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AMINE EXTRACTION PROCESSES FOR URANIUM RECOVERY FROM SULFATE LIQUORS

VOLUME I

D. J. Crouse
K. B. Brown

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AMINE EXTRACTION PROCESSES FOR URANIUM RECOVERY FROM SULFATE LIQUORS

VOLUME I

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ABSTRACT

Bench scale studies have been made of processes for recovery of uranium from ore leach liquors by solvent extracting with long chain amines in an organic diluent. Several process schemes have been evaluated which show considerable promise both from the standpoint of operation and chemical costs.

I. INTRODUCTION

The investigation and evaluation of organonitrogen compounds as solvent extraction agents for the separation of uranium from various aqueous systems has been underway at this laboratory since 1952.[1,2,3] Most of the work has been concerned with acidic sulfate solutions, both because of the extensive use of sulfuric acid in uranium raw material processing operations, and because relatively greater success has been achieved in this system than in systems where chloride, nitrate or phosphate anions are predominant.

The test program for evaluating the organonitrogen compounds may be divided into two main categories: (1) Screening tests aimed at the discovery and selection of reagents most likely to be useful in practical application, and (2) process development studies. Thus far, in the first phase of the program, over 200 different compounds of various classes have been examined with regard to their ability to extract uranium from acidic sulfate solutions. Those reagents exhibiting appreciable extractive power were next examined more critically to determine whether they possessed other important characteristics essential to a useful extractant, e.g., sufficient miscibility with practical diluents, low loss to the aqueous phase through solubility, satisfactory selectivity, satisfactory stability, compatibility with practical stripping methods, etc. A description of these studies has been reported in ORNL-1734[2] and ORNL-1922.[3]

As a result of the screening program, a number of long chain secondary and tertiary amines were found which possessed sufficient extraction power and other favorable characteristics to make them worthy of investigation from a process development viewpoint. Consequently, the more promising of these reagents were subjected to laboratory-scale tests of processes for recovering uranium from acid liquors, the primary interest being in clarified sulfate liquors of the type obtained by sulfuric acid leaching of Western ores. In this work the amount of study afforded each amine candidate has been dictated to a great extent by its potential availability at a reasonable price. Since the start of the program, potential suppliers of amine reagents have become increasingly interested in the work and, from time to time, new compounds have been supplied for study. The advent of these new reagents and new potential suppliers has sometimes caused a change in emphasis in favor of those compounds which could be considered closest to commercial availability at relatively low prices.

At this time the laboratory-scale process studies of uranium extractions by amines are nearly complete. Sufficient information has been accumulated to define reasonably accurately the performance of several extractants and to evaluate various process schemes with respect to reagent usage and operational characteristics. Since the amount of data that has been obtained is rather extensive, descriptions of the work are being reported in two volumes. This report (the first volume) is intended as a summary report wherein the optimum processing schemes are defined but with only limited presentation of supporting experimental data. The second report volume will present the experimental data in detail.

In addition to the work with uranium, attention has been given to the use of amines in extracting other metals, and some preliminary studies have been reported.[4] Studies of vanadium extractions are also underway and will be reported later.

II. SCHEMATIC FLOW DIAGRAMS OF PROPOSED PROCESSES FOR RECOVERY OF URANIUM FROM WESTERN ORE CLARIFIED SULFATE LIQUORS

Figure 1 shows a general schematic process flow diagram for recovery of uranium from an ore. In this diagram the amine solvent extraction process is utilized to separate the uranium from a clarified sulfuric acid leach liquor which has been prepared by methods common to Western mill operations. Five different variations of the amine extraction process, all embodying the same extraction procedure but differing in the method used to recover uranium from the organic extract, are presented in Figures 2, 3, 4, 5 and 6.

In subsequent sections, operation of the extraction system and of each of the suggested stripping systems is considered in detail. Tentative definitions of optimum process conditions are based, for the most part, on data obtained in batch equilibration tests, some of which were patterned to simulate countercurrent operation. Continuous countercurrent demonstration and scale-up of the processes is being conducted by the Engineering Group at the ORNL Raw Materials Test Facility and will be reported separately. It is worthy of note that the experimental results obtained in scaled-up continuous countercurrent runs performed by that group have conformed remarkably well with expected operation as predicted from laboratory bench-scale data. For this reason, it is believed that the estimated reagent consumptions and other operational factors described subsequently (Sections C and D) are a fairly accurate representation of those that would be experienced in larger scale application.

No choice is made, here, among the various stripping methods except to note that the direct precipitation method (sodium or ammonium hydroxide strip, Figure 6) appears less favorable than the others from an operational viewpoint. With this exception, reagent costs for the stripping operation vary over a relatively narrow range and proper choice could be made only after observing, in larger scale operation, the operational characteristics, corrosion problems, etc. of each. Choice of the stripping method can also depend upon differences in the composition of the ore treated and upon variations in unit costs of chemicals at different mill sites.

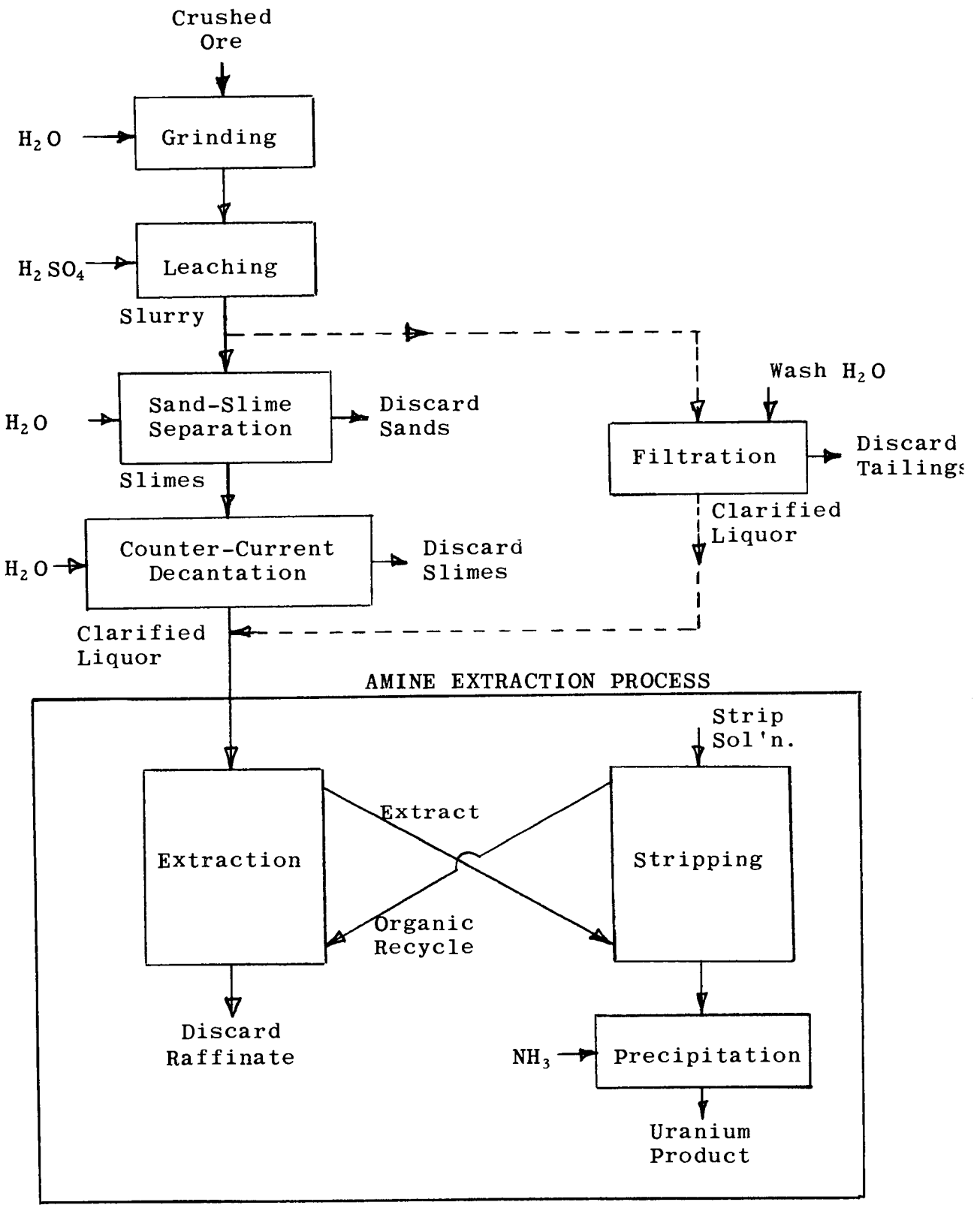

Figure 1

RECOVERY OF URANIUM FROM WESTERN ORES

UTILIZING AN AMINE EXTRACTION PROCESS

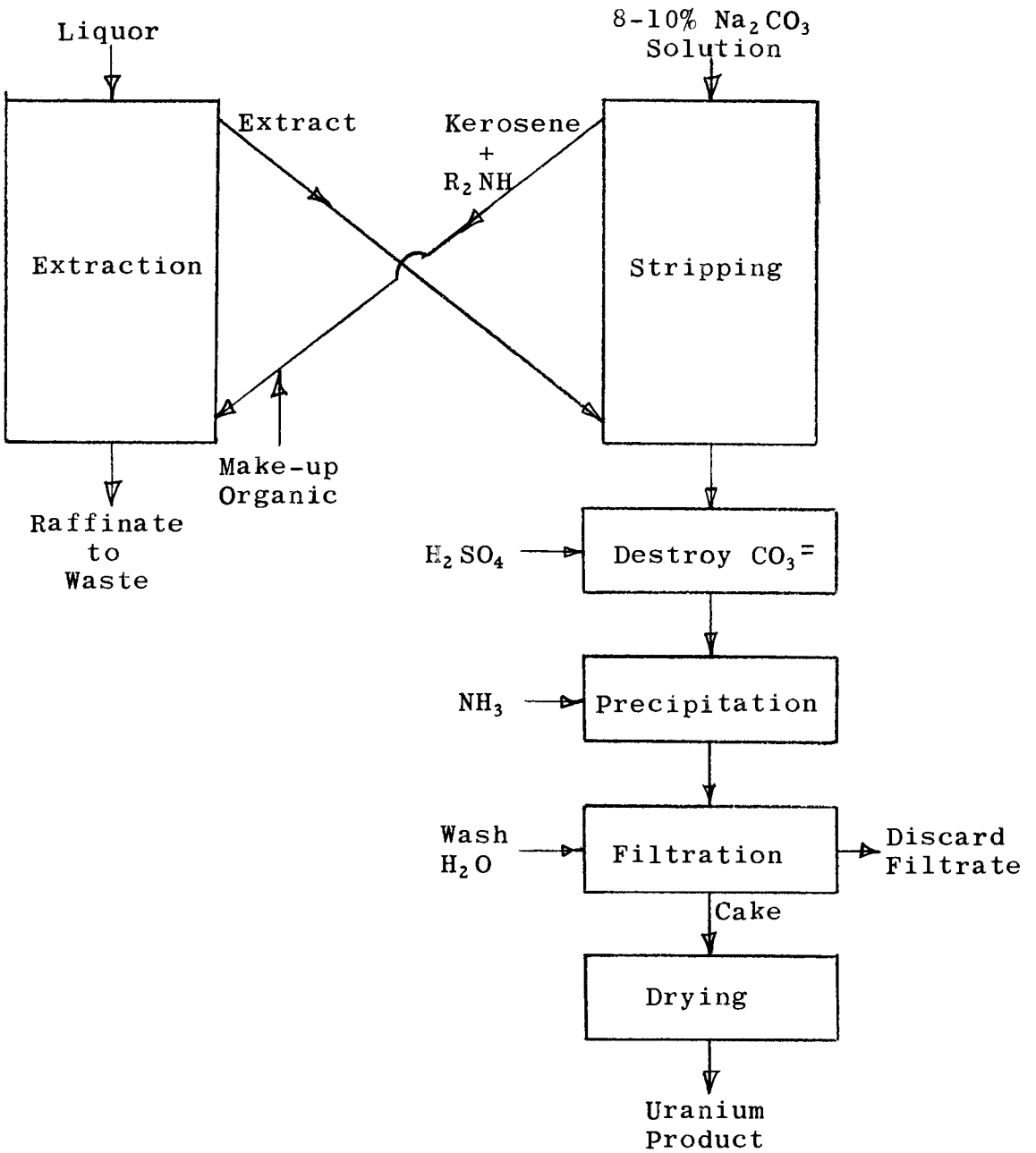

Figure 2

SODIUM CARBONATE STRIPPING METHOD

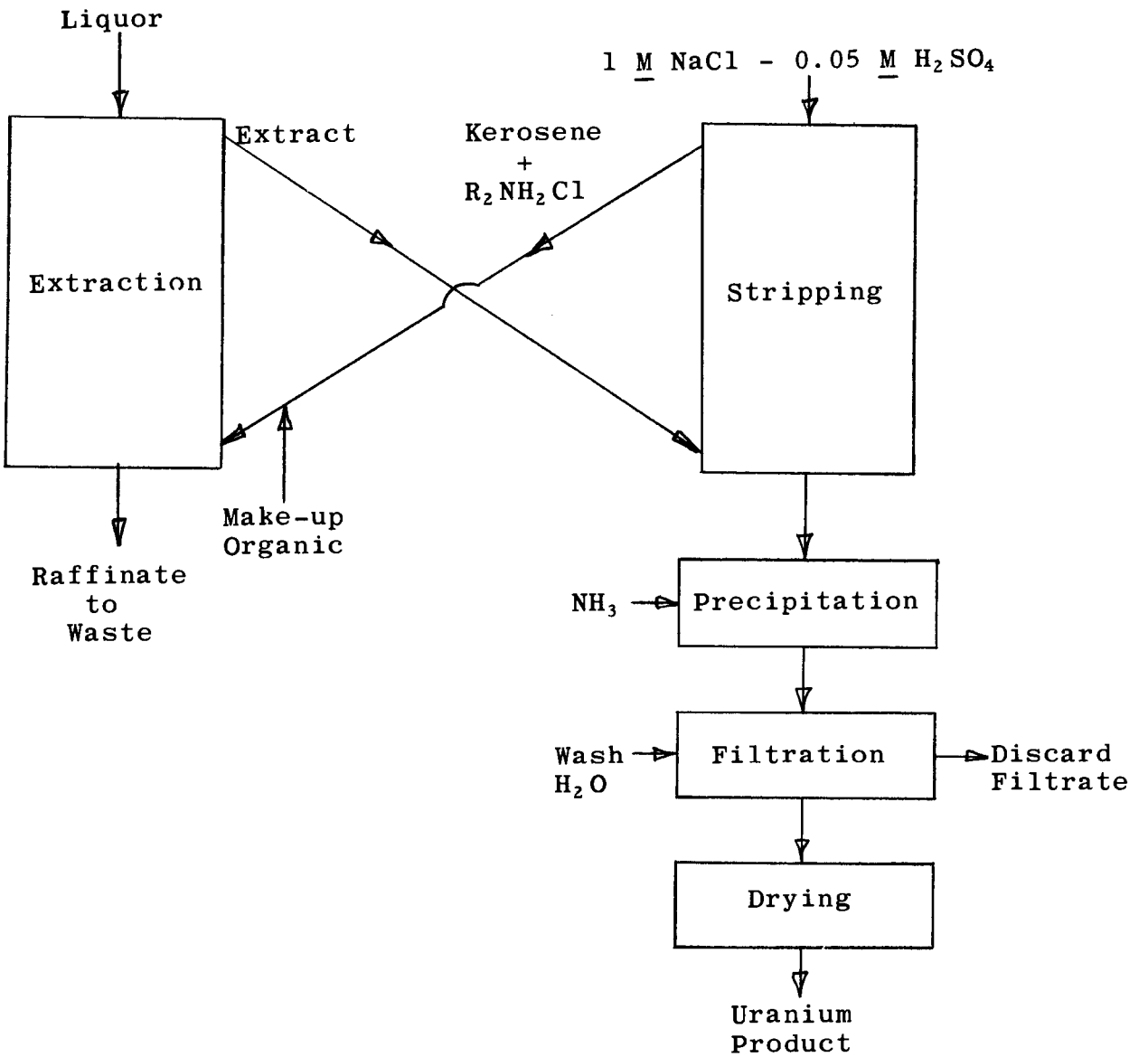

Figure 3

CHLORIDE STRIPPING METHOD

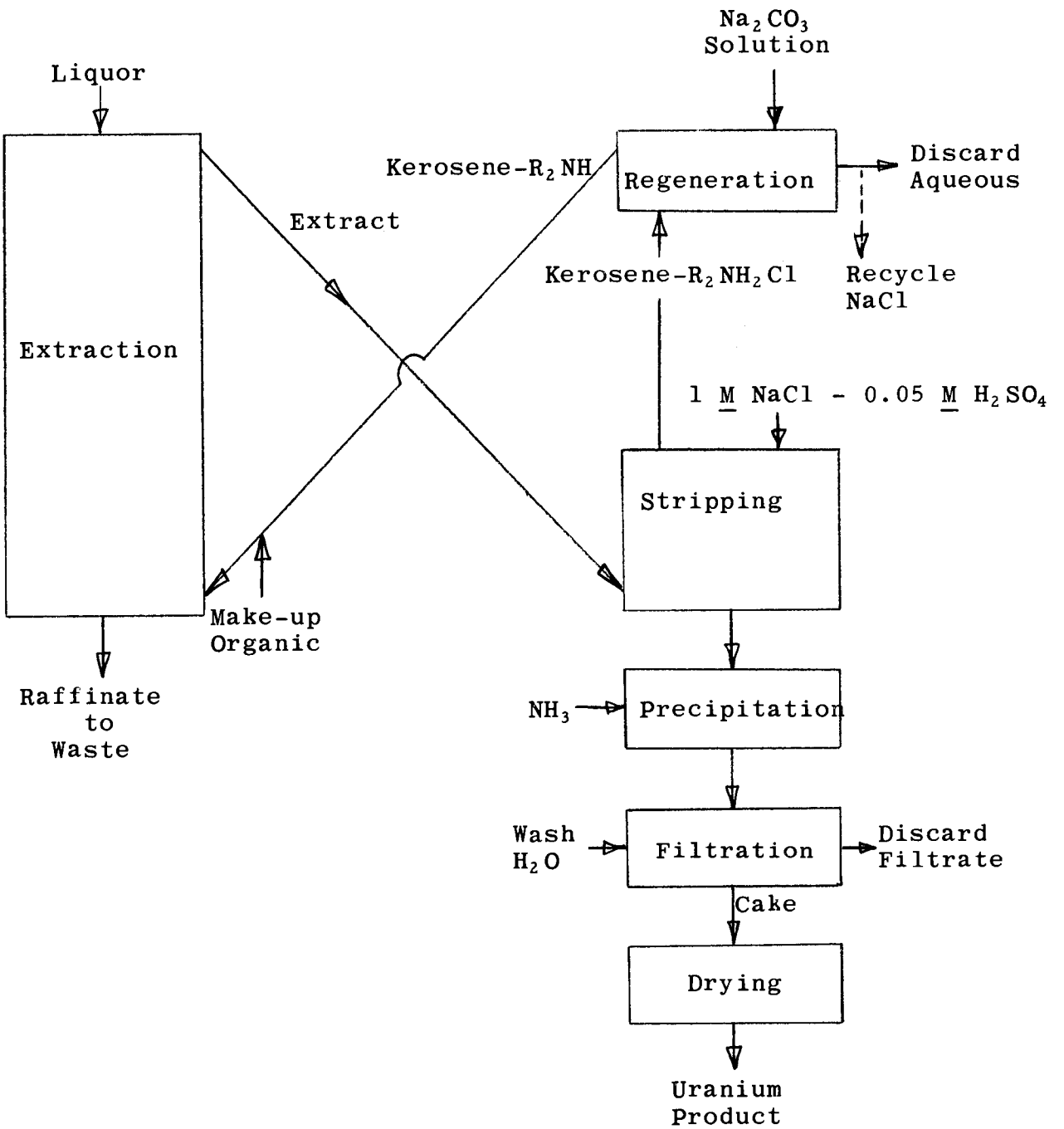

Figure 4

CHLORIDE STRIPPING METHOD

(With Amine Regeneration)

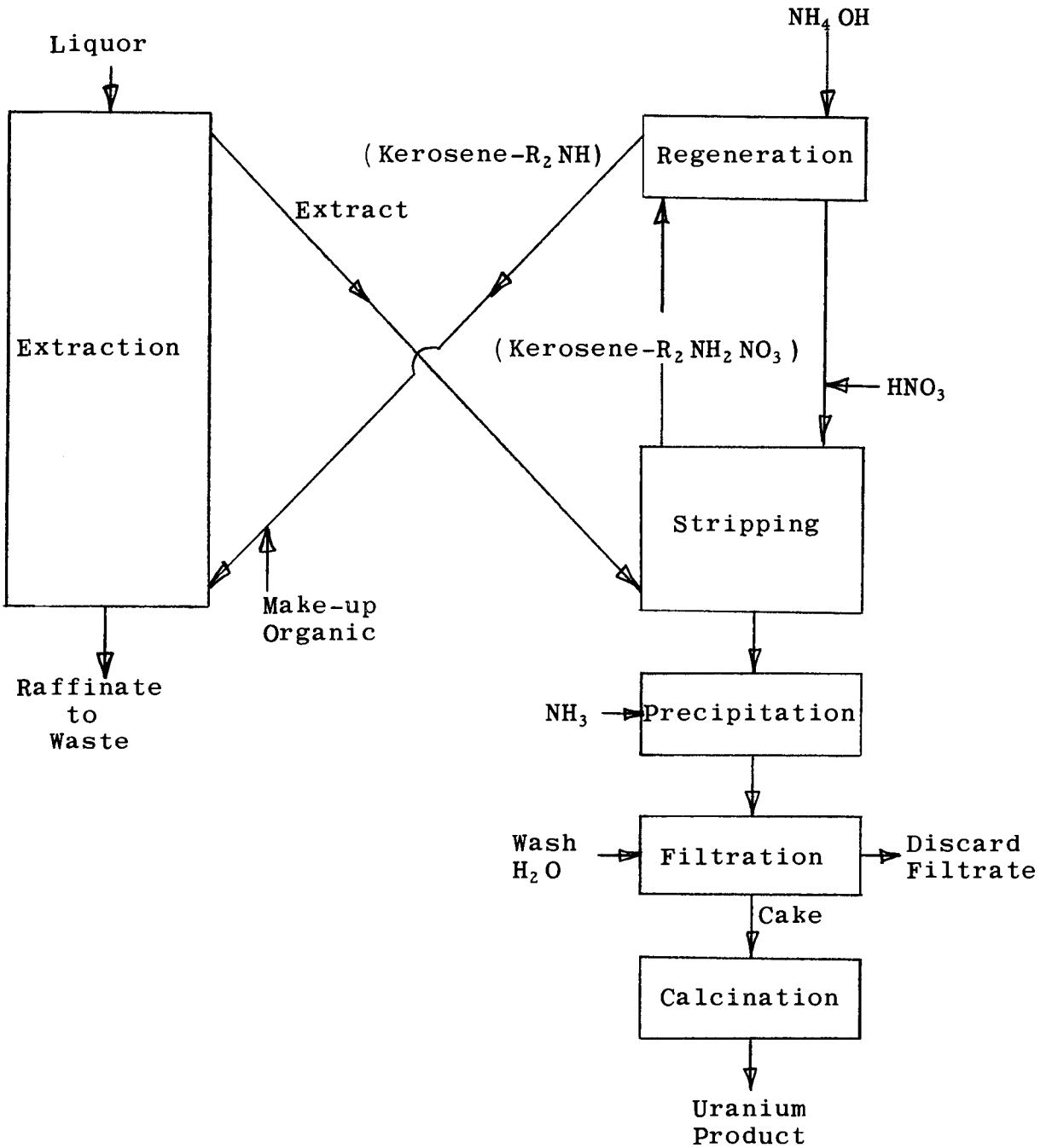

Figure 5

NITRATE STRIPPING METHOD

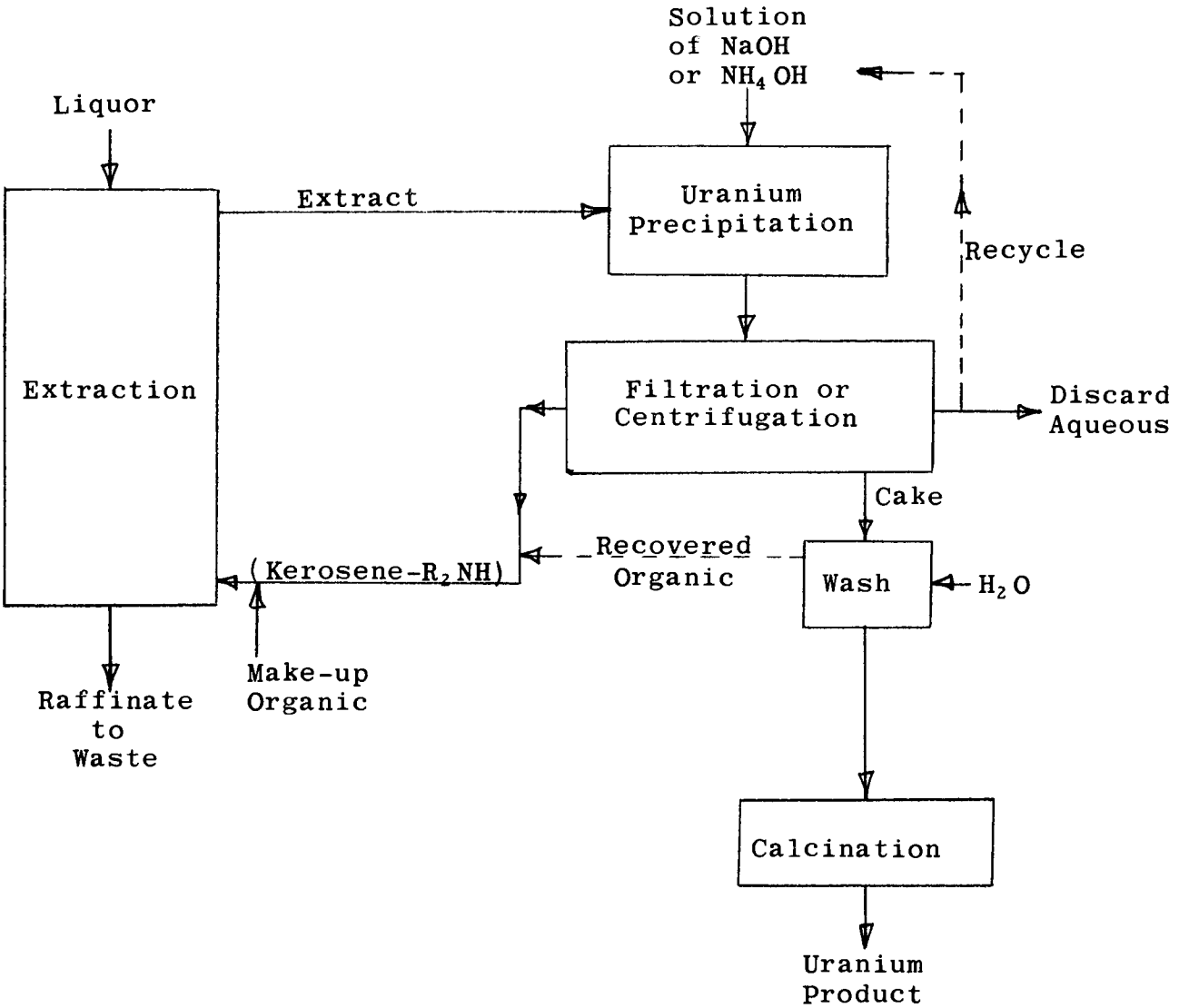

Figure 6

HYDROXIDE STRIPPING METHOD

III. DISCUSSION

A. The Extraction System

1. Extraction of Uranium from Various Liquors

The chemical composition of liquors obtained from digestion of Western ores with sulfuric acid can vary considerably depending on the chemical composition of the ore and the severity of the leaching treatment required for uranium dissolution. Consequently, for broad applicability, a solvent extraction process must be able to handle liquors which are widely variant in acidity, salt concentration, and degree of metal contamination. Some adjustment of liquor characteristics such as pH, sulfate concentration, and redox potential can be made prior to the extraction step, but such adjustments, particularly the last, ordinarily represent an increase in the cost of the operation due to the addition of extra processing steps and increased reagent consumption.*

Since actual leach liquors were not available in sufficient volume to support an extensive development program, most of the test work was conducted on synthetic liquors, particularly one patterned after a sample of leach liquor received from the Vitro Uranium Company which was representative of their plant production when processing Marysvale ore. Analysis of the synthetic liquor, hereafter referred to as "Synthetic Marysvale Liquor," is listed below:

Constituent	Concentration, g/l
U	1.25
Fe(III)	5.8
Al	3.3
SO_4	50
PO_4	2.0
F	1.7

pH = 0.85

Because of the appreciable concentrations of ferric iron and aluminum, the liquor presents a fairly rigorous test of the extraction agent from the standpoint of selectivity for uranium over these most common liquor contaminants.**

---

*Cost of addition of lime for adjustment of pH would not be charged against the solvent extraction process in cases where the waste liquors must be neutralized before discarding.

**For selectivity properties of the amines with regard to other potential metal contaminants, see ORNL-1734, page 32, ORNL-1922, page 46, and Section A-3 of this report.

In addition, the sulfate concentration and acidity are higher than for many liquors obtained in processing Western ores for their uranium content only. Hence, from the chemical standpoint, a solvent extraction process capable of handling this liquor should be applicable to most sulfuric acid liquors likely to be encountered in Western operations. In support of this, numerous extraction tests have been performed successfully on a variety of actual leach liquors which were prepared at this laboratory or received from Western mills.

Typical extractions of uranium from Synthetic Marysvale Liquor by 0.1 M solutions of some of the more promising amines in various diluents are shown in Table 1. In examining these data it should be remembered that, since the aqueous liquors contained an appreciable concentration of ferric iron, the coefficients shown reflect differences in extraction selectivity (with respect to iron) in combination with the differences in uranium extraction power, rather than uranium extraction power alone.* Also, it should be remembered that the type of diluent can affect the extraction power and selectivity properties of the amines. Although the magnitude of this effect ordinarily is less than that shown by major changes in amine structure, measurable differences in the coefficients shown would be expected if other diluents had been used.

Regardless of these limitations, several general observations can be made on the basis of the data in Table 1. Of most importance is the observation that, with the exception of the primary amines, all of the amine-diluent combinations listed gave effective extractions of uranium from the leach liquor. The magnitudes of the coefficients in all cases, at 0.1 M extractant concentration, were sufficiently great for practical process application. Inferior extractions by the primary amines were to be expected since previous studies[2] had shown these reagents to have poor selectivity for uranium over ferric iron. N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine[3] was particularly outstanding as an extractant, the extraction coefficient being much higher than for any other

---

*The extraction coefficients are related fundamentally, of course, to the free reagent rather than total reagent concentration, and thus the coefficients shown in Table 1 are also affected by the partial loading of the extractant with uranium. However, since the experiments were made at constant amine concentrations and constant phase ratios and since almost all of the uranium was extracted in every case ($E_a^o > 30$) the effect from uranium loading would be similar in each of these particular tests.

Table 1

EXTRACTION OF URANIUM FROM SYNTHETIC MARYSVALE LIQUOR

WITH 0.1 M AMINE SOLUTIONS

Amine	Compound No.	Type*	Diluent	Uranium Extraction Coefficient** E_a^o
1-(3-ethyl-pentyl)-4-ethyloctyl (C&C 21F81)	120A	Primary	Benzene	0.04
Primene JMR	6C	"	Kerosene	0.014
Di-n-decyl	Batch C	Secondary	Amsco D-95	30-40
Dilauryl	Batch A	"	" "	30-40
Armeen 2-12	103F	Secondary Amine Mixture	" "	40
Armeen 2C	34A	" " "	" "	30-40
Benzyllauryl	199A	Secondary	97% Kerosene-3% Cap. Alc.	35
Di(oxodecyl)	197A	"	Kerosene	40
Di(tridecyl P)	227A	"	Kerosene	40
Di(2-butyloctyl)	198A	"	"	70
Dodecenyl Primene 81 (R&H 9D-178)	193C	"	"	70
Dodecenyl Primene JM	242A	"	"	25
Bis(1-isobutyl-3,5-dimethylhexyl) (C&C 16F27)	30B	"	"	120

Table 1 (Cont'd.)

EXTRACTION OF URANIUM FROM SYNTHETIC MARYSVALE LIQUOR

WITH 0.1 M AMINE SOLUTIONS

Amine	Compound No.	Type*	Diluent	Uranium Extraction Coefficient** E_a^o
N-benzyl-1-(3-ethylpentyl)-4-ethyloctyl	228A	Secondary	Kerosene	> 2000
Methyldi-n-decyl	97F	Tertiary	Amsco D-95	30
Benzyldilauryl	200A	"	97% Kerosene-3% Cap. Alc.	50
Di-n-hexyllauryl	91A	"	Amsco D-95	160
Tri-n-octyl	125H	"	98% Kerosene-2% Cap. Alc.	200
Tri(iso-octyl)	239A	"	98% Kerosene-2% Cap. Alc.	200
Tri-n-decyl	84D	"	Kerosene	200
Trilauryl	86A	"	Kerosene	140

*For further description of amine structures see ORNL-1922, Appendix C.

**Extraction Conditions: Phase ratio, a/o: 2
Temperature: Room
Contact Time: 2 minutes
Final aqueous pH; ~0.9

amine tested thus far. The coefficients for the different straight chain secondary amines did not vary appreciably and, in these tests, were comparable to those observed for some unsymmetrical tertiary amines, i.e., methyldi-n-decyl and benzyldilauryl amines. Most of the branched secondary amines (those with good selectivity with respect to iron) gave better extractions than the less selective straight chain secondary amines, but were somewhat less effective than the symmetrical tertiary (high selectivity) and the unsymmetrical tertiary amines wherein the alkyl chains are all fairly long, e.g., di-n-hexyllaurylamine.

Further comparisons of several representative amines are shown in the form of extraction isotherms in Figures 7 and 8. These isotherms were obtained by extracting Synthetic Marysvale Liquors of varying uranium content with 0.1 M extractants at a constant phase ratio. Here, the extremely strong extraction power of N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine is again apparent. Of the other secondary amines shown, C&C 16F27 is slightly superior to R&H 9D-178 which in turn is better than di(tridecyl P), dilauryl, and bis(1-methyl-4-ethyloctyl) amines in that order. The performance of tri-n-octylamine is intermediate between that of N-benzyl-1-(3-ethylpentyl)-4-ethyloctyl and C&C 16F27 amines but is more similar to that of the latter.

The maximum loadings shown by most of the amines (0.1 M) from the Synthetic Marysvale Liquor is in the order of 4 g U/l. With some of the tertiary amines, higher loadings have been shown. For example, with tri-n-octyl and tri(isooctyl)* amines (0.1 M) concentrations in the order of 5 g U/l have been obtained in the organic phase.

In Figure 9 the isotherm for R&H 9D-178 amine is used to plot the number of equilibrium extraction stages required to reduce the uranium content of the liquor from the head concentration of 1.25 g U/l to 0.001 g U/l. For simplicity, it is assumed that the organic phase fed into the extraction system contains 0.01 g U/l, i.e., was reduced to this con-

---

*A sample of tri(isooctyl)amine was obtained only a short time ago and has not been described in earlier reports. Preliminary tests indicate the extraction properties of this compound to be similar to those described previously for tri-n-octylamine (see also Table 1). According to preliminary information from the supplier, tri(isooctyl)-amine would be easier to produce than tri-n-octylamine and could probably be offered in the 60¢ - $1.00/lb range.

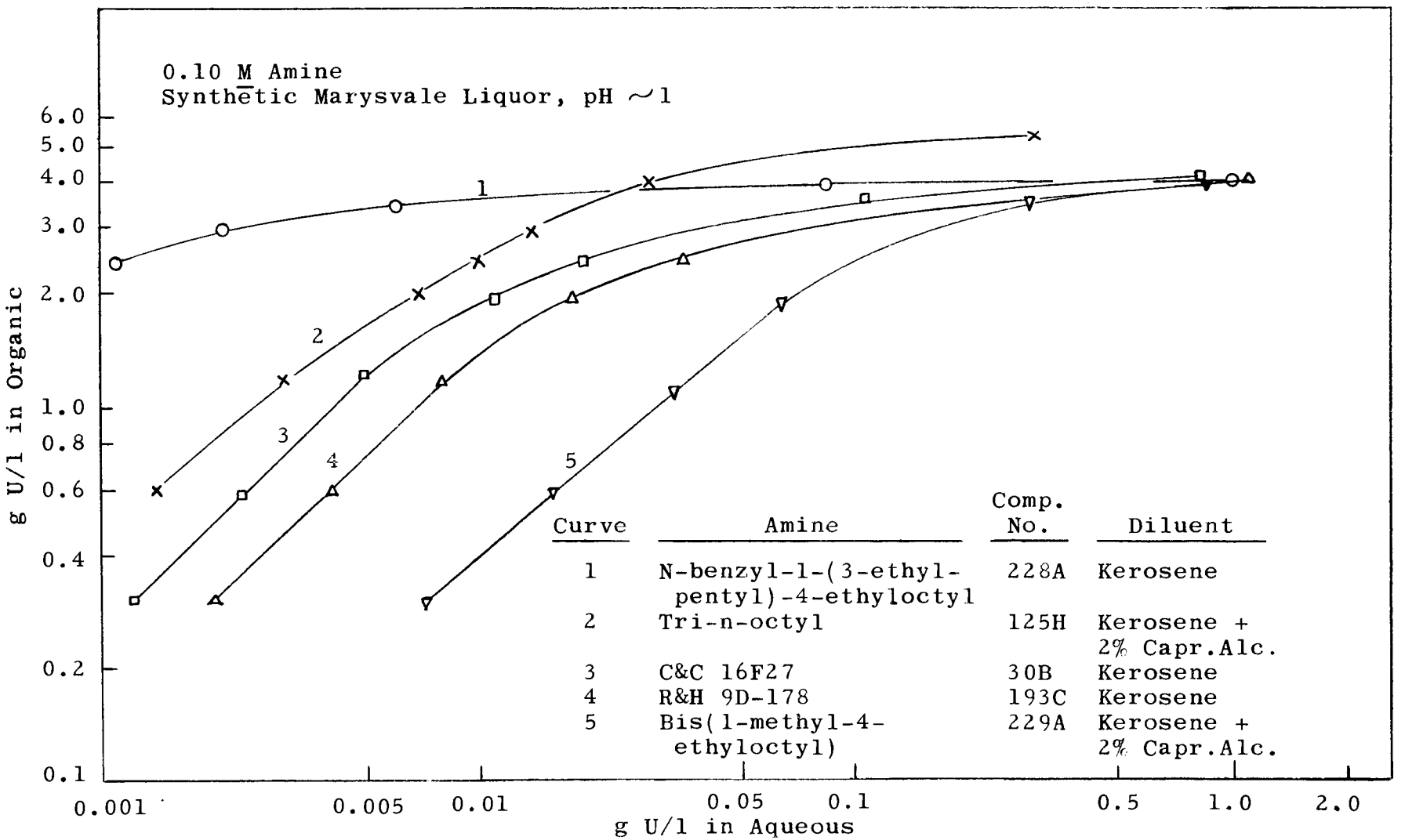

Figure 7

URANIUM EXTRACTION ISOTHERMS

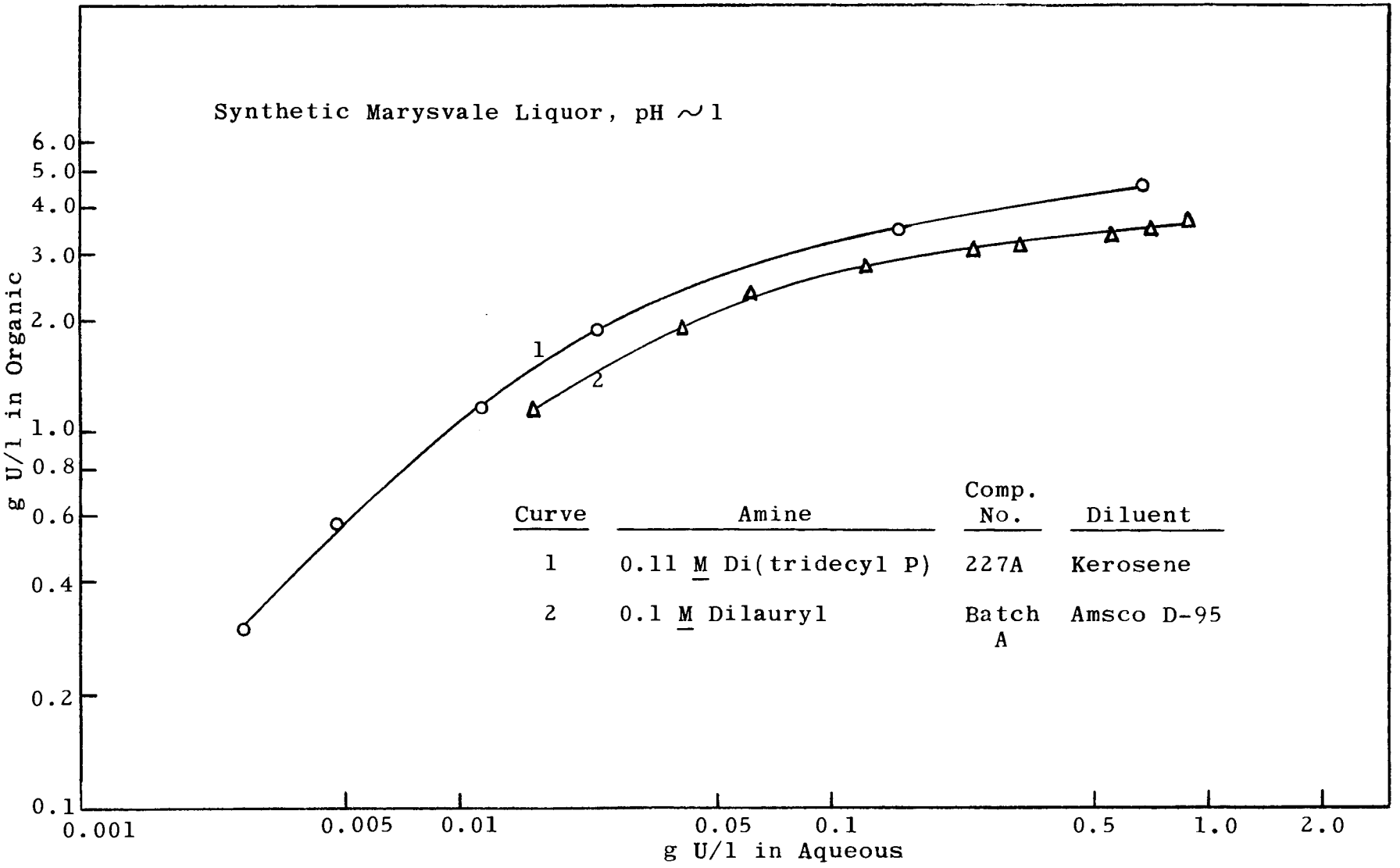

Figure 8

URANIUM EXTRACTION ISOTHERMS

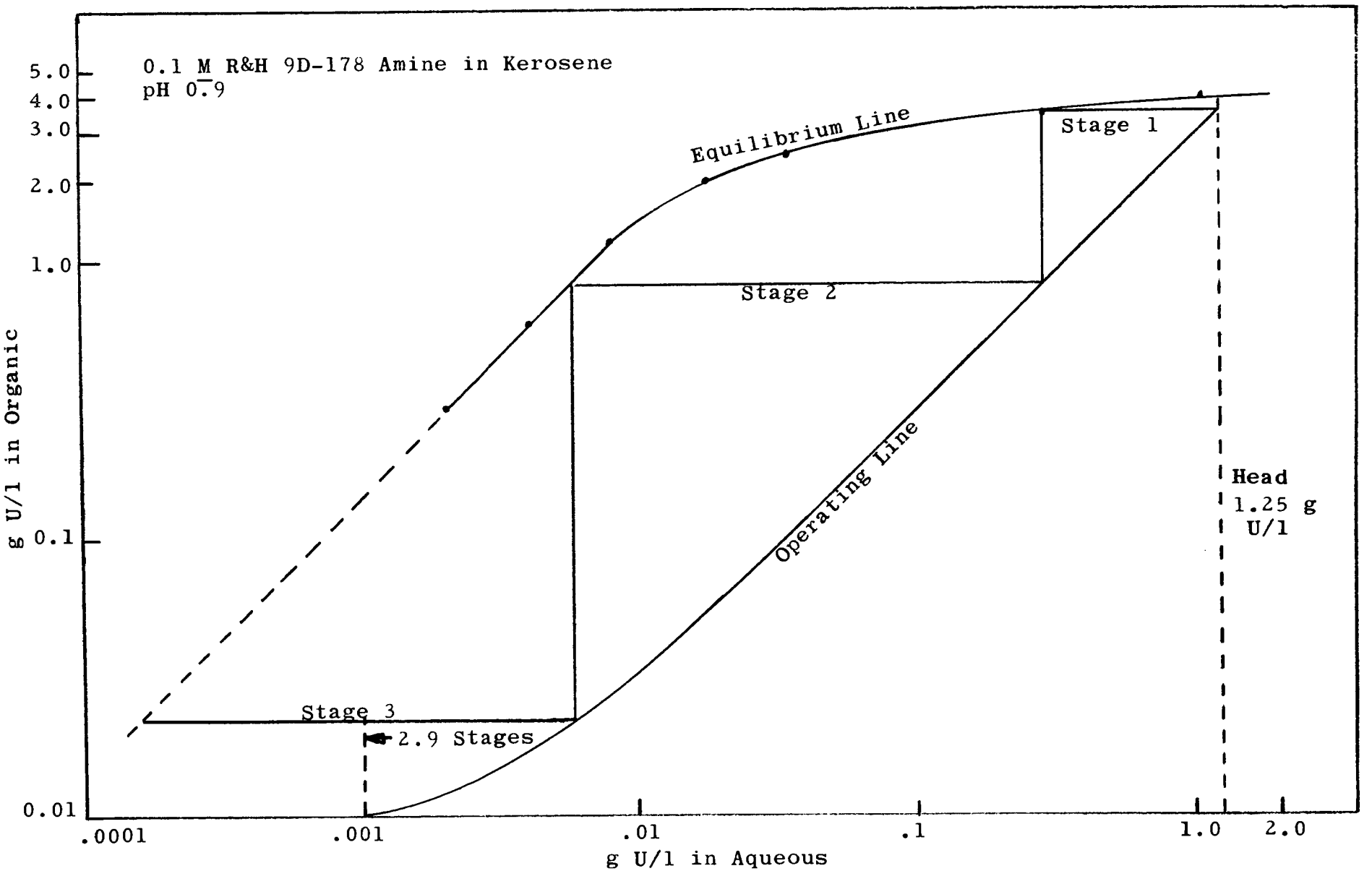

Figure 9

DETERMINATION OF NUMBER OF IDEAL STAGES FOR

URANIUM RECOVERY FROM SYNTHETIC MARYSVALE LIQUOR

centration in the stripping cycle. As shown by the figure, the recovery mentioned would be obtained in 2.9 ideal stages when operating at an aqueous/organic phase ratio of 2.7. At this phase ratio and reagent concentration, loading of the organic extract corresponds to approximately 85% of the maximum uranium loading achievable from this liquor. For comparison, under the same conditions, the theoretical stages required for N-benzyl-1-(3-ethylpentyl)-4-ethyloctyl and bis(1-methyl-4-ethyloctyl) amines are 1.9 and 4.0, respectively.

Other extractions of uranium by several amines from a number of different (actual) leach liquors are described in Table 2. The origin and chemical composition of the liquors are shown in Table 3. In these tests, the general variations in extraction efficiencies as a function of liquor composition were in accordance with previous studies, i.e., extractions were better from liquors lower in sulfate, iron and acidity. However, even with liquors of the highest sulfate, acidity and degree of contamination, the uranium extractions were, in each case, sufficiently high for effective process application.

2. Choice of Diluent

When a solution of a free amine in an organic diluent is contacted with excess aqueous acidic sulfate solution (pH = 1-2) the amine reacts essentially completely to form the sulfate and bisulfate salts, the ratio of bisulfate to sulfate increasing with decreasing pH.[3,8] During chloride or nitrate stripping the sulfate salts are converted to the chloride or nitrate salts. If the original amine concentration is greater than the miscibility level of these salts in the particular diluent employed, the excess will separate from the diluent as a solid precipitate or as a third liquid phase. When the organic phase is in contact with sulfate solutions the tendency toward precipitation or third phase formation increases with decreasing pH and/or increasing total sulfate in the aqueous liquor, indicating lower miscibilities for the bisulfate than for the normal sulfate salts.[3] The tendency appears to decrease, on the other hand, when extracted uranium or, to a lesser extent, iron is present in the organic phase. This latter effect should not be of major significance in a countercurrent extraction process, however, since the liquor in the lower stages would be almost barren of uranium and only iron, in relatively low amounts, would be extracted at this point.

The miscibility level obtainable with the amine salts depends upon the type of diluent employed and upon the type and structure of the amine.[2,3] In regard to the latter, the long branched chain secondary amines have shown the

Table 2

EXTRACTION FROM ACTUAL LEACH LIQUORS

Liquor	Amine	Compound No.	Amine Conc. (M)	Diluent	Phase Ratio a/o	Final pH	Uranium Extrn. Coeff. E_a^o
Lukachukai	Tri-n-octyl	Batch B	0.15	Amsco D-95	1	0.9	170
Lukachukai*	"	"	"	" "	"	1.4	330
"	"	"	"	" "	"	1.9	370
Lukachukai	Di-n-decyl	Batch C	"	" "	"	0.9	70
Lukachukai*	"	"	"	" "	"	1.4	170
"	"	"	"	" "	"	1.7	180
Mary Jane	Tri-n-octyl	Batch D	0.1	" "	2	0.9	250
" "	Dilauryl	Batch A	0.1	" "	"	0.9	130
Mineral Mt.	Tri-n-octyl	Batch D	0.1	" "	"	1.0	180
" "	Dilauryl	Batch A	0.1	" "	"	1.0	80
Marysvale M-2	Tri-n-octyl	116F	0.1	" "	"	0.95	90
" "	Armeen 2-12 Fraction	104	0.1	" "	"	0.95	26
Marysvale M-4	Tri-n-octyl	116F	0.1	" "	"	1.5	70
" "	Armeen 2-12 Fraction	104	0.1	" "	"	1.5	21
Vitro 4	R&H 9D-178	193C	0.1	Kerosene	"	1.2	270
" 5	"	"	0.1	"	"	"	240
" 6	"	"	0.1	"	"	"	210
" 7	"	"	0.1	"	"	"	230
" 8	"	"	0.1	"	"	"	230

Table 2 (Cont'd.)

EXTRACTION FROM ACTUAL LEACH LIQUORS

Liquor	Amine	Compound No.	Amine Conc. (M)	Diluent	Phase Ratio a/o	Final pH	Uranium Extrn. Coeff. E_a^o
Vitro 4	Armeen 2-12	103F	0.1	95% Kerosene-5% Cap. Alc.	2	1.2	50
" 5	"	"	0.1	"	"	"	50
" 6	"	"	0.1	"	"	"	40
" 7	"	"	0.1	"	"	"	50
" 8	"	"	0.1	"	"	"	50

*pH of liquor adjusted with NH_3 gas before extraction.

Table 3

CHEMICAL COMPOSITION OF LEACH LIQUORS

		Lukachukai	Mary Jane	Mineral Mountain	Marysvale M-2	Marysvale M-4	Vitro(4,5,6,7,8)*
Origin		ORNL	ORNL	ORNL	ORNL	ORNL	Vitro Uranium Co.
U	g/l	2.46	0.47	0.69	0.86	1.33	1.0 - 1.1
V(mostly V^{+4})	"	2.4	1.9	2.4	----	----	0.8 - 0.9
$\sum$Fe	"	1.5	2.5	2.1	9.04	14.8	1.7 - 2.3
Fe(II)	"	---	---	---	----	---	0.7
Al	"	2.4	1.9	3.3	3.6	7.1	2.5 - 2.7
Mo	"	---	---	---	0.62	0.27	0.08
Ca	"	---	---	---	0.4	0.9	0.6 - 0.7
Ti	"	---	---	---	---	---	<.005 - 0.032
Si	"	0.23	0.34	0.33	---	---	0.3 - 0.4
SO_4	"	53	46	58	54	86	38 - 40
F	"	0.14	0.02	0.04	2.2	7.5	0.2 - 0.3
PO_4	"	0.26	0.37	0.27	2.0	2.9	0.7 - 1.0
pH		0.8	0.85	0.9	0.9	1.5	1.1

*Representative of plant operations in Dec., 1954, on Temple Mountain ore blend.

greatest compatibilities with the widest variety of practicable diluents whereas the straight chain secondary amines have been perhaps the most limited in this respect. With regard to commercial hydrocarbon diluents, those of high aromatic character, e.g., Amsco D-95, Amsco G, Xylene, etc., have shown generally greater solvent power than aliphatic kerosene solvents. Kerosene is a perfectly satisfactory diluent for a number of amines, however, and is preferable from the cost standpoint. Also, it has been shown that the solvent power of both the aromatic and aliphatic hydrocarbon diluents can be appreciably increased, if desired, by the addition of long chain alcohols in moderate quantities.

Detailed discussions of the miscibilities of a number of specific amine salts in different diluents have been presented in ORNL-1922. For the purposes of this report a summarized discussion of some of the more promising amine-diluent combinations may be given as follows:

1) Kerosene is a suitable diluent for most of the long branched chain secondary amines including:

R&H 9D-178 (dodecenyl Primene 81 amine)*
C&C 16F27 (Bis-(1-isobutyl-3,5-dimethylhexyl)amine)
N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine
Di(tridecyl P)amine
Di(2-butyloctyl)amine

Total amine concentrations greater than 0.6 M are retained by the kerosene even when contacted by sulfate solutions of low pH. Although not yet tested at very high reagent levels, good physical performance (i.e., lack of third phase formation) has been given by these amine-diluent mixtures at moderate reagent levels when treated by the chloride, nitrate (and, of course, carbonate) stripping methods. Other amines similar in type, structure, and molecular weight to those listed would be expected to be generally similar in performance.

2) If the alkyl chains are sufficiently long (decyl or lauryl), the symmetrical tertiary amines may ordinarily be used for extraction in kerosene diluent, although difficulty may be encountered if the aqueous acidity and total sulfate concentration are extraordinarily high. In such instances, modification of the kerosene with a small amount of a long chain alcohol will extend the range of application. Com-

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*Kerosene is not a good diluent for this compound when treating certain liquors - see Section A-3.

pounds of shorter chain length, e.g., tri-n-octylamine and tri(iso-octyl)amine, require addition of alcohol to the kerosene in all except the most favorable circumstances. These amine-diluent combinations (at least at reasonable reagent levels) are also compatible with the chloride and nitrate stripping methods.

3) Of the amines tested, the straight chain secondaries and the unsymmetrical tertiaries containing two straight-chain alkyls and a methyl group have been the least versatile with regard to diluent compatibility. The salts of these compounds are not compatible with kerosene alone but can be used with kerosene containing a moderate amount, i.e., ~ 5 v % of a long chain alcohol. Even in the latter case their range of applicability does not approach that of the compounds described under (1) above. However, for processing liquors of the acidity, uranium concentration and sulfate concentration normally encountered in Western operations, their performance would be acceptable. Examples of compounds in this category are

Di-n-decylamine
Dilaurylamine
Armeen 2-12
Methyldi-n-decylamine

At ambient temperatures, the chloride and nitrate salts of these amines appear to be less miscible with the kerosene-alcohol diluent than the sulfate salts (at least the normal sulfate salts) and it is doubtful that their physical performance during chloride or nitrate stripping would be adequate for process purposes, unless the operation was conducted at temperatures above 35°C. They are, of course, compatible with the carbonate stripping method.

4) Addition of alcohol to the hydrocarbon diluents has been observed to increase the extraction selectivity and, in some cases, the rate of phase separation as well as increasing the solvent power. If a large amount of alcohol is added, a severe loss of extraction efficiency occurs. However, addition of 2-5% alcohol by volume ordinarily causes only a small drop in extraction efficiency and, for the less selective amines, actually may increase the efficiency due to the aforementioned improvement in selectivity. The presence of alcohol would cause an undesirable increase in reagent costs but the amount of increase would not be prohibitive to process application. Losses of capryl alcohol (20¢/lb) to a liquor 0.5 M in SO_4 at pH 1.0 were measured to be about 60 ppm from 98% kerosene - 2% alcohol and about 130 ppm from 95% kerosene - 5% alcohol. Other longer chain alcohols now being tested should give lower losses, e.g., decyl and tridecyl alcohols (21-24¢/lb).

5) As mentioned above, diluents of high aromatic content (Amsco D-95, Amsco G, Amsco F, Solvesso 100, Solvesso 150, Petbyco F-80, Petbyco Hi-Flash Naphtha, etc.) have generally greater solvent power for the amine salts as compared to kerosene, and with several compounds tested relatively better selectivity properties have also been noted. Even with these diluents, however, addition of small amounts of alcohol may be necessary to obtain sufficient miscibilities of the sulfate and bisulfate salts of some of the straight chain secondary amines. Also, even with alcohol present, poor physical performance has been observed with some of the straight chain secondary amines during chloride and nitrate stripping. The solvents listed are priced at 35-40¢/gal. in tank car lots and would have a cost disadvantage in comparison to kerosene. On the other hand, the losses of diluent encountered in the solvent extraction operation are reasonably low and if such solvents were required, they should be suitable for application.

3. Extraction Selectivity

The efficiency with which uranium can be separated by amine extractants from the various metal contaminants is dependent on a number of factors. The type and structure of the extractant is of primary importance, the primary amines being generally the least selective and the symmetrical tertiary amines generally the most selective of the reagents tested. With secondary amines, branching of the alkyl chains on the carbon adjacent to the nitrogen improves the selectivity over that of amines with no branching or with branching farther removed from the nitrogen. Thus, compounds such as C&C 16F27 and R&H 9D-178 amines, are superior in selectivity to compounds such as dilauryl, di(2-butyloctyl) and di(tridecyl P) amines. Also it has appeared that C&C 16F27, in which both chains are branched at the first carbon, has somewhat better selectivity properties than R&H 9D-178, in which only one chain is branched at the first carbon.

Of the metal contaminants normally found in Western ore leach liquors, iron, aluminum, magnesium, and sodium are normally present in highest concentration. Liquors derived from carnotite ores may also contain appreciable amounts of vanadium. In addition, smaller concentrations of numerous other metal ions are present, their occurrence and concentration level depending, as mentioned above, on the composition of the ore and the severity of the leaching treatment.

In previous work[2,3] extractions of a number of metal ions from "pure" sulfate solutions by several representative amines were studied. Of the elements expected to be

associated with uranium in Western ore liquors, only molybdenum, and to a less extent vanadium(V), were extracted significantly by both secondary and tertiary amines. With the least selective secondary amines, low but significant quantities of iron(III) were extracted. Small amounts of titanium can also be extracted by these compounds, but the concentrations found in Western ore liquors are not high enough for consideration. Coefficients for extraction of such elements as iron(II), aluminum, sodium, magnesium, calcium, zinc, nickel(II), copper(II), cobalt(II), manganese(II), chromium(III), and vanadium(IV) by secondary and tertiary amines were so low as to be unimportant.

a. Iron

Extraction of iron(III) by amines has been shown to depend upon amine type and structure[2,3] whereas extraction of iron(II) is weak to negligible with amines in all classes. The variation in selectivity with respect to iron as a function of amine type and structure is similar to those described above for selectivity properties in general. Thus, the extraction of iron(III) by primary amines is so strong as to prevent the application of these reagents to oxidized leach liquors containing significant quantities of this element. In contrast, iron(III) extraction by the tertiary amines, particularly the symmetrical tertiary amines, is so low as to be unimportant. With the secondary amines the extractions, although low, are large enough to be considered unless the alkyl chains are appropriately branched (e.g., branching in close proximity to the nitrogen). In all cases the iron extraction coefficients increase with decreasing acidity of the aqueous liquors.

When the concentration of ferric iron in the liquor is high, it is possible to extract significant quantities into the organic phase even though the extraction coefficient is low. In continuous countercurrent operation, iron extraction is at a maximum in the lower stages of the system where little uranium is present to compete with it for the reagent. However, as the organic passes to regions of higher uranium concentration, the extracted iron is replaced by uranium, the extent of the replacement depending on the relative magnitude of the uranium and iron extraction coefficients and the level of uranium loading obtained. It apparently is not dependent on the rate of uranium-iron exchange since this has proved to be fairly rapid.

Figure 10 illustrates the variation in iron decontamination (Iron decontamination factor $= \frac{\text{Fe(III)/U in the head liquor}}{\text{Fe(III)/U in the extract}}$)

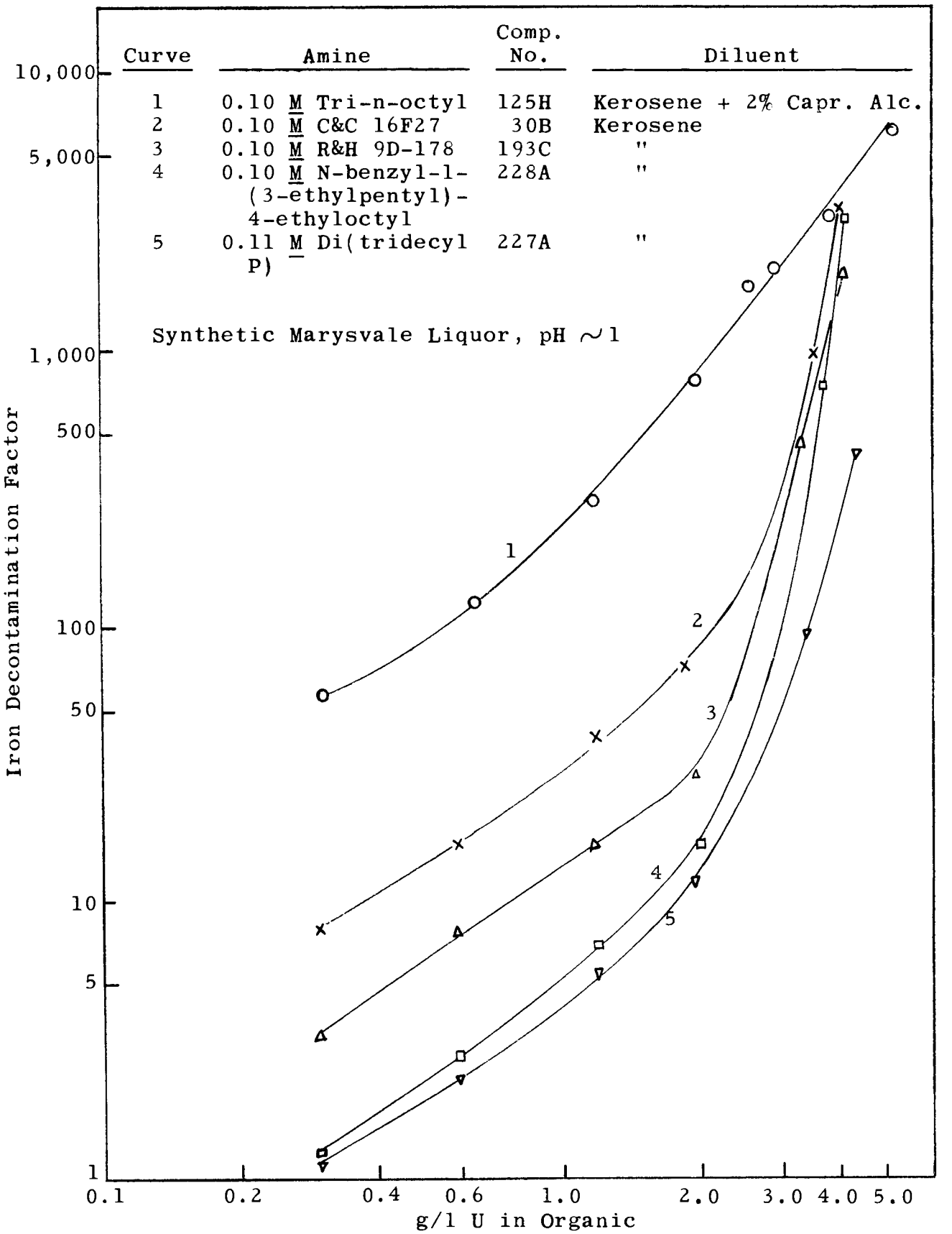

Figure 10

CONTROL OF IRON CONTAMINATION BY URANIUM LOADING

of the extract with uranium loading level for several amines from Synthetic Marysvale Liquor. In Figure 11, from the same experiments, the iron decontamination is shown as a function of the uranium concentration in the liquor at equilibrium with the organic phase. The tests were performed in such a manner that the results approximate those expected in continuous countercurrent operation, i.e., the extractions were performed at constant phase ratio from liquors of varying uranium content. For 0.11 M di(tridecyl P)amine, which is the least selective of the amines shown, the iron decontamination factor increases from 4 to 200 as the uranium concentration in the extract increases from 1 to 4 g U/l. For Synthetic Marysvale Liquor (5.8 g Fe(III) and 1.25 g U/l), a decontamination factor of 200 corresponds to a product containing approximately 2.3% Fe based on the uranium. In comparison, tri-n-octylamine (0.1 M in kerosene + 2% alcohol*) shows a high iron decontamination factor (~200) even when loaded to only about 1 g U/l. The factor increases to ~3000 at a loading of 4 g U/l which corresponds to a product (from Synthetic Marysvale Liquor) containing about 0.15% iron.

In normal application to Western ore liquors a 2 to 4 stage amine extraction process would be operated to give at least 3.5 g U/l in the organic phase if the amine concentration were 0.1 M. For most amines**, this corresponds to about 85% of the maximum loading from liquors of this type (see Section A-1). Under these conditions, it is apparent that all of the secondary and tertiary amines tested, including the least selective secondary amines, would be acceptable for process use. Increased decontamination from iron could be obtained by operating the process to give higher uranium loadings but at the expense of more extraction stages and a closer control of volume flow rates and concentrations.

At higher pH levels, iron is rejected less readily from the organic phase due apparently to a greater rise in the extraction of iron with increasing pH as compared with uranium. In Figure 12, the iron decontamination factor is plotted as a function of uranium concentration in the organic

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*The presence of alcohol in this experiment (added to improve reagent miscibility) was probably of some benefit to the extraction selectivity (see Section A-2). Other tests have demonstrated, however, that tri-n-octylamine is an exceptionally selective extractant without benefit from alcohol addition.

**The maximum uranium loading of tri-n-octylamine was significantly higher under comparable conditions and it would be loaded to a higher level in process use (see Section A-1).

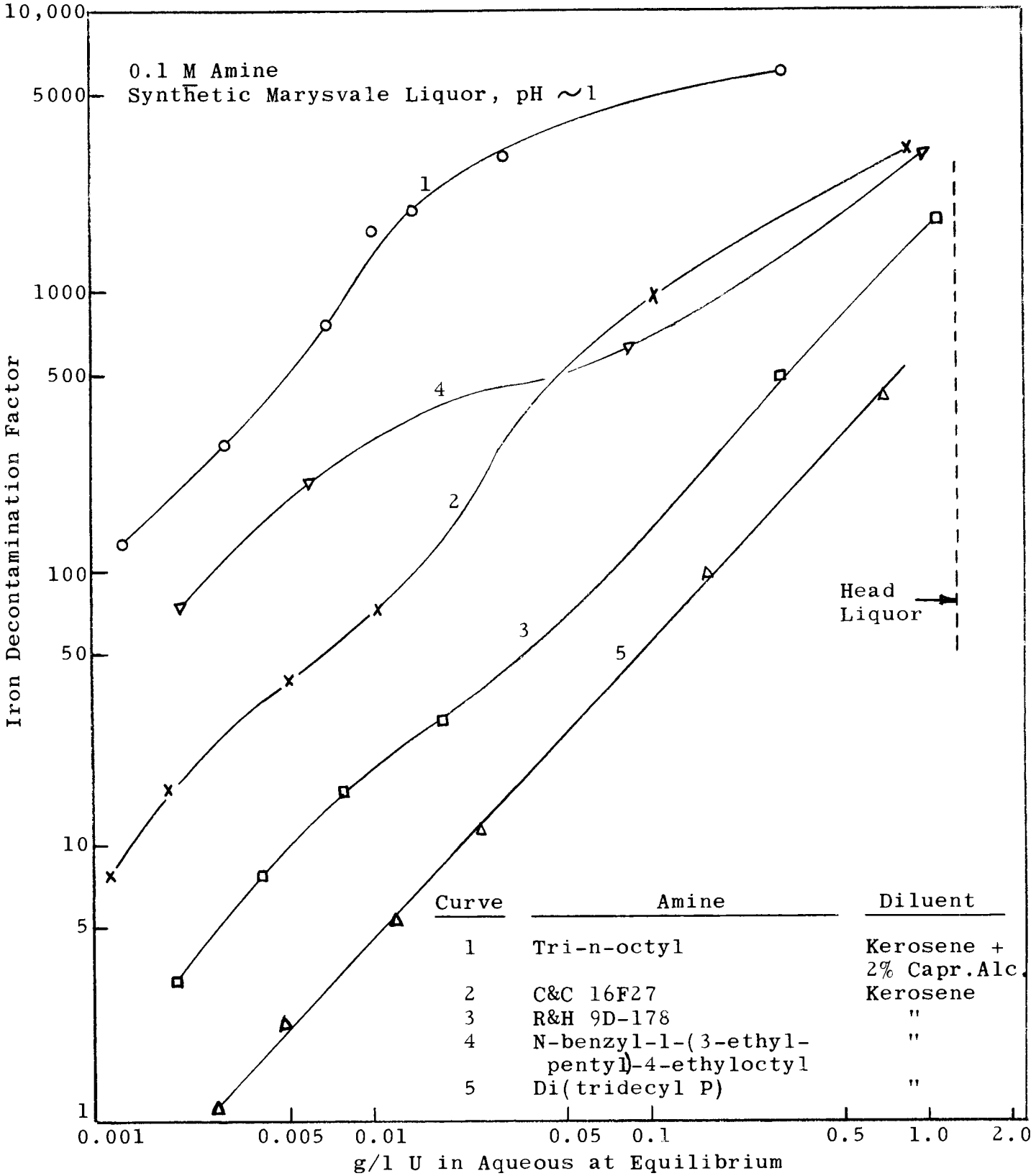

Figure 11

CONTROL OF IRON CONTAMINATION

BY URANIUM LOADING

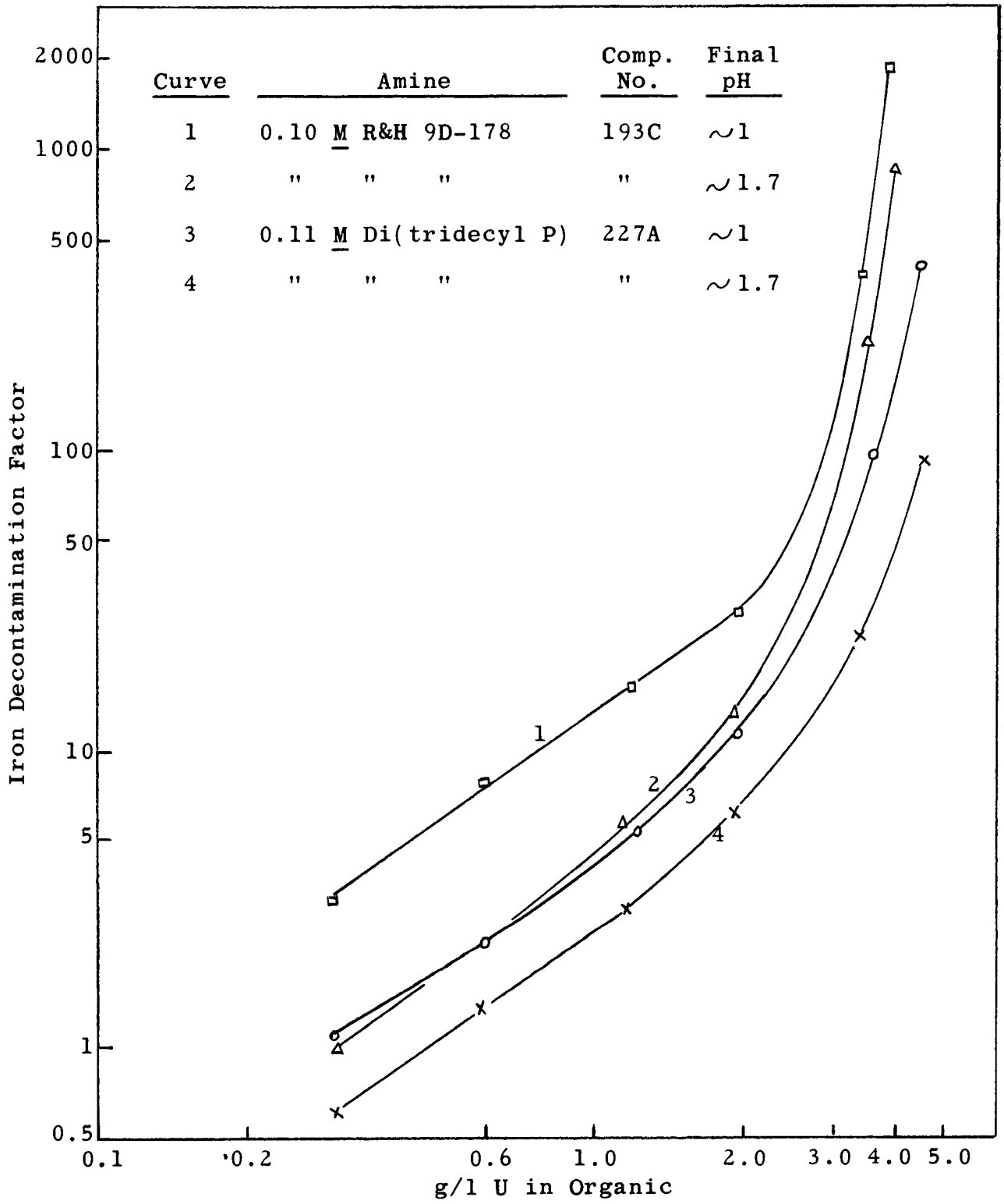

Figure 12

EFFECT OF pH ON SELECTIVITY OF

R&H 9D-178 AND DI(TRIDECYL P) AMINES

phase for di(tridecyl P) and R&H 9D-178 amines at pH 1 and 1.7. At the higher pH levels (considerably higher than would be encountered in practice) the extractions of iron by di(tridecyl P)amine in kerosene were high enough to cause a problem in treating liquors of this type. With the more selective R&H 9D-178 amine, extractions of iron were also significantly greater at the higher pH levels. In this case, however, the magnitude of the effect was not great enough to be of importance in process application (iron decontamination factor = $\sim$170 at a uranium loading of 3.5 g/l). Even better uranium-iron separations at the high pH levels would be given by compounds of even greater selectivity such as tri-n-octylamine, and the order of their effectiveness should be similar to that already shown in Figures 10 and 11 for extractions at pH 1 (see also Section A-4).

In addition to pH, other variables can influence the magnitude of the iron extractions. As noted previously[3] and as shown for di(tridecyl P)amine in Figure 13, the addition of alcohol to the diluent can cause a marked decrease in iron extraction. In other studies of diluent effects (results not shown), increased selectivities have been obtained with several amines when using aromatic petroleum products as compared to kerosene. Also, with respect to variations in aqueous phase composition, it has been shown that the extraction of iron is depressed by the presence of phosphate in the liquor.[2]

If desired, further separation of uranium from iron could be achieved by scrubbing most of the iron from the organic phase with dilute sulfuric acid (2-5%) prior to uranium stripping. Since the volume of scrub solutions would not be large, and the uranium content would be relatively small, it could be recycled either to the leaching step or to the extraction feed liquor. Such a scrubbing operation, as noted from the data given above, would not be required for a milling operation but could be considered for special applications where extremely pure products are required.

b. Molybdenum

As reported previously[2], since the extraction coefficients for molybdenum from sulfate solutions are as high or higher than those for uranium, most of any molybdenum present in the liquor should be extracted into the organic solvent. More recently it has also been observed that, when pentavalent vanadium is present in the liquor, the molybdenum and some vanadium are extracted in an associated form,

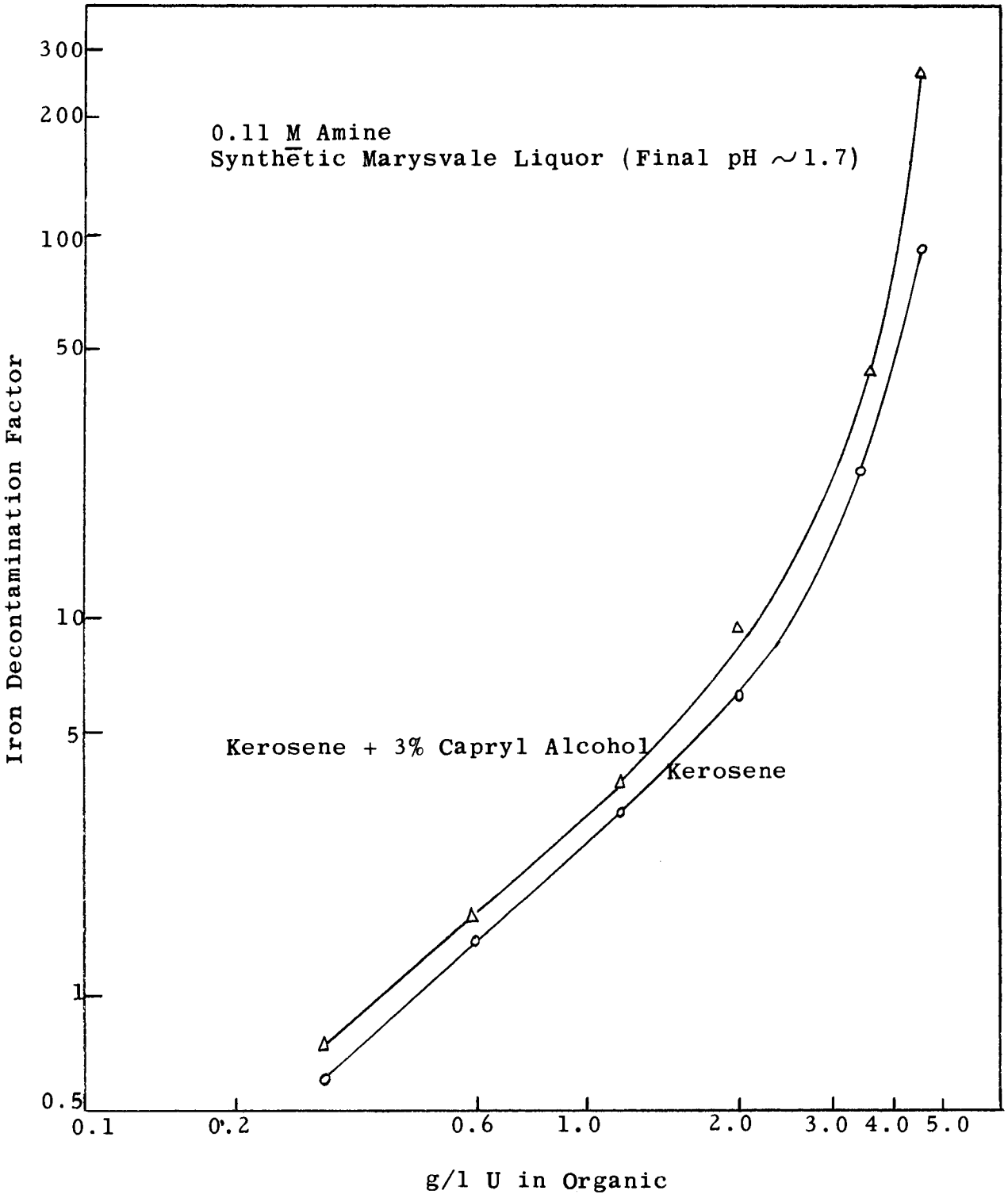

Figure 13

EFFECT OF DILUENT ON SELECTIVITY

OF DI(TRIDECYL P)AMINE

perhaps as a heteropolyacid.* This effect has caused some difficulty when using R&H 9D-178 amine in kerosene since the polyacid-amine complex is apparently only slightly soluble in this diluent and separates out as a green precipitate. Similar precipitations have not been observed, however, with several other reagents such as di(tridecyl P), C&C 16F27, dodecenyl Primene JM, and N-benzyl-1-(3-ethylpentyl)-4-ethyl-octylamine in kerosene and tri-n-octylamine in kerosene plus 2% capryl alcohol. With R&H 9D-178 amine precipitation has been avoided by using an aromatic diluent such as Amsco-G. Also, no precipitate has been noted when the vanadium present in the liquor is in the tetravalent state.

Only small amounts of molybdenum are present in leach liquors from most Western ores whereas appreciable amounts may be present in some, such as those from Arrowhead and Marysvale ores. It is apparent from the foregoing that, in these latter cases, provisions must be made to (1) prevent "build-up" of molybdenum in the amine-diluent phase to the detriment of the uranium extraction and (2) prevent excessive contamination from molybdenum in the uranium product. Fortunately, the preventive measures required are not difficult to provide and as described below they occur to a large extent as a natural result of the process schemes already proposed in Figures 2, 4, 5 and 6.

Molybdenum Build-up: Molybdenum is easily removed from the weak base amine reagents by treating with dilute alkaline solutions. This is true whether it has been extracted from the solution singly or in combination with vanadium(V). Consequently, in the carbonate and hydroxide stripping methods, Figures 2 and 6 respectively, the molybdenum is removed from the solvent in each cycle along with uranium. Also, in the chloride and nitrate stripping methods, Figures 4 and 5, provision is made to regenerate the amine (with a base) prior to its return to the extraction cycle and the molybdenum would be removed in this step. In the chloride stripping method of Figure 3, a regeneration step is not provided and the process would not be suitable for liquors of high molybdenum content. With liquors of intermediate molybdenum concentration a combination of processes 3 and 4 may be possible, i.e., a regeneration of only part of the organic stream in each cycle.

Molybdenum in Product: In the case of carbonate and hydroxide stripping (and also nitrate where molybdenum is returned to the strip solution from the regeneration step) separation of uranium from most of the molybdenum is to be

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*In several continuous extraction tests by the Process Test Group, a combining ratio of 2 moles of Mo/1 mole of V was observed.

expected at the uranium precipitation step since the molybdenum tends to remain in solution at this point. In several laboratory tests, with adequate washing provided, very effective separations have been obtained (see Section A-3-d, for example). With the chloride stripping method (Figure 4) additional opportunity for separation is provided since the molybdenum would be almost entirely expelled at the alkaline regeneration step.

c. Vanadium

Vanadium need not be considered with respect to selectivity unless it occurs in the liquor in its most highly oxidized (pentavalent) state. Unless oxidants are utilized, vanadium is ordinarily present in the sulfuric acid leach liquors as the nonextractable vanadium(IV). However, even if an appreciable concentration of vanadium(V) is present, its extraction is limited to a fairly low value under conditions normally encountered. For instance, the extraction is strongly dependent on the acidity of the liquor, the extraction coefficient with 0.1 M reagent being normally <1 at pH 1 or below, increasing gradually as the pH is raised to 1.8, and increasing very sharply in the pH range of 1.8 - 2.5.* Thus, in treating liquors of normal acidity, only a small amount of vanadium is extracted. Also, if the extraction pH is 1.5 or less the extracted vanadium can be mostly replaced by operating under conditions such that the organic phase becomes loaded to a high level with uranium. (An exception to this would be expected in the particular case of high molybdenum liquors - see previous section.)

If the extraction pH is greater than 1.5, there is evidence that replacement of vanadium with uranium is more difficult than would be predicted by comparison of the relative uranium and vanadium extraction coefficients at that pH. Also, in such instances, it has been noted that the vanadium is replaced with greater difficulty if the extract is aged for a period of time. A change in chemical form of the vanadium apparently occurs in these cases after extraction into the organic phase.

Although additional separation of uranium and vanadium, past that obtainable in the extraction cycle, would not be necessary for meeting product specifications, further separation would, nevertheless, be given by some of the stripping methods. In the chloride stripping method (Figure 3) the vanadium, like molybdenum, ordinarily is not stripped

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*Later (Appendix B) a process will be considered for simultaneous extraction of uranium and vanadium from liquors which have been oxidized and adjusted to high pH levels.

appreciably by the chloride salt solutions. If present in significant quantities it can be removed from the solvent by contacting with an alkaline solution to regenerate the free amine (Figure 4). Some separation of uranium and vanadium might also be expected in the nitrate and carbonate stripping methods during the uranium precipitation step, the degree of separation depending upon the precipitation conditions.

d. Product Grade and Purity

It is apparent from the foregoing discussions that, since the amines are selective extractants, the uranium product obtained from an amine extraction process should be relatively pure and of high grade. The following is a typical product obtained from continuous countercurrent extraction of a Vitro plant liquor (analysis Table 3) with R&H 9D-178 amine in kerosene.* Sodium carbonate was used as

U_3O_8	Fe	Al	V	Mo
81%	0.25%	0.1%	0.1%	0.1%

the stripping agent in this test. No attempt was made to remove the small amounts of ferric hydroxide that may have formed during the strip. The loaded solution was acidified with sulfuric acid to destroy the carbonate, and the uranium was precipitated with sodium hydroxide. The sodium polyuranate product was washed and dried at 120°C prior to analysis. No other metals (except, of course, sodium) were present in quantities as great as 0.1% according to spectrographic analysis.

The low concentrations of molybdenum appearing in the product are of particular interest. Most of the molybdenum present in the liquor (0.08 g/l) was extracted by the amine and stripped by the sodium carbonate to give a concentration in the loaded strip solution equivalent to about 8% by weight of the uranium. The small amount of molybdenum found in the product demonstrates a rather effective rejection in the uranium precipitation and washing steps.

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*Performed by the Process Test Facility Group.

4. Effect of Extraction Variables

a. Amine Concentration

The amine reagents (the amine salts) appear to exist in the hydrocarbon diluents in a form (such as a colloidal dispersion) in which the amine activity is fairly constant over a range of nominal concentrations. Conformably, the extraction coefficients for uranium from sulfate solutions are nearly directly proportional to the free reagent concentration in the organic phase*.[2] In treating Western type sulfate liquors an effective recovery operation can be obtained with 0.1 M reagent in the organic phase, and most of the process test work has been performed using this concentration. It is not intended to imply that this is the general optimum concentration for process operation on liquors of all compositions or grades. On the other hand, it does appear that any gains to be made by increasing the reagent concentration should not be large, at least for liquors of the type and grade normally encountered in treating Western ores, and that the data obtained on operational factors, reagent consumption, etc. at the 0.1 M level should be reasonably representative of those generally expected in application of an amine extraction process.

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*Detailed tests (which will be reported elsewhere) of uranium extraction with di-n-decylamine in benzene from 1 M sulfate solution, pH 1, showed the uranium extraction coefficient proportional to the first power of the free reagent (free amine salt) concentration when that concentration was varied by changing the amount of uranium present at constant total reagent concentration. On the other hand, when the free reagent concentration was varied by varying the total reagent concentration while keeping the ratio of uranium to reagent low and approximately constant, the extraction coefficient was proportional to the first power of the free reagent concentration only up to about 0.03 M amine, and was proportional to about the two-thirds power in the region of 0.1 M. This difference may be provisionally ascribed to a change in the nature of aggregation of the colloidal amine sulfate, causing a relatively small change in the activity of amine sulfate and/or the uranium in the organic phase. This degree of deviation from "constant activity" is not great enough to have an important effect on the process relationships under consideration. It is important to note that the dependence of extraction on the first power of the free amine concentration is in contrast (and the contrast is greater if the power is less than unity) to uranium extraction with such reagents as TBP and organophosphoric acids, wherein the extraction depends on the square of the free reagent concentration.

For a given amine and liquor a final optimization of the extractant concentration would necessarily depend upon a careful balance between the operational advantages and disadvantages which would be encountered at each concentration considered. Some of the advantages and disadvantages from increasing the amine concentration may be mentioned as follows:

1) The volume of organic which must be handled in the extraction and stripping circuits would decrease with increasing extractant concentrations.

2) Since the organic phase is richer in reagent and its unit cost per gallon is greater, the costs arising from entrainment losses would increase with increasing extractant concentration.

3) If there is a tendency toward emulsion formation it ordinarily becomes stronger as the amine concentration is increased.

4) Since the uranium concentration of most Western liquors is in the range of 1.0 - 1.5 g U/l, the use of very high amine concentrations would require operation at extreme aqueous/organic feed ratios in order to insure adequate loading of the organic phase. Throughputs in some types of contactors are limited in respect to operations of this type.

At maximum loadings from the sulfate leach liquors at pH about 1, the molar ratio of amine to uranium in the organic phase does not vary appreciably over a fairly wide range of amine concentrations (e.g., 0.1 - 0.4 M). Thus, in practice, if the extractant concentrations were increased, the same percent of maximum loading must be attained in order to achieve equivalent reagent utilization. In such case, and insofar as the proportionality between extraction coefficient and free amine concentration holds, the number of extraction stages required to obtain the same uranium recovery would be independent of the reagent concentration. In stripping the loaded organic by the quantitative sodium carbonate method the reagent requirements on the basis of uranium recovered would, of course, be independent of reagent concentration when the moles of amine per mole of uranium at loading is the same. Also, in the equilibrium chloride and nitrate stripping methods, the reagent requirements would remain unchanged insofar as the constant activity principle, described above, applies.

b. pH

It has been observed[2] that when uranium is extracted from "pure" sulfate solution, the extraction coefficient increases with increasing pH of the aqueous solution (until an upper limit is reached at a pH which is related to the base strength of the particular amine). However, in extracting from actual liquors where other metal ions, particularly iron, are in competition with the uranium, the total effect of pH variation can be different depending upon the extractant and the quantity of metal present.

Figures 14 and 15 show extractions of uranium by several amines (in benzene) from Synthetic Marysvale Liquor which had been adjusted to various pH levels with ammonia. It may be noted from these tests that the behavior of the tertiary amines and the most selective of the secondary amines (C&C 15F53*) was qualitatively similar to that shown previously when extracting from pure liquors (compare Figures 14 and 15 with Figures 5 and 6, ORNL-1734). On the other hand, with the less selective secondary amines, e.g., dilauryl, di-n-decyl, and di(2-butyloctyl), the uranium extractions decreased rather than increased as the pH was raised from 0.9 to 2.1. This latter behavior is undoubtedly due to an increase in relative amount of iron extraction (competition) as the solution acidity was decreased and would, of course, be less important for liquors of lower iron(III) content. For example, it may be observed from Table 2 that an increase in pH was beneficial to extractions by dilaurylamine (in Amsco D-95) from the comparatively low iron Lukachukai leach liquor.

When an appreciable concentration of vanadium(V) is present in the liquor, the uranium coefficient may also be affected adversely by increasing pH due to increased vanadium extraction, particularly at very high pH levels (i.e., 1.8 - 2). In this case, the effect on the coefficient is similar for all types of amines since the extraction of vanadium does not appear to be substantially dependent on amine structure. If the vanadium were reduced an effect would not be noted, of course, since vanadium(IV) does not extract even at the high pH levels.

Although the data in Figures 14 and 15 show that the uranium extraction efficiency of the amines, particularly the less selective compounds, can vary with changes in the free acid content of the liquor, it is also apparent from these and other data that in the range of acidities

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*Branching off the first carbons of the alkyl chains is identical to that of C&C Amine 16F27 (see Appendix C, ORNL-1922).

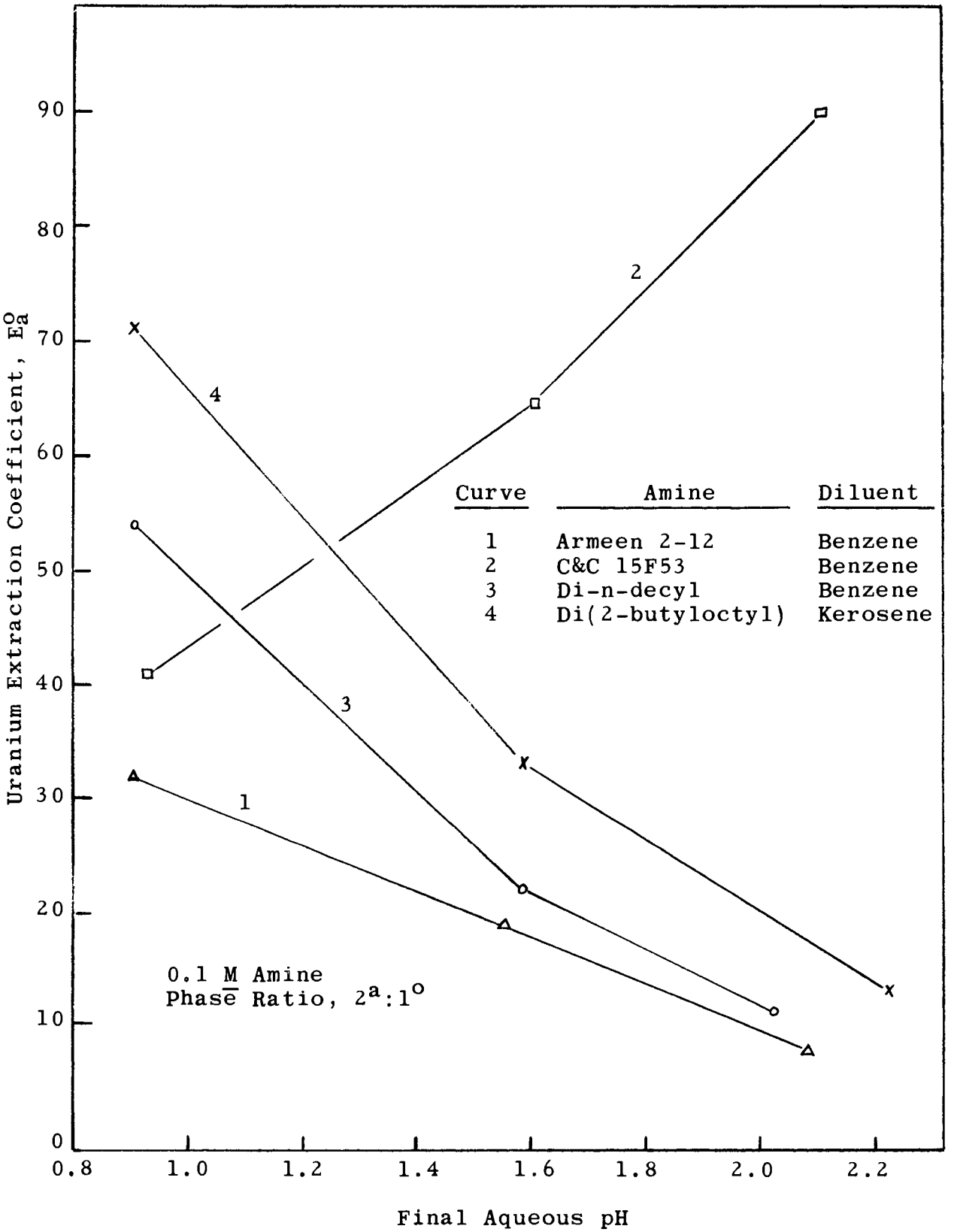

Figure 14

EFFECT OF pH VARIATION ON URANIUM EXTRACTION

BY SECONDARY AMINES FROM SYNTHETIC MARYSVALE LIQUOR

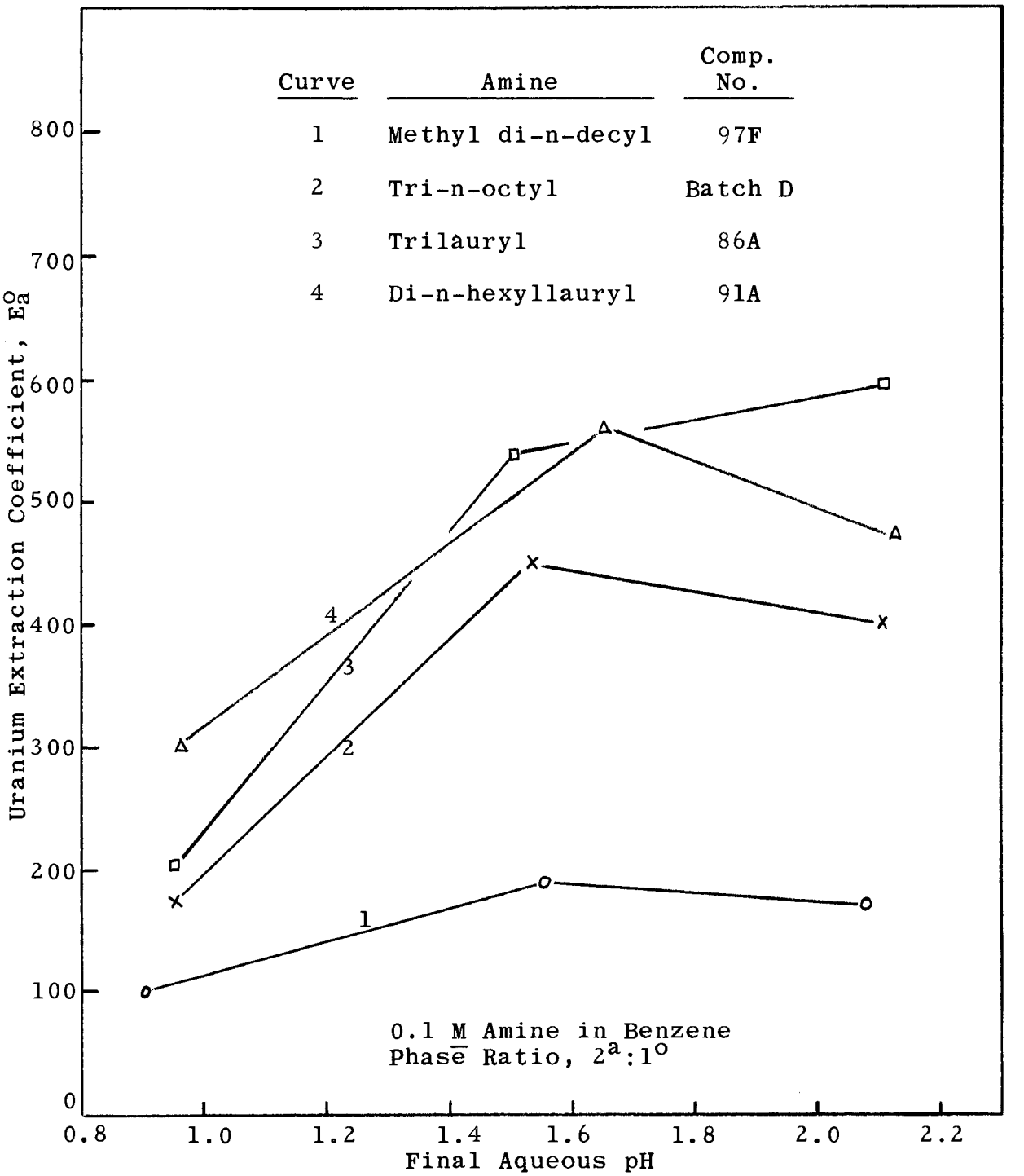

Figure 15

EFFECT OF pH VARIATION ON URANIUM EXTRACTION

BY TERTIARY AMINES FROM SYNTHETIC MARYSVALE LIQUOR

normally encountered (pH 0.8 - 1.5), the coefficients at 0.1 M reagent concentration are entirely adequate for process application. Process tests at pH levels much below 0.8 have not been extensive since Western process liquors ordinarily do not contain excessive quantities of free acid. However, data from the screening experiments reported earlier[2] show that low pH liquors could be handled in the event that they were encountered. Extraction and separation of uranium from liquors higher in pH* can also be made although reduction of vanadium to the tetravalent state would be required with liquors of high vanadium content. If the liquor is at a high pH and oxidized the recovery of vanadium, as well as uranium, may be obtained by amine extraction. Studies are being made of the feasibility of such a process (see Appendix B).

c. Sulfate Concentration

As described previously,[2] the extraction of uranium by the amines decreases as the sulfate concentration in the aqueous liquor increases. This is illustrated again in Figure 16 for R&H Amine 9D-178 (in kerosene) and tri-n-octylamine (in kerosene + 2% alcohol) when extracting from synthetic liquors of varying salt content at pH 1.0. In both cases the coefficients decreased by a factor of about ten as the sulfate concentration was increased from 0.3 M to 1.5 M. However, even at the latter concentration, the coefficients were still fairly high (E_a^o = 25 for R&H 9D-178 and 55 for tri-n-octylamine). Western ore leach liquors are typically much lower in sulfate, the concentration in most cases falling between 0.3 M and 0.7 M.

d. Other Anions

Sulfuric acid leach liquors derived from Western ores frequently contain small concentrations of phosphate and fluoride. Chloride is present in acid leach liquors obtained

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*When the amines are recycled to extraction in the basic form, i.e., after basic stripping or basic regeneration, they react with sulfuric acid to form the sulfate and bisulfate salts and hence there is an increase in the liquor pH. The amine requirements for uranium extraction are small and thus the pH change under most process conditions is minor. However, with liquors of relatively low initial acidity (pH $>$ 1.7) care must be taken that the pH rise during extraction is not sufficient to cause precipitation of some of the hydrolyzable metals. Susceptibility to such precipitation will be greatest, of course, for liquors highest in metal ion concentration and lowest in sulfate concentration.

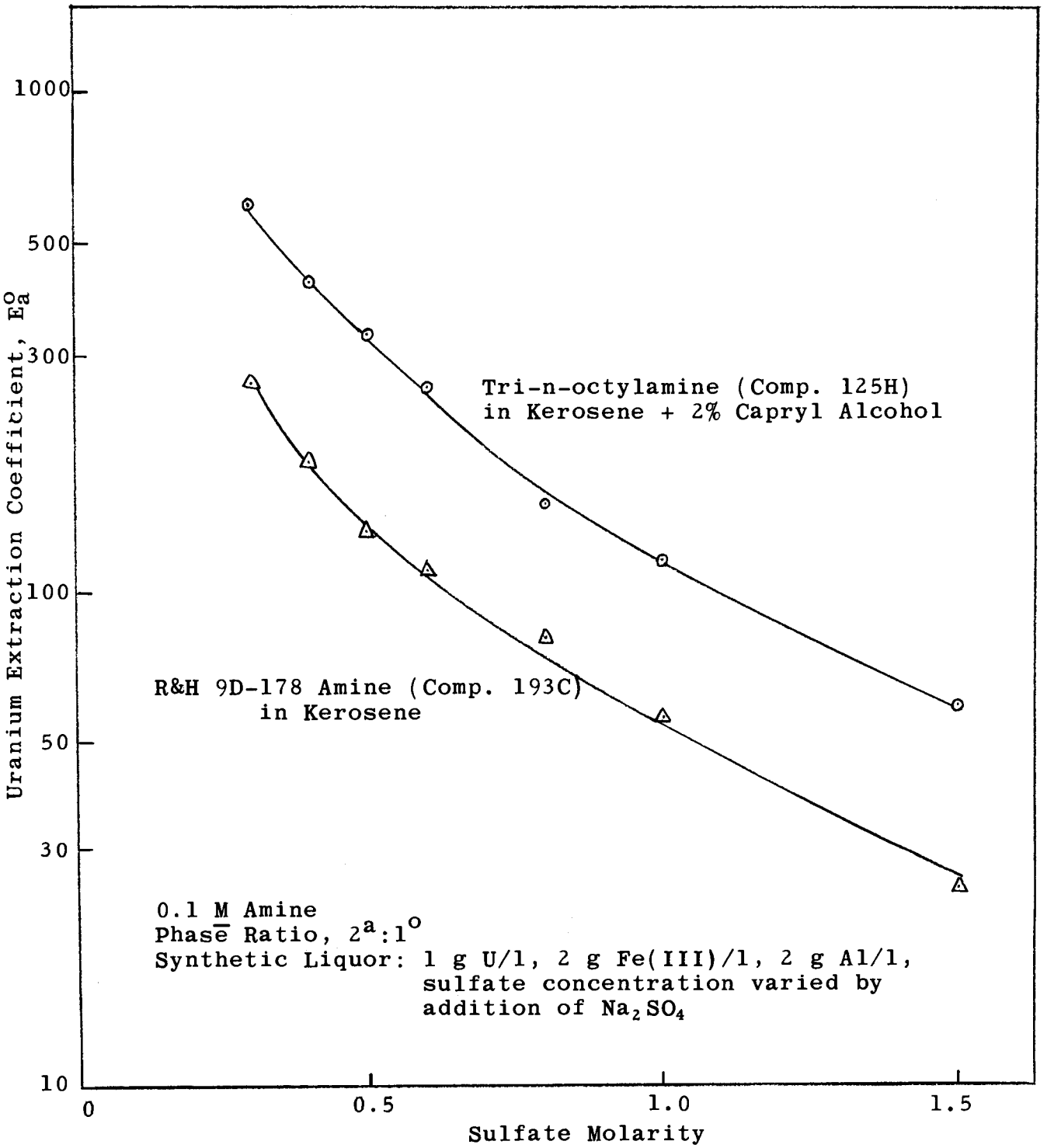

Figure 16

EFFECT OF SULFATE CONCENTRATION ON URANIUM EXTRACTION

in the salt roast-acid leach process[5] and, in addition, chloride or nitrate can be introduced into the extraction system if chloride or nitrate salts are utilized for stripping and the extractant is recycled to the extraction system as the amine salt. For these reasons, the effect of small concentrations of chloride, fluoride, nitrate, and phosphate on uranium extraction from sulfate liquors has been investigated. Studies of these anions in pure uranium sulfate solutions using dilauryl and tri-n-octylamine as extractants were reported previously.[2,3] Figures 17 and 18 below illustrate their effect on uranium extractions from Synthetic Marysvale Liquor with tri-n-octyl (0.1 M in kerosene plus 3% alcohol) and R&H 9D-178 amines (0.1 M in kerosene).

Nitrate: In agreement with its effectiveness as a stripping agent, the presence of small amounts of nitrate in the leach liquor caused a severe deleterious effect on the uranium extraction. The addition of only 0.05 M nitrate to the liquor decreased the extraction coefficient of tri-n-octylamine from approximately 300 to 6 and that of R&H 9D-178 amine from 120 to 1.

Nitrate concentrations of this order could be introduced by amine reagents which had been stripped with a nitrate solution and thus converted to the nitrate salt. Consequently, if nitrate solutions are used for stripping, the organic phase should be scrubbed with a base (to regenerate free amine) prior to its return to the extraction cycle (see Figure 5).

Chloride: The decrease in extraction due to the presence of chloride was appreciable but not so severe as that with nitrate, in conformance with the relative stripping effectiveness of these two ions. The effect from chloride was comparatively greater on the secondary, R&H 9D-178 amine, than the symmetrical tertiary, tri-n-octylamine*. In either case, however, the level of chloride that might be obtained as the result of a chloride stripping cycle should not be prohibitive to the extraction process. Thus, in contrast to

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*Other tests have indicated the "chloride effect" to be stronger in general with the secondary than with the tertiary amines, and stronger for the secondary amines with branching near the nitrogen than for secondary amines with straight chains or branching at a distance from the nitrogen. These results are considered to be tentative, however, since different diluents were used in many of the tests and a sizable effect from the diluent could invalidate several of the comparisons. Further studies are being made.

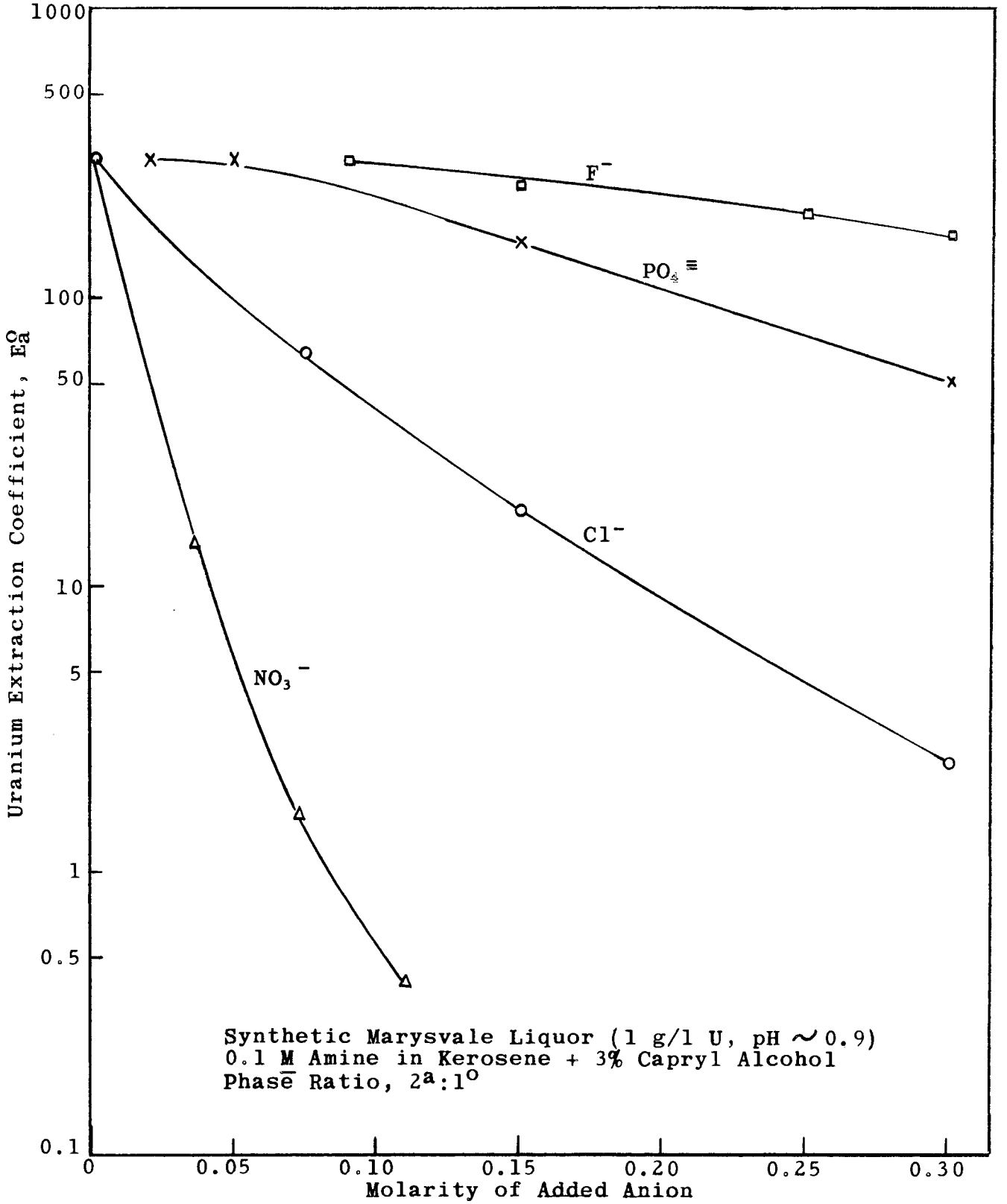

Figure 17

EFFECT OF ADDED CHLORIDE, FLUORIDE, NITRATE, PHOSPHATE ON EXTRACTION OF URANIUM BY TRI-n-OCTYLAMINE (Comp. 125H)

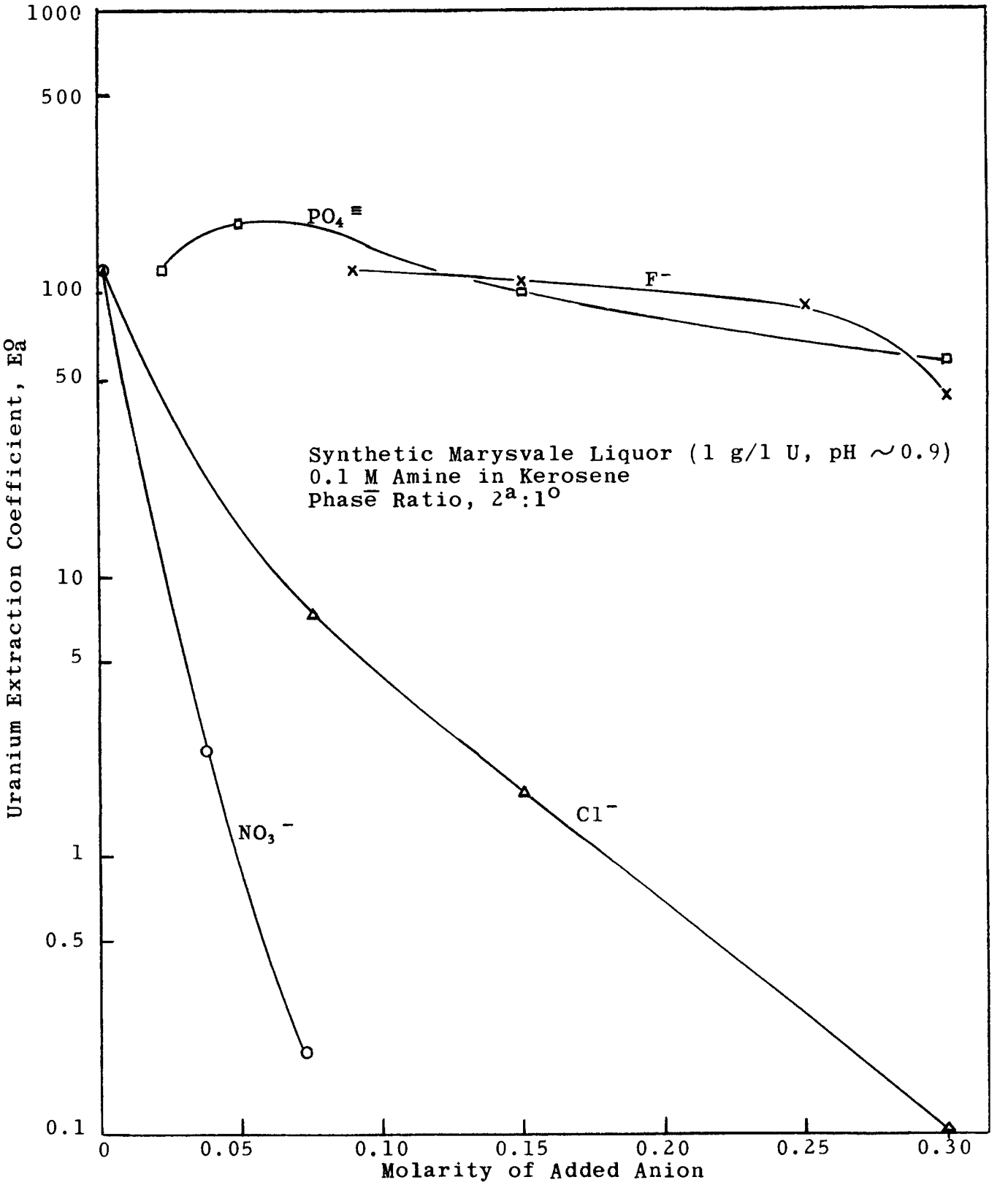

Figure 18

EFFECT OF ADDED CHLORIDE, FLUORIDE, NITRATE, PHOSPHATE ON EXTRACTION OF URANIUM BY R&H AMINE 9D-178 (Comp. 193C)

the case for nitrate, removal of chloride by alkaline regeneration after stripping should not be necessary because of its effect on the uranium extraction coefficient, although such a regeneration might be desirable in some cases for other reasons*.

With liquors which contain chloride as an inherent result of the leaching operation, i.e., those from the salt-roast, acid-leach process, extraction by amines would be worthy of consideration provided the chloride concentration in the liquors did not reach too high a level. As shown in Figure 17, 0.1 M tri-n-octylamine gave a uranium coefficient of approximately 20 when the chloride concentration of the liquor was 0.15 M. In other tests (not reported), N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine (0.1 M in kerosene) was shown to be more effective, coefficients of 175 and 15 being obtained at 0.15 M and 0.3 M chloride, respectively. On a comparative basis the degree of chloride effect on the latter reagent was as large as for other amines tested; the higher coefficients were a result of the greater overall extraction power of this compound (see previous sections).

Fluoride: In tests with "pure" uranium sulfate solutions (p. 79, ORNL-1922), the presence of fluoride was observed to cause an appreciable reduction in uranium extraction, the magnitude of the effect being similar to that from chloride. As shown in Figures 17 and 18, the effect from fluoride in the Synthetic Marysvale Liquor was much smaller. Even at 0.3 M fluoride, a concentration considerably higher than would normally be encountered, the decrease in extraction was not sufficient to cause a problem in process application. The difference in these results in undoubtedly due to the reaction of fluoride with aluminum and iron in the Marysvale liquor to form stable complexes, thus reducing the amount of fluoride available for reaction with the uranium. It is also probable that the extractions of iron were decreased by the presence of fluoride, although specific measurements of this effect have not been made.

Phosphate:, As shown in Figures 17 and 18, the presence of phosphate in the liquor caused only a moderate decrease in uranium extractions, and, as with fluoride, concentrations greater than those ordinarily encountered (i.e., 0.3 M) could be tolerated without undue effect on a process operation. In other tests reported previously,[2] it has

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*For example, to free the reagent from extracted molybdenum (see Section A-3).

been shown that the phosphate complexes with iron(III) and decreases its extraction. When using amines of lower selectivity (with respect to ferric iron) or when extracting at higher pH's, where extractions of iron are enhanced, the presence of phosphate in the liquors can be of an overall benefit to the extraction operation.

e. Extraction Temperature

The effect of temperature on extraction has been examined for four different amines over the range of 20 to 50°C (Figure 3, ORNL-1734). Although the extraction efficiency decreased appreciably with increasing temperature, the extraction power of each amine, even at 50°C, was sufficiently high for process use. Reagent stability would probably be a more important factor in setting an upper limit on the temperature of operation (see Section C-3).

f. Extraction Rate

The rate of uranium transfer from the aqueous to the organic phase is rapid if adequate mixing is provided. With efficient agitation, equilibrium distribution of the uranium has been achieved in only a few seconds, using either free amine or the amine sulfate salt as the initial extractant. It is apparent that the throughputs obtainable in an extraction apparatus will be limited by the rate of phase disengagement rather than by the rate of uranium transfer. The extraction of iron(III) is rapid but somewhat slower than uranium. With vanadium the extractions are apparently complicated by a slow change in the chemical nature of the vanadium after its extraction into the organic phase. Although an appreciable percentage of the vanadium(V) can be rapidly extracted (at a high pH), complete equilibrium was not obtained in several tests even after 5-10 minutes of vigorous mixing.

B. The Stripping System

1. Stripping with Solutions of Sodium Carbonate (Figure 2)

The uranium-loaded organic extract may be effectively stripped with solutions of sodium carbonate, the uranium reporting to the aqueous phase as the soluble carbonate complex. Simultaneously, the amine salt, including that portion combined with the uranium, is converted to free amine which remains dissolved in the organic phase and is recycled to the extraction system. At a temperature of 25-30°C and with a

reasonable contact time (5 minutes/stage) quantities of sodium carbonate which are equal to or in slight excess of the stoichiometric quantities represented by equations (1), (2) and (3) below are ordinarily sufficient to accomplish complete stripping.

$$(R_2NH_2)_2UO_2(SO_4)_{2\,org}^{*} + 5Na_2CO_{3\,aq} = 2R_2NH_{org} + Na_4UO_2(CO_3)_{3\,aq} + 2Na_2SO_{4\,aq} + 2NaHCO_{3\,aq} \quad (1)$$

$$(R_2NH_2)_2SO_{4\,org} + 2Na_2CO_{3\,aq} = 2R_2NH_{org} + Na_2SO_{4\,aq} + 2NaHCO_{3\,aq} \quad (2)$$

$$(R_2NH_2)HSO_{4\,org} + 2Na_2CO_{3\,aq} = R_2NH_{org} + Na_2SO_{4\,aq} + 2NaHCO_{3\,aq} \quad (3)$$

As indicated by the above equations, most of the sodium carbonate is used in converting the amine salts to free amine, while a smaller fraction is required for formation of the soluble uranium tricarbonate complex. Therefore, it is evident that most efficient utilization of the sodium carbonate strip is obtained when the organic phase is loaded as high as practicable with uranium. In Figure 19 typical results are shown for a two stage system where an 8% sodium carbonate solution is used for stripping 0.1 M R&H 9D-178 amine in kerosene. The organic phase in this test contained 4.1 g U_3O_8/l (3.5 g U/l), the approximate level anticipated in practice for amines at this concentration, and the amount of sodium carbonate supplied was approximately 5% in excess of the stoichiometric requirements shown by equations (1), (2) and (3). It is apparent from the results that essentially complete removal of uranium from the organic phase was effected in the first stripping stage. Under the conditions of the experiment, the total amount of sodium carbonate supplied amounted to 3.9 lb/lb U_3O_8 or 8.6¢/lb of U_3O_8, when taking a unit cost of 2.2¢/lb Na_2CO_3.

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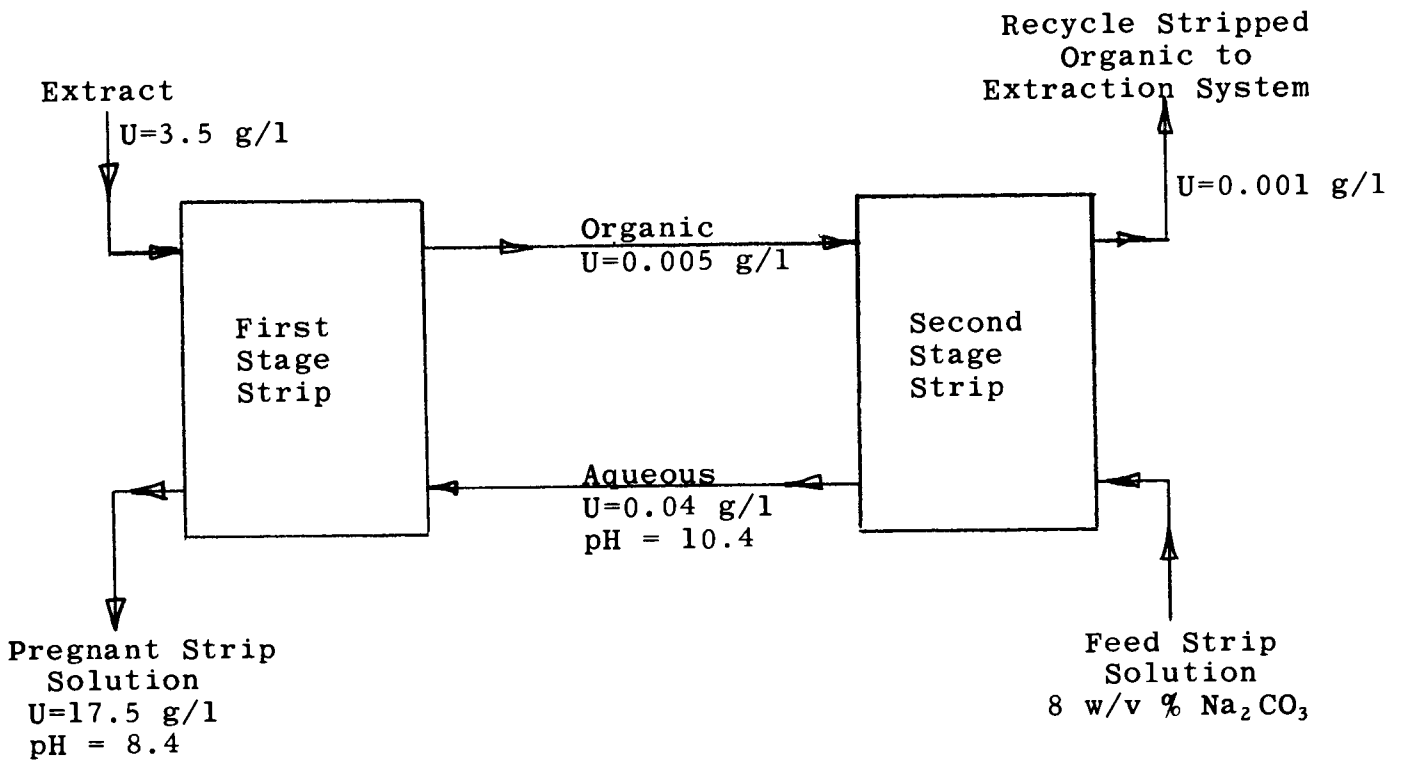
*$(Amine)_2UO_2(SO_4)_2$ is not meant to represent the actual uranium complex species in the organic phase and is used here only for simplicity in presentation. This choice is not important to the discussion since any other formulation leads to an equation equivalent to a combination of equations (1)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

(0.1 M R&H amine 9D-178 (Comp. 193C) in kerosene)

Feed Ratio: Organic/Aqueous = 5



Chemical Consumption:

lb Na_2CO_3/lb U_3O_8 = 3.9

Figure 19

URANIUM DISTRIBUTION IN CARBONATE STRIPPING

With longer contact times and/or higher temperatures, almost complete utilization of the sodium carbonate base strength may be made as follows:

$$(R_2NH_2)_2UO_2(SO_4)_{2\,org} + 4Na_2CO_{3\,aq} = 2R_2NH_{org} + Na_4UO_2(CO_3)_{3\,aq} + 2Na_2SO_{4\,aq} + H_2O + CO_2 \quad (4)$$

$$(R_2NH_2)_2SO_{4\,org} + Na_2CO_{3\,aq} = 2R_2NH_{org} + Na_2SO_{4\,aq} + H_2O + CO_2 \quad (5)$$

$$(R_2NH_2)HSO_{4\,org} + Na_2CO_{3\,aq} + RNH_{org} + Na_2SO_{4\,aq} + H_2O + CO_2 \quad (6)$$

In several tests where the sodium carbonate was only slightly in excess of the stoichiometric amounts shown in equations (4) - (6), complete stripping of uranium was attained. It was also noted, however, that the phase separation rate was much slower under these conditions, the effect being more pronounced for some amines than for others. Further studies will be necessary to determine whether this more effective utilization of the sodium carbonate reagent can be made to perform in a manner acceptable for large scale practice.

Elements other than uranium which may be extracted into the organic phase are also stripped effectively by the sodium carbonate solutions. Vanadium(V) and molybdenum are removed and dissolved by the alkaline solution whereas iron is precipitated as ferric hydroxide. Precipitation of the iron might be considered a minor advantage since some further reduction in iron contamination of the uranium product could be obtained by removing the iron precipitate prior to uranium precipitation. On the other hand, the formation of appreciable amounts of precipitate at this point might produce operational difficulties since it tends to collect at the organic-aqueous interface. In actual continuous large scale process tests on Vitro type liquor with fairly selective amine-diluent combinations, e.g., R&H 9D-178 amine in kerosene and Armeen 2-12 in 95% Amsco G - 5% alcohol*, the amount of iron extracted was small and

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The selectivity of Armeen 2-12 with respect to iron is much better when alcohol is present in the hydrocarbon diluent than when used in hydrocarbon diluents alone.

no problems were encountered. With less selective extractants some difficulty would be anticipated unless precautions were taken to decrease the iron extraction. As described in a previous section, this can be accomplished by loading the organic phase to near saturation with uranium, and, if necessary in extreme cases, by utilization of a dilute sulfuric acid scrub to remove most of the iron prior to the stripping operation.

2. Stripping with Chloride Solutions (Figures 3 and 4)

Dilute solutions of sodium chloride, hydrochloric acid, or mixtures of salt* and acid are also effective stripping agents for uranium. Simplified expressions for the stripping reactions may be written as follows:

$$(R_2NH_2)_2UO_2(SO_4)_{2\,org} + 2NaCl_{aq} \rightleftharpoons 2R_2NH_2Cl_{org} + UO_2SO_4\,aq + Na_2SO_4\,aq \qquad (7)$$

and

$$(R_2NH_2)_2SO_4\,org + 2NaCl_{aq} \rightleftharpoons 2R_2NH_2Cl_{org} + Na_2SO_4\,aq \qquad (8)$$

$$(R_2NH_2)HSO_4\,org + NaCl_{aq} \rightleftharpoons R_2NH_2Cl_{org} + NaHSO_4\,aq \qquad (9)$$

Although sodium chloride is somewhat less efficient than hydrochloric acid, it is the preferred reagent due to lower cost and lower base requirements for precipitating uranium from the pregnant strip solution. In practice, a small amount of sulfuric acid ($\sim$ 0.05 M) would probably be added to the sodium chloride strip solution, since it gives improved phase separation in some cases as well as an improvement in stripping coefficient. This quantity of acid, and the quantity of additional base required for its neutralization in the uranium precipitation operation, are so small as to be unimportant costwise.

Analogous to the elution of anion exchange resins, chloride stripping of uranium from the amines occurs by an equilibrium (competition) process, the stripping efficiency increasing as the amount of excess chloride is increased.**

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*Other chloride salts, e.g., NH_4Cl, $MgCl_2$, can also be used.

**The concentration of chloride that may be used for stripping is subject to limitations, however, since uranium is extracted by the amines from concentrated chloride solutions, again analogous to anion exchange resins.

In order to obtain complete stripping, while holding the chloride requirements to a low level, a multistage operation is used. Figure 20 shows typical uranium distributions obtained during stripping of R&H 9D-178 amine with 0.95 M NaCl - 0.05 M HCl in a 3-stage system*. In this test the sodium chloride supplied to the system was 100% in excess of the stoichiometric quantities shown in equations (7) - (9). Stripping was essentially complete in two stages, yielding a pregnant strip solution containing ~20 g U/l. As indicated previously (Section A-4) the tertiary amines are usually somewhat less responsive to the chloride strip than are the secondary amines**. Had a compound of this type been used in the test described, a slightly greater excess of chloride and/or more stripping stages would probably have been required for complete uranium removal.

At the conclusion of the stripping operation the extractant is in the form of the chloride salt. It may be recycled to the extraction system as such (Figure 3) or may first be regenerated to the free amine (Figure 4) by single-stage contact with a base***, e.g., solutions of NH_3, Na_2CO_3, or possibly a lime slurry****. A direct recycle of the reagent (Figure 3) would have an advantage in reagent requirements but could also have certain disadvantages, e.g., (1) the introduction of chloride into the extraction system causes a decrease in the overall extraction efficiency due to the interference of chloride ions, (2) corrosion in the extraction system might be increased by the addition of chloride, and (3) molybdenum is not stripped from the extract

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*Batch shake-outs performed in a manner simulating a countercurrent system. Equivalent results have been obtained in continuous countercurrent equipment by the Engineering Group using H_2SO_4 in place of the HCl.

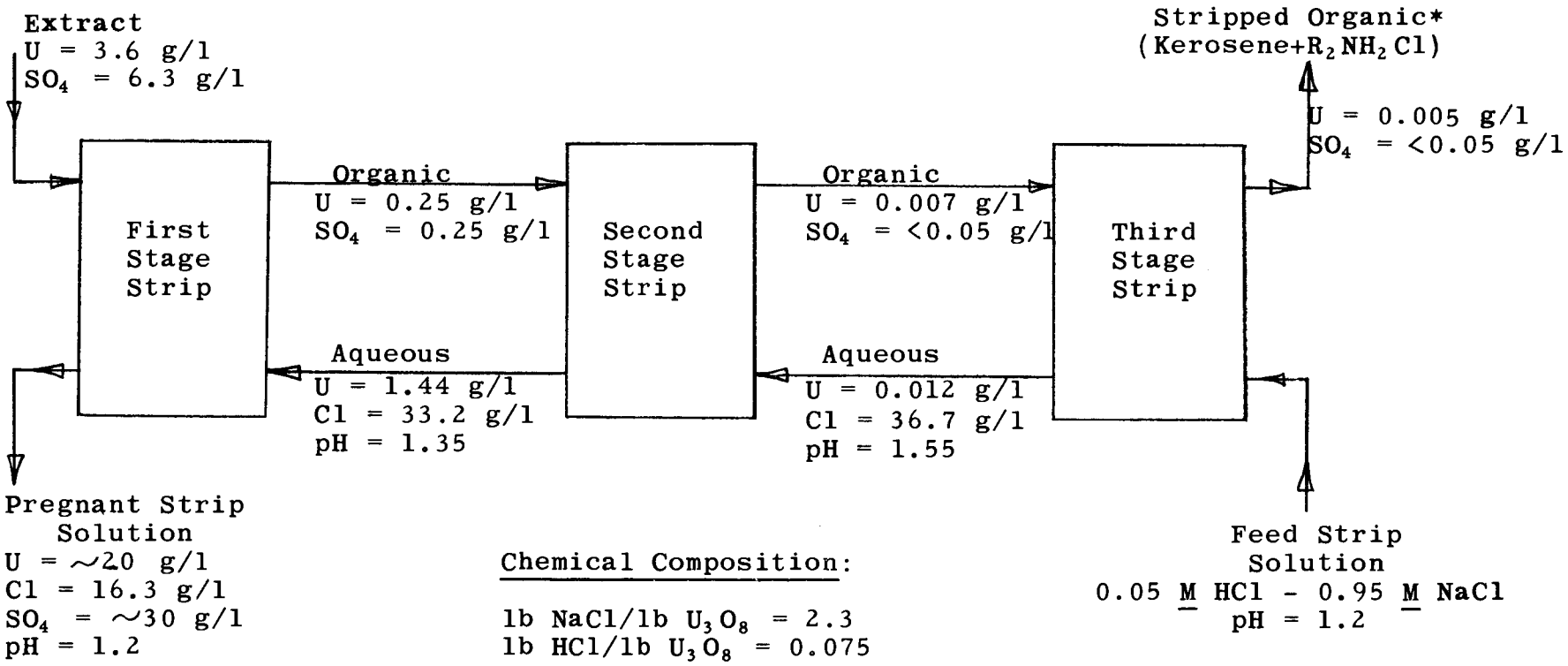
**Even less response has been shown by very strong extractants such as N-benzyl-1-(3-ethylpentyl)-4-ethyl-octylamine. Again, it should be mentioned, however, that the efficiency of chloride stripping can be appreciably affected by the diluent, and further studies with a variety of diluents are being made.

***The chloride salts formed in the regeneration step could be recycled to the strip solution but the cost advantage to be gained by such a procedure would be so small as to be of questionable value.

****Preliminary studies of regeneration with a lime slurry (at high org/aq phase ratios to prevent emulsions) have been encouraging, but the work thus far has not been sufficient to establish operational feasibility.

(0.1 M R&H 9D-178 Amine (193C) in kerosene + 2% capryl alcohol)

Feed Ratio: Organic/Aqueous = 5



Chemical Composition:

lb NaCl/lb U_3O_8 = 2.3
lb HCl/lb U_3O_8 = 0.075

*Recycle to the extraction system as amine chloride salt (Fig. 3) or regenerate to free amine (Fig. 4).

Figure 20

URANIUM DISTRIBUTION IN A CHLORIDE STRIPPING SYSTEM

with chloride solutions and, if present in sufficient quantity, it could build up in the organic phase and impair the extraction efficiency. Actually, the first two objections are probably of minor importance since the amount of chloride involved is not large enough to cause serious interference with the extraction and most of the chloride would be removed in (and confined to) the bottom extraction stage. The third objection would be an important one if the liquor treated contained appreciable molybdenum. Even in this case a regeneration of only a fraction of the organic stream would probably be sufficient unless the concentrations of molybdenum were unusually high (see Section A-3).

As pointed out previously,[3] chloride stripping may not be applicable to some amine-diluent mixtures due to limited miscibility of some of the amine chloride salts at ordinary temperatures. For example, attempts to strip the straight-chain secondary amines, e.g., didecyl- and dilauryl-, when held in any of the common diluents (kerosene, kerosene plus alcohol, Amsco D-95 and Amsco G) have resulted in the formation of slow breaking emulsions due to partial separation of these salts. To avoid this difficulty, even at low amine concentrations in diluents of high solvent power (e.g., 0.1 M amine in Amsco D-95), it was necessary to perform the stripping operation at temperatures in excess of 35°C. Similar difficulties would be expected with many of the tertiary amines when kerosene is employed as the diluent*. Good compatibilities with the chloride strip have been obtained, however, with tertiary amines in kerosene plus alcohol and with the highly branched secondary amines in any of the common solvents including kerosenes.

3. Stripping with Nitrate Solutions (Figure 5)

In continued analogy with the elution of anion exchange resins, nitrate solutions (salt, acid, or salt-acid mixtures) are much more efficient stripping agents than chloride solutions at corresponding concentrations. Similar to the case with chloride, the extractant, at the conclusion of the stripping operation, is in the form of the amine (nitrate) salt. Unlike the chloride process, however, direct recycle of the reagent in this form would not be practicable, and only a process involving regeneration to free amine has been considered, for two reasons: (1) the effect of nitrate in the

*Long chain tertiary amines such as tri-n-decyl and trilauryl may be operable, but have not been tested.

extraction system is much more deleterious than that of chloride, the presence of even small amounts causing a severe decrease in extraction efficiency, and (2) the relatively expensive nitrate is recovered from the amine in the regeneration step as a nitrate salt which may be utilized for further stripping. In such a process the only nitrate actually consumed is that which is removed with the uranium in the pregnant strip solution and this quantity can be held to a low level due to the high efficiency of the nitrate strip. Solutions of ammonia or sodium carbonate are economical regenerants. With the latter reagent a provision for destruction of excess carbonate might be needed prior to precipitation of uranium from the pregnant strip solution.

Typical uranium distributions obtained during stripping of R&H 9D-178 amine with NH_4NO_3-HNO_3 (NH_4OH regeneration) in a simulated 3-stage countercurrent system are shown in Figure 21. Stripping of uranium was essentially complete in two stages and the nitric acid consumption was only 0.25 lb/lb U_3O_8. Some difficulty with slow phase separation was encountered in the test especially if the pH of the aqueous phases drifted too close to the neutral point. To obtain proper balance of the acid-base reactions, a close control of the reagent feeds was required. Further tests of nitrate stripping on a larger scale are planned to determine whether this factor could cause an important disadvantage in process operation.

Variations in physical and chemical response to nitrate stripping have been observed for amines of different structures and types, and, from limited data, the general trends in these variations would appear to be similar to those observed (and described above) for chloride stripping. Thus, in the few cases tested organic miscibilities appeared to be lower for nitrate salts of straight chain secondary amines as compared to tertiary or highly branched secondary amines, and stripping efficiencies were higher for secondary amines as compared to tertiary amines. Again, the variations found in stripping effectiveness did not appear to be an important criteria in determining process utilization, however, since even with the tertiary amines the efficiencies were high*.

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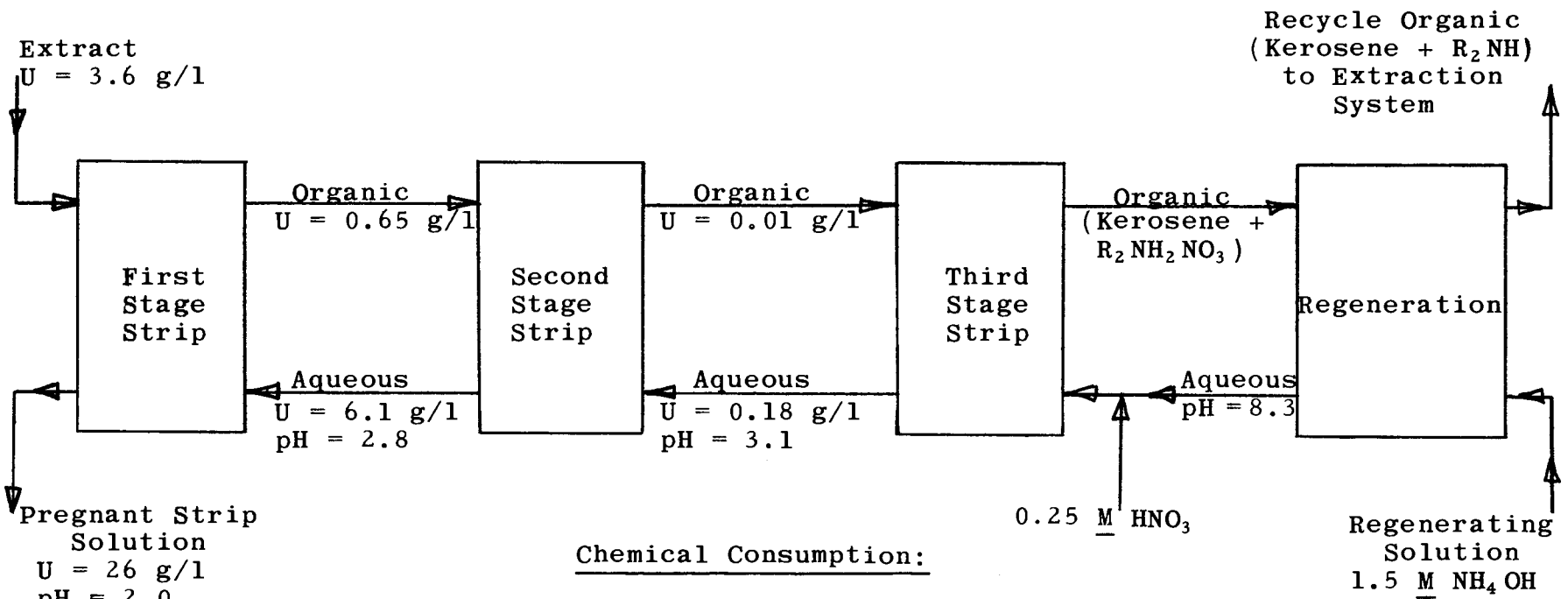
*As with chloride stripping, some exception to this might be given by very strong extractants such as N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine.

(0.1 M R&H 9D-178 Amine (Comp. 193C) in Kerosene)

Feed Ratios: Extract/0.25 M HNO_3/1.5 M NH_4OH = 14/1/1



Chemical Consumption:

lb HNO_3/lb U_3O_8 = 0.25
lb NH_3/lb U_3O_8 = 0.4

Due to analytical variations and the large number of transfers, the material balance of this flow sheet is not exact but is sufficient for the purpose of this discussion.

Figure 21

URANIUM DISTRIBUTION IN A NITRATE STRIPPING SYSTEM

4. Stripping with Sodium or Ammonium Hydroxide (Figure 6)

Treatment of the organic phase with solutions of sodium or ammonium hydroxide results in direct precipitation of the uranium as sodium or ammonium polyuranates.(2) The extractant is converted to free amine and is recycled to the extraction system. Assuming formation of the diuranate, hydroxide requirements for stripping may be defined by the following equations:

$$2(R_2NH_2)_2UO_2(SO_4)_{2\,org} + 10NaOH_{aq} \longrightarrow 4R_2NH_{org} + Na_2U_2O_7 + 4Na_2SO_{4\,aq} + 7H_2O \qquad (10)$$

and

$$(R_2NH_2)_2SO_{4\,org} + 2NaOH_{aq} \longrightarrow 2R_2NH_{org} + Na_2SO_{4\,aq} + 2H_2O \qquad (11)$$

$$(R_2NH_2)HSO_{4\,org} + 2NaOH_{aq} \longrightarrow R_2NH_{org} + Na_2SO_{4\,aq} + 2H_2O \qquad (12)$$

Complete stripping may be achieved with either dilute or concentrated hydroxide solutions provided a sufficient quantity of base is supplied in excess of that necessary to satisfy equations (10), (11) and (12). With sodium hydroxide, a 20% excess is ordinarily sufficient to give complete stripping in a reasonable time ($\sim$ 5 min) at room temperature. With ammonium hydroxide, under the same conditions, as much as 200% excess is required. In either case, particularly with ammonium hydroxide, the excess can be reduced by increasing the contact time and/or temperature.

The hydroxide stripping method provides a simple process flow pattern, since the organic phase may be stripped in a single-stage operation and the uranium product is obtained as a direct result of the stripping step. However, physical difficulties have been encountered which present serious disadvantages. When dilute sodium or ammonium hydroxide are used, the uranium precipitate tends to collect predominantly at the interface making separation of the liquid phases extremely difficult. If concentrated bases are used, such a small volume is required that essentially only two distinct phases are present, i.e., a wet precipitate dispersed in the organic phase. This precipitate settles rapidly in the organic phase and can be recovered fairly easily by filtra-

tion or centrifugation. However, tests by the Process Test Facility group[6] have indicated that a considerable amount of the organic phase is occluded or adsorbed by the precipitate so that the cost associated with these organic losses is rather excessive. Also, the precipitate would have to be calcined to eliminate the organic material in order to meet product specifications. Unless means are found for overcoming these disadvantages, the hydroxide stripping method must be considered inferior to the other stripping methods discussed.

Preliminary tests on the use of a dilute magnesium oxide slurry for stripping uranium from the organic phase have shown some promise. A high organic/aqueous ratio is maintained in the system to prevent emulsion formation. The uranium strips effectively with only a small excess of magnesium oxide, and the precipitate formed is readily filtered. Measurements of organic losses to this precipitate are being made but are not available at this time.

C. Losses of Amine and Diluent

An important requisite for successful operation of any solvent extraction process is that the extractant and diluent be recycled without excessive loss. This is particularly true of uranium raw material processing operations where the concentration of uranium in the process liquors is ordinarily quite low.

Losses of the extractant and diluent during process operation may occur in the following ways:

1) Solubility of the extraction reagent in the aqueous solutions with which it is contacted.

2) Physical entrainment of the organic phase (i.e., reagent plus diluent) in these aqueous solutions.

3) Reagent degradation.

4) Spillage.

In cases 1 and 2, and to a large extent in 3, the losses encountered are proportional to the volume of liquor processed, and thus the costs associated with these losses on a per-pound-of-uranium basis are inversely proportional to the concentration of uranium in the head liquor.

1. Losses of Amine by Solubility in the Aqueous Phase

A description of the method used for determining reagent losses to aqueous liquors and a listing of these losses for various amine compounds has been presented in detail in ORNL-1734 and ORNL-1922. It has been shown, in general, that the amount of amine going to the aqueous phase increases as the acidity of the aqueous solution increases and as its salt concentration decreases. Appreciable variations have also been noted with respect to the diluent used, whereas moderate changes in amine concentration and temperature have exhibited little effect.

In the process development studies, attention has been given only to those amines (in appropriate diluents) which, in the screening tests, have exhibited negligible or tolerably low losses to the acidic liquors. (Losses of all of these amines to basic solutions are negligible.) Measured losses of some of the more promising amines to uranium-barren Synthetic Marysvale Liquor have been excerpted from previous data and are listed in Table 4. As described previously, the initial amine losses shown in the table are attributed to the presence of amines of lower molecular weight which are distributed to the aqueous phase more readily than the principal constituent. From a process development viewpoint, this loss, when it is of reasonable magnitude, would be reflected only as a moderate increase in the purchase price of the amine. It may be noted that, for the compounds listed, the highest steady-state loss is 31 ppm. Such a loss in processing a liquor containing 1.25 g U_3O_8/l would amount to 2.0¢/lb U_3O_8 for an amine costing 80¢/lb.

2. Entrainment Losses

The amount of organic phase which would be entrained in the aqueous raffinate during process operation is difficult to estimate from laboratory measurements since it would depend, to a large extent, on the manner in which the extraction system is operated. For example, as might be expected, the time required for essentially complete phase disengagement is greater when the phases are mixed violently, as in a pump mixer, than when milder agitation is provided. Typical results from large scale tests by the Process Test Facility group have indicated that losses of organic may be kept to $<$ 0.02% of the aqueous raffinate volume ($<$ 0.2 ml organic/liter of aqueous) by allowing sufficient hold-up time of the aqueous raffinate[7]. Under conditions of relatively mild mixing of the phases (mixing still adequate to give rapid uranium transfer) the required hold-up time

Table 4

LOSS OF AMINE TO THE AQUEOUS PHASE*

Amine	Compound No.	Diluent	Loss of Amine: Fraction Readily Lost, % of Initial	Loss of Amine: Steady State Loss, ppm/Aqueous
Armeen 2-12	103F	Kerosene + 5% Cap. Alc.	< 1	13
Di(2-butyloctyl)	198A	Kerosene	2.5	< 5
C&C 16F27	30B	"	24	14
R&H 9D-178	193B	"	3	24
" "	193C	"	7	31
" "	193D	"	10	16
N-benzyl-1-(3-ethylpentyl)-4-ethyloctyl	228A	"	< 1	< 5
Di(tridecyl P)	227A	"	10	5
Bis(1-methyl-4-ethyloctyl)	229B	"	5	< 5
Tri-n-octyl	125H	Kerosene + 5% Cap. Alc.	< 1	17
Tri(iso-octyl)	239A		1	23

*From Table 6, ORNL-1922[2].

was in the order of ten minutes. With very violent agitation, a 2-4 hour hold-up was necessary to give the same low entrainment level.

Entrainment losses in the stripping cycle would be unimportant from a cost standpoint since the aqueous volume handled is relatively small and the uranium concentration in the loaded strip solution is relatively high.

3. Reagent Degradation

When used as extraction agents the amines can be exposed to the oxidizing action of dissolved air and of such metals as are present in their higher oxidation states. To determine whether amine loss by chemical reaction might be important under conditions of process use, several representative compounds of different types and structures were examined in multicycle extraction (and stripping) tests on liquors of variant compositions. The results of these tests (presented in detail in ORNL-1922) indicate that, although appreciable degradation may occur under extreme circumstances, e.g., elevated temperatures, the degradation losses under conditions likely to be encountered in uranium* processing should be unimportantly low. In some tests the tertiary amines appeared to have somewhat lower resistance to oxidation than the secondary amines, but the effect was not sufficiently great to prohibit the consideration of these compounds for process use.

D. Estimated Process Reagent Costs

Reagent costs for each of the proposed processes shown in Figures 2, 3, 4, 5 and 6 have been estimated on the basis of data accumulated in batch and simulated countercurrent tests. In arriving at these estimates the following general assumptions were made.

1) That the organic solution used for the operation would consist of a 0.1 M solution of an amine in kerosene diluent. Cost of the amine and kerosene were taken as 80¢/lb and 14¢/gal, respectively.

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*If the amines were used for vanadium recovery (see Appendix B) the oxidizing conditions encountered might be more severe. Tests of amines under these conditions are incomplete.

2) That the head liquor would contain 1.25 g U_3O_8/l.

3) That the organic phase would be loaded to 4.0 g U_3O_8/l, i.e., about 85% of maximum loading for most amines. (With some amines, e.g., tri-n-octyl and tri(iso-octyl), the loadings would be higher and the reagent costs proportionally lower.)

4) That losses of diluent through evaporation (and, of course, aqueous solubility) would be negligible.

The Extraction System: The reagent costs associated with the extraction operation are those incurred from loss of amine and diluent by the mechanisms outlined in the previous section.

1) The steady-state losses of some of the more promising amines (Table 4) to a 0.5 M sulfate liquor varies from <5 to 31 ppm. On the basis of the amine price and head liquor concentration shown above, the latter figure corresponds to a loss of 1 lb of amine/40 lb U_3O_8 recovered or 2.0¢/lb U_3O_8.

2) In multicycle uranium extraction-stripping tests under normal process conditions, the loss of the amine reagents through decomposition has been negligibly low. The assumption of decomposition equivalent to 10 ppm of liquor or 0.6¢/lb of U_3O_8, as used in this estimate, is higher than indicated by experimental data.

3) Tests at the ORNL Process Test Facility indicate that, under good operational conditions, the entrainment of the organic phase should not exceed 0.02% of the aqueous raffinate volume or, for the liquor described above, one gallon/52 lb of recovered U_3O_8. Since the organic solution (amine + diluent) is valued at about 38¢/gallon, this amounts to 0.7¢/lb U_3O_8. To allow for occasional periods of bad operation and for spillage, the organic entrainment loss in this estimate is taken at double the above value or 1.4¢/lb U_3O_8.

4) In accordance with the above, the total cost of reagents for the extraction cycle (including entrainment, spillage, decomposition and reagent solubility losses) are estimated at 2 to 4¢/lb of U_3O_8.

The Stripping System: Several methods for stripping uranium from the amines were discussed in Section B. Chemical flowsheets and typical reagent requirements for some of these methods are shown in Figures 19, 20 and 21.

From a combination of the extraction and stripping estimates, the total estimated reagent costs (including the base required for product precipitation) may be itemized for each of the proposed processes as shown below:

Process with Sodium Carbonate Stripping - Figure 2

Chemical	Use	Unit Cost ¢/lb	Consumption* lb/lb U_3O_8	¢/lb U_3O_8
Na_2CO_3	Stripping	2.2	2.9-3.9**	6.4-8.6
H_2SO_4	Precipitation	1.5	1.2-2.0	1.8-3.0
NH_3	"	6.5	0.25	1.6
Amine + Kerosene	Extraction			2-4
			Total	12-17

*The sodium carbonate requirements are still lower for those amines which give greater uranium loadings, e.g., tri-n-octylamine and tri(iso-octyl)amine.

**For different amines, at equivalent loadings, the sodium carbonate requirements can vary within this range depending upon the amount of excess required for attaining good phase separations (see Section B-1).

Process with Chloride Stripping (1.0 M NaCl - 0.05 M H_2SO_4) - Figure 3

Chemical	Use	Unit Cost ¢/lb	Consumption lb/lb U_3O_8	¢/lb U_3O_8
NaCl*	Stripping	0.8	2.3	1.9
H_2SO_4	"	1.5	0.2	0.3
NH_3	Precipitation	6.5	0.25	1.6
Amine + Kerosene	Extraction			2-4
			Total	6-8

*For the same number of extraction stages, sodium chloride requirements may be somewhat lower with some amines, e.g., less branched secondary amines, and somewhat higher with others, e.g., tertiary amines. With the exceptionally strong extractant, N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine, or similar compounds, appreciably larger amounts of sodium chloride might be required.

Process with Chloride Stripping with Amine Regeneration - Figure 4

Chemical	Use	Unit Cost ¢/lb	Consumption lb/lb U_3O_8	¢/lb U_3O_8
NaCl	Stripping	0.8	2.3	1.9
H_2SO_4	"	1.5	0.2	0.3
Na_2CO_3 *	Regeneration	2.2	1.5	3.3
NH_3	Precipitation	6.5	0.25	1.6
Amine + Kerosene	Extraction			2-4
			Total	9-11

*If a lime slurry could be used instead of sodium carbonate a saving of ~2¢/lb U_3O_8 would be obtained.

Process with Nitrate Stripping (NH_4NO_3-HNO_3) - Figure 5

Chemical	Use	Unit Cost ¢/lb	Consumption lb/lb U_3O_8	¢/lb U_3O_8
HNO_3	Stripping	6	0.25	1.5
NH_3	Regeneration	6.5	0.5	3.3
NH_3	Precipitation	6.5	0.25	1.6
Amine + Kerosene	Extraction			2-4
			Total	8-11

Process with Hydroxide Stripping - Figure 6

Chemical	Use	Unit Cost ¢/lb	Consumption lb/lb U_3O_8	¢/lb U_3O_8
NH_3	Precipitation	6.5	1.5	9.7
Organic Loss to Uranium Precipitation			Unknown*	?
Amine + Kerosene	Extraction			2-4
			Total	12-14+?

*Indications to date are that complete recovery of organic from the uranium precipitate would be difficult and that loss of the organic phase by this mechanism could be an appreciable cost item. Preliminary experiments using MgO slurries have been encouraging and are receiving further study.

E. Considerations on Reagent Choice

As discussed in the foregoing sections, effective application of the Amine Extraction Process for recovery of uranium from Western ore sulfate liquors can be made with several different amine reagents. The most promising reagents examined thus far are

R&H Amine 9D-178	(secondary)
Tri(iso-octyl)amine	(tertiary)
C&C Amine 16F27	(secondary)
Tri-n-octylamine	(tertiary)
Dodecenyl Primene JM Amine	(secondary)
N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine	(")
Di(2-butyloctyl)amine	(")
Di(tridecyl P)amine	(")
Armeen 2-12	(")

Most of these reagents are presently available in experimental quantities only. However, as discussed in ORNL-1922, the compounds could be made available in large quantities in the event of a demand. The anticipated price range is of a very reasonable order for many of the reagents (see ORNL-1922 and Table 5 of this report) and in each case the specific price eventually set within the range would be expected to depend upon the size of the demand.

In the process development work conducted thus far at this laboratory, both bench scale and large scale, the most intensive studies have been made with R&H Amine 9D-178 (kerosene diluent). This amine was selected both because it was obtainable in sufficient quantities for large scale testing and because it offered a favorable combination between good extraction properties and potential availability at a reasonable price. Sufficient studies have been carried out with this compound to permit sizing of the extraction and stripping equipment, determination of reagent costs (see Section D), evaluation of other operational factors and, finally, the estimation of total processing costs for a full scale plant operating on Western ores.[9,10] The results obtained from this work are extremely promising

Table 5

ANTICIPATED PRICE RANGES FOR SEVERAL AMINES AND THE REFLECTION OF THESE PRICES IN COST PER POUND OF U_3O_8 RECOVERED FROM A TYPICAL LIQUOR BY THE AMINE EXTRACTION PROCESS

Amine	Approx. Price Range Anticipated for Quantity Production ($/lb)	Estimated Amine* Cost per lb U_3O_8 Recovered from Typical Liquor		
		Entrainment and Spillage	Distribution to Aqueous	Total
R&H 9D-178	0.60 - 1.00	1.0	1.5***	2.5
Tri(iso-octyl)	0.60 - 1.00	0.9	1.5	2.4
C&C 16F27	0.60 - 1.00	0.9	0.9	1.8
Tri-n-octyl	1.00 - 1.50	1.4	1.7	3.1
Dodecenyl Primene JM	---	---	--- **	---
N-benzyl-1-(3-ethylpentyl)-4-ethyloctyl	1.50 - 2.00	2.0	< 0.7	< 2.7
Di(tridecyl P)	0.60 - 1.00	1.0	0.3	1.3
Di(2-butyloctyl)	1.00 - 1.50	1.4	< 0.5	< 1.9
Armeen 2-12	0.60 - 0.70	0.8	0.7	1.5

*Calculated losses are based on the assumptions listed in Section III-D, p. 60 and the distribution losses shown in Table 4. Prices of the amines were taken as the average of the maximum and minimum values of the ranges shown in the second column of this table.

**The anticipated price for dodecenyl Primene JM is somewhat greater than for R&H 9D-178.

***Average of the three batches.

and being based on a typical amine extractant they may be considered as representative of those to be generally expected from application of the Amine Extraction Process to Western sulfate liquors.*

From discussions of comparative reagent properties in the previous section of this report, it is apparent that some of the other reagents listed above might offer advantages over the R&H 9D-178 amine with respect to general process performance and range of potential applicability. The magnitude of these possible advantages from reagent variation would not be expected to exert a major controlling influence on the cost of recovered U_3O_8 - at least from Western liquors of usual compositions. More likely the gains anticipated would be of the order usually categorized as improvements on a process already considered to be promising and competitive. Because of the large number of dependent variables that must be considered, further studies (primarily larger scale continuous cyclic tests) will be required before a close definitive comparison of reagents can be made with regard to their influence on overall processing costs. In the first instance, a closer interbalance than is thus far available must be obtained between costs associated with such properties as selectivity, extraction power, diluent limitations, reagent stability, losses to aqueous liquors, loading levels, response to stripping methods, etc. These costs must be balanced, in turn, against those arising from differences in physical performance and differences in reagent price. At the present time, information of this type is being obtained with tri-n-octylamine. (If the similarity between tri-n-octyl and tri(iso-octyl) amines persists the information may be transcribable to the latter compound.) C&C 16F27, tri(iso-octyl)amine, dodecenyl Primene JM amine (and other compounds that may be suggested by the screening program) will be included at such time as sufficient experimental quantities of these materials can be obtained. Later, it is hoped that N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine can be obtained for similar tests. Although the anticipated

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*The only major limitation on the use of R&H 9D-178 amine for Western application is in the treatment of liquors containing significant quantities of Mo and V(V), in which case a molybdenum-vanadium(V)-amine sulfate complex is formed which is insoluble in the kerosene diluent (see Section A3-b). This limitation can be circumvented, however, by using diluents of high aromatic content. Also other amines, which are generally similar to R&H 9D-178 in other extraction properties, have not shown insolubility of the molybdenum-vanadium(V)-amine sulfate complex in kerosene (see Section A3-b).

selling price is considerably greater for this amine than any of the others mentioned, the costs associated with reagent (amine) losses in the process cycle have been small (see Table 5) and it is possible that the initial costs for more expensive reagents could be offset by advantages in operational performance.

In extending the Amine Extraction Process to applications other than the usual Western sulfate liquors, additional considerations can influence the choice of amine extractant. For example, in treating liquors of decreasing uranium content, reagents with very high extraction coefficients would become increasingly more valuable since lower reagent concentrations could be used (resulting in lower reagent losses) and more efficient reagent loadings could be obtained. As another example, in treating chloride-sulfate liquors the presence of chloride can have an important effect on reagent behavior. In this case the performance of the symmetrical alkyl tertiary amines were markedly superior to the alkyl secondaries with even better performance being shown by the strong extractant, N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine. Further general studies of reagent performance in other applications are being continued in conjunction with the work on Western liquors.

IV. SUMMARY

A number of long chain secondary and tertiary amines have been examined in laboratory-scale process studies to define their practicability as extraction reagents for recovery of uranium from clarified sulfate liquors such as those obtained by sulfuric acid leaching of Western ores. Only those compounds which proved promising in previous screening tests (ORNL-1734, ORNL-1922) were included in this work. Initial survey tests were first made wherein the performance of each amine compound was characterized relative to, 1) extraction of uranium and contaminants from synthetic and actual leach liquors, 2) compatibility with practicable diluents and, 3) response to various stripping methods. Certain representative compounds were also examined with respect to their stability under a variety of simulated process conditions. From the results of this initial work, several realistic process flowsheets were established and subsequent tests (mostly of the batch equilibrium type) were directed toward a closer definition and evaluation of these processes, particularly from the standpoint of physical operability and reagent requirements.

Some of the principal conclusions which may be drawn from the laboratory process development studies are listed below:

1) Efficient and rapid extraction of uranium from synthetic and actual leach liquors of widely varying composition can be obtained with a number of secondary and tertiary amines of varying structure when used at moderate concentrations in several diluents.

2) Kerosene is a suitable diluent for many of the more promising amines under normal processing conditions. Amines which are incompatible with kerosene alone can be used in kerosene which has been modified with a small amount of a long chain alcohol, or can be used in hydrocarbon diluents of high aromatic content such as Amsco G, Solvesso 100, etc.

3) All of the common liquor contaminants, with the exception of molybdenum, can be separated from uranium satisfactorily in the extraction operation. Molybdenum, when present, can be separated from uranium either in or after the stripping operation.

4) Uranium can be stripped effectively from the extract with solutions of several different chemical agents, e.g.,

carbonates, chlorides, nitrates, and hydroxides. With the possible exception of hydroxide stripping, all of the methods appear operationally feasible at a low reagent cost.

5) Estimates of total reagent costs for recovery of uranium from clarified Western ore sulfate leach liquors by the amine extraction process have been made based on data obtained in batch and simulated countercurrent tests. These estimates have ranged from 6¢ to 17¢ per pound of U_3O_8, depending upon the choice of reagent and the stripping method.

From the process development studies in general, it has been concluded that the long chain amines show considerable promise as practicable extractants for the recovery of uranium from sulfate leach liquors. Of the compounds studied to date, those which appear to be the best potential candidates for process application are:

R&H Amine 9D-178	(secondary)
Tri(iso-octyl)amine	(tertiary)
C&C Amine 16F27	(secondary)
Tri-n-octylamine	(tertiary)
Dodecenyl Primene JM Amine	(secondary)
N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine	(")
Di(2-butyloctyl)amine	(")
Di(tridecyl P)amine	(")
Armeen 2-12	(")

Several of the processing schemes described here are being examined in a larger scale process test facility by the Engineering Group of this division. The compounds tested thus far have performed successfully in the larger scale tests and the results from this work will be described in separate reports.

V. ACKNOWLEDGEMENTS

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Many of the reagents which were obtained from outside sources were furnished as product samples by the manufacturers. In addition, special reagents were contributed by the research laboratories of Carbide and Carbon Chemicals Company and Rohm and Haas Company.

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APPENDIX A

Preparation of Amine Solutions

Description of the amine compounds and discussion of their purity has been presented previously in ORNL-1734 and ORNL-1922. It was shown that many of the reagents contained appreciable amounts of lower molecular weight amines (some of which were amines of a different type) which gave higher distribution losses to the aqueous phase than did the major component. In process use, these more soluble constituents would distribute readily to the aqueous raffinate and would be effectively removed from the organic phase in relatively few cycles. In laboratory batch experiments, however, the presence of these impurities could cause spurious conclusions with regard to the reagent performance. Therefore, in order to obtain a more representative evaluation of the compounds with reference to process application, the amine solutions were scrubbed prior to testing in all cases where it was evident that the presence of impurities could exert an important effect on the test results. In such instances the amine was dissolved in a diluent at a concentration higher than that desired for use and scrubbed by contact with 2% sulfuric acid (10-15 volumes). The scrubbed organic phase was contacted with a solution of sodium carbonate to convert the amine salt to free amine, washed with water, and titrated to determine its amine concentration. The concentration was then adjusted, by addition of diluent, to the level desired for test purposes.

APPENDIX B

Other Studies of Amines as Extractants

Although most of the work with amines thus far has been concerned with the recovery of uranium from clarified sulfuric acid leach liquors from Western ores, other possibilities for utilizing these compounds as extractants have been considered to some extent.

1. Extraction of Uranium from Lower Grade Sulfate Liquors

In recovery of uranium with sulfuric acid from low grade uranium sources such as Rand gold ore residues, Florida Leached Zone ores, shales, lignites, etc., liquors are produced which ordinarily are very dilute with respect to uranium and which contain extremely high contaminant/uranium ratios. For some of these materials, the uranium level in the head liquor may be considerably below 100 ppm. Certain of the amines, because of their strong uranium extraction power and good selectivity, are promising extractants for recovery of uranium from such liquors. Thus far no specific effort at this laboratory has been directed toward development of complete processes for handling these particular liquors although the possibilities have been discussed with representatives from Columbia University (in regard to shale) and representatives from Rohm and Haas (in regard to Rand ores).

Rand Liquors: Difficulties have been encountered in the use of strong base anion exchange resins for processing leach liquors derived from Rand gold ore residues due to "poisoning" of the resin by sorption of cobalticyanide and polythionate complexes. These "poisons" are not removed in the regular eluting cycle and the cobalticyanide complexes are difficult to remove even by other chemical treatments. Extractions of uranium from a synthetic Rand leach liquor (0.25 g U/l) have been investigated using 0.1 M solutions of tri-n-octylamine. Uranium extraction coefficients greater than 500 were obtained. The cobalticyanide was also extracted ($E_a^o > 50$) but it was easily removed from the organic phase by contacting with dilute alkaline solutions. Thus, if a sodium carbonate solution were used for uranium stripping, the organic phase would be stripped of the potential "poisons" in each cycle. If chloride stripping of the uranium were utilized, and the extracted "poisons" were not removed in the regular stripping cycle, they could easily be kept at a tolerable concentration level by continuous regeneration of a small fraction of the organic recycle stream.

Resin blinding from materials such as sulfur and silica, another difficulty in the Rand operation, would also be absent in a solvent extraction process. Chemical reagent costs for solvent extraction promise to be lower.

Leached Zone Sulfate Liquors: Efficient extractions of uranium from dilute Leached Zone sulfate liquors have been achieved using 0.1 M solutions of tri-n-octyl and N-benzyl-1-(3-ethylpentyl)-4-ethyloctyl amines. For the latter reagent the extraction coefficient was greater than 500 from a liquor containing 0.05 g U/l, 21 g PO_4/l, and 47 g SO_4/l at a pH of 0.8. Uranium coefficients greater than 100 were observed for tri-n-octylamine in extractions from another Leached Zone liquor which contained 0.05 g U/l, 4 g PO_4/l, and 21 g SO_4/l, at a pH of 1.0.

2. Recovery of Thorium and Uranium from Sulfuric Acid Leach Liquors

Studies on the recovery of thorium and uranium from sulfuric acid digests of monazite sands and on the recovery and separation of thorium and uranium in other sulfate liquors have been discussed previously.[3,4]

3. Recovery of Uranium and Vanadium from Sulfate Liquors

Because of the AEC's diminishing interest in vanadium recovery, the development effort on vanadium extraction with amines has been conducted on a low priority basis. At this time the work is incomplete and the data are insufficient to support final conclusions as to optimum process conditions or process feasibility. Many of the results obtained have been encouraging, however, and these are briefly summarized with respect to their process significance below.

As described previously[2] extraction of vanadium with amines is strongly dependent upon the valence state of the vanadium and the acidity of the aqueous liquor. Since V(IV) does not extract, the vanadium must be completely oxidized to the pentavalent state. In addition, to achieve extraction coefficients of appreciable magnitude, the operation must be performed at relatively high pH levels (close to 2).

Figure 22 shows a flow diagram for a uranium-vanadium recovery process which has shown promise, but which has been only partially evaluated and consequently must be considered tentative at this time. Prior to extraction, the liquor is oxidized and its acidity adjusted with a base. Manganese dioxide appears to be a favorable oxidant. The oxidation proceeds fairly readily at a temperature of 25-30°C if a three to four-fold excess of manganese dioxide is added over the amount theoretically required to oxidize the vanadium and other oxidizable metal ions present in the liquor. The excess manganese dioxide may be separated from the oxidized liquor and recycled. Uranium and vanadium are co-extracted at a pH of 1.8 - 2.0 and then separated by selective stripping.

Under proper conditions, it has been possible to strip uranium from the organic phase into chloride solutions without removing important amounts of vanadium. In some tests, however, the results have been erratic and further study is needed. The separation attainable seems to depend upon some, or all, of the following factors: amine type and structure, nature of the diluent, extraction pH and time, and the concentration and residence time of vanadium in the organic phase. Once uranium is removed from the solvent, the vanadium is readily stripped by a single-stage contact with a solution of sodium carbonate. High concentrations of vanadium can be obtained and the resulting solutions should be suitable for precipitation of vanadium red cake.

If desired, the uranium and vanadium can be stripped simultaneously using a solution of sodium carbonate. The separation of uranium and vanadium can then be achieved by methods now used in Western mill operations.

Preliminary tests in which the extract is contacted with an acidic sulfite solution to reduce and strip the vanadium have also shown promise. The uranium may then be stripped by one of the methods described in previous sections.

Although the discussions above are concerned with simultaneous extraction of the uranium and vanadium, their separate recovery in a two-cycle operation should be equally

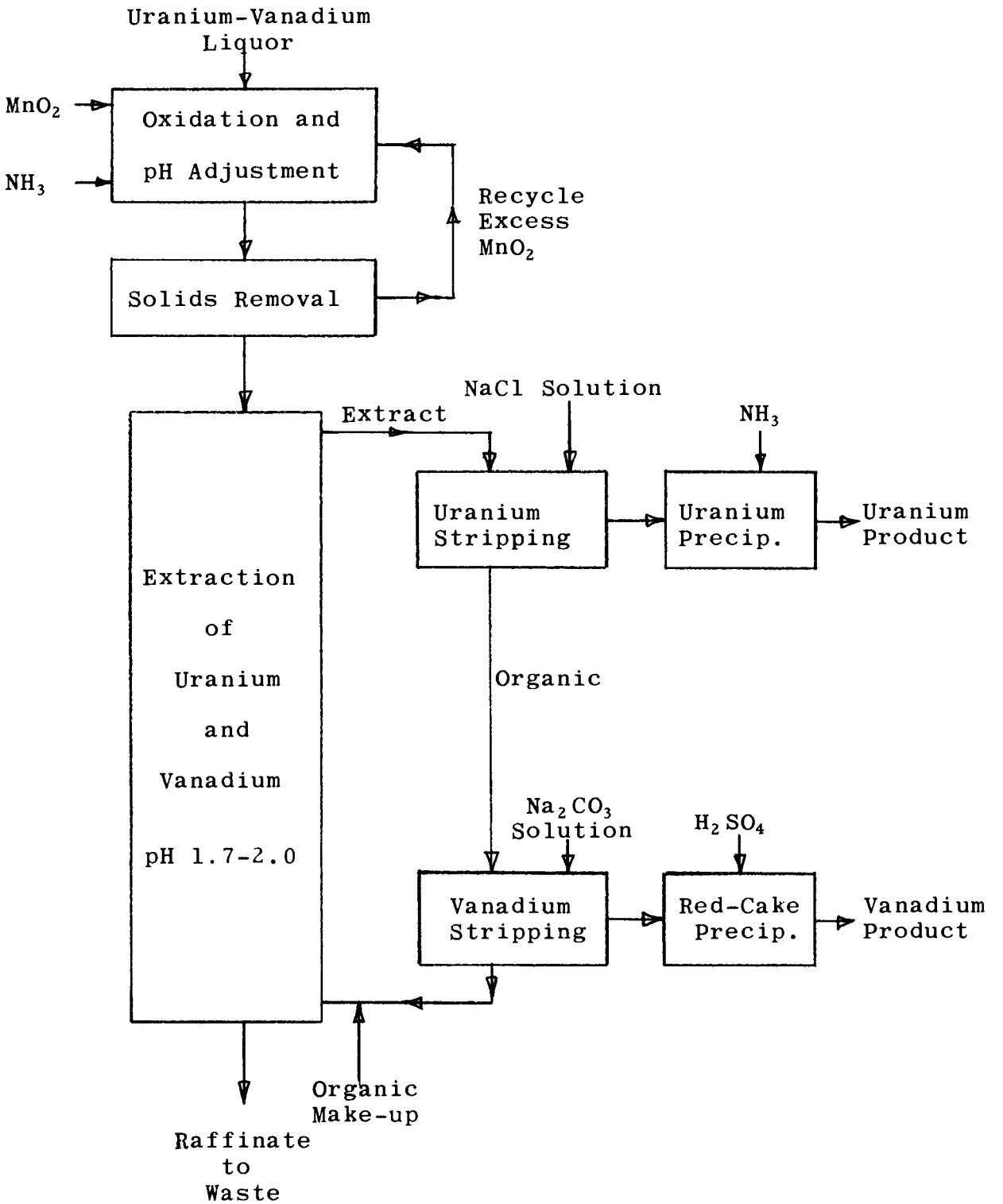

Figure 22

RECOVERY OF URANIUM AND VANADIUM WITH AMINES

possible, the redox potential and acidity of the liquors being adjusted for vanadium recovery after the uranium extraction.

Further studies of vanadium recovery are being made. First in importance are studies on (1) Reagent stability; it has not yet been shown that the amines are stable under conditions encountered in a vanadium circuit. (2) Selectivity with respect to iron at the high extraction pH; the studies thus far have been made with amines of high selectivity and it is not known whether those of lower selectivity would be suitable. (3) Problems in process control at the high pH level; depending upon liquor compositions several metals, including vanadium(V), can be near the point of precipitation.

4. Extraction of Uranium from Western Ore Leach Slurries

Recovery of uranium from desanded Western ore leach slurries with amine extractants in hydrocarbon diluents has been investigated to a limited extent. Most of these tests were conducted on -200 mesh Lukachukai slime slurries at approximately 10% pulp density. When the organic phase was contacted with the slurry in a turbine agitated vessel at a high organic/slurry ratio (>3), the primary separation of the phases was rapid and good extraction of uranium was obtained. However, other features of the process were discouraging. For example, the slurry raffinate contained an abnormally high volume of entrained organic which was extremely difficult to recover. This volume loss was much higher than that experienced with the diluent alone or with diluent containing certain organophosphorus extractants, e.g., di(2-ethylhexyl)phosphoric acid. Also, in addition to the high volume loss of organic phase, an appreciable decrease in amine concentration in the recovered organic volume has been observed indicating a preferential chemisorption of the extractant salt by some of the solid particles.

In some tests, losses of both the amine and diluent have been decreased considerably by coagulating the ore slimes with a guar gum prior to extraction. However, even with impracticably large additions of the coagulant, the losses were higher than could be tolerated. At present, a limited amount of further study is being made on other additives and a variety of amine-diluent combinations.

5. "Non-Aqueous" Extraction of Uranium from Western Ores with Amines

Limited studies have been conducted on the use of amines for recovery of uranium from ores by non-aqueous extraction techniques. An organic phase containing the amine (pretreated with sulfuric acid to form the sulfate salts) was contacted with an ore which had been pugged with sulfuric acid and air dried. Greater than 90% extraction of uranium was realized from samples of Uravan ore (0.19% U_3O_8) and Marysvale ore (0.28% U_3O_8) using 0.1 M and 0.2 M solutions of amines in benzene or Amsco D-95 diluents. Di(2-ethylhexyl), tri-n-hexyl, methyldi-n-octyl, and tri-n-octyl amines were tested. The first three of these amines had been found unacceptable for liquid-liquid extraction due to high solubility losses to aqueous solutions, but were considered potentially suitable for "non-aqueous" application because of the small amount of aqueous phase present.

Thus far, no studies have been made of the problem of organic recovery from the ore tailings. Presumably, as in slurry extraction, chemi-sorption of the amine extractant onto the ore particles will present additional, perhaps prohibitive, complications to the task of reagent recovery.

6. Scavenging of Iron from Beryllium Solutions

The Brush Beryllium Company has developed a solvent extraction process for removing iron from beryllium sulfate solutions prior to precipitation of beryllium hydroxide. The iron is oxidized to the ferric state, NH_4SCN is added as complexing agent, and the iron extracted with a TBP-kerosene mixture.

From consideration of the selectivity data presented previously,[2] it is indicated that amine extractants might be useful in separating iron from beryllium. The primary amines, for example, give appreciable extractions of iron(III) from sulfate solutions whereas the extractions of beryllium are comparatively weak. Some of the secondary amines might also be considered. Coefficients for iron(III) with these compounds are smaller, but the extractions of beryllium are almost negligible. If successful, an amine extraction cycle should be more economical in reagent consumptions than those indicated for the TBP-NH_4SCN process.

Some other possibilities for application of amine extractants might include (1) removal of chloride contamination from process sulfuric acids, (2) separation of other inorganic and organic acids and (3) recovery and separation of other metals. Further investigations along these lines are being considered. Much of the knowledge already gained concerning effects from amine type and structure on solubilities, diluent compatibilities, extraction power, selectivities, etc. should be of considerable value in such work.