structurally similar group, increased extraction power can be expected, at least when benzene is used as the diluent. Also, it may be noted that highest extractions with this type reagent have been obtained when the aliphatic radical is branched and actually, in the cases cited, when the attachment to the nitrogen is through a secondary carbon. The type of diluent is shown to play a major role in extraction performance and substantiates earlier opinions that effects from this source may be of an importance equal to those from changes in structure alone. Further screening tests of the type described are continuing.

B. Comparison of Uranium Extraction Isotherms

Isotherms for the extraction of uranium from synthetic Marysvale liquor* with several amine reagents have been reported previously.[2] Additional isotherms, shown in Figure 1, have been obtained for the same liquor with other

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*1.25 g U/l, 5.8 g Fe(III)/l, 3.3 g Al/l, 50 g SO_4/l, 2.0 g PO_4/l, 1.7 g F/l, pH $\sim$1.

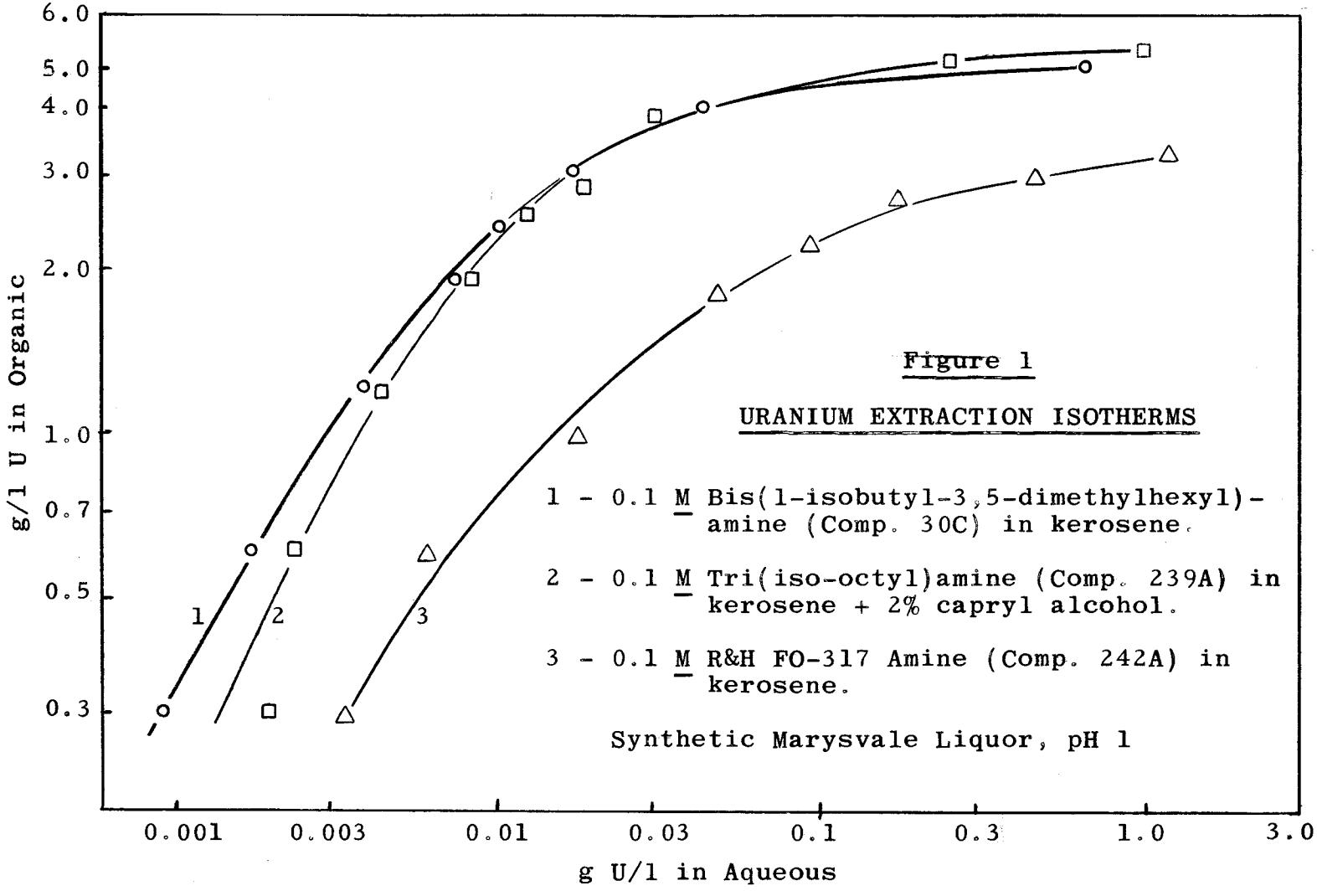

Figure 1

URANIUM EXTRACTION ISOTHERMS

1 - 0.1 M Bis(1-isobutyl-3,5-dimethylhexyl)-amine (Comp. 30C) in kerosene.

2 - 0.1 M Tri(iso-octyl)amine (Comp. 239A) in kerosene + 2% capryl alcohol.

3 - 0.1 M R&H FO-317 Amine (Comp. 242A) in kerosene.

Synthetic Marysvale Liquor, pH 1

reagents, i.e., tri(iso-octyl)amine in kerosene + 2% capryl alcohol, R&H FO-317 amine (dodecenyl Primene JM) in kerosene, and a new sample* of bis(1-isobutyl-3,5-dimethylhexyl)amine in kerosene.

It may be observed from Figure 1 that the uranium loading (4.8 g U/l for 0.1 M amine) achieved with the new sample of bis(1-isobutyl-3,5-dimethylhexyl)amine was somewhat higher than that observed in tests with earlier impure samples[1,2,3]. The overall extraction isotherm for this amine is quite similar to that for tri(iso-octyl)amine. Also, in turn, the isotherm for tri(iso-octyl)amine is essentially the same as that obtained earlier with tri-n-octylamine.[2] Considerably poorer extraction efficiency and lower loadings were observed for R&H FO-317 amine.

In Figure 2, from the same experiments described above, the iron decontamination factor** is shown as a function of the uranium loading in the organic phase. Here, it may be noted that, as previously observed with tri-n-octylamine, the tri(iso-octyl)amine extracted almost negligible quantities of iron even at low uranium loadings.*** The selectivity of bis(1-isobutyl-3,5-dimethylhexyl)amine, although not as good as that of tri(iso-octyl)amine, was still excellent and this compound would give a very effective separation from iron at loadings typical of process operation. On a comparative basis, poorer selectivity was shown by the dodecenyl Primene JM amine. However, this material would also be expected to give reasonable performance in many process applications.

C. Effect of Diluent Additives on Extraction of Uranium and Iron by Di(tridecyl P)amine

In previous studies,[1,2] it has been noted that the addition of capryl alcohol in small amounts to amine-diluent (e.g., kerosene) systems can cause a marked increase in the extraction selectivity shown by the amine for uranium over iron(III). This effect was particularly noticeable with an extractant of comparatively poor selectivity such as di(tridecyl P)amine.

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*This compound is now called Amine S-24 and was previously identified as C&C 16F27. See footnote on page 41 for further comments.

**Iron decontamination factor = $\frac{\text{Fe(III)/U in the head liquor}}{\text{Fe(III)/U in the organic phase}}$

***As predicted previously[2] the properties of tri(iso-octyl)-amine in general have been similar to tri-n-octylamine, i.e., with respect to selectivity, uranium loading, loss to aqueous, diluent compatibility, etc. (see other sections of this report).

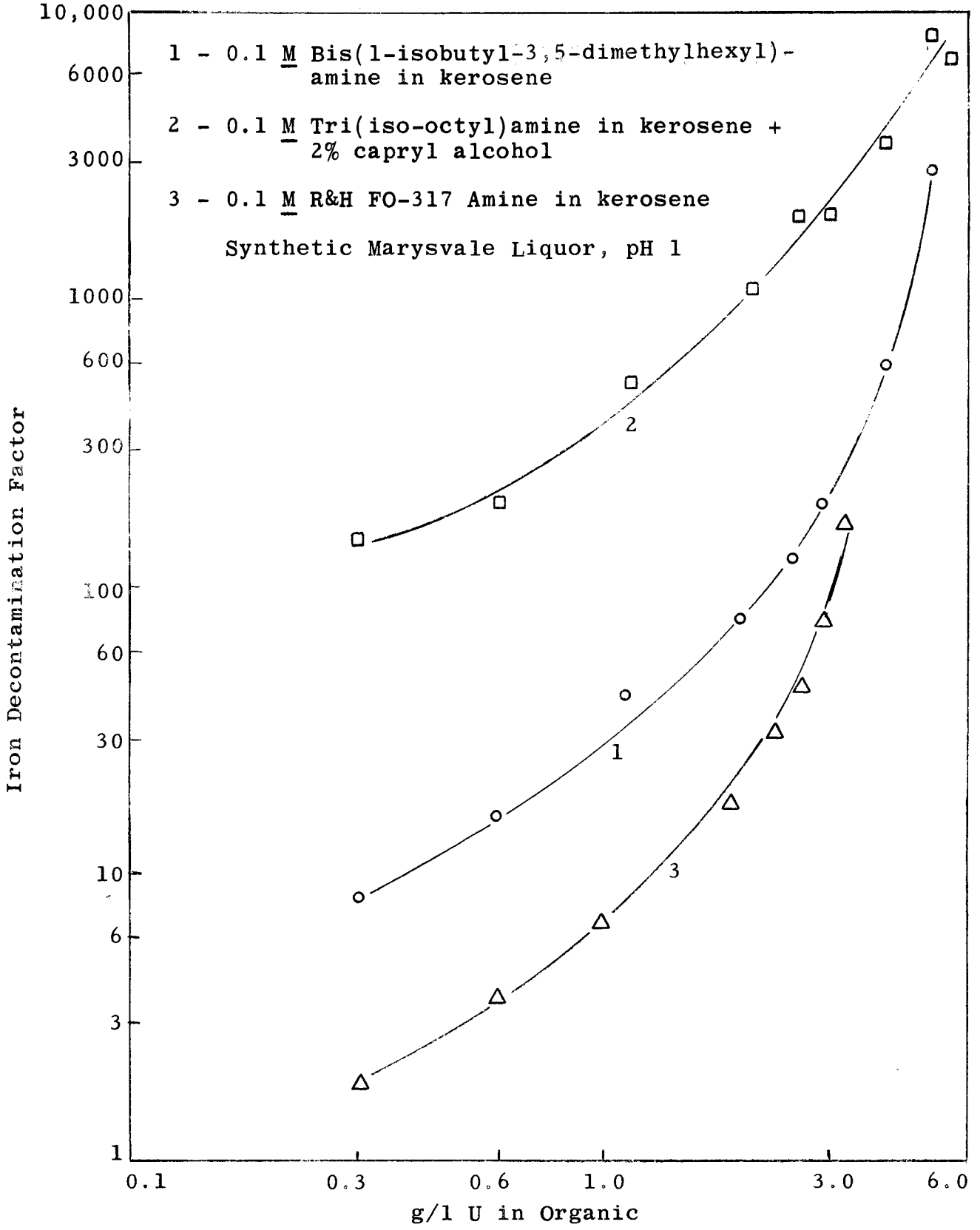

Figure 2

CONTROL OF IRON CONTAMINATION BY URANIUM LOADING

Recently, additional studies have been made on the addition of other organic additives to the kerosene diluent to determine if different types of compounds would exert a similar, and possibly even greater, beneficial effect on the selectivity. In these tests, 0.1 M solutions of di(tridecyl P)amine in kerosene, spiked with 1, 2, or 3 volume per cent of the various additives, were contacted with a synthetic liquor (Table 2) and the distribution of iron and uranium were measured after two minutes of vigorous mixing. It should be noted that the additives selected for study were not necessarily compounds which in themselves would be practical additives from the economic and operational standpoint (i.e., compounds with low aqueous solubility, high flash point, etc.).

Most of the compounds tested, including trichloroethylene, methyl n-hexyl ketone, n-butyl acetate, nitrobenzene, TBP, "Flexol" plasticizer TOF, dioctyl phthalate, n-butyl ether, benzyl chloride, n-butyl succinate, and cumene, were found to exert a negligible or very minor effect on both iron and uranium extraction. However, as shown in Table 2, a considerable decrease in iron extraction (and corresponding increase in uranium extraction) was obtained when capryl alcohol, nonyl phenol, benzyl alcohol, or 2-ethylhexyl chloride was added to the organic phase. Of these compounds the strongest beneficial effect, on a volume percent basis, was exerted by nonyl phenol.

D. Uranium Loading of Tri-n-octylamine

The maximum uranium loading of tri-n-octylamine from an acidic sulfate solution of very high uranium content has been determined using 0.3 to 0.6 M solutions of the amine in 95% kerosene - 5% capryl alcohol. In each test the organic solution was cascaded against fresh volumes of aqueous solution (96 g U/l, 0.94 M SO_4, pH $\sim$1) until the uranium content of the aqueous phase in equilibrium with the organic was approximately equal to that of the head aqueous solution. Results showing the composition of the organic phase at the point representing essentially maximum uranium loading from this solution are shown in Table 3.

It may be noted that at each amine concentration the maximum uranium loading was close to one mole of uranium per four moles of amine. Three moles of sulfate per mole of uranium were present in the organic phase.

E. Extraction of Uranium from "Plant C" Liquor

A brief investigation was made of uranium extraction with amines from a sample of liquor received from an operating Western mill (designated "Plant C"). The chemical composition of the liquor is listed directly below and extraction isotherm

Table 2

EFFECT OF DILUENT ADDITIVES ON URANIUM

AND IRON EXTRACTION BY DI(TRIDECYL P)AMINE

Additive	Volume % of Additive	Organic g/l U	Organic g/l Fe	Aqueous g/l U	Extraction Coefficient Uranium	Extraction Coefficient Iron
None	-	1.75	0.64	0.059	30	0.12
"	-	1.75	0.54	0.050	35	0.10
Capryl Alcohol	1	1.76	0.51	0.037	48	0.09
" "	2	1.75	0.46	0.029	60	0.08
" "	3	1.76	0.34	0.027	65	0.06
Nonyl Phenol	1	1.90	0.49	0.027	70	0.09
" "	2	1.84	0.32	0.018	100	0.06
" "	3	1.88	0.15	0.027	70	0.03
2-Ethylhexyl Chloride	1	1.71	0.55	0.036	48	0.10
" " "	2	1.71	0.45	0.027	63	0.08
" " "	3	1.69	0.36	0.028	60	0.06
Benzyl Alcohol	1	1.76	0.50	0.029	60	0.09
" "	2	1.73	0.38	0.028	62	0.07
" "	3	1.71	0.21	0.028	61	0.04

Table 2 (Cont'd.)

EFFECT OF DILUENT ADDITIVES ON URANIUM

AND IRON EXTRACTION BY DI(TRIDECYL P)AMINE

Extraction Conditions:

Organic: 0.1 M Di(tridecyl P)amine in kerosene with indicated concentration of additive.

Aqueous: Synthetic liquor (1.0 g U/l, 5.8 g Fe(III)/l, 3.3 g Al/l, 50 g SO_4/l, 2.0 g PO_4/l, 1.7 g F/l, pH 0.9).

Phase Ratio: $2^a/1^o$.

Temperature: Room.

Contact Time: 2 minutes.

Table 3

URANIUM LOADING OF TRI-n-OCTYLAMINE SOLUTIONS

Amine Conc.	Aqueous		Organic		Molar Ratios in Organic	
	g/l U	pH	g/l U	g/l SO_4	Amine/U	SO_4/U
0.3	94	1.05	17.3	20.2	4.1	2.90
0.4	91	1.0	22.8	27.8	4.3	3.02
0.5	90	1.05	28.1	33.9	4.2	2.99
0.6*	95	0.95	33.9	40.3	4.2	2.96

Extraction Conditions:

Organic: Indicated concentration of tri-n-octylamine in 95% kerosene - 5% capryl alcohol.

Aqueous: Uranyl sulfate solution, U = 96 g/l, SO_4 = 0.94 M, pH $\sim$1.

Procedure: Organic phase cascaded against fresh volumes of aqueous until saturation with uranium was reached. Above results show distribution on the final contact.

*Rate of phase separation was very slow.

data obtained with 0.1 M tri-n-octylamine in kerosene + 3 v % tridecyl alcohol and 0.1 M R&H 9D-178 amine in kerosene are given in Table 4 and Figure 3.

Analysis of "Plant C" Liquor

	g/l
U	6.2
$\sum V$	4.6
V(V)	3.7
$\sum Fe$	0.40
Fe(III)	0.40
Al	2.9
Mo	0.022
Ti	0.11
Ca	0.31
Si	0.04
SO_4	71
Cl	1.3
F	0.32
PO_4	3.05
pH	0.65

The data show that "Plant C" liquor could be effectively handled by the Amex process. The uranium in the organic phase built up to a maximum of 4.8 g U/l with tri-n-octylamine and 3.7 g U/l with R&H 9D-178 amine. Using the isotherm plots of Figure 3, it may be determined that, with either of the amines tested, three ideal extraction stages should be sufficient to achieve a raffinate of <5 ppm U (>99.9% recovery) when loading the organic phase to approximately 90% of its loading limit. In all tests, phase separation, although not exceptionally rapid, was reasonably fast, falling in the range of 3/4 - 1-1/2 minutes when the solutions were contacted by vigorous shaking in separatory funnels. Although only two amines were tested with the Plant C liquor, similar results would be expected for compounds of similar structure.

Since the vanadium(V) content of the Plant C liquor is high, some competition for the amine reagents was offered by vanadium even though the liquor pH was fairly low. Part of the vanadium could be displaced by "saturating" the organic phase with uranium, but even at maximum uranium loading, the vanadium content of the extract was still significant. Several alternative methods are available to prevent the vanadium from reporting with the uranium product. For example:

1) Avoiding vanadium extraction in the first place by prior reduction of the vanadium in the liquor to the quadrivalent state.

2) Removal of extracted vanadium from the organic phase by scrubbing with sulfurous acid prior to uranium stripping.

Table 4

EXTRACTION OF URANIUM FROM "PLANT C"

LIQUOR WITH AMINES*

0.1 M Tri-n-octylamine in kerosene + 3 v % tridecyl alcohol

Contact	g/l U		g/l V		Uranium Extraction Coefficient, E_a^o
	Aqueous	Organic	Aqueous	Organic	
1	0.040	1.47	4.2	0.39	37
2	0.23	2.9	4.5	0.39	13
3	0.90	4.2	5.0	0.26	4.7
4	2.7	4.8	5.1	0.15	1.8

0.1 M R&H 9D-178 Amine in kerosene

Contact	g/l U		g/l V		Uranium Extraction Coefficient, E_a^o
	Aqueous	Organic	Aqueous	Organic	
1	0.13	1.5	3.6	0.23	12
2	0.79	2.8	4.8	0.17	3.5
3	3.0	3.5	4.8	0.106	1.2
4	4.8	3.7	4.8	0.086	0.8

*The extraction isotherm data were obtained by contacting the organic solutions with successive increments of liquor at a phase ratio of $4^o/1^a$ and determining the uranium distribution between the phases after each contact. In order to avoid excessive pH changes, the amines, prior to extraction, were converted to the salt form by contact with dilute sulfuric acid.

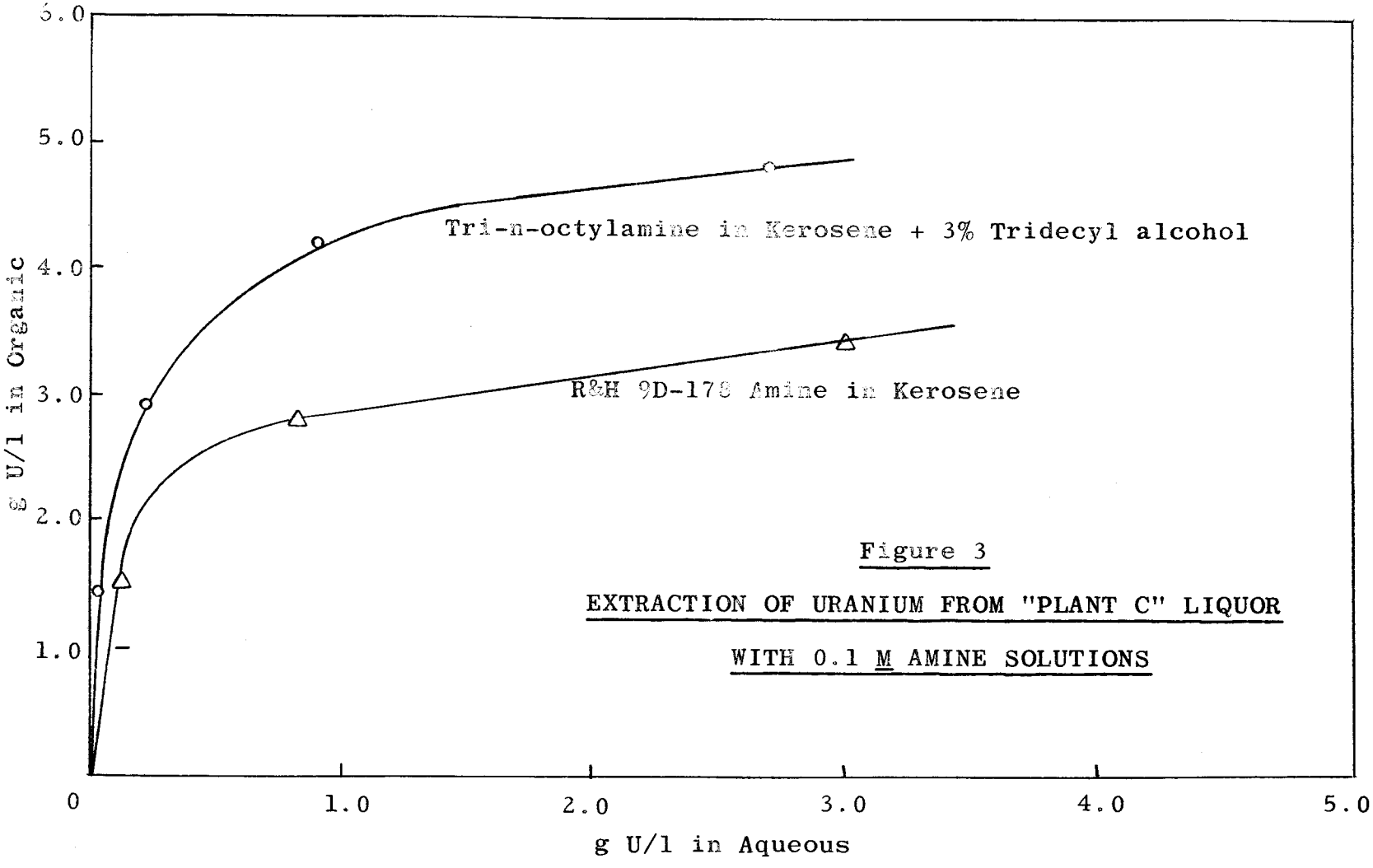

Figure 3

EXTRACTION OF URANIUM FROM "PLANT C" LIQUOR

WITH 0.1 M AMINE SOLUTIONS

3) Utilization of chloride salt solutions for uranium stripping since vanadium ordinarily is not stripped effectively with chloride solutions.[2]

F. Extraction of Uranium from 1.0 M Sulfuric Acid

Sulfuric acid elution of the resin in the RIP circuit and solvent extraction of uranium from the sulfuric acid eluate is under development at the Winchester Laboratory. The di(2-ethylhexyl)phosphoric acid reagent has given good performance in this application and a process using this extractant has been proposed.[4] Preliminary studies at Winchester of eluate extraction with an amine extractant were not encouraging due primarily to poor phase separation properties.[4] A few additional studies of amine extractants for this purpose have been conducted at this laboratory to determine whether better performances could be obtained with some of the reagents available here.

Prior to the uranium extraction studies, a preliminary examination was made of the rate of phase separation of a number of different amine-diluent solutions when contacted with a solution of 1.0 M H_2SO_4. The amine concentration in these tests was varied from 0.15 M to 0.3 M. Each organic solution was shaken vigorously for two minutes with an equal volume of 1.0 M H_2SO_4 in a separatory funnel and the phases were then allowed to separate. Results are listed in Table 5. The time for complete separation varied considerably depending on the particular amine-diluent combination chosen and the amine concentration. In most instances the rate of phase separation became slower as the amine concentration was increased. R&H 9D-178 amine in kerosene formed very slow breaking emulsions at an amine concentration of 0.2 M or 0.3 M but gave satisfactory separation when the concentration was lowered to 0.15 M. In Amsco G diluent this same amine separated fairly rapidly at 0.2 M but again formed a semi-permanent emulsion at 0.3 M concentration. The other secondary amine tested (N-benzyl-1-(3-ethylpentyl)-4-ethyl-octylamine) was used only in kerosene. Separations were satisfactorily rapid at 0.15 M and 0.2 M but very slow at 0.3 M concentration. Tri-n-octylamine in kerosene + 5% tridecyl alcohol and tri(iso-octyl)amine in Amsco G gave fairly rapid phase separation at 0.15 M, 0.2 M, and 0.3 M amine concentration.

The extraction of uranium from 1.0 M H_2SO_4 solutions containing 1.0 and 8.0 g U/l was next investigated using some of the amine-diluent combinations which had shown satisfactory phase separations in the tests described above. Results are presented in Table 6. The coefficients for extraction of uranium from the 1 g U/l solution are of course more representative of the true extraction power of the amine than those from the 8 g U/l solution since, in the latter tests, the

Table 5

RATE OF PHASE SEPARATION OF AMINE SOLUTIONS

FROM 1.0 M H_2SO_4

Amine	Diluent	Separation Time in Seconds 0.15 M	0.2 M	0.3 M
Tri-n-octyl	Kerosene + 3% tridecyl alcohol	*	*	*
"	" " 4% " "	30	*	*
"	" " 5% " "	55	65	30
Tri(iso-octyl)	Kerosene + 5% tridecyl alcohol	*	*	*
" "	Amsco G	40	45	60
R&H 9D-178	Kerosene	70	>300	>300
"	Amsco G	55	70	>300
N-benzyl-1-(3-ethylpentyl)-4-ethyloctyl	Kerosene	60	80	>300

*Third liquid phase formed since miscibility of the amine salt with the diluent was exceeded.

Table 6

EXTRACTION OF URANIUM FROM 1.0 M H_2SO_4 WITH AMINES

Amine	Diluent	M Amine	Phase Ratio a:o	Sep. Time Sec.	g/l Uranium Head Aq.	Org.	Aq.	E_A^O
Tri-n-octyl	Kerosene + 5% Tridecyl alcohol	0.3	3:1	85	1	2.57	0.10	26
"	"	0.2	2:1	70	"	1.85	0.075	23
"	Amsco G	"	"	60	"	1.93	0.057	34
Tri(iso-octyl)	Amsco G	"	"	55	"	1.71	0.10	17
R&H 9D-178	"	"	"	60	"	1.67	0.13	13
N-benzyl-1-(3-ethyl-pentyl)-4-ethyloctyl	Kerosene	"	"	70	"	2.0	0.005	400
Tri-n-octyl	Kerosene + 5% Tridecyl alcohol	0.3	3:1	100	8	14.1	3.8	3.7
"	"	0.2	2:1	90	"	10.4	3.3	3.0
"	Amsco G	"	"	75	"	10.8	3.2	3.4
Tri(iso-octyl)	Amsco G	"	"	55	"	10.0	3.5	2.9
R&H 9D-178	"	"	"	85	"	7.3	4.4	1.6
N-benzyl-1-(3-ethyl-pentyl)-4-ethyloctyl	Kerosene	"	"	115	"	8.0	4.1	1.9

coefficients are much more severely limited by loading of the amine reagent with uranium. The latter tests do, however, serve to define the approximate maximum uranium loadings which could be achieved in countercurrent operation since the aqueous phase at equilibrium is at the uranium level (~4 g U/l) which the Winchester group has estimated will be obtained in 1.0 M H_2SO_4 eluates. The extraction coefficients (at low loading) of all of the amine solutions tested were sufficiently high for practical process application. Here, as in tests with other liquors,[1,2] the extraction power of N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine was exceptionally strong. As observed previously[2] the tertiary amines can be loaded to a higher level with uranium than the secondary amines. With the latter, maximum loadings of 0.2 M amine solutions were 7-8 g U/l whereas 0.2 M solutions of the tertiary amines loaded to 10-11 g U/l.

G. Extraction of Uranium from Sulfate-Chloride Liquors

Results previously reported[1,2,3] have shown that the presence of chloride can cause a considerable decrease in the efficiency of extraction of uranium from sulfate solutions since the chloride competes with the uranyl sulfate complex for the amine reagent. The extent of the "chloride effect" was shown to be different for amines of different types, the effect being in general more pronounced for secondary than for tertiary amines. (In a chloride stripping cycle, this effect, of course, becomes an advantage rather than a disadvantage.)

Further data on the extraction of uranium from sulfate-chloride liquors with a wider variety of amines in different diluents is presented in Table 7. Of the amines tested, only N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine and tri-n-octylamine gave effective extraction of uranium when the chloride concentration was 0.15 M. The former compound showed reasonably effective extraction even when the chloride concentration was increased to 0.3 M.

When compared to extraction results obtained from chloride free liquors, the results thus far for the secondary amines show a greater depressing of the uranium coefficient when the amine reagent has branching near the nitrogen, e.g., R&H 9D-178 and bis(1-isobutyl-3,5-dimethylhexyl) amines, than when the branching is at a distance from the nitrogen, e.g., di(tridecyl P)amine.

H. Further Studies of the Compatibility of Several Amines with Different Diluents

As described briefly in ORNL-1959, some physical limitations were encountered in applying R&H 9D-178 amine in kerosene

Table 7

EXTRACTION OF URANIUM FROM SULFATE-CHLORIDE LIQUORS

Amine	Diluent	Approx. Final pH	Uranium Extraction Coefficient, E_a^o		
			No Cl^-	0.15 M Cl^-	0.3 M Cl^-
R&H 9D-178	Kerosene	1.0	115	1.3	--
"	Kerosene + 2% capryl alcohol	"	---	0.8	--
"	Amsco 123-15	"	---	2.0	--
"	" "	1.6	---	3.3	--
Bis(1-isobutyl-3,5-dimethylhexyl)	Kerosene	1.0	180	0.7	--
"	Kerosene + 2% capryl alcohol	"	---	0.5	--
Di(tridecyl P)	Kerosene	"	80	4.4	--
"	Kerosene + 2% capryl alcohol	"	---	2.9	--
"	" " " " "	1.6	---	4.9	--
N-benzyl-1(3-ethyl-pentyl)-4-ethyl-octyl	Kerosene	1.0	>2000	170	--
	"	1.6	---	175*	15*
"	Kerosene + 2% capryl alcohol	1.0	---	60	--
Tri-n-octyl	Kerosene + 2% capryl alcohol	1.0	310	24	--
"	" " " " "	1.6	---	41	--

Table 7 (Cont'd.)

EXTRACTION OF URANIUM FROM SULFATE-CHLORIDE LIQUORS

Extraction Conditions:

Aqueous:	Synthetic liquor containing 1.0 g U/l, 5.8 g Fe(III)/l, 3.3 g Al/l, 2.0 g PO_4/l, 1.7 g F/l, 0.5 M SO_4, chloride concentration as indicated above (added as NaCl), pH as indicated above.
Organic:	0.1 M amine
Phase Ratio:	$2^a/1^o$
Contact Time:	2 minutes
Temperature:	Room

*Uranium concentration in liquor was 1.25 g U/l.

diluent to the recovery of uranium from certain liquors containing both molybdenum and vanadium(V). Extractions were accompanied by precipitation of some of the amine reagent due apparently to the very limited solubility of a molybdenum-vanadium polyacid-amine complex in kerosene.

A more detailed study of the compatibility of several amines with molybdenum liquors has been made to define the degree of compatibility with respect to reagent and diluent choice and to variations in composition of leach liquors.

In preliminary tests, each amine solution was contacted with a synthetic liquor (Table 8) and, after a brief standing period (5-10 minutes), examined for precipitate formation. In two instances, when no precipitation was observed, the organic phase was separated and contacted with fresh volumes of liquor to determine if a precipitate would form at higher molybdenum loadings. Results of the tests are presented in Table 8.

With R&H 9D-178 amine, precipitation occurred after a single contact at $2.5^a/1^o$ when either kerosene or Amsco 123-15 (aliphatic petroleum fraction) was used as diluent. On addition of 2 v % capryl alcohol to the kerosene, no precipitate formed after a single contact, but precipitation did occur when the extract was contacted with another fresh volume of liquor, again at a phase ratio of $2.5^a/1^o$. In benzene or Amsco G diluent, no precipitate resulted even at high molybdenum loadings, i.e., after contacting a single volume of the solvent with ten volumes of the aqueous liquor, a condition which would result in high molybdenum loadings. Bis(1-isobutyl-3,5-dimethylhexyl)*, dodecenyl Primene JM**, and ditridecyl amines in kerosene and tri-n-octylamine in kerosene + 2 v % capryl alcohol showed no precipitation on a single contact at $2.5^a/1^o$. N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine in kerosene gave no precipitate after contact with ten liquor volumes.

To determine the effects from variations in composition of the aqueous phase, e.g., such as those expected in both the extraction and stripping operations, a series of experiments were performed wherein a number of amine diluent combinations were contacted with a liquor containing molybdenum, and then stripped, first with an acidic chloride solution and next with a solution of sodium carbonate.*** Approximately two hours was allowed to elapse between each contact, and during this time the organic phase was observed for precipitate formation. Four different synthetic liquors, differing

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*C&C Amine S-24.

**R&H FO-317 Amine.

***The latter contact would correspond to the amine regeneration step in a chloride stripping flow sheet.

Table 8

COMPATIBILITY OF AMINES WITH MOLYBDENUM-VANADIUM(V)-PHOSPHATE LIQUOR

Amine	Diluent	Contact	Total Aqueous Volume Contacted		
			$2.5^a/1^o$	$5^a/1^o$	$10^a/1^o$
R&H 9D-178	Kerosene	Single	P	--	--
"	Kerosene + 2% Cap. Alc.	Two stage at $2.5^a/1^o$	NP	P	--
"	Amsco 123-15	Single	P	--	--
"	Benzene	"	--	--	NP
"	Amsco G	"	NP	--	--
"	" "	"	--	--	NP
Bis(1-isobutyl-3,5-dimethylhexyl) (Compound 30B)	Kerosene	"	NP	--	--
R&H FO-317	"	"	NP	--	--
Tri-n-octyl	Kerosene + 2% Cap.Alc.	"	NP	--	--
N-benzyl-1(3-ethylpentyl)-4-ethyloctyl	Kerosene	4 stage at $2.5^a/1^o$	NP	NP	NP
Di(tridecyl P)	Kerosene	Single	NP	--	--

P = precipitate formed; NP = no precipitate formed.

Extraction Conditions:

Organic: 0.1 M amine in indicated diluent.

Aqueous: Synthetic liquor (1.2 g U/l, 1.07 g V(V)/l, 0.37 g V(IV)/l, 0.25 g Mo/l, 2.3 g Fe(III)/l, 2.1 g PO_4/l, 36 g SO_4/l, pH 1.1).

Contact Time: 2 minutes.

only in phosphate content and oxidation state of the contained vanadium, were examined. Compositions of the liquors are shown below.

	Liquor A	Liquor B	Liquor C	Liquor D
U	0.5 g/l	0.5 g/l	0.5 g/l	0.5 g/l
Mo	0.46 "	0.46 "	0.46 "	0.46 "
V(V)	0.0 "	1.0 "	0.0 "	1.0 "
V(IV)	1.0 "	0.0 "	1.0 "	0.0 "
Fe(III)	3.0 "	3.0 "	3.0 "	3.0 "
Al	3.0 "	3.0 "	3.0 "	3.0 "
PO_4	0.0 "	0.0 "	2.0 "	2.0 "
SO_4	0.5 M	0.5 M	0.5 M	0.5 M
pH	1	1	1	1

Results of the tests are listed in Tables 9, 10, 11, and 12. In all tests most (>80%) of the molybdenum was extracted corresponding to a molybdenum loading in the organic phase of 1.1-1.4 g Mo/l. The more important observations which may be made from examination of the data are as follows:

Tri-n-octylamine

1) Precipitation during the extraction cycle was not observed with any of the leach liquors tested, no matter which diluent was used.

2) When the amine was in kerosene or kerosene-alcohol diluent, precipitation occurred during the chloride stripping cycle after extraction from Liquors B, C, and D but not after extraction from Liquor A. In Amsco G diluent, no precipitation resulted during chloride stripping after extraction from any of the liquors. However, a precipitate did form on contact of the organic phase with sodium carbonate* solution if the extraction had been performed from liquors containing

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*If the organic extract is stripped with a carbonate solution directly, e.g., without an intermediate chloride strip, no precipitation occurs. Because of this and, since the cost associated with carbonate stripping of tertiary amines is comparable to that of chloride stripping, the former stripping method would appear to be a better choice for use with tertiary amines.

Table 9

COMPATIBILITY OF AMINES WITH MOLYBDENUM-VANADIUM(IV) LIQUOR (LIQUOR A)

Amine	Diluent	Elapsed Time After Separation of Phases					
		Extraction		Chloride Strip		Carbonate Strip	
		10 min	~2 hrs	10 min	~2 hrs	10 min	~2 hrs
Tri-n-octyl	Kerosene + 2% Tridecyl Alc.	NP	NP	NP	NP	NP	NP
"	" " 5% " "	NP	NP	NP	NP	NP	NP
"	" " 8% " "	NP	NP	NP	NP	NP	NP
"	" " 2% Decyl Alc.	NP	NP	NP	NP	NP	NP
"	" " 5% " "	NP	NP	NP	NP	NP	NP
"	" " 2% Capryl Alc.	NP	NP	NP	NP	NP	NP
"	" " 5% " "	NP	NP	NP	NP	NP	NP
"	Amsco G	NP	NP	NP	NP	NP	NP
"	Amsco G + 2% Tridecyl Alc.	NP	NP	NP	NP	NP	NP
Tri(iso-octyl)	Kerosene + 2% Capryl Alc.	NP	NP	NP*	NP*	NP	NP
"	" " 5% " "	NP	NP	NP	NP	NP	NP
"	Amsco G	NP	NP	NP	NP	NP	NP
"	Amsco G + 2% Tridecyl Alc.	NP	NP	NP	NP	NP	NP
R&H 9D-178	Kerosene	NP	NP	NP	NP	NP	NP
"	" + 2% Tridecyl Alc.	NP	NP	NP	NP	NP	NP
"	" " 5% " "	NP	NP	NP	NP	NP	NP
"	" " 2% Decyl Alc.	NP	NP	NP	NP	NP	NP
"	" " 5% " "	NP	NP	NP	NP	NP	NP
Bis(1-isobutyl-3,5-dimethyl-hexyl) (Comp. 30C)	Kerosene	NP	NP	NP	NP	NP	NP
"	" + 2% Tridecyl Alc.	NP	NP	NP	NP	NP	NP

Table 9 (Cont'd.)

COMPATIBILITY OF AMINES WITH MOLYBDENUM-VANADIUM(IV) LIQUOR (LIQUOR A)

*Third liquid phase formed because the solubility of the amine chloride salt in kerosene + 2% capryl alcohol was exceeded.

P = precipitate formed; NP = no precipitate formed; TP = trace of precipitate formed.

Test Conditions:

Organic:	0.1 M Amine.
Liquor:	Analysis p. 25.
Chloride Strip Solution:	1.0 M NaCl + 0.05 M H_2SO_4.
Carbonate Strip Solution:	5 w/v % Na_2CO_3 solution.
Phase Ratios:	Liquor/organic/chloride strip/carbonate strip = 3/1/1/1.
Contact Time:	5 minutes.

Table 10

COMPATIBILITY OF AMINES WITH MOLYBDENUM-VANADIUM(V) LIQUOR (LIQUOR B)

Amine	Diluent	Elapsed Time After Separation of Phases					
		Extraction		Chloride Strip		Carbonate Strip	
		10 min	~2 hrs	10 min	~2 hrs	10 min	~2 hrs
Tri-n-octyl	Kerosene + 2% Tridecyl Alc.	NP	NP	P	P	--	--
"	" " 5% " "	NP	NP	TP	P	--	--
"	" " 8% " "	NP	NP	NP	P	--	--
"	" " 2% Decyl Alc.	NP	NP	TP	P	--	--
"	" " 5% " "	NP	NP	NP	TP	--	--
"	" " 2% Capryl Alc.	NP	NP	P	P	--	--
"	" " 5% " "	NP	NP	NP	TP	--	--
"	Amsco G	NP	NP	NP	NP	NP	--
"	Amsco G + 2% Tridecyl Alc.	NP	NP	NP	NP	TP	--
Tri(iso-octyl)	Kerosene + 2% Capryl Alc.	NP	NP	P	P	--	--
"	" " 5% " "	NP	NP	P	P	--	--
"	" " 5% Tridecyl Alc.	NP	NP	P	P	--	--
"	" " 8% " "	NP	NP	P	P	--	--
"	" " 5% Decyl Alc.	NP	NP	P	P	--	--
"	" " 8% " "	NP	NP	P	P	--	--
"	Amsco G	NP	NP	NP	NP	TP	--
"	Amsco G + 2% Tridecyl Alc.	NP	NP	NP	NP	TP	--
R&H 9D-178	Kerosene	NP	NP	NP	NP	NP	NP
"	" + 2% Tridecyl Alc.	NP	NP	NP	NP	NP	NP
"	" " 5% " "	NP	NP	NP	NP	NP	NP

Table 10 (Cont'd.)

COMPATIBILITY OF AMINES WITH MOLYBDENUM-VANADIUM(V) LIQUOR (LIQUOR B)

Amine	Diluent	Elapsed Time After Separation of Phases					
		Extraction		Chloride Strip		Carbonate Strip	
		10 min	~2 hrs	10 min	~2 hrs	10 min	~2 hrs
R&H 9D-178	Kerosene + 2% Decyl Alc.	NP	NP	NP	NP	NP	NP
"	" " 5% " "	NP	NP	NP	NP	NP	NP
Bis(1-isobutyl-3,5-dimethyl-hexyl) (Compound 30C)	Kerosene	NP	NP	NP	NP	NP	NP
"	" + 2% Tridecyl Alc.	NP	NP	NP	NP	NP	NP

P = precipitate formed; NP = no precipitate formed; TP = trace of precipitate formed.

Test Conditions: Refer to Table 9.

Table 11

COMPATIBILITY OF AMINES WITH MOLYBDENUM-PHOSPHATE-VANADIUM(IV) LIQUOR (LIQUOR C)

Amine	Diluent	Elapsed Time After Separation of Phases: Extraction 10 min	Extraction ~2 hrs	Chloride Strip 10 min	Chloride Strip ~2 hrs	Carbonate Strip 10 min	Carbonate Strip ~2 hrs
Tri-n-octyl	Kerosene + 2% Tridecyl Alc.	NP	NP	P	P	--	--
"	" " 5% " "	NP	NP	P	P	--	--
"	" " 8% " "	NP	NP	P	P	--	--
"	" " 2% Decyl Alc.	NP	NP	P	P	--	--
"	" " 5% " "	NP	NP	P	P	--	--
"	" " 2% Capryl Alc.	NP	NP	P	P	--	--
"	" " 5% " "	NP	NP	P	P	--	--
"	Amsco G	NP	NP	NP	NP	P	P
"	" + 2% Tridecyl Alc.	NP	NP	NP	NP	P	P
"	Esso "Heavy Aromatic Naphtha"	NP	NP	NP	NP	NP	NP
Tri(iso-octyl)	Kerosene + 2% Capryl Alc.	NP	NP	P	P	--	--
"	" " 5% " "	NP	NP	P	P	--	--
"	" " 5% Tridecyl Alc.	NP	NP	P	P	--	--
"	" " 8% " "	NP	NP	P	P	--	--
"	" " 5% Decyl Alc.	NP	NP	P	P	--	--
"	" " 8% " "	NP	NP	P	P	--	--
"	Amsco G	NP	NP	NP	NP	P	P
"	" + 2% Tridecyl Alc.	NP	NP	NP	NP	P	P

Table 11 (Cont'd.)

COMPATIBILITY OF AMINES WITH MOLYBDENUM-PHOSPHATE-VANADIUM(IV) LIQUOR (LIQUOR C)

Amine	Diluent	Elapsed Time After Separation of Phases					
		Extraction		Chloride Strip		Carbonate Strip	
		10 min	~2 hrs	10 min	~2 hrs	10 min	~2 hrs
R&H 9D-178	Kerosene	NP	NP	NP	NP	TP	TP
"	" + 2% Tridecyl Alc.	NP	NP	NP	NP	TP	TP
"	" " 5% " "	NP	NP	NP	NP	NP	NP
"	" " 2% Decyl Alc.	NP	NP	NP	NP	NP	NP
"	" " 5% " "	NP	NP	NP	NP	NP	NP
Bis(1-isobutyl-3,5-dimethyl-hexyl) (Compound 30C)	Kerosene	NP	NP	NP	NP	NP	NP
"	" + 2% Tridecyl Alc.	NP	NP	NP	NP	NP	NP

P = precipitate formed; NP = no precipitate formed; TP = trace of precipitate formed.

Test Conditions: Refer to Table 9.

Table 12

COMPATIBILITY OF AMINES WITH MOLYBDENUM-PHOSPHATE-VANADIUM(V) LIQUOR (LIQUOR D)

Amine	Diluent	Elapsed Time After Separation of Phases: Extraction 10 min	Extraction ~2 hrs	Chloride Strip 10 min	Chloride Strip ~2 hrs	Carbonate Strip 10 min	Carbonate Strip ~2 hrs
Tri-n-octyl	Kerosene + 2% Tridecyl Alc.	NP	NP	P	P	--	--
"	" " 5% " "	NP	NP	P	P	--	--
"	" " 8% " "	NP	NP	P	P	--	--
"	" " 2% Decyl Alc.	NP	NP	P	P	--	--
"	" " 5% " "	NP	NP	P	P	--	--
"	" " 2% Capryl Alc.	NP	NP	P	P	--	--
"	" " 5% " "	NP	NP	P	P	--	--
"	Amsco G	NP	NP	NP	NP	TP	TP
"	" + 2% Tridecyl Alc.	NP	NP	NP	NP	TP	TP
"	Esso "Heavy Aromatic Naphtha"	NP	NP	NP	NP	NP	NP
Tri(iso-octyl)	Kerosene + 2% Capryl Alc.	NP	NP	P	P	--	--
"	" " 5% " "	NP	NP	P	P	--	--
"	" " 5% Tridecyl Alc.	NP	NP	P	P	--	--
"	" " 8% " "	NP	NP	P	P	--	--
"	" " 5% Decyl Alc.	NP	NP	P	P	--	--
"	" " 8% " "	NP	NP	P	P	--	--
"	Amsco G	NP	NP	P	P	--	--
"	" + 2% Tridecyl Alc.	NP	NP	P	P	--	--

Table 12 (Cont'd.)

COMPATIBILITY OF AMINES WITH MOLYBDENUM-PHOSPHATE-VANADIUM(V) LIQUOR (LIQUOR D)

Amine	Diluent	Elapsed Time After Separation of Phases					
		Extraction		Chloride Strip		Carbonate Strip	
		10 min	~2 hrs	10 min	~2 hrs	10 min	~2 hrs
R&H 9D-178	Kerosene	P	P	--	--	--	--
"	" + 2% Tridecyl Alc.	NP	NP	NP	NP	NP	NP
"	" " 5% " "	NP	NP	NP	NP	NP	NP
"	" " 2% Decyl Alc.	NP	NP	NP	NP	NP	NP
"	" " 5% " "	NP	NP	NP	NP	NP	NP
Bis(1-isobutyl-3,5-dimethyl-hexyl) (Compound 30C)	Kerosene	NP	NP	NP	NP	NP	NP
"	" + 2% Tridecyl Alc.	NP	NP	NP	NP	NP	NP

P = precipitate formed; NP = no precipitate formed; TP = trace of precipitate formed.

Test Conditions: Refer to Table 9.

phosphate (Liquors C and D). In Esso "Heavy Aromatic Naphtha"* no precipitation occurred during either chloride or carbonate stripping after extraction from Liquors C and D. This diluent was not tested with Liquors A and B.

Tri(iso-octyl)amine

1) No precipitation was observed during the extraction cycle in any test.

2) In kerosene or kerosene-alcohol diluents, precipitation resulted during chloride stripping after extraction from Liquors B, C, and D but not after extraction from Liquor A. In Amsco G or Amsco G-alcohol, no precipitate occurred in chloride stripping except after extraction from the molybdenum-vanadium(V)-phosphate liquor (Liquor D). In two instances where precipitation did not occur during chloride stripping (Liquors B and C), precipitation did result on contact with sodium carbonate solution.

3) In general, the behavior pattern of tri(iso-octyl)-amine was very similar to that of tri-n-octylamine, the tendency toward precipitate formation with the iso-compound being slightly greater.

R&H Amine 9D-178

1) In kerosene diluent, precipitation was observed during extraction only when the liquor contained molybdenum, vanadium(V), and phosphate (Liquor D). Upon addition of 2 v % alcohol to the kerosene, precipitation during extraction from Liquor D was avoided.

2) In kerosene-alcohol diluent no more than a trace amount of precipitation resulted during chloride and carbonate stripping after extraction from any of the four liquors.

Bis(1-isobutyl-3,5-dimethylhexyl)amine (Amine S-24)

1) With the amine in kerosene or kerosene-alcohol diluent, no precipitation was observed during the extraction or stripping cycles with any of the four liquors tested.

In general, the compatibility studies described above have shown that some caution must be observed in application of certain amines to solvent extraction recovery of uranium from

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*An inexpensive (~13¢/gal) high-boiling, high-flash point aromatic petroleum product.

liquors of relatively high molybdenum content, particularly if vanadium(V) and/or phosphate also are present. On the other hand, with some compounds, e.g., Amine S-24, no difficulties have been experienced in any of the tests made thus far. Also, in many instances where difficulties have been experienced, it has been possible to avoid them by proper choice of the diluent used.

It should be mentioned that, since the precipitate formation encountered is dependent on the molybdenum (and probably vanadium(V) and phosphate) concentration in the liquor, the tests described above cannot possibly define the performance expected with liquors of all compositions. The liquors selected for study contained high concentrations of molybdenum (0.3 - 0.46 g Mo/l) compared to those encountered in most Western ore liquors and, hence, molybdenum loading of the organic phase was higher* and the compatibility tests were, therefore, rather stringent with respect to that application. However, in operations wherein molybdenum recovery is desired (see Section J), molybdenum loading of the organic phase might be greater than in the above tests and the compatibility requirements more severe. Studies of the performance of various amines and diluents at higher molybdenum loadings (and from liquors relatively high in phosphate content) are being made.

I. Extraction of Zirconium, Cerium(III) and Uranium(IV)

Extractions of zirconium, cerium(III) and uranium(IV) from 0.5 M sulfate solutions have been measured using several amines of different types and structure.** From the experimental results in Table 13, it may be noted that strong extraction of zirconium was exhibited by all of the amines tested. Similar to uranium, effective stripping of zirconium from the amine extracts has been obtained with acidified chloride solutions (results not shown). Nitrate stripping should also be effective.

High extraction coefficients (>1000) for uranium(IV) were shown by the primary amine both at pH 1.0 and 1.6. Strong extraction of uranium(IV) was also observed for the secondary amines, particularly at the higher pH level. Relatively weak extraction of uranium(IV) was obtained with tri-n-octylamine.

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*High molybdenum concentration in the organic phase could be attained from liquors of relatively low molybdenum content if a chloride stripping flow sheet is utilized and the amine is not regenerated to free amine prior to its return to the extraction system.

**Results for extraction of zirconium and uranium(IV) from 1.0 M sulfate solution by other representative amine compounds were reported in ORNL-1734 (p. 37-38).

Table 13

EXTRACTION OF Zr, Ce(III), AND U(IV) WITH AMINES

Amine	Amine Type	Diluent	Extraction Coefficient, E_a^g Zr* Final pH 1.0	Ce(III) Final pH 1.1	U(IV) Final pH 1.0	U(IV) Final pH 1.6
Primene JM-T (Comp. 6C)	Primary	Kerosene	>60	14	>1000	>1000
Armeen 2-12 (Comp. 103F)	Secondary	Kerosene + 5% Tridecyl Alcohol	>60	0.025	220	310
Bis(1-isobutyl-3, 5-dimethylhexyl) (Comp. 30C)	"	Kerosene	>60	<0.003	44	490
R&H 9D-178	"	Kerosene	>60	0.006	79	480
Tri-n-octyl	Tertiary	Kerosene + 2% Tridecyl Alcohol	>60	<0.003	1.1	2.3

Extraction Conditions:

Organic: 0.1 M Amine.

Aqueous: 0.003 - 0.004 M metal in 0.5 M SO_4 solution at indicated pH.

Phase Ratio: 1:1.

Temperature: Room.

*Exact extraction coefficients for zirconium were not calculable due to uncertainties in the analytical measurements at the low concentrations of zirconium in the aqueous phase.

The primary amine showed an extraction coefficient of 14 for cerium(III) whereas extraction of this element by the other amines tested was essentially negligible.

J. Recovery of Molybdenum

As reported previously[2,3] the amines are strong extractants for molybdenum from sulfate liquors. Since some uranium ores and the resulting acid leach liquors contain appreciable amounts of molybdenum, consideration may be given to the possibilities for recovering a molybdenum by-product in these cases.

Preliminary tests on molybdenum extraction have been made from 1.1 M and 1.5 M sulfate solutions at pH ~1, using 0.1 M R&H 9D-178 amine in kerosene. These data, in the form of extraction isotherms, are shown in Figure 4. It may be noted that the extraction efficiency was high for both liquors and particularly from the liquor of lower sulfate content. Also, it may be noted that the isotherms have an unconventional shape, i.e., a relatively low slope at low molybdenum loadings with the slope increasing as the loading increases.* (The isotherms were not extended sufficiently far to indicate the maximum molybdenum loading achievable.) Similar isotherms have been noted for vanadium extraction.** It is believed that these effects might be attributed to a change in chemical form of the metals, e.g., polymerization, after their extraction into the organic phase.

It is apparent that in application of the Amex process to recovery of both uranium and molybdenum from liquors wherein they coexist, both of these metals would report to the organic phase in the extraction step and separation must be achieved later, either during or subsequent to the stripping step. One method which suggests itself for this purpose is the use of chloride strip solutions which previously have been shown to be effective in removing uranium from the organic phase but relatively ineffective with respect to molybdenum. After the removal of uranium, molybdenum removal should be readily obtained by contacting with an alkaline solution such as sodium carbonate. A few preliminary tests have been completed which demonstrate the separation achievable by this method. Thus, when a 0.1 M solution of R&H 9D-178 amine in kerosene which had been loaded to 1.9 g U/l and 2.3 g Mo/l was contacted with a 0.9 M NaCl - 0.1 M HCl strip solution at a phase ratio of $2^{o}/1^{a}$, 99% of the uranium and only 2% of the molybdenum was stripped from the organic phase. A second contact of the organic phase with fresh strip solution, again at $2^{o}/1^{a}$, removed essentially all of the remaining uranium and 3%

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*It should be noted that the great difference in the scales in Figure 4 exaggerates the effect described. E_a^Q for the lowest points shown is still above 25 for raffinates below 5 ppm molybdenum.

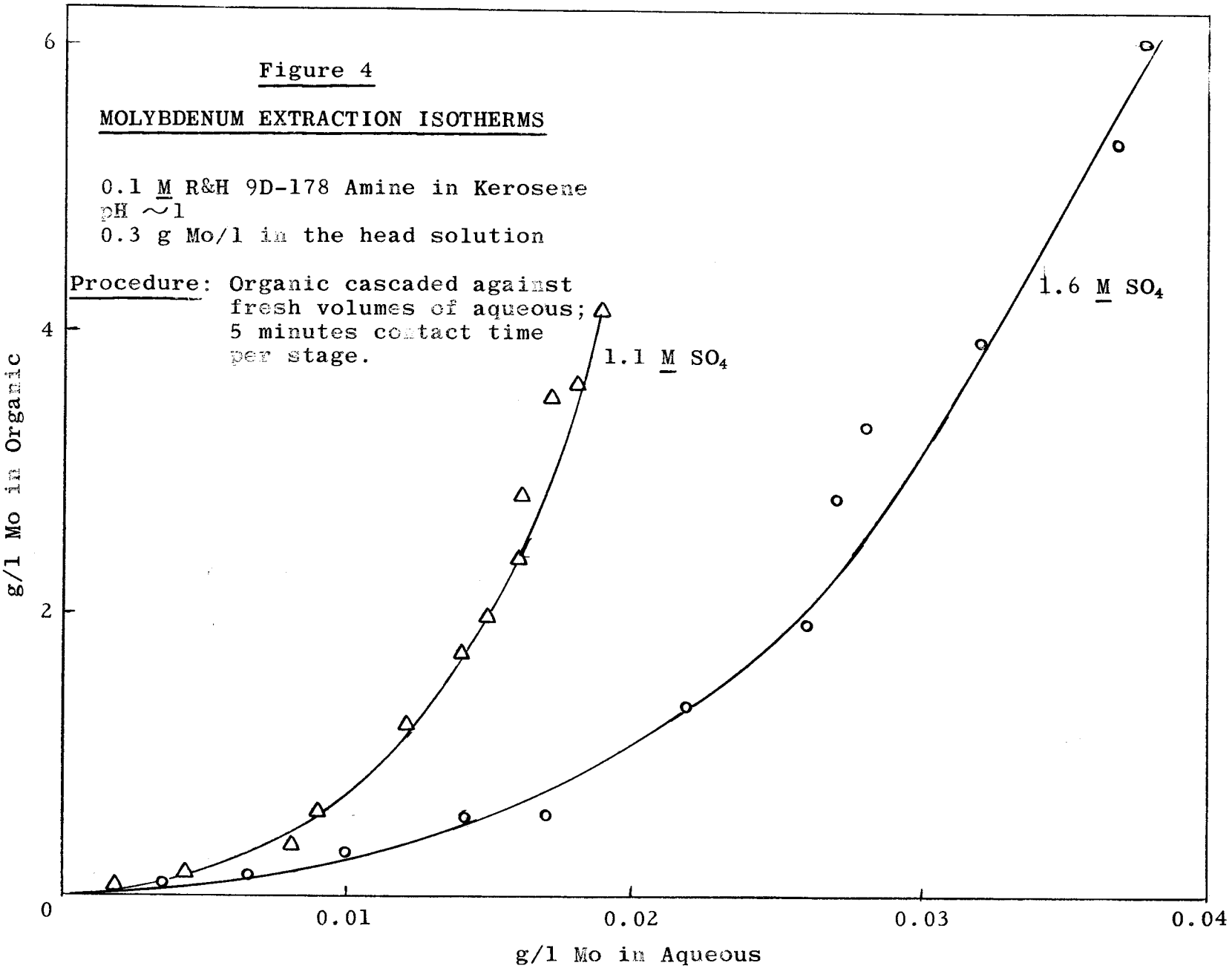
**Progress report being prepared.

Figure 4

MOLYBDENUM EXTRACTION ISOTHERMS

0.1 M R&H 9D-178 Amine in Kerosene
pH ~1
0.3 g Mo/l in the head solution

Procedure: Organic cascaded against fresh volumes of aqueous; 5 minutes contact time per stage.



more of the molybdenum. Subsequent contact of the organic phase with a solution of sodium carbonate stripped >99% of the remaining molybdenum in a single stage. With 0.1 M tri-n-octylamine in Amsco G* (loaded to 1.9 g U/l and 3.3 g Mo/l) stripping of uranium with 0.9 M NaCl - 0.1 M HCl, as expected,[2] was somewhat more difficult, i.e., 96% of the uranium and 1% of the molybdenum was stripped at a phase ratio of $2^{o}/1^{a}$. However, a second contact with fresh strip solution at the same phase ratio increased uranium removal to >99% while stripping little additional molybdenum. A subsequent carbonate strip removed 99% of the remaining molybdenum in a single stage.

Another method for separate recovery of uranium and molybdenum might be one wherein both metals are stripped simultaneously by, e.g., sodium carbonate with separation being attained during the uranium precipitation step. Previous experiments[2] have indicated that most of the molybdenum might be left in solution during uranium precipitation if conditions are properly controlled.

Further tests are in progress to better define the uranium-molybdenum separations and recoveries achievable and also to study molybdenum product recovery from the various aqueous solutions after it has been separated from uranium.

K. Extraction of Vanadium(IV) by a Primary Amine

Previous experiments[3] have shown that vanadium(IV) is extracted to a negligible degree from sulfate liquors by secondary and tertiary amines. To obtain comparative data with primary amines, a series of cursory tests were made wherein a 0.25 M solution of a typical primary amine (Primene JM-T) in kerosene was contacted with a 0.5 M sulfate solution which contained 2 g V(IV) per liter and which had been adjusted to various pH levels.

As observed from the test results in Table 14, the extraction coefficients for V(IV) with the primary amine appear to increase slightly with increasing pH. However, even at the highest pH level tested, i.e., pH 3.4, the extractions were too low to be of practical interest.

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*As described in Section H, some physical difficulties have been encountered in stripping certain amines with chloride solutions and under certain conditions with carbonate solutions, when the extract contains molybdenum. In many cases these difficulties can be alleviated by proper choice of diluent.

Table 14

EXTRACTION OF VANADIUM(IV) WITH PRIMENE JM-T

Final Aqueous pH	Phase Ratio a:o	Vanadium Extraction Coefficient, E_a^o
1.7	1	0.35*
1.9	1	0.40*
2.1	1	0.43*
2.2	1	0.50
3.4	4	0.70

Extraction Conditions:

Organic: 0.25 M Primene JM-T in kerosene.

Aqueous: Vanadium(IV) sulfate solution, 2 g V/l, 0.5 M SO_4, pH adjustment made with sodium hydroxide.

Contact Time: 2 minutes.

*At 20 minutes contact time distribution was essentially unchanged.

L. Losses of Amines to Aqueous Liquors

Further measurements of the distribution of several amines to various aqueous solutions are listed in Table 15. The method used for these measurements, as well as data for a variety of other amine-solvent-aqueous systems, has been described previously.(1,2,3)

Observations which may be made from the data in Table 15 are as follows:

1) Further evidence of the influence of sulfate concentration on the distribution of amine to aqueous sulfate liquors is given in the tests with R&H 9D-178 amine (Batch 193D). Thus, the steady state loss of this compound was 16 ppm to a liquor containing 0.5 M SO_4 and 39 ppm to a liquor containing 0.2 M SO_4, but otherwise similar in composition.

2) Significant differences in both initial and steady-state losses were obtained between different batches of R&H 9D-178 amine.

3) The higher molecular weight R&H FO-317 amine (dodecenyl Primene JM) showed about the same initial loss as R&H 9D-178 amine but the steady-state loss was appreciably less.

4) Distribution losses to an acid chloride solution, such as might be used in chloride stripping, were negligibly low for all of the amines tested.

5) The new sample of bis(1-isobutyl-3,5-dimethylhexyl)-amine (Amine S-24) exhibited much lower losses (both initial and steady-state) than had been shown by earlier impure samples.* The low losses combined with other favorable properties such as relatively high loadings (see Sections B and N), high selectivity (see Section B), good diluent compatibilities and phase separations, etc. made this compound a particularly desirable extractant among the secondary amines. It has been reported previously that this reagent is one of those which could be made available at a reasonable price in the event of a demand. Information has been requested from the supplier to ascertain whether this new sample is representative of the compound purity that would be obtained in actual practice.

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*The new sample of bis(1-isobutyl-3,5-dimethylhexyl)amine (now called Amine S-24) is estimated to be about 97% pure by equivalent wt. measurements and differential titration. Previous samples of this compound (called Amine 16F-27, see ORNL-1734 and ORNL-1922) showed evidence of containing appreciable amounts of -C=N- compounds and one of the samples appeared to contain a significant amount of a primary amine.

Table 15

LOSSES OF AMINE THROUGH DISTRIBUTION TO AQUEOUS SOLUTIONS

Amine	Comp. No.	Diluent	Aqueous Solution	Loss of Amine: Fraction Readily Lost % of Initial	Loss of Amine: Steady State Loss, ppm/ Aqueous
Bis(1-isobutyl-3,5-dimethyl-hexyl)*	30C	Kerosene	0.5 M SO_4 Syn. Liquor**	3	6
Tri(iso-octyl)	239A	Kerosene + 2% Capryl Alc.	" " " "	2	15
Tri-n-octyl	125H	" " 3% Tridecyl Alc.	" " " "	4	11
"	"	" " " " "	" " " " (45°C)	2	16
R&H 9D-178	193D	Kerosene	" " " "	10	16
"	193E	"	" " " "	13	20
"	193F	"	" " " "	9	31
R&H FO-317	242A	"	" " " "	8	5
N-Benzyl(7-ethyl-2-methyl-undecyl-4)	243A	"	" " " "	3	120

Table 15 (Cont'd.)

LOSSES OF AMINE THROUGH DISTRIBUTION TO AQUEOUS SOLUTIONS

Amine	Comp. No.	Diluent	Aqueous Solution	Loss of Amine: Fraction Readily Lost % of Initial	Loss of Amine: Steady State Loss, ppm/ Aqueous
N-n-Decyl(7-ethyl-2-methyl-undecyl-4)	245A	Kerosene	0.5 M SO_4 Syn. Liquor	4	6
N-(p-sec.-amyl-benzyl)-1-iso-butyl-3,5-dimethylhexyl	251A	Kerosene	" " " "	9	11
N-(2-naphthyl-methyl)-1-iso-butyl-3,5-di-methylhexyl	252A	Kerosene	" " " "	14	80
R&H 9D-178	193D	Kerosene	0.2 M SO_4 Syn. Liquor***	10	39
"	"	"	0.1 M HCl - 0.9 M NaCl	7	8
Tri(iso-octyl)	239A	Kerosene + 2% Tridecyl Alc.	" " " "	2	5
N-Benzyl-1(3-ethylpentyl)-4-ethyloctyl	228A	Kerosene	" " " "	1	5

Table 15 (Cont'd.)

LOSSES OF AMINE THROUGH DISTRIBUTION TO AQUEOUS SOLUTIONS

*Amine S-24 (C&CCC).

**Uranium barren synthetic Marysvale Liquor, pH 1 (5.8 g Fe(III)/l, 3.3 g Al/l, 50 g SO_4/l, 2 g PO_4/l, 1.7 g F/l). Room temperature, except where otherwise indicated.

***Uranium barren synthetic liquor (2 g Fe(III)/l, 2 g Al/l, 0.2 M SO_4, pH 1).

6) Steady-state losses of tri-n-octylamine, from kerosene + 3 v % tridecyl alcohol may have been slightly higher at 45°C than at room temperature (measurements indicated 16 ppm versus 11 ppm).

7) In spite of the large (14 carbon) alkyl group the steady-state loss of N-benzyl(7-ethyl-2-methylundecyl-4)-amine was surprisingly high, i.e., 120 ppm.

M. Stability of Amines

Recently an automatic reagent testing apparatus has been devised for studying the stability of extraction agents in cyclic operation. The equipment involves a single mixer-settler stage for extraction and a single mixer-settler stage for stripping and is designed to provide cyclic flow of the organic extractant without attention from an operator. Flow of the phases is regulated with micro-bellows pumps. Sufficient hold-up time is provided in the settlers to minimize organic losses by entrainment in the aqueous phase. Also, the units are tightly enclosed to insure that evaporation of the diluent is negligible. The complete apparatus is mounted in a closed transite chamber equipped with a heater and blower to maintain the desired temperature conditions. Since the total organic volume in the system is low ($\sim$300 ml), the organic phase may be subjected to a large number of extraction-stripping cycles in a reasonable time period, and without the expenditure of inconveniently large volumes of leach liquor.

Such equipment eliminates the laborious procedure, previously utilized, of performing a large number of extraction-stripping cycles in separatory funnels. In addition, some of the uncertainties in the latter procedure introduced by mechanical losses of the organic phase and potential evaporation of the diluent are reduced to an unimportant level.

First tests with the new apparatus have been devoted to studies of tri-n-octylamine since this compound had shown the least resistance to oxidation of those previously tested. Three separate 200-cycle runs were made using a 0.1 M solution of the amine reagent in kerosene plus 3 v % tridecyl alcohol. The leach liquors treated in each test were different with respect to pH and concentration and oxidation state of the vanadium. Composition of the liquors and temperature conditions for each of the runs are shown below.

	Run 1	Run 2	Run 3
U	1.2 g/l	1.2 g/l	1.2 g/l
V(IV)	0.5	0.0	0.0
V(V)	0.0	1.5	1.5
Fe(III)	1.5	1.5	1.5
Al	1.5	1.5	1.5
Mo	0.1	0.1	0.1
Cu	0.02	0.02	0.02
Ni	0.02	0.02	0.02
SO_4	0.4 M	0.4 M	0.4 M
pH	0.9	1.7	1.5
Operating Temperature	45°C	R.T. (25-30°C)	45°C

A 5 w/v % sodium carbonate solution was employed as the stripping agent. The flow rates were 30 ml/min for the liquor, 10 ml/min for the organic, and 5 ml/min for the strip solution. The organic residence time was fifteen minutes in each of the extraction and stripping systems giving a total cycle time of approximately one-half hour.

Changes in amine concentration during the course of the runs were measured by removing samples of the organic phase after every 50 cycles for amine titration. The decrease in amine concentration may be attributed to the sum of the losses through distribution* to the aqueous phase and to degradation. As shown in Figure 5, the rate of this decrease was fairly uniform throughout each of the 200 cycle operations. The decreases in organic phase volumes (entrainment) suffered during the tests were measured after the completion of 200 cycles. The amounts of amine lost by this means are combined

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*It should be noted that, in these tests, the organic phase in contact with the aqueous raffinate is loaded with uranium. Previous studies[1] have shown that amine solubility loss to the aqueous phase is less when the organic phase contains uranium than when it is barren of uranium. Thus, the solubility losses in these tests were somewhat less than those which would occur in multi-stage countercurrent operation where the uranium content of the organic phase in the bottom stage is small.

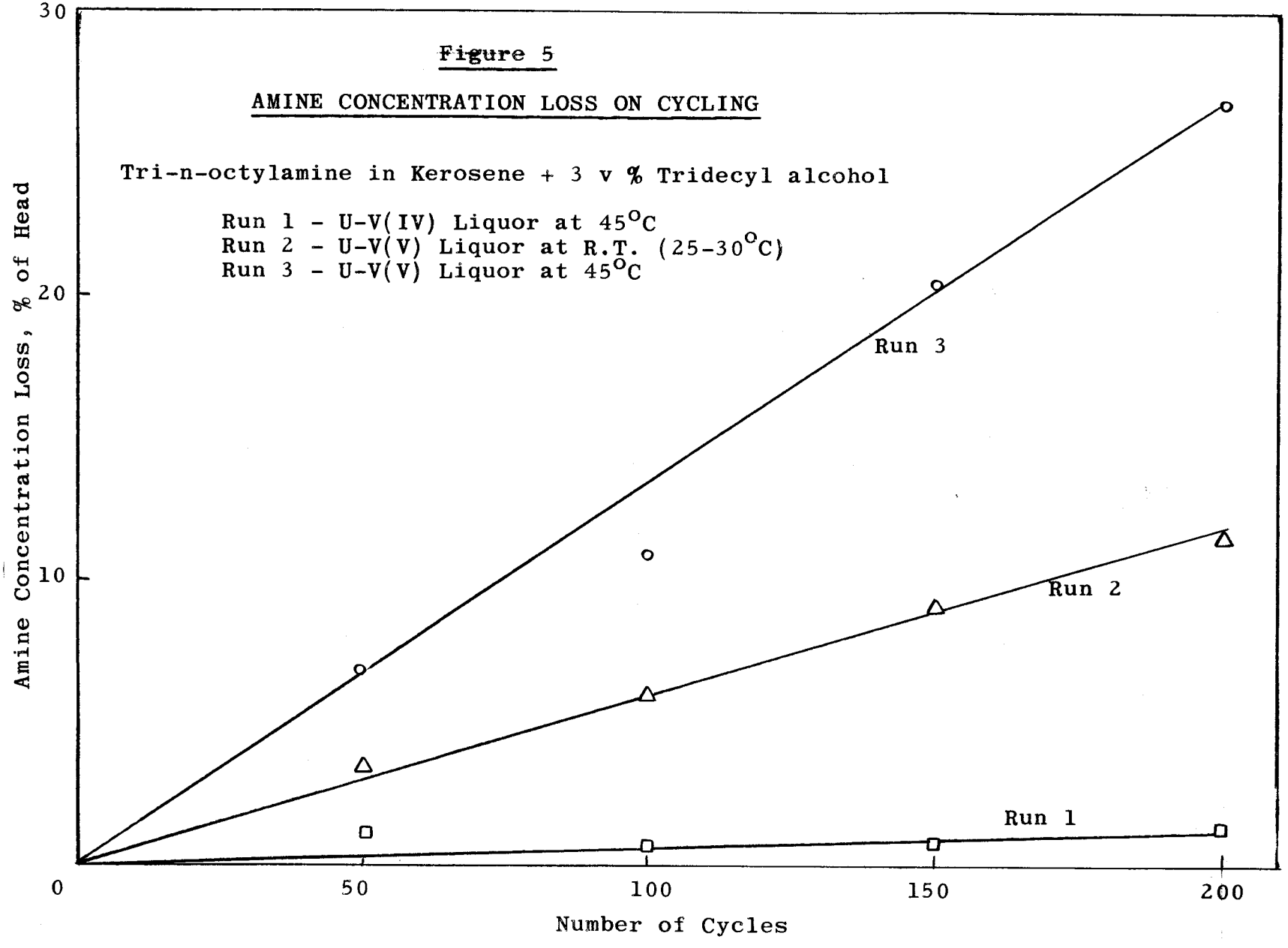
Figure 5
AMINE CONCENTRATION LOSS ON CYCLING
Tri-n-octylamine in Kerosene + 3 v % Tridecyl alcohol
Run 1 - U-V(IV) Liquor at 45°C
Run 2 - U-V(V) Liquor at R.T. (25-30°C)
Run 3 - U-V(V) Liquor at 45°C
Amine Concentration Loss, % of Head
30
20
10
0
50
100
150
200
Number of Cycles
Run 3
Run 2
Run 1

with the amounts lost by concentration change to give the total loss of reagent for the experiments (see Table 16). It may be noted that the volume decrease of the organic phase was very low (5-8% in 200 cycles) in each of the tests and contributed to only a minor portion (except in Run 1) of the total extractant loss. Samples of the head organic solutions and the organic samples after 200 cycles were subjected to standardized uranium extraction tests. In each case, uranium loading (moles uranium/mole amine) of the cycled samples was equivalent to that of the head sample.

Examination of Table 16 shows that in Run 1, where the vanadium was in the quadrivalent state and the operating temperature was 45°C, the total amine loss was only 4 ppm.* As observed in previous tests,(1) the loss of amine was increased in the presence of vanadium(V) particularly at the higher temperature. For example, with vanadium(V) present, and at temperatures of 25-30°C and 45°C, the measured total amine losses were 11 and 24 ppm, respectively. Differential titration measurements (Table 16) indicate that the increased losses in these latter tests were a result of increased degradation of the tri-n-octylamine to more soluble primary and secondary amine.

Even under the most extreme conditions, however, the total loss of amine was of a reasonable order (24 ppm). For example, in processing a liquor containing 1.25 g U_3O_8/l, such a loss would correspond to one pound of amine per 50 pounds of U_3O_8 recovered. Further stability tests including study of different amines and other stripping cycles are in progress. From previous experience, it is expected that the secondary amines will demonstrate even greater resistance to degradation than tri-n-octylamine.

N. Stripping Amines with Sodium Carbonate Solution

In previous measurements of carbonate requirements for stripping uranium from R&H 9D-178 amine-kerosene extracts,(2) very slow phase separations were encountered when the amount of excess sodium carbonate in the stripping system was small. Consequently, to avoid physical difficulties, it was necessary to supply more sodium carbonate to the system than was otherwise required for the attainment of complete uranium stripping.

To determine if the physical performance of R&H 9D-178 in kerosene is typical of the performance to be expected for other reagents and diluents, additional stripping tests have been made with a variety of amine-diluent combinations. In each of these tests the organic solutions, loaded to approxi-

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*Parts of amine per million parts of raffinate passed.

Table 16

ORGANIC LOSSES IN CYCLIC TESTS

Run	Organic Volume Start (ml)	Organic Volume After 200 Cycles* (ml)	Organic Volume % Loss	Amine Concentration Start (M)	Amine Concentration After 200 Cycles (M)	Amine Concentration % Loss	Amine Loss(1) Due to Volume Loss	Amine Loss(1) Due to Conc. Loss(2)	Amine Loss(1) Total	Total Amine Loss lbs/lb U_3O_8(3)
1	320	305	5	0.1090	0.1077	1.2	3	1	4	0.003
2	320	305	5	0.1106	0.0980	11.4	3	8	11	0.009
3	320	295	8	0.1100	0.0785	28.7	5	19	24	0.019

(1) Parts of amine per million parts of raffinate passed.
(2) Sum of losses by solubility loss to aqueous phase and degradation loss.
(3) Assuming (as in ORNL-1959) a head liquor containing 1.25 g U_3O_8/l.

Differential Titration of Organic Samples

	% Primary	% Secondary	% Tertiary
Run 1 - Head	-	-	>99
After 200 cycles	2	-	98
Run 2 - Head	3	Trace	>96
After 200 cycles	1	3	>95
Run 3 - Head	-	-	>99
After 200 cycles	2	6	92

*Listed volume is corrected for samples removed during the run. Ten ml. samples were withdrawn at 50, 100, and 150 cycles.

mately the same level with uranium, were contacted (by vigorous shaking in separatory funnels) with 8 w/v % Na_2CO_3 solution at three different phase ratios.* The rate and cleanness of separation of the phases was then noted. Results are presented in Table 17.

As observed previously, R&H 9D-178 amine in kerosene formed very slow-breaking emulsions when only a small excess of sodium carbonate was supplied to the system; with a large excess, reasonably rapid and clean separation was obtained. The performance of this amine was also very poor in kerosene-tridecyl alcohol and Amsco D-95 diluents. However, when used in Amsco 123-15 (a high boiling aliphatic solvent), separations were markedly improved and were reasonably rapid even at the highest organic/aqueous ratio (lowest excess carbonate) tested. With bis(1-isobutyl-3,5-dimethylhexyl)amine (Amine S-24) in kerosene, tri-n-octylamine in kerosene + 3% capryl alcohol and N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine in kerosene, rapid and clean phase separation was obtained at each phase ratio, i.e., at each level of excess sodium carbonate. Di(tridecyl P)amine in kerosene + 3% capryl alcohol gave slower but still reasonably rapid separation, although some interfacial scum was formed in the test with the lowest amount of excess carbonate.

In general, then, it is apparent that the physical limitations observed in stripping R&H 9D-178 in kerosene with sodium carbonate solutions are not experienced with the same amine in a better diluent or with several other amine-diluent combinations. Consequently, the carbonate requirements for stripping the more favorable combinations would be somewhat lower than predicted from some of the earlier tests (see ORNL-1959).

As mentioned previously[2] carbonate requirements for stripping certain tertiary amines, e.g., tri-n-octyl and tri-iso-octyl amines would be even lower since these compounds may be loaded with uranium to a higher level than the secondary amines.** To demonstrate this, several carbonate stripping tests were performed on a solution of tri-n-octylamine in kerosene + 2% capryl alcohol which had been loaded to $\sim$5 g U/l. Results are shown in Table 18. Complete

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*At this uranium loading ($\sim$3.6 g U/l), stripping phase ratios of $4^o/1^a$, $5^o/1^a$, and $6^o/1^a$ correspond respectively to approximately 100, 60, and 30% excess carbonate assuming the carbonate requirements are calculated on the basis of complete utilization of the sodium carbonate base strength as shown in Equations (4) and (5) on page 49 of ORNL-1959.

**Loadings of one secondary amine, i.e., bis(1-isobutyl-3,5-dimethylhexyl)amine (Amine S-24) have approached those achieved with the tertiary amines (see pages 7 and 8).

Table 17

RATE OF PHASE SEPARATION IN STRIPPING AMINES WITH Na_2CO_3 SOLUTION

Amine	Diluent	Phase Ratio of 4°/1[a] Sepn. Time (sec)	Final pH	Sepn.	Phase Ratio of 5°/1[a] Sepn. Time (sec)	Final pH	Sepn.	Phase Ratio of 6°/1[a] Sepn. Time (sec)	Final pH	Sepn.
R&H 9D-178 (Comp. 193C)	Kerosene	90	8.8	Clean	200	8.4	*	>600	7.7	*
"	Kerosene + 3% Tridecyl Alc.	115	8.8	Clean	200	8.4	*	>600	7.7	*
"	Amsco D-95	125	8.8	Clean	110	8.4	*	>600	8.0	*
"	Amsco 123-15	30	8.8	Clean	25	8.5	Clean	65	7.9	*
Tri-n-octyl	Kerosene + 3% Capryl Alc.	40	8.7	Clean	20	8.1	Clean	25	7.5	Clean
N-Benzyl-1(3-ethylpentyl)-4-ethyloctyl	Kerosene	25	8.7	Clean	35	8.1	Clean	15	7.5	Clean
Di(tridecyl P)	Kerosene + 3% Capryl Alc.	85	8.8	Clean	35	8.4	Clean	90	7.9	*
Bis(1-isobutyl-3,5-dimethyl-hexyl) (Amine S-24)	Kerosene	17	9.1	Clean	20	8.2	Clean	25	7.45	Clean

*Some interfacial scum formed which may actually be an extremely slow-breaking emulsion.

Stripping Conditions: Extracts: 0.1 M amine solutions loaded to ~3.6 g U/l from synthetic Marysvale liquor.
Stripping Solution: 8 w/v % Na_2CO_3.
Temperature: Room.
Contact Time: 2 minutes.

Table 18

Na_2CO_3 STRIPPING OF TRI-n-OCTYLAMINE

Sodium Carbonate Concentration, w/v %	Phase Ratio o/a	Contact Time	Final pH	g/l U		% Stripped	lbs Na_2CO_3/lb U_3O_8
				Aqueous	Organic		
6	4.8	5 min.	7.1	24.7	0.0004	>99.9	2.1*
6	"	30	7.1	24.5	0.0004	"	2.1
6	4.1	5	7.9	21.2	0.0001	"	2.4
6	"	30	8.0	21.2	0.0002	"	2.4
6	3.4	5	8.5	17.3	0.0004	"	2.9
6	"	30	---	----	0.0002	"	2.9
8	6.3	5	7.2	32.1	0.0003	"	2.1
8	"	30	7.2	32.2	0.0003	"	2.1
8	5.4	5	7.9	27.9	0.0003	"	2.4
8	"	30	7.9	27.7	0.0005	"	2.4
8	4.5	5	8.5	22.8	0.0003	"	3.0
8	"	30	8.5	22.9	0.0003	"	3.0

Extract: 0.10 M Tri-n-octylamine (Comp. 125H) in kerosene + 2% capryl alcohol loaded to 4.9 g U/l from synthetic Marysvale liquor.

Stripping Conditions: R.T. (33°C). Contact in separatory funnels shaken by machine.

Phase Separation: Clean and rapid (~15 seconds) in all tests.

*Corresponds to 5% excess sodium carbonate based on Equations (4) and (5) on page 49 of ORNL-1959.

removal of uranium from the organic phase was accomplished in all tests and in each case the phase separation was clean and very rapid ($\sim$15 seconds). Stripping was accomplished with expenditure of as little as 2.1 lbs Na_2CO_3/lb U_3O_8. In a two-stage stripping system even more efficient utilization of the carbonate should be possible.

O. Stripping Amines with Magnesium Oxide Slurry

Previous tests[2,3] on direct precipitation of uranium from the loaded organic extracts with hydroxides (NaOH, NH_4OH) showed that, although precipitation of the uranium was rapid and complete, the slimy precipitates formed did not settle into the aqueous phase but collected predominantly at the interface making separation of the three phases difficult. In contrast, an aqueous slurry of magnesium oxide has been found to produce a granular uranium precipitate which settles in the aqueous phase and may be easily filtered. Maintenance of a high organic/aqueous ratio in the mixing contactor prevents formation of emulsions which otherwise might be expected because of the solids present.

On contact of the amine extract with a sufficient amount of the magnesium oxide slurry, the uranium precipitates as magnesium polyuranates and, simultaneously, both the amine salt combined with uranium and the excess amine salt are converted to free amine which remains dissolved in the organic phase and may be recycled directly to the extraction system. The reactions occurring may be expressed by the following equations:*

$$2(R_3NH)_2UO_2(SO_4)_{2(org)} + 5\underline{MgO}_{(aq)} \longrightarrow$$
$$4R_3N_{(org)} + \underline{MgU_2O_7} + 4MgSO_{4(aq)} + 2H_2O \qquad (1)$$

$$(R_3NH)_2SO_{4(org)} + \underline{MgO}_{(aq)} \longrightarrow$$
$$2R_3N_{(org)} + MgSO_{4(aq)} + H_2O \qquad (2)$$

If there were a slight deficiency of magnesium oxide, complete stripping of uranium from the organic phase and complete

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*Here, as in similar equations used previously, $(R_3NH)_2UO_2(SO_4)_2$ is not meant to represent the actual uranium complex species in the organic phase, but is used only for simplicity in the presentation. This choice is not important to the discussion since any other formulation leads to an equation equivalent to a combination of equations (1) and (2), and the stoichiometric quantities to be calculated would be identical.

regeneration of amine salt to free amine might still be expected, with a small fraction of the stripped uranium remaining dissolved in the aqueous phase instead of precipitating:

$$(R_3NH)_2UO_2(SO_4)_{2(org)} + \underline{MgO}_{(aq)} \longrightarrow$$
$$2R_3N_{(org)} + UO_2SO_{4(aq)} + MgSO_{4(aq)} \qquad (3)$$

Batch Tests

A number of preliminary batch tests were made to examine the completeness of stripping and to compare the physical performance with different amine-diluent combinations. The tests were conducted in baffled beakers at a phase ratio of $5^O/1^a$ and an agitator speed of 400 R.P.M. for a ten minute contact period. The pregnant organic solutions were prepared by contacting 0.1 M amine solutions with synthetic Marysvale liquor so that the uranium concentration resulting in the organic phase was 85-90% of the loading limit. The stoichiometric amount of magnesium oxide to react with each pregnant organic solution was calculated according to equations (1) and (2), neglecting the possible presence of some bisulfate.

Samples of one pregnant organic solution (0.1 M tri(iso-octyl)amine in kerosene + 2% capryl alcohol, loaded to ~5 g U/liter) were stripped with magnesium oxide slurries containing 100, 110, and 120% of the stoichiometric quantity calculated. In each case essentially all of the uranium was stripped from the organic phase, as shown in Table 19, and a high grade uranium precipitate was obtained. (The completeness of uranium precipitation from the aqueous solution was not measured in these tests.) The washed and calcined (1000°C) products corresponded closely to the compositions expected for MgU_2O_7 plus the estimated excess MgO.

The rate and cleanness of phase separation varied considerably with different amine-diluent combinations. Table 20 summarizes the data obtained when several different extracts were stripped with magnesium oxide at 20% in excess of the calculated amounts. All of the tests were accompanied by the formation of at least a very small amount of interfacial scum. The amount of interfacial scum formed was almost negligible for tri(iso-octyl), tri-n-octyl, and N-benzyl-1-(3-ethylpentyl)-4-ethyloctyl amines, but was appreciable for R&H 9D-178 amine and heavy for di(tridecyl P)amine. In general, phase separation was slightly better when Amsco 123-15 was used as diluent rather than ordinary kerosene.

Stripping of uranium was essentially complete in all tests where the phase separation was good. Incomplete stripping in the tests with di(tridecyl P)amine, especially

Table 19

MAGNESIUM OXIDE REQUIREMENTS FOR

STRIPPING TRI(ISO-OCTYL)AMINE

% Excess MgO	lb MgO/ lb U_3O_8	g/l U in Stripped Organic	% of U Stripped	Product Analysis (Dried at 110°C) % U_3O_8	% Mg	% L.O.I. (1000°C)	After Calcination (Calculated) % U_3O_8	% MgO
0	0.56	0.014	99.8	81.0	3.2	11.6	91.7	6.0
10	0.62	0.007	99.9	76.2	5.4	12.3	87.0	10.2
20	0.67	0.006	99.9	72.3	6.7	14.3	84.5	13.0

Stripping Conditions:

Extract: 0.1 M Tri(iso-octyl)amine in kerosene + 2% capryl alcohol loaded to ~5 g U/l.

Aqueous: MgO slurry contained indicated excess of MgO, calculated on basis of Equations (1) and (2).

Phase Ratio: $5^{o}/1^{a}$.

Contact Time: 10 minutes.

Temperature: Room.

Table 20

STRIPPING AMINES WITH MAGNESIUM OXIDE - BATCH TESTS

Amine, 0.1 M	Diluent	g/l U in Head Organic	g/l U in Stripped Organic	% U Stripped	Phase Separation
Tri(iso-octyl)	Kerosene + 2% C.A.*	~5	0.006	99.8	Excellent
"	Amsco 123-15 + 2% C.A.	~5	0.002	99.9	"
Tri-n-octyl	Kerosene + 2% C.A.	~5	0.003	99.9	"
"	Amsco 123-15 + 2% C.A.	~5	0.002	99.9	"
"	Esso "Heavy Naphtha"	~5	0.035	99.3	Fair
N-Benzyl-1(3-ethylpentyl)-4-ethyloctyl	Kerosene	~3.6	-	--	Excellent
R&H 9D-178	Amsco 123-15	~3.6	0.045	98.7	Fair
"	Kerosene	~3.6	-	--	Fair
Di(tridecyl P)	Kerosene	~3.6	0.43	88	Poor
"	Kerosene + 2% C.A.	~3.6	0.105	97	"
"	Amsco 123-15 + 2% C.A.	~3.6	0.109	97	"

Stripping Conditions: 20% excess MgO over quantity calculated according to Eqs. (1) and (2).

$5^{O}/1^{a}$ Phase Ratio.

400 R.P.M.

10 minutes contact.

*C.A. = Capryl alcohol.

with unmodified kerosene as the diluent, is considered to have been caused by incomplete contacting of the phases due to poor mixing properties rather than by any difference in the chemical reactions.

Although most tests were performed with C.P. magnesium oxide, nearly equivalent results have been obtained with two commercial grades of magnesium oxide (i.e., a sample of "seawater calcined magnesite" from Westvaco and No. 15 calcined magnesite from Michigan Chemical Co.). A third commercial sample (No. 2663 light burnt magnesia from Westvaco) gave poorer stripping results under the same test conditions, showing that the source of magnesium oxide can be an important variable. Other samples of commercial grade magnesium oxide are being obtained for study.

Continuous Tests

Two runs were made to determine the practicality of the process in continuous operation. The stripping equipment consisted of two co-current baffled mixers (400 R.P.M.) and one settler. Residence time in each mixer was approximately ten minutes giving a total contact time of approximately twenty minutes. In each run the system was operated for a total of three extraction-stripping cycles. Tri(iso-octyl)-amine in kerosene + 2% capryl alcohol and R&H 9D-178 amine in Amsco 123-15 were tested using approximately 20% excess MgO and a feed ratio of $5^{o}/1^{a}$. Results of the runs are listed in Table 21.

In Run 1 (R&H 9D-178 amine), stripping was 98-99% complete, leaving the uranium content of the stripped organic phase higher than desired but sufficiently low to allow recycle to the extraction system. Stripping was essentially complete in Run 2. No operational difficulties were encountered in either test although some interfacial scum formed in the settler. An encouraging observation was that the amount of interfacial scum did not tend to build up in the settler as the run progressed but, after its initial formation, remained about constant.

Only limited information is available on the amount of organic entrained by the precipitate. The results that have been obtained indicate the losses of organic from this source to be low and essentially negligible from the cost standpoint. For example, in Run 1 the slurry discharge from the settler was filtered and the precipitate washed with water. Determination of the amount of amine associated with the wet washed precipitate showed it to contain 0.002 lbs of amine/lb of U_3O_8. No measurement was made of the amount of organic discharged with the filtrate. It seems probable that any material expelled at that point could be easily recovered.

Table 21

CONTINUOUS MgO STRIPPING RUNS

Run No.	Extract	Sampled at Cycle	g/l Uranium		% U Stripped	Calcined (400°C) Product % U_3O_8
			Extract	Stripped Organic		
1	0.1 M R&H 9D-178 Amine in Amsco 123-15	1	~3.6	0.075	98	
		2	"	0.076	98	70.0
		3	"	0.046	99	
2	0.1 M Tri(iso-octyl)amine in kerosene + 2% capryl alcohol	1	~5	0.023	99.5	
		2	"	0.015	99.5	81.5
		3	"	0.013	99.5	

Stripping Conditions: 20% excess MgO over quantity calculated according to Eqs. (1) and (2). MgO concentration in the slurry was 0.435 M in Run 1 and 0.485 M in Run 2.

Two co-current mixers at 400 R.P.M.

~10 Min. contact time per mixer.

P. Extraction of Uranium from Sodium Carbonate Solutions With Quaternary Ammonium Compounds

Tests on the extraction of uranium from sodium carbonate solutions with several of the strong base quaternary ammonium compounds were described previously.[1] Appreciable extraction power for uranium was shown by some of the compounds when chloroform was used as the diluent. However, none of the reagents performed well when used in hydrocarbon diluents which are less expensive and more practical for process use.

Recently, a new quaternary ammonium compound (Rohm and Haas, Quaternary B-104*) has been received and subjected to preliminary evaluation tests. As shown in Table 22 the results with this new reagent have been encouraging in that appreciable uranium extractions and reasonable phase separation rates were obtained even when an aromatic petroleum fraction, Amsco G, was used as the diluent. Further evaluation studies of this compound are now being made with regard to (1) losses through distribution to (or solubility in) the aqueous liquor and (2) extraction performance over a wider range of conditions.

Since stripping of uranium from the pregnant quaternary ammonium compound extracts (from carbonate solutions) had not been previously examined, preliminary studies were made of the effectiveness of several reagents for this purpose. A chloroform solution of Hyamine 10X (0.1 M) was used in these particular tests. The solvent had been loaded to 3.6 g U/l by prior extraction from a sodium carbonate liquor containing 1 g U/l, 0.5 M CO_3, pH = 10.7. Experimental results are presented in Table 23.

As expected (analogous to strong base anion exchange resins), effective stripping of uranium was obtained with solutions of HCl, HNO_3, HCl-NH_4Cl and HNO_3-NH_4NO_3. Also as expected, the nitrate solutions were more effective than the chloride solutions.

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*An isopropanol solution of didodecenyldimethylammonium chloride.

Table 22

EXTRACTION OF URANIUM FROM CARBONATE SOLUTION

WITH ROHM AND HAAS QUATERNARY B-104*

Diluent	% U Ext'd.	Extraction Coefficient	Separation Time
$CHCl_3$	50%	1.0	< 1 min.
Benzene	66%	2.0	< 1 min.
Kerosene	Third Phase		< 1 min.
Amsco G	81%	4.3	2 min.

*Isopropanol solution of didodecenyl dimethyl ammonium chloride.

Extraction Conditions:

Organic: Isopropanol solution diluted 1:10 with diluents named.

Aqueous: 1.11 g/l U, 0.5 M Na_2CO_3, pH 10.7.

Phase Ratio: 1/1.

Table 23

URANIUM STRIPPING FROM QUATERNARY AMMONIUM COMPOUND

Stripping Solution	% U Stripped	Stripping Coefficient	Separation
H_2O	<0.1	<0.001	Poor
1 M NaOH	64 (as ppt.)	--	Poor
1 M HCl	76	3.1	Good
1/3 M HCl - 2/3 M NH_4Cl	82	4.5	Good
1 M HNO_3	>99	340	Good
1/3 M HNO_3 - 2/3 M NH_4NO_3	>99	370	Good

Stripping Conditions:

Organic: 0.1 M solution of Hyamine 10X in chloroform containing 3.6 g/l U.

Phase Ratio: 1/1.

III. REFERENCES

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3. Brown, K. B., 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 - A Preliminary Report," ORNL, ORNL-1734, May 27, 1954.

4. Conversations with A. M. Ross and Henry Petrow, Winchester Raw Materials Laboratory, National Lead Company, Inc.

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APPENDIX A

DESCRIPTION OF NEW COMPOUNDS

Amine	Source[c]	Formula	Description[b]	Mol. Wt.[a] Theo.	App.
Di(α-methylbenzyl)	C	$(C_6H_5-\underset{\displaystyle CH_3}{\underset{\vert}{CH}})_2NH$	Laboratory sample	225	247
N-1-isobutyl-3,5-dimethylhexyl-α-methylbenzyl	C	$C_6H_5-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-NH-\left[(CH_3)_2-CHCH_2\underset{\displaystyle CH_3}{\underset{\vert}{CH}}CH_2\underset{\displaystyle CH_3}{\underset{\vert}{CH}}CH_2CH(CH_3)_2\right]$	Laboratory sample	289	285
N-Benzyl-n-tetradecyl	OR	$C_6H_5CH_2NH(CH_2)_{13}CH_3$	Analysis - C 84.5, H 11.8, N 4.6 Theo. - C 83.1, H 12.3, N 4.61	304	310
N-(p-sec.-amylbenzyl)-1-isobutyl-3,5-dimethylhexyl	C	$(C_2H_5)_2CH-C_6H_4-CH_2-NH-\left[(CH_3)_2-CH-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}CH_2CH(CH_3)_2\right]$	Laboratory sample	348	526
N-(2-naphthylmethyl)-1-isobutyl-3,5-dimethylhexyl	C	$C_{10}H_7CH_2-NH-\left[(CH_3)_2-CH-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}CH_2CH(CH_3)_2\right]$	Laboratory sample	327	340
N-Benzyl(7-ethyl-2-methylundecyl-4)	OR	$(CH_3)_2CH-CH_2-\underset{\displaystyle NH\\ \vert\\ CH_2-C_6H_5}{\underset{\vert}{CH}}-CH_2-CH_2-\underset{\displaystyle C_2H_5}{\underset{\vert}{CH}}-C_4H_9$	2% Primary, 97% Secondary, 1% Tertiary Analysis - C 83.2, H 11.9, N 4.67 Theo. - C 83.1, H 12.3, N 4.61	304	311
N-n-Decyl(7-ethyl-2-methylundecyl-4)	OR	$(CH_3)_2CH-CH_2-\underset{\displaystyle NH\\ \vert\\ (CH_2)_9CH_3}{\underset{\vert}{CH}}-CH_2-CH_2-\underset{\displaystyle C_2H_5}{\underset{\vert}{CH}}-C_4H_9$	Analysis - C 82.0, H 14.0, N 4.0 Theo. - C 81.6, H 14.5, N 4.0	354	353
R&H FO-317 (dodecenyl Primene JM)	RH	$C_{12}H_{23}-NH-\underset{\displaystyle R''}{\underset{\vert}{\overset{\displaystyle R'}{\overset{\vert}{C}}}}-R$ where R is a highly branched 15-21 carbon alkyl group	Laboratory sample	506	570

a) Molecular Weight: Where an indefinite formula or a mixture is listed, the "theoretical mol. wt." is an average value, either quoted by the vendor or calculated from the stated percent distribution of alkyls. The "apparent mol. wt." is a titrated acid equivalent obtained in this laboratory.

b) Values determined in this laboratory.

c) Source of Compounds: C - Carbide and Carbon Chemicals Co., New York
OR - Oak Ridge National Laboratory
RH - Rohm and Haas Company, Philadelphia