CONFIDENTIAL

822863
File: 503.03
F. C. VonderLage
J. P. Nupp
Date Rec'd JUN 22 1955 gw

OAK RIDGE NATIONAL LABORATORY LIBRARIES
3 4456 0570417 3

3H4560360757 7

ORNL-1903
Metallurgy-Raw Materials

THE EXTRACTION AND RECOVERY OF URANIUM (AND VANADIUM) FROM ACID LIQUORS WITH DI(2-ETHYLHEXYL) PHOSPHORIC ACID AND SOME OTHER ORGANOPHOSPHORUS ACIDS

C. A. Blake
K. B. Brown
C. F. Coleman

DECLASSIFIED
Per Letter Instructions Of
AEC-6-5-56
For: N. T. Bray, Supervisor
Laboratory Records Dept.
ORNL

OAK RIDGE NATIONAL LABORATORY
U.S. ATOMIC ENERGY COMMISSION

ORNL LIBRARIES DIVISION
Y-12 TECHNICAL LIBRARY
Document Reference Section

LOAN COPY ONLY

Do NOT transfer this document to any other person. If you want others to see it, attach their names, return the document, and the Library will arrange the loan as requested.

RESTRICTED DATA
This document contains Restricted Data as defined in the Atomic Energy Act of 1954. Its unauthorized use or the disclosure of its contents in any manner to an unauthorized person is prohibited.

CONFIDENTIAL

[redacted]

ORNL-1903
This document consists of 130 pages.
This is copy 73 of 385, Series A.

Subject Category: Metallurgy-
Raw Materials

THE EXTRACTION AND RECOVERY OF URANIUM (AND VANADIUM) FROM ACIDIC LIQUORS WITH DI(2-ETHYLHEXYL)PHOSPHORIC ACID AND SOME OTHER ORGANOPHOSPHORUS ACIDS

Report Prepared By: C. A. Blake
K. B. Brown
C. F. Coleman

Work Done By: D. E. Horner
J. M. Schmitt

May 13, 1955

Date Issued
JUN 21 1955

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

MATERIALS CHEMISTRY DIVISION
G. H. Clewett, Division Head

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

Contract No. W-7405-eng-26

[redacted]

INTERNAL DISTRIBUTION

1. C. E. Center
2. Biology Library
3. Health Physics Library
4-5. Central Research Library
6. Reactor Experimental Engineering Library
7-63. Laboratory Records Department
64. Laboratory Records, ORNL R.C.
65. C. E. Larson
66. L. B. Emlet (K-25)
67. J. P. Murray (Y-12)
68. A. M. Weinberg
69. E. H. Taylor
70. E. D. Shipley
71. G. H. Clewett
72. W. H. Jordan
73. E. C. VonderLage
74. J. A. Swartout
75. A. C. Lind
76. F. L. Culler
77. A. Hollaender
78. A. H. Snell
79. M. T. Kelley
80. J. A. Lane
81. K. Z. Morgan
82. J. H. Frye, Jr.
83. C. E. Keim
84. R. S. Livingston
85. T. A. Lincoln
86. A. S. Householder
87. C. S. Harrill
88. C. E. Winters
89. D. W. Cardwell
90. E. M. King
91. A. J. Miller
92. D. D. Cowen
93. M. L. Skinner
94. S. J. Cromer
95. G. E. Boyd
96. C. A. Blake
97. K. B. Brown
98. C. F. Baes
99. C. F. Coleman
100. D. J. Crouse
101. D. E. Horner
102. A. D. Kelmers
103. J. M. Schmitt
104. A. D. Ryon
105. H. M. McLeod
106. B. B. Klima
107. R. H. Guymon
108. V. A. DeCarlo
109. J. R. Buchanan
110. R. W. Dodson (consultant)
111. H. Eyring (consultant)
112. J. W. Kennedy (consultant)
113. G. T. Seaborg (consultant)
114. J. H. Rushton (consultant)
115. J. Bigeleisen (consultant)

EXTERNAL DISTRIBUTION

116-123. Argonne National Laboratory
124. Arthur D. Little, Inc.
125-128. Atomic Energy Commission, Washington
129. Battelle Memorial Institute
130. Bureau of Mines, Salt Lake City
131-134. Carbide and Carbon Chemicals Company (K-25 Plant)
135. Chicago Patent Group
136. Division of Research and Medicine, AEC, ORO
137-138. Columbia University (Hassialis)
139-145. Division of Raw Materials, Washington
146. Dow Chemical Company, Pittsburgh
147-152. General Electric Company, Richland

153-15[illegible] Grand Junction Operations Office
157. Hanford Operations Office
158. Iowa State College
159-160. Los Alamos Scientific Laboratory
161. Mallinckrodt Chemical Works
162-163. National Lead Company, Inc., Winchester
164. National Lead Company of Ohio
165. New Brunswick Area Office
166. New York Operations Office
167. Patent Branch, Washington
168. Rohm and Haas Company
169. Tennessee Valley Authority (Walthall)
170. Texas City Chemicals, Inc.
171-172. U. S. Geological Survey
173-174. University of California Radiation Laboratory, Berkeley
175. Virginia-Carolina Chemicals, Inc.
176-385. Technical Information Service, Oak Ridge

[redacted]

[redacted]

TABLE OF CONTENTS

		Page
I.	INTRODUCTION	1
II.	URANIUM EXTRACTION FROM PURE SULFATE SOLUTIONS	4
	Choice of Diluent	6
	Effect of Alcohol Concentration	6
	Effect of Sulfate Concentration	10
	Effect of pH Level	10
	Effect of Reagent Concentration	13
	Effect of Temperature	18
	Rate of Uranium Extraction	19
III.	SELECTIVE EXTRACTION OF URANIUM	20
	Extraction of Iron	22
	Extraction of Aluminum	31
IV.	URANIUM STRIPPING	38
	Stripping with Sodium Carbonate	38
	Modification of the Kerosene Diluent	40
	Uranium Loading in Sodium Carbonate Strip Solutions	47
	Removal of Metals Other Than Uranium by the Sodium Carbonate Strip	50
	Stripping with Other Alkaline Stripping Reagents	51
	Compatibility of Other Organophosphorus Acids with Alkaline Stripping	51
	Stripping with Mineral Acids	52
V.	LOSSES OF EXTRACTANT (AND ALCOHOL) THROUGH SOLUBILITY IN THE LEACH LIQUOR AND STRIP SOLUTIONS	57
	Loss of Extractant to Acid Liquors	57
	Solubility of Di(2-ethylhexyl)phosphate in Alkaline Solutions	58

[redacted]

[redacted]

[redacted]

[redacted]

TABLE OF CONTENTS (Cont'd.)

Page

Determination of Alcohol Concentrations in Organic Phase..... 60
Distribution of Alcohol to Acidic Solutions..... 61
Distribution of Alcohol to Alkaline Solutions.... 64

VI. EXTRACTION OF URANIUM FROM LEACH LIQUORS..... 65

Sulfate Liquors..... 65
Sulfate-Chloride Liquors..... 69
Bench-Scale Countercurrent Extraction Studies.... 70
Slurry Extraction..... 76

VII. ESTIMATED REAGENT COSTS FOR RECOVERY OF URANIUM FROM SULFATE LIQUORS WITH DI(2-ETHYLHEXYL)-PHOSPHORIC ACID USING AN ALKALINE STRIP..... 77

VIII. VANADIUM EXTRACTION AND STRIPPING..... 81

IX. SUMMARY..... 88

X. FUTURE WORK..... 95

XI. ACKNOWLEDGEMENTS..... 96

XII. REFERENCES..... 97

APPENDICES:

A. PREPARATION, PURITY, STABILITY, AND AVAILABILITY OF REAGENTS..... 99

B. EXTRACTIONS FROM NITRATE, CHLORIDE, AND PHOSPHATE SOLUTIONS..... 109

C. COMPARISON OF URANIUM EXTRACTION ABILITY OF SEVERAL ALKYLPHOSPHORIC ACIDS..... 117

[redacted]

[redacted]

[redacted]

ABSTRACT

Bench scale studies have been made of the recovery of uranium from acid leach liquors (and slurries) by solvent extracting with di(2-ethylhexyl)phosphoric acid in an organic diluent. Uranium may be stripped from the organic solvent by either alkaline or acidic reagents, the former having been studied in greater detail. On the basis of these tests, a recovery process may be considered which shows promise both from the standpoint of operation and chemical costs.

Under proper conditions, vanadium can also be extracted by the di(2-ethylhexyl)phosphoric acid and stripping again may be accomplished with either acidic or alkaline reagents. Preliminary studies have been made of these possibilities.

In addition to di(2-ethylhexyl)phosphoric acid, some other organophosphorus acids have been cursorily examined in respect to their extraction and/or stripping performance.

[redacted]

[redacted]

I. INTRODUCTION

The investigation and evaluation of new reagents for the separation of uranium from various aqueous systems by solvent extraction methods have been underway for some time at this laboratory. As a part of this program, since August 1951, a number of classes of organophosphorus compounds have been examined and some of this work has been described in previous progress reports[1-4]. It is the purpose of this report to describe in greater detail the extraction studies with one particular class of organophosphorus compounds, i.e., the dialkylphosphoric acids and, in particular, di(2-ethylhexyl)phosphoric acid. Brief descriptions of comparative tests with several other organophosphorus acids are also included. Additional studies with these latter compounds, as well as several other compound classes, will be described in a series of later reports.

In 1949, in connection with studies of tributylphosphate, it was recognized that the acid hydrolysis products of tributylphosphate were excellent extractants for uranium from nitrate solutions and later a report was issued from the Hanford Engineering Works[5] describing the effect of the butyl acid phosphates as being so large as to obscure extractions with tributylphosphate. Extractions from nitrate solutions with mixtures of other alkylphosphoric acids were then reported by the University of California Radiation Laboratory[6]. Later, pure alkylphosphoric acids were used in studies of extractions and the extraction mechanism from nitrate solutions,[7-11] and preliminary tests were also made with other aqueous acid solutions including acetate, sulfate, chloride, phosphate, and fluoride.[9]

In early 1951, Dow Chemical Company initiated extraction experiments with alkylphosphoric acid mixtures in phosphate systems which led to the development of a process for the recovery of uranium from commercial phosphoric acid with mixtures of the alkylortho- and pyrophosphoric acids[12]. Subsequently, a process has been proposed by the same group for the recovery of uranium from Western ore leach liquors and slurries with the long-chain monoalkylphosphoric acids,[13] and this process is in pilot plant development by the Bureau of Mines at Salt Lake City, Utah.

[redacted]

Workers at Argonne National Laboratory[14] have since reported studies of dibutylphosphoric acid as a uranium extractant from sea water.

As mentioned in previous reports, the general program on organophosphorus and other reagents at this laboratory has in the first instance been concerned with comparative testing of a wide variety of individual compounds (representing many classes) in regard to their uranium extraction ability. Those reagents showing promise in these initial tests are next examined (as soon as time permits) with respect to their utility in practicable processes for the recovery of uranium from liquors or slurries such as those obtained in the leaching of uranium ores. The dialkylphosphoric acids were one of the compound types showing promise in this regard and the results from these studies are reported below.

Di(2-ethylhexyl)phosphoric acid has been used in most of the experiments because of its potential availability in quantity at reasonable cost. It is not intended to imply, however, that its attractive features, process-wise, may not be possessed by some other reagents within this class. Because of the frequent use of sulfuric acid in uranium raw material processing, most of the extraction studies have been made on uranium-bearing sulfate solutions, in some cases "pure," and in other cases containing appreciable amounts of those contaminants which are often dissolved from an ore during leaching, e.g., iron, aluminum, phosphate, fluoride, etc. Extractions from nitrate, chloride, and phosphate solutions have also been studied, but only briefly. Survey tests of extraction from nitric acid leach liquors of calcium-aluminum phosphate ore with di(2-ethylhexyl)phosphoric acid and other organophosphorus reagents were reported previously[15].

For purposes of discussion, the data presented in this report have been divided into categories leading logically to the development of a tentative flowsheet describing a solvent extraction process for recovering uranium from acid liquors with di(2-ethylhexyl)phosphoric acid. The categories are: (1) extraction of uranium from pure sulfate solutions, showing the effects of variables such as pH and sulfate concentration (at levels usually encountered in process liquors) and reagent concentration, (2) extraction of other contaminant metals such as iron and aluminum under the same conditions, (3) extractions from actual and synthetic leach liquors, (4) removal of extracted metal values from the organic phase by both alkaline and acid

stripping methods, and (5) the integration of these data into a tentative process flowsheet which has received preliminary testing in a bench-scale continuous countercurrent extraction apparatus.

It has not been within the scope of this work to examine, fundamentally, the factors governing extraction by these reagents with respect to structure and other variables. Although certain conclusions may be drawn from these data, it is anticipated that a more thorough study of the pertinent fundamentals will be undertaken when time allows.

II. URANIUM EXTRACTION FROM PURE SULFATE SOLUTIONS

For the present purposes, the extraction of uranium from acid liquors by dialkylphosphoric acids may be regarded as a reversible chemical reaction such as the following,

$$UO_2^{++}{}_{(aq)} + 2HR_2PO_{4\,(org)} \rightleftharpoons (UO_2)(R_2PO_4)_{2\,(org)} + 2H^+_{(aq)} \qquad (1)$$

in which uranium enters the organic phase as an oil-soluble salt of the organic acid. It should be understood that this is a simplified postulation, which may be neither complete nor exclusively correct. The mass action expressions corresponding to this reversible reaction are

$$K_c = \frac{[(UO_2)(R_2PO_4)_2][H^+]^2}{[UO_2^{++}][HR_2PO_4]^2} \qquad (2)$$

$$E_a^o = \frac{[(UO_2)(R_2PO_4)_2]}{[UO_2^{++}]} = K_c \frac{[HR_2PO_4]^2}{[H^+]^2} \qquad (3)$$

where the quantities in brackets represent the concentrations at equilibrium. These equations state that for uranium extractions by the reaction shown the extraction coefficient should increase in proportion to the square of the reagent concentration and decrease in proportion to the square of the hydrogen ion concentration.

In actual extraction systems, particularly in extraction from solutions containing other complexing agents, the reaction as written may not properly describe the system,

and the results may deviate considerably from the indicated proportionalities.* For instance, in solutions of high nitrate concentration (v. Appendix B) a different type of uranium extraction reaction appears to become effective. Again, in sulfate solutions the formation of aqueous sulfate complexes competes for the uranyl ion, and hence (even if the equations were exactly correct) the apparent uranium concentration as given by chemical analysis is not the correct concentration for use in the equations shown. Furthermore, such side equilibria may be interdependent, as with the sulfate and hydrogen ion concentrations in a sulfate solution. At any given total sulfate level, the sulfate-bisulfate equilibrium and hence the degree of sulfate complexing of uranyl will depend on the hydrogen ion concentration, and the observed dependence of the extraction coefficient on pH will contain indirect effects of the varying sulfate complexing as well as the expected direct effect of the varying hydrogen ion concentration. Nevertheless, in spite of the complexities which must be expected with the types of solutions considered below, the simple reaction and mass action equations as written serve to point out the major extraction variables: reagent concentration, pH, factors which can change the equilibrium constant K_C (e.g., nature of diluent, temperature), and concentrations of substances which can change the amount of

---

*Stewart and Hicks[9] have reported extraction results with dibutylphosphoric acid which show the extraction coefficient proportional to the square of the reagent concentration under some conditions and to a power higher than the square under others. The former was in extractions from either 2 or 0.6 M nitric acid solution with dibutyl ether as the diluent, the latter, from 0.06 M nitric acid with dibutyl ether and also from all three acid levels with hexane as the diluent. A similar proportionality to a power greater than the square has been found in this laboratory in extractions with di(2-ethylhexyl)phosphoric acid/kerosene from 0.5 M nitric and 0.5 M hydrochloric acid solutions, as well as from a variety of sulfate solutions. At the same time, the extraction isotherm presented below as well as related measurements arising in various process development tests appear best consistent with assumption of a stoichiometry of two reagent molecules per uranium molecule in the extracted complex and variation of the extraction coefficient in proportion to the square of the free reagent concentration. Obviously, there is need for a detailed fundamental investigation of the one or more reactions which are actually taking place.

free uranyl ion (e.g., sulfate, phosphate). The following section describes the effects of these variables through ranges pertinent to uranium extraction from raw materials process liquors.

Choice Of Diluent

Uranium extractions from sulfate solutions (0.5 M SO_4, pH = 1.1) with 0.1 M di(2-ethylhexyl)phosphoric acid in several types of diluents are shown in Table 1. The extraction coefficients were highest with the aliphatic hydrocarbons (kerosene and hexane), and were extremely low with long-chain alcohols as the diluent. Since kerosene provided the highest coefficient and also possesses characteristics desirable in an extraction process (e.g., immiscibility with the aqueous solution, low cost, relatively high flash point, etc.), most of the experiments described in this report have utilized kerosene as the primary diluent. In addition, however, in order to maintain reagent-diluent compatibility during alkaline stripping operations, it may be useful to modify the kerosene with a small amount of an additional solvent (see section on stripping). Certain long-chain alcohols are suitable for this purpose, and 2-ethylhexanol has been used in most of the following experiments.

Effect Of Alcohol Concentration

The addition of alcohol to the organic solvent depresses the uranium extraction. Table 2 and Figure 1 show the effect on extraction of uranium from sulfate solutions when 2-ethylhexanol was added in varying amounts to di(2-ethylhexyl)phosphoric acid solutions in kerosene. Because of the regular effect at each level of sulfate and reagent concentration, it is possible to summarize the data with the following empirical equation:

$$\log E_p = \log E_o - 0.27P \qquad (4)$$

Where at a particular sulfate and reagent level, and pH level close to 1,

$P \equiv$ w/v % 2-ethylhexanol in the range 0-3%.
$E_p \equiv$ uranium extraction coefficient at P % alcohol.
$E_o \equiv$ uranium extraction coefficient at zero % alcohol.

Table 1

CHOICE OF DILUENT FOR EXTRACTIONS WITH DI(2-ETHYLHEXYL)PHOSPHORIC ACID

0.1 M Di(2-ethylhexyl)phosphoric Acid, Batch G
0.004 M Uranium(VI)
0.5 M SO_4, pH = 1.1

Phase Ratio, aqueous/organic = 1

Agitation Time = 10 min. (wrist-action shaker)

Diluent	Extraction Coefficient, E_a^o
Kerosene	135
Hexane	110
Carbon tetrachloride	20
Isopropyl ether	17
Benzene	13
Chloroform	3
2-Ethylhexanol	0.1
Octanol-2 (capryl alcohol)	0.08

Table 2

EFFECT ON EXTRACTION COEFFICIENT OF ADDITION OF 2-ETHYLHEXANOL TO ORGANIC DILUENT

Di(2-ethylhexyl)phosphoric Acid, Batch G, in kerosene
Aqueous sulfate solution, pH as indicated
0.004 M Uranium(VI)
Phase Ratio = 1
Agitation Time = 10 min. (wrist-action shaker)

w/v percent 2-Ethylhexanol	Reagent Conc. (M)	0.5 M SO_4 pH 1.1	1.5 M SO_4 pH 0.9
0	0.05	20	--
	0.10	135	18
	0.20	800	--
0.5	0.10	95	12
1.0	0.05	10	--
	0.10	70	9
	0.20	480	--
2.0	0.05	---	--
	0.10	40	--
	0.20	320	--
2.8	0.10	---	3

[redacted]

ORNL-LR-Dwg. 7073

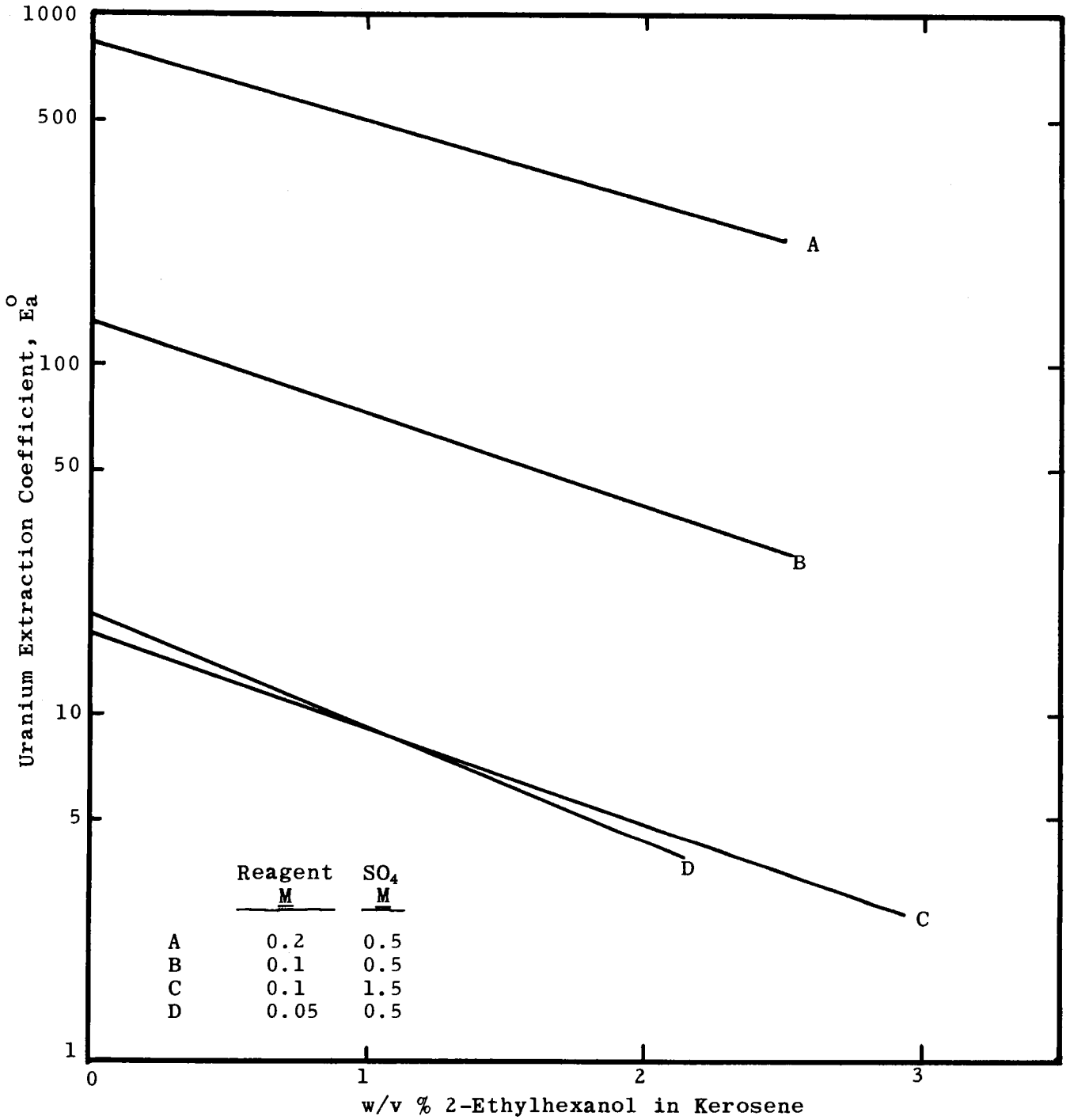


Figure 1

EFFECT OF 2-ETHYLHEXANOL ON EXTRACTION

with

Di(2-ethylhexyl)phosphoric Acid, Batch G

At alcohol levels contemplated for processes employing an alkaline strip, the extraction coefficients are significantly decreased. However, even with the alcohol present, the extractions are sufficient for effective process utility.

Effect Of Sulfate Concentration

Extractions from sulfate solutions, showing the variation of uranium extraction coefficient as a function of sulfate concentration, reagent concentration and pH, are presented in Table 3.

As the sulfate concentration was increased, the increased competition for uranium between sulfate ions in the aqueous phase and the reagent in the organic phase was apparent. With 0.1 M di(2-ethylhexyl)phosphoric acid in kerosene (aqueous pH = 1), the extraction coefficient dropped from 135 in 0.5 M sulfate to 18 in 1.5 M sulfate, a decrease of over 7-fold. Under similar conditions, with 2 w/v % 2-ethylhexanol in the diluent, extraction coefficients were lower but the order of change with sulfate concentration was about the same, e.g., E_a^o = 30 at 0.5 M sulfate and 4 at 1.5 M sulfate. For other pH and reagent levels, the order of change between these same sulfate concentrations varied from 7-fold to 2-fold.

Although solutions having a wide range of sulfate concentrations may be extracted with di(2-ethylhexyl)phosphoric acid, it is obvious that the most effective application could be made to solutions of low sulfate level. The leach liquors obtained in ore processing ordinarily contain only moderate concentrations of sulfate (usually 0.2 - 0.5 M) and the data show that satisfactory uranium coefficients can be obtained at these levels with moderate reagent concentrations.

Effect Of pH Level

The uranium extraction coefficients in Table 3 are plotted in Figure 2, on a log scale, as a function of the pH level in the range 0.5 to 1.8. Within this range, the resulting curves are nearly linear with a slope close to 1. The pH of ore leach liquors generally varies from about 1 to 1.5 (with sulfate between 0.2 and 0.5 M) and the extraction coefficients at these conditions are satisfactory. With liquors of lower than usual pH, or even with liquors

Table 3

EXTRACTIONS FROM SULFATE SOLUTIONS WITH DI(2-ETHYLHEXYL)PHOSPHORIC ACID

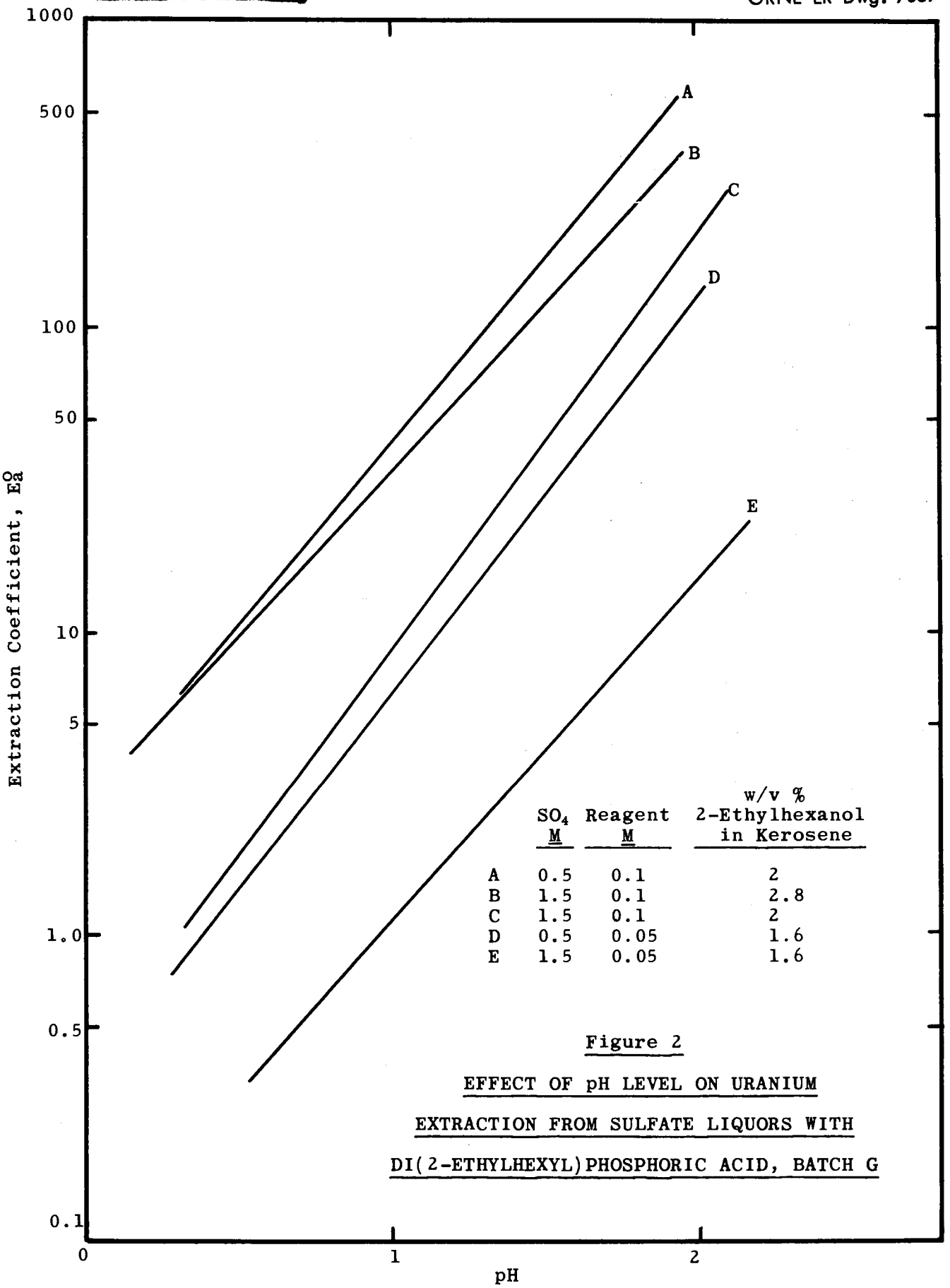
Di(2-ethylhexyl)phosphoric Acid, Batch G, in kerosene
Phase Ratio, aqueous/organic = 1
Uranium(VI) = 1 g/liter (0.004 M)

Reagent Conc. M	2-Ethyl-hexanol,[a] w/v %	0.5 M SO_4 Initial pH[b]	0.5 M SO_4 E_a^o	1.5 M SO_4 Initial pH[b]	1.5 M SO_4 E_a^o	Agitation Time[c] (min)
0.05	0	1.0	20	---	-----	10
	1.6	0.4	1	0.5	0.5	2
	1.6	0.9	5	1.0	1	2
	1.6	1.8	60	1.9	11	2
0.1	0	1.0	135	0.9	18	10
	2.0	0.4	8	0.5	2	2
	2.0	0.9	30	1.0	4	2
	2.0	1.8	300	1.9	82	2
0.2	0	1.0	800	---	-----	10
	2.8	---	---	0.5	10	2
	2.0	1.0	320	---	-----	2
	2.8	("	est. 200)[d]	1.0	32	2
	2.8	---	---	1.9	200	2

a) Twice the quantity of 2-ethylhexanol called for by Equation (8), p. 43.
b) The pH decreased during extraction by less than 0.1 unit.
c) Agitation by wrist-action shaker (10 min) or by hand (2 min).
d) Estimated by means of Equation (4), p. 6.

[redacted]

ORNL-LR-Dwg. 7089



	SO_4 M	Reagent M	w/v % 2-Ethylhexanol in Kerosene
A	0.5	0.1	2
B	1.5	0.1	2.8
C	1.5	0.1	2
D	0.5	0.05	1.6
E	1.5	0.05	1.6

Figure 2

EFFECT OF pH LEVEL ON URANIUM EXTRACTION FROM SULFATE LIQUORS WITH DI(2-ETHYLHEXYL)PHOSPHORIC ACID, BATCH G

of pH ~1, addition of calcium carbonate might be considered as a means of obtaining increased extraction efficiency by adjustment of both pH and sulfate to more desirable levels. Calcium carbonate used for this purpose could presumably be considered cost-free since neutralization of the acid liquor after the extraction may be considered necessary to precipitate vanadium and/or to prepare the liquor for waste disposal.

As indicated by the data of Figure 2, and shown directly by Table 4, di(2-ethylhexyl)phosphoric acid at moderate concentrations is an ineffective extractant from solutions containing moderate to high concentrations of sulfuric acid. The low extraction coefficients suggest the possibility of sulfuric acid as a stripping agent and further studies in this regard are included in a later section.

Effect Of Reagent Concentration

Data from Tables 3 and 4 are plotted (on log scale) in Figure 3 to show the variation of uranium extraction with reagent concentration. At each sulfate and pH level tested, the extraction coefficients increased by a factor of 20 or more as the reagent concentration was increased from 0.05 to 0.2 M. It should be noted that these extractions were made with 2-ethylhexanol present in the diluent and that the amount of 2-ethylhexanol was varied with the reagent concentration; thus, these data are not appropriate for exact mass-action calculations. On the other hand, the presence of the 2-ethylhexanol in quantities suitable for use in processes involving alkaline stripping (q.v.) makes these curves pertinent for showing how the reagent concentration can be chosen to obtain usefully high extraction coefficients in this type of process application.

In Figure 3 as in Tables 3 and 4, the initial concentration of reagent is shown without correction for the fraction tied up by uranium complex formation. In these tests, with 0.004 M uranium and 1:1 phase ratio, the difference between the final concentration of uncomplexed reagent and the initial concentration was small. In process application, on the other hand, extraction will normally be carried out so that a large proportion of the reagent will be loaded with uranium. It is useful to represent the extraction behavior under such conditions by an extraction isotherm. Table 5 and Figure 4 show an isotherm for uranium extraction with 0.1 M di(2-ethylhexyl)-

Table 4

EXTRACTION WITH DI(2-ETHYLHEXYL)PHOSPHORIC ACID FROM SULFURIC ACID SOLUTIONS

Di(2-ethylhexyl)phosphoric Acid, Batch G, in kerosene

Uranium = 0.004 M

Phase Ratio, aqueous/organic = 1

Agitation Time = 2 minutes by hand-shaking.

Reagent M	w/v percent 2-Ethylhexanol	H_2SO_4 (M) 0.5	1.5	4.0	6.0
0.05	1.6	1.1	0.2	----	----
0.10	2.0	5.4	0.7	0.09	0.03
0.20	2.8	---	3.6	0.45	0.14

[redacted]

ORNL-LR-Dwg. 7071

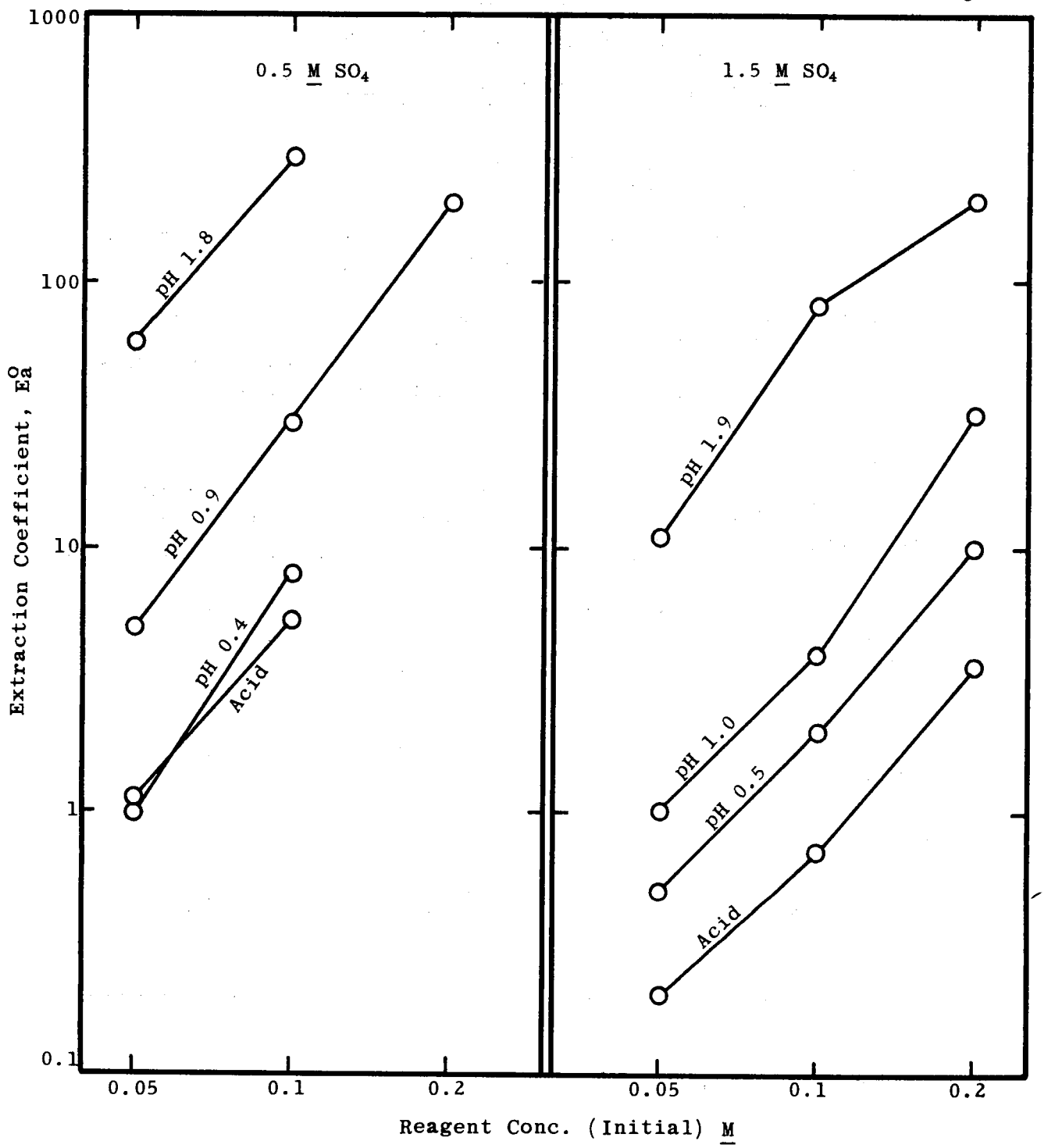


Figure 3

EFFECT OF REAGENT CONCENTRATION

ON URANIUM EXTRACTION

with

Di(2-ethylhexyl)phosphoric Acid

Table 5

URANIUM EXTRACTION ISOTHERM

WITH DI(2-ETHYLHEXYL)PHOSPHORIC ACID

Aqueous: 2 g U/liter (0.008 M)
0.3 M Sulfate, pH 1

Organic: 0.1 M Di(2-ethylhexyl)phosphoric Acid, Batch G, in kerosene with 2% 2-ethylhexanol.

Cascade extraction (organic phase contacting successive volumes of aqueous phase) at phase ratio of 2 aqueous/1 organic and contact time of 10 minutes per stage, agitation by wrist-action shaker.

Stage	Uranium Distribution g/l Aqueous	Uranium Distribution g/l Organic	E_a^o	Estd. Free Reagent M	Corresponding E_a^{o*} for 0.1 M Free Reagent
1	0.15	3.8	25.3	0.068	50
2	.67	6.5	9.7	.046	47
3	1.44	7.7	5.4	.035	43
4	1.77	8.2	4.6	.031	48
5	1.84	8.6	4.7	.028	59

*(E_a^o measured) x (0.1/M free reagent)^2.

[redacted]

ORNL-LR-Dwg. 7080

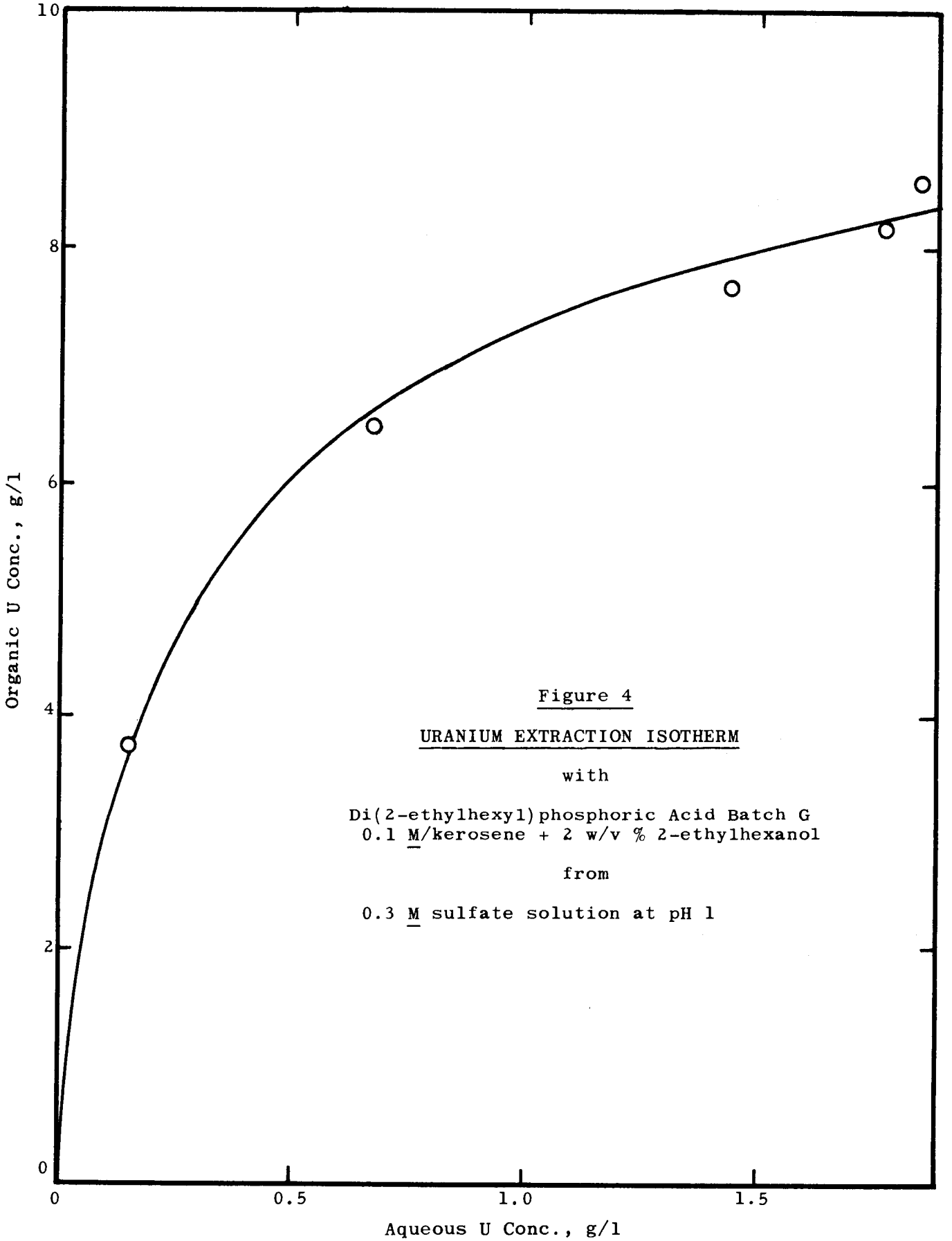


Figure 4

URANIUM EXTRACTION ISOTHERM

with

Di(2-ethylhexyl)phosphoric Acid Batch G
0.1 M/kerosene + 2 w/v % 2-ethylhexanol

from

0.3 M sulfate solution at pH 1

phosphoric acid in kerosene (modified with 2% 2-ethylhexanol) from a solution containing 2 g uranium per liter and 0.3 M sulfate, pH 1. The decrease of the extraction coefficient as the uranium concentration in the organic phase increased is attributed to the decrease in free reagent concentration. As such, the extent of decrease in E_a^o may be compared to that calculated from the assumption that the extraction occurred by the mechanism proposed in Equation (1). According to that equation, each mole of uranium in the organic phase has bound two moles of reagent. Thus, the molarity of free reagent is (initial M reagent) minus (2 x M U_o), as listed in the next to last column of Table 5. According to Equation (3), the extraction coefficient is proportional to the square of the free reagent concentration. Thus, for each of the coefficients and free reagent concentrations found, the corresponding inherent coefficient at 0.1 M free reagent is

$$E_a^o \text{ (at 0.1 M)} = E_a^o \text{ (measured at m M)} \times \left(\frac{0.1}{m}\right)^2$$

The last column of Table 5 shows the results of this calculation, which are in relatively good agreement at $E_a^o \approx 50$ for 0.1 M free reagent. Using this average value, and the same equations, the theoretical extraction was calculated for a series of uranium levels. The resulting theoretical extraction isotherm is shown as the continuous curve in Figure 4, and the experimental points are seen to be in relatively good agreement throughout.

The theoretical curve of Figure 4 approaches an organic uranium concentration of about 8.5 g/l, corresponding to the head aqueous uranium concentration of 2 g/l. The level of this limit will vary with the inherent extraction coefficient, e.g., it would be higher for a solution of higher pH or lower sulfate concentration and lower for a solution of lower pH or higher sulfate concentration. In addition, however, it should be noted that, regardless of the inherent coefficient, an asymptotic upper limit would be imposed by the stoichiometry of the extracted complex. If two moles of reagent are bound by each mole of uranium as suggested by Equation (1), the stoichiometric loading limit is about 12 g U/l in 0.1 M reagent, 24 g U/l in 0.2 M reagent, etc.

Effect Of Temperature

The effect of temperature upon extraction from a single aqueous solution has been observed in the range 15 - 40°C.

The data of Table 6 show that in 0.5 M sulfate solutions at

Table 6

EFFECT OF TEMPERATURE ON URANIUM EXTRACTION COEFFICIENT FROM 0.5 M SULFATE SOLUTIONS

0.52 M Sulfate, pH 0.9
0.004 M Uranium(VI)
0.1 M Di(2-ethylhexyl)phosphoric acid, Batch G, in kerosene + 2 w/v % 2-ethylhexanol.
10 min Agitation Time (by hand in constant temperature water bath)
Phase Ratio, aqueous/organic = 1

Temp., °C	Extraction Coefficient
15	30
20	29
25	28
30	25
35	23
40	21

pH 1 there was a moderate decrease in extraction coefficient with increasing temperature, the coefficient changing from 30 to 20 over the range studied.

Rate Of Uranium Extraction

With good mixing, the extraction of uranium from sulfate liquors by di(2-ethylhexyl)phosphoric acid takes place at a fairly rapid but measurable rate. Under conditions such as that provided by vigorous hand-shaking in a separatory funnel, the extraction was at equilibrium in 2 minutes at room temperature. Slightly longer agitation times were required at lower temperatures.

III. SELECTIVE EXTRACTION OF URANIUM

The ability of a reagent to extract uranium without excessive extraction of other solution components, i.e., its selectivity for uranium, is particularly important in the treatment of ore leach liquors, which ordinarily contain a number of other metal ions such as iron, aluminum, calcium, copper, vanadium, etc. The distribution and quantities of these ions vary widely, being dependent on both the composition of the ore and the type of leaching treatment used, but many of them (notably iron, aluminum, and vanadium) are often as high or even much higher in molar concentration than the uranium.

In the preceding section it was demonstrated that di(2-ethylhexyl)phosphoric acid is an effective extractant for uranium(VI) from pure acidic sulfate solutions. Tests of the extraction of some other metal ions from similar sulfate solutions are presented below. For several of these only preliminary survey tests have been made, while the extraction of iron, aluminum, and vanadium has been examined in more detail. (Vanadium extractions are described in Section VIII.)

Extraction tests from a series of 0.5 M sulfate solutions at pH $\sim$1, each containing a single metal ion at a concentration in the order of 0.01 M, are described in Table 7. The extractant was di(2-ethylhexyl)phosphoric acid in kerosene, which in most of the tests was modified with 2% 2-ethylhexanol. Under the conditions of these tests, thorium, titanium(IV), and iron(III) were extracted by 0.1 M reagent with coefficients (E_a^o =>26, 16, and 6) approaching that obtained for uranium(VI) (E_a^o = 30). Extractions of molybdenum(VI) and cerium(IV) were lower but still significant (E_a^o = 1.8 and 1.1). Vanadium(IV) was also extracted (E_a^o = 1.1 when the reagent concentration was increased to 0.2 M), but vanadium(V) was not appreciably extracted even by 0.2 M reagent.

The extraction time for the above tests (excepting iron and aluminum) was arbitrarily set at two minutes, which had been found sufficient to attain equilibrium in uranium extractions. Since no attempt was made to study the rates of extraction, and since an appreciable time effect has been found in iron and aluminum extractions (see below), the data should be considered qualitative. The effects of varying pH, sulfate concentration, and alcohol content in the diluent were not examined.

Table 7

EXTRACTIONS OF METAL IONS WITH DI(2-ETHYLHEXYL)PHOSPHORIC ACID

Extraction Conditions:

Organic reagent concentration = 0.1 M (Batch G)
Diluent = kerosene with 2% 2-ethylhexanol.
Aqueous solutions 0.5 M SO_4, pH ~1.
Phase Ratio, aqueous/organic = 2.
Agitation Time = 2 minutes by hand.

	Distribution (g/l)			
	Aqueous	Organic	E_a^o	
Al	2.75	0.014	0.005	a,d
Ca	.34	< .002	< .006	
Ce(IV)	.39	.42	1.1	
Cr(III)	.69	< .02	< .03	
Cu(II)	.97	~ .02	~ .02	
Fe(III)	.086	.49	6	a,c
Fe(II)	2.5	< .0005	< .001	b,c
Mn(II)	1.00	< .02	< .02	
Mo(VI)	.59	1.06	1.8	
Ni(II)	1.19	.013	.01	
Th	< .05	1.3	> 26	
Ti(IV)	.06	1.00	16	
Zn	1.00	< .1	< .1	
V(V)	1.8	0.36	0.2	e,f
V(IV)	1.4	1.3	1.1	e,f
U(VI)	0.03	0.97	30	a
"	0.014	0.99	135	a,e

a) Phase ratio, aqueous/organic = 1.
b) Phase ratio, aqueous/organic = 0.25.
c) Agitation time = 4 hours on wrist-action shaker.
d) " " = 16 hours on wrist-action shaker.
e) Diluent = kerosene without 2-ethylhexanol.
f) Organic reagent concentration = 0.2 M.

Extraction Of Iron

Significant extractions of iron(III) and inappreciable extraction of iron(II) by several alkylphosphoric acids were reported previously.[2,3] Workers at Dow Chemical Company later reported data for monoalkylphosphoric acids which showed that the iron(III) extractions occurred at a measurably slow rate, and that the extraction coefficients at equilibrium were large.[16] In process application interference from iron extraction can be almost completely avoided by reduction to the ferrous state. However, even without such a reduction, or with only partial reduction, it may be possible to keep iron interference within tolerance levels by proper control of the extraction conditions, if the iron concentration is sufficiently low. Hence, the extraction of Fe(III) has been examined in some detail.

Effects Of Extraction Variables. Table 8 presents iron(III) extraction data from 0.5 M sulfate solutions, at pH levels of 0.6, 1.0, and 1.5, with 0.1 M di(2-ethylhexyl)-phosphoric acid. A series of extractions was made at each pH level, the contact time varying from 10 seconds to 16 hours. The iron was extracted slowly, equilibrium apparently being reached in one-half to one hour, with indication that the rate was slowest at the lowest pH*. Through the range tested, the amount of iron extracted at equilibrium increased with pH, and in each series the pH dropped slightly as the extraction progressed. These results indicate that the extracted iron displaced hydrogen ion from the organic acid into the aqueous solution, i.e., they indicate that the iron was extracted as a cation complexed with the anion of the organic acid (cf. the extraction reaction proposed for uranium).

The equilibrium extraction coefficients are not shown in Table 8 since in those tests the molarity of iron in the organic phase reached a significant fraction of the reagent molarity, and the concentration of free reagent may have been considerably decreased, especially if the extracted

---

*These data (in terms of iron concentration in the organic phase) are consistent with a first order rate of approach to equilibrium, indicating 99% of the maximum iron extracted under these conditions in about 20, 30, and 60 minutes at pH 1.5, 1.0, and 0.6, respectively. However, the variables affecting the extraction rate have not been examined.

Table 8

EXTRACTION OF IRON(III) FROM SULFATE SOLUTIONS -

RATE OF EXTRACTION AT VARIOUS pH LEVELS

0.1 M Di(2-ethylhexyl)phosphoric Acid, Batch G, in kerosene, with 2% 2-ethylhexanol.

[Fe(III)] = 4 g/l (0.07 M)

[$SO_4^=$] = 0.5 M

Phase Ratio, aqueous/organic = 1.

Agitation by wrist-action shaker.

		Conc. of Fe in Organic Phase:	
Time	pH	g/l	% of Max. Conc. Reached
0	0.6		
10 sec	.6	0.046	5
30 "	.6	.051	6
1 min	---	.078	9
10 "	.6	.44	51
30 "	.6	.80	93
1 hr	.5	.85	99
16 "	.5	.86	100
0	1.0		
10 sec	1.0	0.052	4
30 "	1.0	.066	5
1 min	1.0	.18	14
10 "	.9	1.04	81
30 "	.9	1.28	100
1 hr	.9	1.26	98
16 "	.9	1.18	92
0	1.5		
10 sec	1.5	0.140	8
30 "	1.5	.188	11
1 min	1.4	.431	25
10 "	1.3	1.53	88
30 "	1.3	1.73	100
1 hr	---	1.70	98
16 "	1.3	1.71	99

complex involves more than one mole of reagent per mole of iron. A series of extractions was made from a similar sulfate solution (0.5 M sulfate, pH 1) with a lower concentration of iron(III), 0.001 M, so that nearly all of the reagent molecules would remain uncomplexed. In this series the concentration of reagent in the organic phase (no alcohol added) was varied in order to determine its effect on the extraction coefficient. The results, Table 9, show the coefficient proportional to a power of the reagent concentration between the square and the cube. However, the extraction coefficient obtained with 0.1 M reagent and 0.001 M iron was very much higher than that obtained in the corresponding test with 0.1 M reagent and 0.07 M iron, the difference being greater than can be ascribed to decrease in free reagent concentration on the basis of binding of even three moles of reagent per mole of iron. These and several other iron(III) distribution coefficients (all from tests with 0.5 M sulfate, pH ~1, and 0.1 M initial reagent concentration, some with and some without added alcohol) are compared in Figure 5 as a function of the equilibrium aqueous iron concentration. This comparison supports the suggestion that the extraction of iron does indeed vary (inversely) with its absolute concentration. Thus, the extraction of iron appears to be a more complicated process than the extraction of uranium, and specific tests under conditions close to each set of operating conditions will probably be required to evaluate the selectivity for uranium in the presence of iron. Such empirical tests and also studies of the fundamentals of the iron extraction will both be continued.

Comparison Of Reagents. Iron(III) extraction by three monoalkylphosphoric acids and by di(2-ethylhexyl)phosphoric acid are compared in Table 10. The aqueous solution contained 0.001 M iron and 0.5 M sulfate, pH 1; the reagents were used at 0.1 M in kerosene (no alcohol added). Equilibrium was reached more slowly with di(2-ethylhexyl)phosphoric acid in this test than in the corresponding test with 0.1 M iron, and equilibration with mono(heptadecyl)phosphoric acid was still slower. All three monoalkylphosphoric acids showed much higher extraction power for iron under these conditions than did the dialkylphosphoric acid, which is similar to the relative extraction powers for uranium shown by the same reagents.

Tests of iron(II) extraction by the same four reagents are shown in Table 11. These extractions were all made under an atmosphere of carbon dioxide. No iron(II) was detected in the organic phase with di(2-ethylhexyl)phosphoric acid, and

Table 9

EXTRACTION OF IRON(III) AT LOW LEVEL CONCENTRATION WITH DI(2-ETHYLHEXYL)PHOSPHORIC ACID

Di(2-ethylhexyl)phosphoric Acid, Batch G, in kerosene

[Fe(III)] = 0.001 M

[$SO_4^=$] = 0.5 M

pH = 1

Agitation Time = 6.5 to 7.5 hours in wrist-action shaker.

Reagent Conc. (M)	Phase Ratio Aqueous/Organic	Fe Distribution (ppm)		Extraction Coefficient
		Aqueous	Organic	
0.1	4	0.9	232	250
0.01	0.4	19.5	14	0.72
0.0033	0.133	42.0	3.2	0.076
0.0020	0.08	49.5	1.2	0.024

[redacted]

ORNL-LR-Dwg. 7087

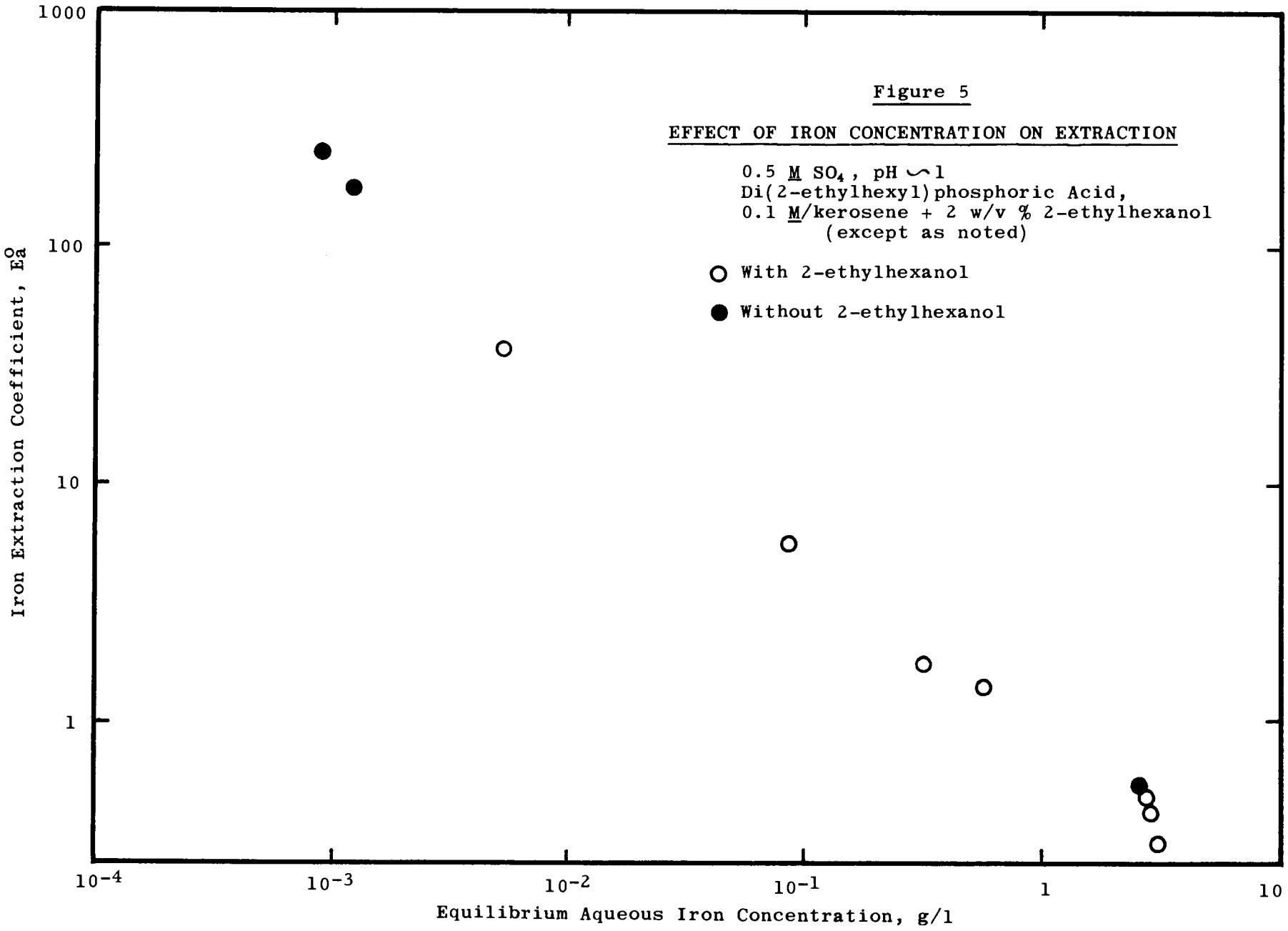


Figure 5

EFFECT OF IRON CONCENTRATION ON EXTRACTION

Table 10

EXTRACTION OF Fe(III) FROM SULFATE SOLUTIONS

WITH ALKYL PHOSPHORIC ACIDS

0.5 M SO_4, pH = 1

0.001 M Fe(III)

Phase Ratio, aqueous/organic = 4

Agitation by wrist-action shaker

0.1 M Reagent in Kerosene	Time (hrs)	E_a^o
Mono(2-ethylhexyl), Batch F	4	~ 1300
	7.5	~ 1300
Mono(dodecyl), Batch B	0.5	~ 130
	1	~ 200
	2	~ 250
	4	~ 1000
	7.5	~ 1000
Mono(heptadecyl), Batch B	0.5	4
	1	9
	4	~ 725
	7.5	~ 1400
Di(2-ethylhexyl), Batch G	0.5	4
	1	13
	2	51
	4	250
	7.5	250

Table 11

EXTRACTION OF REDUCED IRON WITH ALKYLPHOSPHORIC ACIDS

Aqueous: 2.54 g Fe(II)/liter (0.05 M)
0.03 g Fe(III)/liter
0.4 M SO_4, pH 1

Organic: 0.1 M Reagent in kerosene

Phase Ratio, aqueous/organic = 1/4

Extraction time, 4 hours (under CO_2 atmosphere) in wrist-action shaker

Alkylphosphoric Acid	Batch	Iron Distribution,* g/liter				E_a^o Fe(II)	% of Fe(II) Oxidized
		Aqueous Phase		Organic Phase			
		Fe(II)	Fe(III)	Fe(II)	Fe(III)		
Mono(2-ethylhexyl)	F	1.52	<0.01	0.002	0.254	0.001	40
Mono(dodecyl)	B	2.29	.01	.018	.042	.008	6
Mono(heptadecyl)	B	2.26	.01	.020	.048	.009	7
Di(2-ethylhexyl)	G	2.49	.01	< .0005	.013	< .0002	1
Di(2-ethylhexyl)**	G	2.46	.02	< .0005	.018	< .0002	2
Kerosene Blank		2.52					< 1

*Each phase analyzed for total Fe and for Fe(II); Fe(III) by difference.
**With 2% 2-ethylhexanol in the kerosene diluent.

only very small amounts were detected in the tests with the other reagents. However, more iron(III) was found in each extract than had been initially available, the amount of oxidation being greatest in the extraction with mono(2-ethylhexyl)phosphoric acid and lowest in that with di(2-ethylhexyl)phosphoric acid. The manner in which the reagents (or possibly impurities in the reagents) enhanced the oxidation has not been determined.

Displacement Of Extracted Iron(III). In a countercurrent system barren organic extractant enters the last extraction stage to contact liquor which is nearly barren of uranium but which contains iron at nearly the head concentration. Thus, if the liquor has not been reduced, the extractant has an opportunity to become partially loaded with iron(III) before extracting much uranium. It is important to determine whether or not the uranium present at higher concentrations in the upper stages has the ability to displace the iron to a sufficient extent and sufficiently fast so that the final loaded extractant will not exceed a tolerable iron content.

Table 12 shows tests in which, first, iron(III) was extracted from sulfate solution (0.1 M Fe, 0.5 M SO_4, pH 1) with 0.1 M di(2-ethylhexyl)phosphoric acid/kerosene - 2% 2-ethylhexanol, and next, the extractant containing iron was used to extract uranium from sulfate solution (0.004 M U, 0.5 M SO_4, pH 1). To follow the rate of equilibration, the organic solutions containing iron were split and separate uranium extractions were run for times ranging from 10 seconds to 16 hours. The results show that under these conditions the displacement of iron by uranium was not rapid, about 10 minutes being required to displace one-half of the iron that could be displaced.* It should be noted, however, that the conditions during actual countercurrent operation may be more favorable in at least one respect than those in the batch equilibration tests. That is, since the iron extraction is slow, the organic phase in the lower stages may not approach equilibrium iron loading. Certainly, it is apparent that the combination of these many factors governing the extraction of iron, particularly the rate factors, make it difficult to simulate actual process

---

*Comparison of the distribution coefficients for iron at 16 hours, E_a^o = 1.4 and 1.8, with other extraction coefficients in Figure 5 supports the belief that both of these tests reached equilibrium.

Table 12

DISPLACEMENT OF IRON BY URANIUM

0.1 M Di(2-ethylhexyl)phosphoric Acid, Batch G, in kerosene with 2% 2-ethylhexanol.

Uranium Solution: 0.004 M U(VI), 0.5 M SO_4, pH 1

Phase Ratio, aqueous/organic = 1

Agitation by wrist-action shaker

Time	Organic Phase, g/l		Aqueous Phase, g/l	
	U[a]	Fe	U	Fe
0	0	1.41[b]	1.00	0
10 sec	0.43	1.39	.57	0.022
20 "	.48	1.37	.52	.038
1 min	.54	1.32	.46	.069
10 "	.67	1.09	.33	.32
20 "	.70	.95	.30	.41
16 hr	.81	.81	.19	.57
0	0	0.95[c]	1.01	0
20 min	0.78	.71	.23	0.19
1 hr	.83	.65	.18	.28
4 "	.85	.59	.16	.32
16 "	.85	.57	.16	.32

a) Organic uranium concentration by difference.

b) Organic Iron Solution prepared by extraction from aqueous solution containing 4.00 g Fe/l, 0.5 M SO_4, pH 1.0, phase ratio aqueous/organic = 1, contact time 30 minutes.

c) Organic Iron Solution prepared by extraction from aqueous solution containing 4.00 g Fe/l, 0.5 M SO_4, pH 1.1, phase ratio aqueous/organic = 1, contact time 60 minutes.

conditions in simple batch contact experiments. Consequently, tests are now being made in countercurrent extraction equipment to establish the tolerance levels for iron(III) in the extraction system both from the standpoint of its effect on extraction efficiency (through competition with uranium for the reagent) and the effect on product purity (see below).

It is sometimes practicable to reduce the level of contaminants in an organic extract by means of a scrubbing step. (Depending on the conditions, the spent scrub solution may be discarded or it may be recycled to the pregnant liquor or to some other part of the process.) So used, scrubbing is essentially a selective stripping operation requiring that the contaminant be stripped more readily than the uranium. Stripping coefficients (S_o^a) for iron with sulfuric and hydrochloric acids are shown in Table 13, together with coefficients for uranium from comparable tests. The results of these preliminary tests do show preferential stripping of iron, and thus the chemical feasibility of a scrubbing operation. Considerable additional study would be necessary to determine the economic advisability.

Extraction Of Aluminum

Table 14 shows extractions of aluminum from sulfate solutions at pH 0.6, 1.0, 1.5, and 1.9 by di(2-ethylhexyl)-phosphoric acid in kerosene, with and without 2-ethylhexanol. The amounts of aluminum extracted by 0.1 M reagent were so low as to cause analytical difficulty; hence, 0.4 M reagent was used for most of the tests. At 0.1 M (and even at 0.4 M), aluminum extraction was very low in comparison with uranium extraction; i.e., di(2-ethylhexyl)phosphoric acid is a selective reagent for the extraction of uranium in the presence of aluminum. The results in Table 14 also show that the aluminum extractions approached equilibrium even more slowly than did the iron extractions. Qualitatively, the effects of pH and reagent concentration on aluminum extraction were similar to their effects on iron extraction, and the presence of 2-ethylhexanol in the diluent depressed the extraction to an appreciable extent.

Aluminum extractions from sulfate solutions by several mono- and dialkylphosphoric acids in kerosene are compared in Table 15. At corresponding reagent concentration and pH levels, the monoalkyl acids extracted more aluminum than

Table 13

SCRUBBING OF IRON FROM THE ORGANIC PHASE

WITH MINERAL ACIDS

0.1 M Di(2-ethylhexyl)phosphoric Acid, Batch G, in kerosene with 2% 2-ethylhexanol.

1.0 g Fe(III)/l.

Phase Ratio, aqueous/organic = 1

Agitation by wrist-action shaker

	Scrubbing Coefficients			
Time	0.5 M H_2SO_4	1.0 M H_2SO_4	0.5 M HCl	1.0 M HCl
2 min	---	---	0.3	2.0
30 "	1.2	4.1	0.7	2.8
1 hr	1.6	4.5	0.8	2.4
4 "	2.0	7.0	0.7	2.9
Comparison coefficients with uranium* (Table 4, and Table 4, Appendix B).				
2 min	0.2	0.7	0.01	0.06

*Assuming reversible extraction equilibria,

$$\text{Scrub coefficient} \equiv \frac{1}{E_a^o}$$

Table 14

EXTRACTION OF ALUMINUM FROM SULFATE SOLUTIONS

Di(2-ethylhexyl)phosphoric Acid, Batch G

Aqueous Solutions: 2.7 g Al/l (0.1 M);
0.5 M SO_4

Phase Ratio, aqueous/organic = 1

Agitation by wrist-action shaker

Reagent Conc. M	Alcohol[a] %	Time	pH	g Al/l Organic Phase	E_a^o
0.1	2	0	1.0		
		2 min	1.0	0.002[b]	
		16 hr	1.0	.014	0.005
0.4	4	0	0.6		
		16 hr	0.6	0.06	0.02
0.4	4	0	1.1		
		1 min	1.1	<0.05	
		1 hr	1.1	< .05	
		1.5 "	1.1	.05	
		16 "	1.0	.37	0.16
0.4	0	0	1.1		
		16 hr	1.0	0.75	0.37
0.4	4	0	1.5		
		1 min	1.5	0.05	
		1 hr	---	.36	
		1.5 "	1.4	.44	
		16 "	1.3	.67	0.33
0.4	4	0	1.9		
		16 hr	1.5	0.93[c]	0.54
0.4	0	0	1.9		
		16 hr	1.4	1.14[c]	0.70

a) w/v % 2-Ethylhexanol added to the kerosene diluent.
b) Batch C reagent.
c) Organic aluminum concentration by difference from raffinate analysis.

Table 15

COMPARISON OF ALUMINUM EXTRACTIONS WITH

MONO- AND DIALKYLPHOSPHORIC ACIDS

FROM SULFATE SOLUTIONS

Organic: Reagent in kerosene (no alcohol used)

Aqueous: 2.7 g Al/liter (0.1 M)
0.5 M Sulfate

Phase Ratio, aqueous/organic = 1

Agitation by wrist-action shaker, 16 hours

Alkylphosphoric Acid	Batch	Reagent M	Initial pH	E_a^o
Di(2-ethylhexyl)	G	0.4	1.1	0.37
		0.4	1.9	0.70
Di(3,5,5-trimethylhexyl)	A	0.4	1.1	0.28
Di(diisobutylmethyl)	D	0.4	1.1	0.03
Mono(2-ethylhexyl)	F	0.1	1	$\leqslant$ 0.3[b]
		0.4	1.1	4
		0.4	1.5	10
Mono(dodecyl)[a]	A	0.1	1	$\leqslant$ 0.1[b,c]
		0.4	1.1	1.1
		0.4	1.5	1.5

a) Dodecyl = 2,6,8-trimethylnonyl-4.

b) From aqueous head and raffinate analysis.

c) Six hours contact time.

did the dialkyl acids. The mono(2,6,8-trimethylnonyl-4) acid extracted less than did the mono(2-ethylhexyl) acid, and the di(diisobutylmethyl) acid extracted less than did the di(2-ethylhexyl) and di(3,5,5-trimethylhexyl) acids, suggesting decreased aluminum extraction with increased branching and/or molecular weight. It should be noted that in some of these tests, particularly with the mono(2-ethylhexyl)phosphoric acid, the amount of aluminum extracted was sufficient to decrease the free reagent concentration to considerably below the initial concentration, especially if several reagent molecules are bound to each extracted aluminum ion.

Aluminum extractions from various solutions by di(2-ethylhexyl)phosphoric acid in kerosene (2% 2-ethylhexanol) are shown in Table 16. The extraction coefficients with 0.1 M reagent were all low (measured after 16 hours contact) and were of about the same magnitude from the 4 M acid solutions as from the 0.5 M salt solutions at pH 1.

Aside from the question of uranium product purity, aluminum is an important consideration in process application because it forms precipitates with some of the alkylphosphoric acids. Workers at Dow Chemical Company have reported aluminum precipitation with dialkylorthophosphoric acids.[13] In this laboratory, sulfuric acid leach liquors of calcium-aluminum phosphate ("Leached Zone") ore were found to form stable gels, presumably due to precipitates, with kerosene solutions of di-n-octylphosphoric acid, but not with di(2-ethylhexyl)phosphoric acid nor with several branched-chain monoalkylphosphoric acids. Similarly, in preliminary extraction tests with 0.1 M reagents (in carbon tetrachloride) from aluminum nitrate, sulfate and phosphate solutions,[3] either precipitates or emulsions which may have been due to precipitates were encountered with both di-n-butyl- and di-isoamyl- but not with di(2-ethylhexyl)phosphoric acid. (Under the same conditions, extractions with mono(2-ethylhexyl)phosphoric acid gave turbid organic phases which cleared slowly but completely.)

In a test with pure aluminum solution (2.74 g Al/l, 0.5 M SO_4, pH 1.1, extracted with 0.4 M di-n-octylphosphoric acid in kerosene, phase ratio 1:1), a precipitate began to form within a few minutes. In an hour the entire organic phase had formed a gel, from which a gummy residue was obtained. Analysis of the clarified organic and aqueous phases indicated that about 60% of the organic acid and about 85% of the aluminum were removed by the precipitate. Negligible aluminum was found in the clear

Table 16

EXTRACTION OF ALUMINUM FROM VARIOUS SOLUTIONS

0.1 M Di(2-ethylhexyl)phosphoric Acid*
in kerosene with 2% 2-ethylhexanol

Phase Ratio, aqueous/organic = 1

Anion	M	pH	Time	g Al/l Aqueous Head	g Al/l Organic Extract	E_a^o
Chloride						
HCl	4		2 min	2.65	0.001	
"	"		16 hr	"	.012	0.005
HCl-NaCl	0.5	1.0	2 min	2.54	.002	
"	"	"	16 hr	"	.013	.005
Nitrate						
HNO_3	4		2 min	2.59	.002	
"	"		16 hr	"	.010	.004
HNO_3-$NaNO_3$	0.5	1.0	2 min	2.68	.003	
"	"	"	16 hr	"	.034	.01
Sulfate						
H_2SO_4	4		2 min	2.74	<0.001	
"	"		16 hr	"	.003	.001
H_2SO_4-Na_2SO_4	0.5	1.0	2 min	2.76	.002	
"	"	"	16 hr	"	.014	.005
Phosphate						
H_3PO_4	4		2 min	1.88	.002	
"	"		16 hr	"	.022	.01
H_3PO_4	0.7	1.0	2 min	1.99	.007	
"	"	"	16 hr	"	.008	.004

*Two-minute tests: Reagent Batch C, agitation by hand.
Sixteen-hour tests: Reagent Batch G, agitation in wrist-action shaker.

organic phase. The acid:aluminum mole ratio indicated for the precipitate was 2.8, suggesting a normal aluminum salt. In a parallel test in which the kerosene diluent was modified with 4% 2-ethylhexanol, precipitation and gelation occurred similarly but in smaller amount, about 30% of the aluminum and 20% of the organic acid being removed by the precipitate. It may be noted that the conditions of these tests matched the one-hour, pH 1.1 test shown in Table 14, and that none of the aluminum extractions with the branched-chain dialkylphosphoric acids listed in Tables 14, 15, and 16, tested at up to 16 hours contact time, either with or without 2-ethylhexanol in the kerosene diluent, showed any precipitation or difficult emulsions.

IV. URANIUM STRIPPING

For a solvent extraction system to be successful, it must be possible to remove the extracted uranium from the organic solvent by techniques which are economically and operationally practicable. Methods which have been examined for recovering the uranium from di(2-ethylhexyl)phosphoric acid in kerosene have included the use of sodium carbonate, sodium hydroxide, mineral acids and mixtures of mineral acids with their salts. The results from these studies are described below.

Stripping With Sodium Carbonate

When solutions of sodium carbonate are used as the stripping agent the uranium in the organic phase is transferred to the aqueous phase as a soluble carbonate complex. At the same time, the organophosphate complexed with the uranium together with any excess organophosphorus acid is converted by the alkaline sodium carbonate solution to the sodium salt. Equations depicting these reactions, sufficiently accurate for the purposes of the present discussion, may be given as follows:

$$UO_2(Org)_2 + 3Na_2CO_3 = 4Na^+ + UO_2(CO_3)_3^{\equiv\equiv} + 2Na(Org) \quad (5)$$

$$2H(Org) + Na_2CO_3 = 2Na(Org) + H_2O + CO_2 \quad (6)$$

where (Org) = the dialkylphosphate radical

If the alkyl chains are sufficiently long, the sodium dialkylphosphate salts formed by the above reactions are essentially insoluble in the aqueous sodium carbonate strip solutions (e.g., around 30 ppm sodium di(2-ethylhexyl)phosphate in 10% sodium carbonate solution). On the other hand, these salts have certain solubility characteristics in respect to the organic diluents which require special consideration. For example, as shown in Table 17, the sodium salt of di(2-ethylhexyl)phosphoric acid is appreciably soluble in solvents such as isopropyl ether, hexone and carbon tetrachloride. However, when the reagent was used in diluents more suitable for process use, such as kerosene, a third liquid phase was formed upon contact with the sodium carbonate solution. This third phase,

Table 17

SOLUBILITY OF THE SODIUM SALT OF DI(2-ETHYLHEXYL)-PHOSPHORIC ACID IN VARIOUS DILUENTS

Test Procedure

Equal volumes of 0.1 M reagent (Batch F) in diluent and 10% sodium carbonate shaken together for 2 minutes (by hand), centrifuged, and observed for third layer formation.

Diluents in which no third phase was observed:

Ligroin (Eastman D-.72-.74)
Toluene
Hexone
Toluol (Esso)
Carbon tetrachloride
n-Butyl acetate
iso-Propyl ether

Diluents in which third phase was observed:

Kerosene
n-Decane
n-Hexane*
n-Octane*
Amsco-127-5
-190-10
-122-15
-119-90N
-149-92-BR
-125-90-W
-119-92-BR
-160-82
-110-15
-Solvent G
-Naphtha-125-82
Gulf Solvent-BT
" Stoddard Solvent
Esso-Varsol
-Solvesso xylol
-Solvesso 100
-Solvesso 150
Shell Hi Flash Mineral Spirits
" 8233-Dispersol
" TS-28R Solvent
Petbyco Hi Flash Naphtha
" Solvent F-80
Kopper's Hi Flash Naphtha
Socony-Vacuum Sovaspray-100
Ultracene
Tetrachloroethylene

---

*No third phase with Batch C di(2-ethylhexyl)phosphoric acid. This reagent contained about 9% inert material. Assuming this to be 2-ethylhexanol, the 0.1 M solution of reagent would contain ~0.3 w/v % alcohol.

containing the sodium dialkylphosphate salt with some organic diluent and water, lay between the organic diluent and the strip solution. A number of other alkylphosphoric acids which were tested in the same manner gave similar results, the third phase appearing sometimes as a viscous liquid between the kerosene and aqueous phases and sometimes as a solid.* Operation of a process may be possible in spite of the third phase formation and attention is being given to this. Mechanical operation should be better, however, if the separation of a third phase could be prevented.

Modification Of The Kerosene Diluent. It is possible to eliminate the formation of the third phase during alkaline stripping in most cases (certainly with di(2-ethylhexyl)phosphoric acid) by adding a prescribed quantity of a long-chain branched alcohol, e.g., 2-ethylhexanol or capryl alcohol, to the kerosene, thus permitting a ready recycle of the organic solvent to the extraction system.** The quantity of alcohol that must be added to kerosene*** varies with the type of organic reagent, the reagent concentration, the type of alcohol, and the temperature. The requirements as determined for several alcohols when used with 0.1 M di(2-ethylhexyl)phosphoric acid in kerosene are given in Table 18. Requirements for a particular alcohol, 2-ethylhexanol, when used with three different dialkylphosphoric acids are shown in Table 19.

In general (see Table 18) the branched chain primary alcohols such as 2-ethylhexanol and 4-ethyloctanol are effective additives whereas (apart from capryl alcohol) the longer chain, more highly branched secondary alcohols were not as efficient. In regard to the differences between different reagents, it may be noted (Table 19) that the alcohol requirements for the branched compounds, di(2-ethylhexyl)phosphoric acid and di(diisobutylmethyl)phosphoric acid, were similar whereas third phase formation was not prevented with the straight-chained di(n-octyl)-

---

*Liquid third phases were obtained with three branched-chain dialkylphosphoric acids, i.e., 2-ethylhexyl-, diisobutylmethyl-, and 3,5,5-trimethylhexyl-. The straight-chained di(n-octyl)phosphoric acid gave a solid precipitate.

**Additives other than alcohol may also be useful for this purpose and will receive study.

***The quantities of alcohol required would also be different for diluents other than kerosene. See footnote, Table 17.

Table 18

USE OF ALCOHOLS TO MAINTAIN MISCIBILITY

OF SODIUM SALT OF DI(2-ETHYLHEXYL)PHOSPHORIC ACID

AND KEROSENE

Test Conditions

Di(2-ethylhexyl)phosphoric Acid (Batch F) = 0.1 M.
Equal volumes of organic phase and 10% sodium carbonate solutions.

Alcohol	Type[a]	% (wt/vol) To Prevent 3rd Phase
n-Octanol	1°	0.9[b]
2-Ethylhexanol	1°	1.0
Capryl	2°	1.0
4-Ethyloctanol	1°	0.9
Tridecyl B (3-Neopentyl-5,5-dimethyl hexanol)	1°	1.5
Undecanol (5-ethyl-nonanol-2)	2°	2.5
Diisobutylcarbinol	2°	3.5 - 4.0
Trimethylnonanol (2,6,8-trimethyl-nonanol-4)	2°	7.5
Tetradecanol (7-ethyl-2-methyl-undecanol-4)	2°	7.5
Heptadecanol (3,9-diethyl-tridecanol-6)	2°	>12[c]

a) Standard notation: 1° = primary alcohol
2° = secondary alcohol

b) Batch J reagent.

c) Third phase at all levels tested.

Table 19

2-ETHYLHEXANOL REQUIRED TO MAINTAIN MISCIBILITY IN KEROSENE WITH SODIUM SALTS OF SEVERAL DIALKYLPHOSPHORIC ACIDS

Test Conditions

0.1 M Reagent in kerosene

Equal volumes of reagent phase and 10% sodium carbonate

Dialkylphosphoric Acid	2-Ethylhexanol % (wt/vol) To Prevent 3rd Phase
2-Ethylhexyl, Batch F	1
Diisobutylmethyl, Batch D	1
n-Octyl, Batch A	>10*

*Emulsion or precipitate at all levels tested.

phosphoric acid even at alcohol concentrations in excess of 10% (wt/vol). Although the data here are limited, it is felt that the effect of chain-branching as indicated is significant and of general import. Somewhat similar effects from chain-branching on diluent compatibilities have been observed in studies with other types of extractants.

Measurements of alcohol requirements as a function of reagent (di(2-ethylhexyl)phosphoric acid) concentrations are given for three different alcohols in Figures 6, 7, and 8. In each case, at a given temperature, the amount of alcohol required could be related to the reagent concentration by a linear equation, i.e.,

$$\text{w/v \% capryl alcohol} = 0.5 + 4.0\ \underline{M} \text{ at } 26^{\circ}\text{C} \qquad (7)$$

$$\text{w/v \% 2-ethylhexanol} = 0.6 + 4.0\ \underline{M} \text{ at } 30^{\circ}\text{C} \qquad (8)$$

$$\text{w/v \% 4-ethyloctanol} = 0.5 + 4.0\ \underline{M} \text{ at } 27^{\circ}\text{C} \qquad (9)$$

where $\underline{M}$ = the molar concentration of the reagent in kerosene.

Conformity of the data to the above expressions, in the cases cited, is exceptionally close and reproducible. Also, the appearance and disappearance of the third phase, created by the sodium organophosphate salt, was sufficiently sensitive to the threshold alcohol level given by the equations so as to permit the use of ordinary titration techniques in the experimental measurements. In some cases the reagent-kerosene solution in contact with aqueous sodium carbonate solution was titrated directly with alcohol. In others the reagent-kerosene solution already containing alcohol was titrated with an alcohol-free reagent-kerosene solution. Sharp and reproducible endpoints were given by visual observation of third phase formation or disappearance.

The measurements described above for 2-ethylhexanol were made at a temperature of 30°C. At lower temperature slightly less alcohol is required (see Figure 7). In actual practice, of course, the quantity of alcohol used would be in reasonable excess of the threshold requirements for third phase prevention as shown. Ordinarily in studies at this laboratory, 2 w/v % alcohol was used with 0.1 $\underline{M}$ di(2-ethylhexyl)phosphoric, 3% for 0.3 $\underline{M}$ and 4% for 0.4 $\underline{M}$.

[redacted]

ORNL-LR-Dwg. 7075

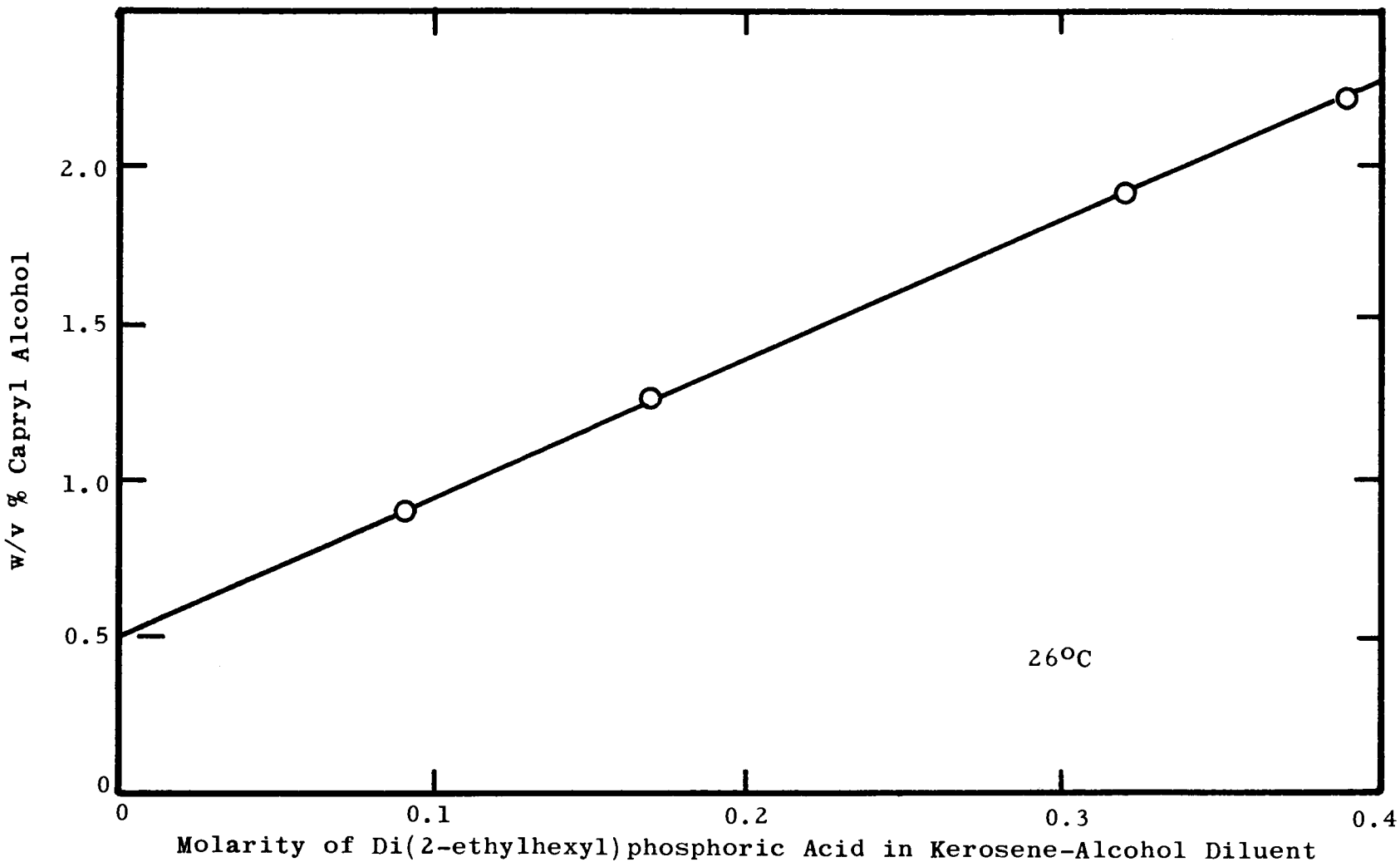


Figure 6

CAPRYL ALCOHOL REQUIREMENT FOR MISCIBILITY

Sodium di(2-ethylhexyl)phosphate in kerosene vs. 10% sodium carbonate

[redacted]

ORNL-LR-Dwg. 7072

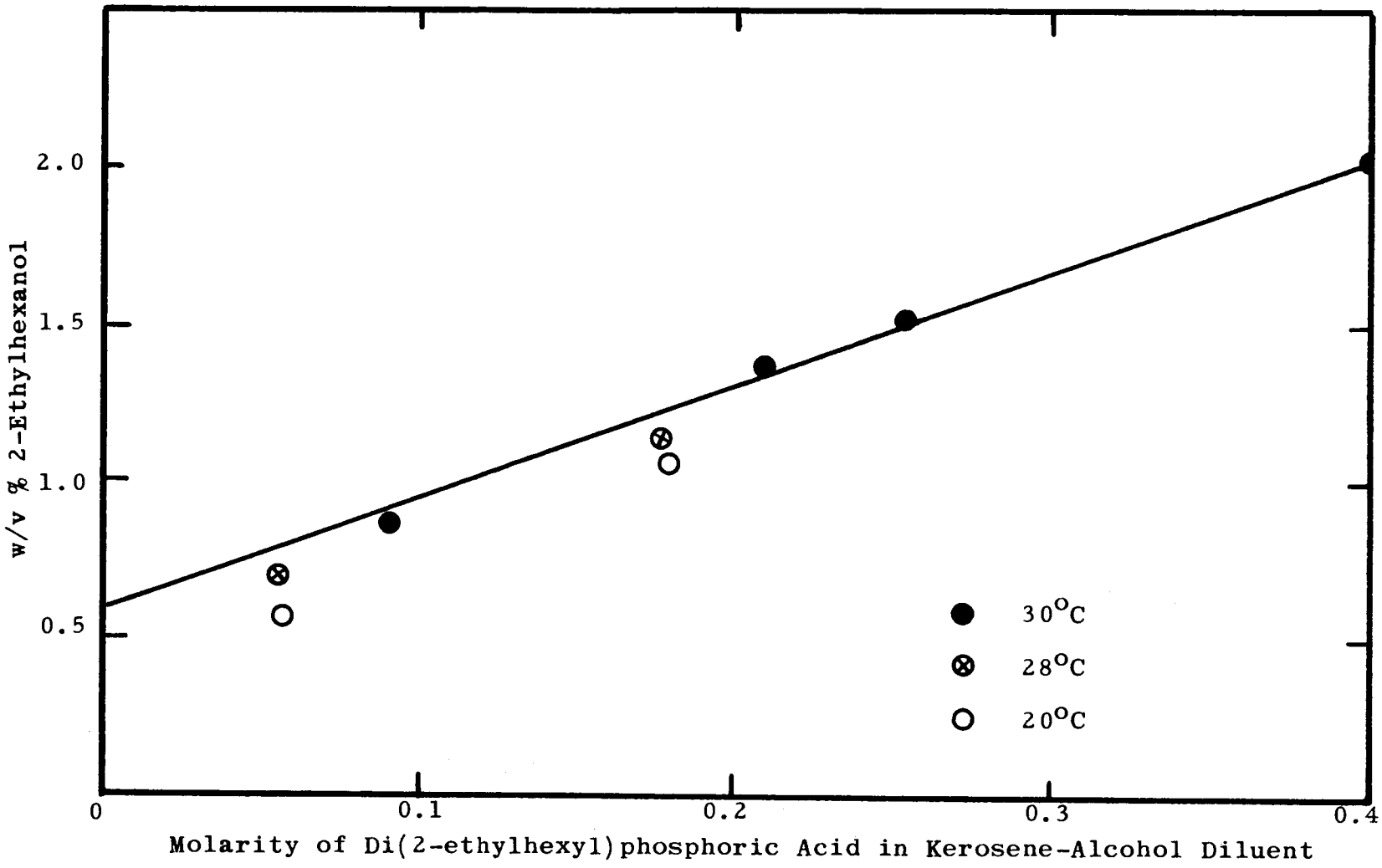


Figure 7

2-ETHYLHEXANOL REQUIREMENT FOR MISCIBILITY

[redacted]ylhexyl)phosphate in kerosene vs. 10% sodium carbonate

[redacted]

ORNL-LR-Dwg. 7076

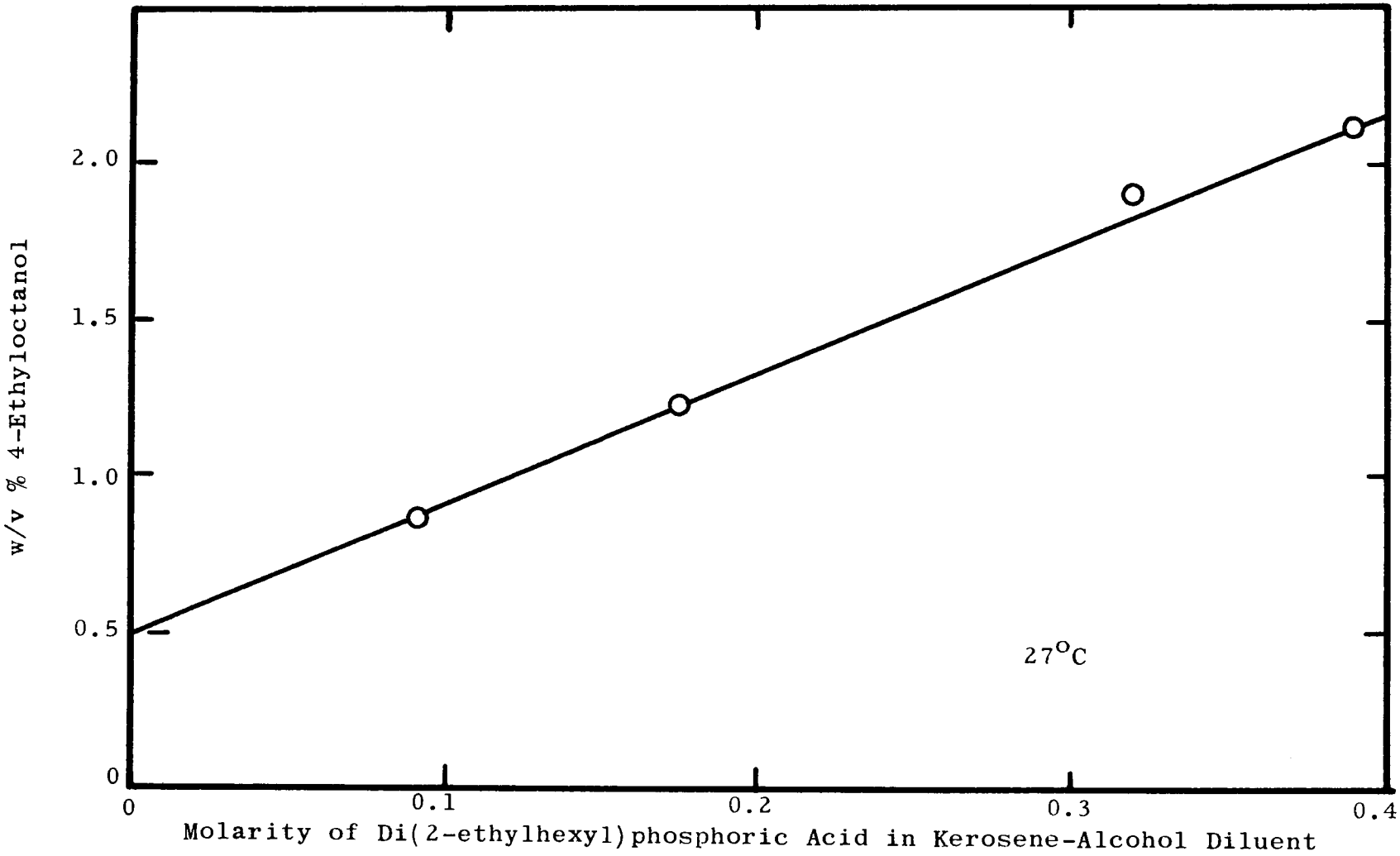


Figure 8

4-ETHYLOCTANOL REQUIREMENT FOR MISCIBILITY

[redacted]thylhexyl)phosphate in kerosene vs. 10% sodium carbonate

Uranium Loading In Sodium Carbonate Strip Solutions. As shown by the data in Table 20, relatively high concentrations of uranium can be obtained in the sodium carbonate strip solution. In the series of tests described a given volume of 10% Na_2CO_3 solution was contacted successively with equal volumes of a kerosene-alcohol solution 0.1 M in di(2-ethylhexyl)phosphate and containing 5.7 grams of uranium per liter. With each successive contact the amount of uranium taken into the strip solution increased uniformly, and the uranium left in the organic remained low, until a concentration of 44 g U/l (52 g U_3O_8/l) was obtained in the aqueous phase. At this point about 80% of the sodium carbonate stripping agent (by calculation on basis of Equations (5) and (6)) had been consumed. With further contacts the stripping efficiency fell off markedly but the uranium in the aqueous increased slowly to 51 g U/l (60 g U_3O_8/l). By this time, according to calculations, 100% of the sodium carbonate should have been consumed, and this was confirmed by direct analysis for carbonate in the liquor (see Table 20). Also, it should be noted that the final uranium concentration was very close to the solubility limit for sodium uranyl tricarbonate in water.(17)

From these data, it is apparent that stripping with sodium carbonate could be achieved in a single stage operation if the concentration and phase ratio were appropriately adjusted. Thus, if the loaded organic solution utilized above were contacted for an equivalent period of time with 10% sodium carbonate at an organic/aqueous phase ratio of 8, a concentration of 45 g U/l would be expected in the aqueous phase, i.e., essentially the same concentration observed after 8 contacts in the cascade tests. An experiment confirming this expectation is described in Table 21. In actual practice more than one contacting stage (probably two stages) would ordinarily be used. The additional stage, or stages, would permit a greater command of the contact time, further reduction of the uranium concentration remaining in the organic, somewhat greater loadings of uranium in the aqueous strip solution (dependent upon the contact time) and thus more efficient utilization of the stripping agent.

Although 10% Na_2CO_3 solutions appear to be about optimum for the stripping operation, lower concentrations may also be used subject to the slight increase in extractant loss as shown in Table 23. For example, when four volumes of the uranium-bearing organic solution described above was contacted with one volume of 5% sodium carbonate solution (Table 21), the resulting aqueous phase contained ~23 g U/l and the uranium concentration in the

Table 20

URANIUM LOADING OF A SODIUM CARBONATE STRIP SOLUTION

Aqueous Phase = 10% Na_2CO_3

Organic Phase = 0.1 M Di(2-ethylhexyl)phosphoric Acid, Batch G
5.75 g U/liter
0.056 g Al/liter
in kerosene with 2 w/v % 2-ethylhexanol

Phase Ratio, equal volumes at each stage.

Contact Time, 10 minutes (wrist-action shaker)

Temperature = 25°C

Contact No.	Conc. of U in Carbonate Solution g/l	Conc. of U in Stripped Organic g/l
1	5.7	0.015
2	11.5	.04
3	17.1	.06
4	22.8	.10
5	28.4	.12
6	33.9	.14
7	39.4	.18
8	(44.9)	(.20)
9	48.0	3.1
10	49.6	3.5
11	50.8	4.1
12	51.0	5.6

Loaded strip solution:

51 g U/liter
42.2 g CO_3/liter (mole ratio CO_3/U = 3)
Final pH = 7.1 (initial pH of 10% Na_2CO_3 = 11.5)

Table 21

SINGLE-STAGE STRIPPING TESTS WITH

SODIUM CARBONATE SOLUTIONS

Organic Phase = 0.1 M Di(2-ethylhexyl)phosphoric Acid, Batch G, 2% (wt/vol) 2-ethylhexanol
5.7 g U/l
0.056 g Al/l

Contact Time = 5 min (wrist-action shaker)

Temperature = 25°C

% Na_2CO_3	Phase Ratio organic/aqueous	Uranium Distribution (g/l)	
		Organic Phase	Aqueous Phase
10	8	0.17*	45
5	4	0.10	23

*A second extraction with fresh 10% Na_2CO_3 reduced the uranium level to 0.007 g U/l.

organic had been reduced to 0.1 g U/l. The concentration of uranium attainable in the strip solution decreases directly with decreasing sodium carbonate concentration as prescribed by Equations (5) and (6). The consumption of sodium carbonate per pound of uranium, on the other hand, should be almost independent of the sodium carbonate concentration over the range considered.

Concentrations of sodium carbonate greater than 10% would become comparatively less favorable as stripping agents. Previous work[18] has shown a decreased solubility of uranium (sodium uranyl tricarbonate) in aqueous systems when the salt concentration (ionic strength) is increased. As a consequence, lower loadings and less efficient reagent utilization would be expected at the high sodium carbonate levels.

Methods for recovering the uranium from the loaded carbonate strip solutions are not reported here. Such methods are well established and are in use in several plants.

Removal Of Metals Other Than Uranium By The Sodium Carbonate Strip. Metals other than uranium that have been extracted into the organic phase are effectively and irreversibly removed by the sodium carbonate strip. For example, any vanadium present, dependent upon oxidation state, is dissolved or precipitated by the alkaline solution whereas any extracted iron, aluminum, titanium, etc. are precipitated as their hydrous oxides.

In preliminary continuous countercurrent (mixer-settler) runs on the extraction-stripping process, significant quantities of ferric hydroxide have been precipitated in the stripping cycle without causing appreciable difficulty. A weak emulsion appeared in the first stripping settler but remained at a constant level after the first two hours of operation. The ferric hydroxide precipitate formed was wet by and expelled with the aqueous carbonate phase. Performance of the process under conditions wherein very large amounts of hydrolyzable metals are extracted by the organic is not known. Since ferric iron is the important offender, it is anticipated at this time that the leach liquor or slurry would be reduced, or partly reduced, in order to optimize performance in both the extraction (see above) and stripping steps. Further studies of the tolerable limits for ferric iron are being made in continuous closed cycle extraction-stripping tests (see below).

Stripping With Other Alkaline Stripping Reagents

Aqueous sodium hydroxide precipitates uranium directly from the organic phase as sodium uranates. Subject to the loss of reagent to the alkaline solution, discussed in the following section, 2-15% aqueous solutions of sodium hydroxide were very effective in stripping uranium from di(2-ethylhexyl)phosphoric acid. (Since the sodium salt of the reagent is formed in this stripping operation, as in that described in the previous section, the addition of a modifier is needed to maintain reagent-diluent compatibility.) Chemically, this presents an attractive method of stripping, since the uranium product is obtained directly with a consumption of reagent which is limited to the amount required to form the sodium salt of the extractant and the stoichiometric equivalent of the extracted metals. Barring excessive build-up of alkali-soluble metal ions (e.g., aluminate) the stripping solution could presumably be recycled to obtain essentially complete reagent utilization. On the other hand, large quantities of precipitate obtained under such conditions are sometimes difficult to handle in scaled-up operations and, as experienced in tests with some other reagents, may occlude excessive amounts of the organic solvent. Further information would be necessary in order to weigh the relative advantages and disadvantages.

In other tests of sodium hydroxide stripping, it was found that solution concentrations greater than 15% (w/v) were less effective than the dilute solutions described above. Limited tests with ammonium hydroxide solutions, dilute or concentrated, and ammonia gas have shown these reagents to be less effective than sodium hydroxide.

Compatibility Of Other Organophosphorus Acids With Alkaline Stripping. The extension of the alkaline stripping method to other organophosphorus acids such as monoalkylphosphoric acids hinges on two factors - the ability to prevent separation of a third phase, and the extent of loss of the sodium organophosphate to the alkaline solution (cf. measurements of loss of di(2-ethylhexyl)phosphoric acid to aqueous solutions, below). As previously reported,[3] the sodium salt of mono(2-ethylhexyl)phosphoric acid is very soluble in 10% sodium carbonate solutions. As a matter of fact, its solubility has been used at this laboratory to separate mono- and di(2-ethylhexyl)phosphoric acids. On the other hand, the solubility of such compounds in aqueous systems can generally be decreased by increasing the chain length (molecular weight). For example, in one preliminary

test with a 14-carbon mono compound (mono(4-ethyl-1-isobutyloctyl)phosphoric acid), the sodium salt solubility has been found to be only about 1 g/l in 10% sodium hydroxide. At the same time, 2-3% of 4-ethyloctanol was required to prevent separation of the 0.1 M sodium organophosphate as a third phase. Monoalkylphosphoric acids with longer branched alkyl chains would presumably be even less soluble. More tests would be necessary to determine whether the performance with somewhat shorter chain compounds would fall between the very soluble 8-carbon compound and the less soluble 14-carbon compounds.

As might be expected, the response of the dialkyl phosphinic acids to alkaline stripping has been very similar to the dialkylphosphoric acids. In the extraction cycle, some of the phosphinic acids have given indications of performance superior to the phosphoric acids. However, according to estimates by the Virginia-Carolina Chemical Corporation, the cost of producing these reagents, even in commercial quantities, would be rather high. Alkaline stripping of the monoalkyl phosphonic acids has not been examined but, presumably, their response would be qualitatively similar to the monoalkylphosphoric acids.

Stripping With Mineral Acids

Stripping with acids may be assumed to follow a reversible reaction as described by the following equation:

$$2H^{+}_{(aq)} + UO_2(R_2PO_4)_{2(org)} \rightleftharpoons 2HR_2PO_{4(org)} + UO_2^{++}_{(aq)} \qquad (10)$$

Since this is simply the reverse of the reaction described by Equation (1), the same factors which affect uranium extraction from acid liquors will also be important in determining stripping efficiency of mineral acids.* Stripping coefficients from a particular extraction reagent will, therefore, increase with increasing acidity and increasing concentration of aqueous complexing anions (e.g., sulfate), and decrease as the concentration of the organic reagent increases.

Acid stripping studies of both mono- and dialkyl phosphoric acids were reported sometime ago.(4) The portion

---

*Obviously, the stripping coefficient is the reciprocal of the extraction coefficient, $S_o^a = 1/E_a^o$, if the system reaches true reversible equilibrium.

of these studies dealing with di(2-ethylhexyl)phosphoric acid is present along with more recent studies below.

Useful stripping coefficients have been obtained when moderately concentrated mineral acid solutions were used to strip uranium from di(2-ethylhexyl)phosphoric acid, as shown in Table 22 and Figure 9. In addition to the measured stripping coefficients, Table 22 includes estimated coefficients obtained from the extractions from sulfuric acid solutions, Table 4, and from phosphoric and hydrochloric acid solutions, Appendix B. The measured stripping coefficients are in good enough agreement with those estimated from extractions to show that the uranium stripping (like the uranium extraction) was essentially at equilibrium within the contact time used.

As expected on basis of the considerations mentioned above, and as has been reported previously,(4) the order of stripping effectiveness at a given molarity was phosphoric acid > sulfuric acid > hydrochloric acid, and the effectiveness of each increased rapidly with increasing acid concentration. Replacing a part of the sulfuric acid with sulfate salt did not impair the stripping efficiency. However, replacing a part of the hydrochloric acid with chloride salt did impair its stripping efficiency, at least in the absence of alcohol. These results are in line with the much more extensive complexing of uranyl ion by sulfate than by chloride. The presence of alcohol increased the stripping coefficients with sulfuric and phosphoric acids as expected. The effect was similar with 3 M hydrochloric acid, but the presence of alcohol had little effect on stripping with 6 M, and decreased the stripping coefficient with 10 M, hydrochloric acid. (This suggests a shift in extraction mechanism at high concentration, which might be related to the effect of high nitrate concentration, Appendix B.)

The cursory iron stripping tests given above in Table 13 showed that iron was more completely stripped than uranium by dilute hydrochloric or sulfuric acid. Thus, all iron extracted will report with uranium to the strip solution.

If uranium is recovered from the strip solution by simple hydrolytic precipitation, neutralization of the moderately high acid concentrations needed would involve a considerable chemical expense. In sulfate stripping, the results indicate that this cost can be decreased by the use of acid-salt mixtures, decreasing the amount of base required for neutralization and also permitting the recycle of some portion of the sulfate. Further tests would be

Table 22

STRIPPING URANIUM WITH ACIDIC SOLUTIONS FROM DI(2-ETHYLHEXYL)PHOSPHORIC ACID

Organic: Reagent Batch J in kerosene containing 2.0 g U/liter, 2-ethylhexanol as indicated
Phase Ratio: aqueous/organic = 1
Agitation = 10 min (wrist-action shaker)

Stripping Agent	Stripping Coefficient, S_o^a			
	from 0.1 M reagent		from 0.2 M reagent	
	No Alcohol	2% Alcohol	No Alcohol	2.8% Alcohol
3 M HCl	0.6	1.3	0.1	0.4
1.5 M HCl + 0.75 M $CaCl_2$	0.2	1.4	---	---
6 M HCl	6.4	7.7,(6.7)[a]	1.6	2.5
3 M HCl + 1.5 M $CaCl_2$	2.2	---	---	---
10 M HCl	35	5.9	11	2.7
1.5 M H_2SO_4	1.0	1.8,(1.4)[b]	0.1	0.4,(0.3)[b]
3 M H_2SO_4	2.5	6.2	0.6	1.7
1.5 M H_2SO_4 + 1.5 M $(NH_4)_2SO_4$	2.1	---	---	---
6 M H_2SO_4	14	44,(34)[b]	3.6	9.2,(7.2)[b]
2 M H_2SO_4 + 4 M $(NH_4)_2SO_4$	18	---	---	---
1.5 M H_3PO_4	2.1	5.1,(5.0)[a]	0.5	1.1
3.3 M H_3PO_4	15	---	---	---
5.3 M H_3PO_4	100	330,(>100)[a]	20	90

a) Estimated from extraction coefficients ($S_o^a = 1/E_a^o$), Appendix B.
b) Estimated from extraction coefficients ($S_o^a = 1/E_a^o$), Table 4.

[redacted]

ORNL-LR-Dwg. 7077

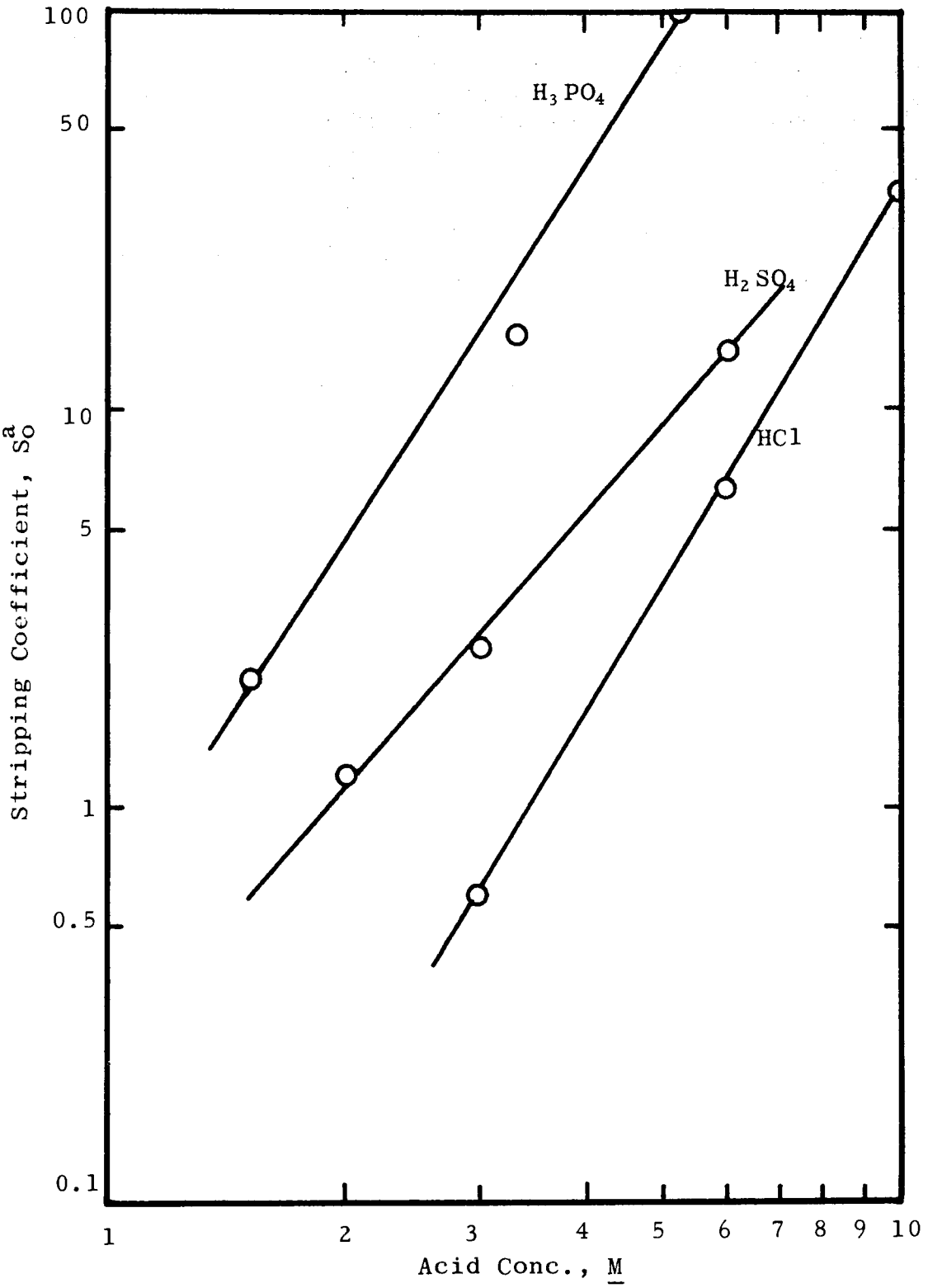


Figure 9

URANIUM STRIPPING WITH MINERAL ACIDS

from
0.1 M Di(2-ethylhexyl)phosphoric Acid/Kerosene

required to indicate the feasible limit of this procedure. The use of acid-salt mixtures may not be suitable in hydrochloric acid stripping. Workers at the Dow Chemical Company have studied the recovery of uranium from 10 M hydrochloric acid strip solution by distillation of the HCl and subsequent reconcentration of the distillate to 10 M for recycle.[19] (They have also considered the recovery of uranium from acid strip solutions by ion exchange or by a separate solvent extraction cycle.[20]) Since 6 M (i.e., constant-boiling) hydrochloric acid could be used for stripping 0.1 M di(2-ethylhexyl)phosphoric acid, a similar but simpler system might be feasible, with direct recycle of the distillate.

Sufficient attention will be given to acid stripping in future work to permit economical comparisons with the alkaline stripping methods.

V. LOSSES OF EXTRACTANT (AND ALCOHOL) THROUGH SOLUBILITY IN THE LEACH LIQUOR AND STRIP SOLUTIONS

For acceptable economic performance of a solvent extraction system, it is necessary that the losses of extraction reagents incurred during the operation be low. One of the ways in which reagents may be lost is by distribution to (solubility in) the aqueous solutions with which they come in contact. In contrast to entrainment losses, which are a function of the physical operation of the system, this loss by aqueous solubility involves an equilibrium process which can be evaluated in terms of the solvent and aqueous compositions. Such evaluations for the reagents and liquors described in this report are presented under the appropriate headings below.

Loss Of Extractant To Acid Liquors

Tests have been made to determine the solubility (distribution) of di(2-ethylhexyl)phosphoric acid in acidic sulfate liquors similar in composition to those ordinarily encountered during ore processing. In one test a volume of accurately titrated 0.1 M di(2-ethylhexyl)phosphoric acid in kerosene (2% 2-ethylhexanol) was contacted with 200 volumes of solution (0.5 M SO_4, pH = 1), after which the organic phase was retitrated for reagent content. Two other tests were identical to the first except for a difference in aqueous-organic phase ratio (400) and in the aqueous composition (0.2 M SO_4, pH = 1, and 0.2 M SO_4, pH = 1.7). A fourth test employed the latter test conditions but the organic diluent contained no modifying alcohol.

In all of the tests described, any difference from the original reagent concentration in the organic phase, after contacting with the aqueous liquor, was beyond the limits of detection by the titration method used. Since the sensitivity of the method should be sufficient for detection of a 4% change in concentration, it may be calculated from the volume employed that the amount of reagent lost must correspond to a concentration of less than 5 ppm* in the

---

*As indicated from semiqualitative tests, the solubility of di(2-ethylhexyl)phosphoric acid in pure water is about 60 ppm. Similar measurements for di(2-ethylhexyl)phosphinic acid showed a solubility, in water, of about 35 ppm. Distribution of phosphinic acid from a 0.1 M kerosene solution was 3-14 ppm to water and 1-4 ppm to acidic sulfate liquors.

aqueous phase. From a process application standpoint, such a loss would be insignificantly low. For example, if a liquor containing 1 g U/l was extracted the amount of reagent lost through solubility would amount to less than 0.01 lb/lb of uranium recovered. Other measurements (although inherently less accurate than those described above) have also indicated low losses of di(2-ethylhexyl)-phosphoric acid to acidic solutions somewhat different in composition. Cyclic extraction on liquors prepared by sulfuric acid leaching of Florida Leached Zone ores have been carried through numerous contacts with no detectable change in reagent concentration. Similarly, stripping tests utilizing concentrated mineral acids have been made repeatedly without detectable reagent loss.

The solubilities shown above for the di-substituted phosphoric acid, i.e., di(2-ethylhexyl)phosphoric acid, are much lower than those which would be obtained with the mono-substituted, mono(2-ethylhexyl)phosphoric acid and the two reagents should not be confused. For example, under similar conditions the solubility of the mono(2-ethylhexyl)phosphoric acid in the acidic liquors would be in the order of 2-3 g/l. Within either compound class, the solubilities would increase or decrease with decreasing or increasing chain lengths (molecular weight). Diethyl-phosphoric acid, for instance, is fairly soluble in aqueous acidic liquors whereas monotetradecylphosphoric acid has a low solubility.

Solubility Of Di(2-ethylhexyl)phosphate In Alkaline Solutions

Losses of the di(2-ethylhexyl)phosphate reagent to alkaline solutions of the type that might be employed in alkaline stripping operations have been measured according to a procedure similar to that described in the preceding section. In each case the reagent-kerosene phase was contacted with large volumes of the solutions listed in Table 23 after which it was acidified (to reconvert the sodium organophosphate to the acid form) and titrated for concentration change.

Although sodium di(2-ethylhexyl)phosphate is quite soluble in water, the solubility losses to the ionic solutions in Table 23 were in all cases low. A general decrease in loss was observed as the concentration of ions in the aqueous phase increased. The solubility loss to 10% sodium carbonate solution was also measured from 0.1 M solution in kerosene without alcohol. As previously described, the reagent separated as a third liquid phase of highly-concen-

Table 23

SOLUBILITY OF SODIUM DI(2-ETHYLHEXYL)PHOSPHATE

IN ALKALINE SOLUTIONS

Reagent: 0.1 M Di(2-ethylhexyl)phosphoric Acid (Batch G) with 2% 2-ethylhexanol.

Phase Ratio, aqueous/organic = 100

Alkaline Reagent	% (wt/vol)	Temp., °C	Solubility* of Di(2-ethylhexyl)phosphoric Acid (mg/l)
Na_2CO_3	2	33	325
	5	"	125
	10	"	27
	15	"	7
NaOH	2	29	270
	5	"	55
	10	"	7
	15	"	1
NH_4OH	10	30	325
$(NH_4)_2CO_3$	10	25	70
$Na_4UO_2(CO_3)_3$ + Na_2CO_3**		20	75

*By titration difference.

**Corresponds to 5% Na_2CO_3 strip solution loaded with uranium to 20 g U/l. Phase ratio, aqueous/organic = 17.

trated sodium di(2-ethylhexyl)phosphate,* from which the distribution to the aqueous phase would be expected to be at a maximum. The solubility found was 26 ppm at 27°C, essentially identical with the 27 ppm (Table 23) in equilibrium with the homogeneous 0.1 M solution containing 2% alcohol. Thus, the reagent loss appears to be limited by saturation of the aqueous carbonate solution rather than to be a distribution proportional to its concentration in the organic phase. This conclusion is further supported by essentially identical results from other tests in which (because of different phase ratios used) the final concentration of reagent in the organic phase varied from 0.1 to 0.06 M.

Table 23 also demonstrates that the losses in uranium stripping operations may be even lower than those indicated to pure sodium carbonate solutions. A uranium solution was prepared to simulate the composition of a carbonate strip solution initially 5% Na_2CO_3 (0.47 M), after sufficient stripping had taken place to reach a uranium level of 20 g/l. The uranium was added as sodium uranyl tricarbonate, $Na_4UO_2(CO_3)_3$, and the carbonate was adjusted to 0.47 M by the addition of sodium carbonate. The loss to this solution from 0.1 M reagent was but 75 ppm which was considerably less than the indicated 125 ppm to 5 percent sodium carbonate.

In any case, from an application viewpoint, the losses to 5 and 10% sodium carbonate solutions are unimportant. If 10% sodium carbonate were used as a strip solution, the uranium loading (see page 47) should be in the order of 50 g U_3O_8/l. A loss several times greater than that shown could be tolerated to a solution this rich in uranium.

Determination Of Alcohol Concentrations In Organic Phase

The concentrations of alcohol remaining in the organic phase after contacts with aqueous liquor or strip solution have been measured by an indirect titration which uses as an end point the critical miscibility point of the sodium organophosphate with the organic diluent, as described in Section IV and Figures 6, 7, and 8. The procedure was as follows:

---

*The reagent-rich third phase also contains small amounts of kerosene and water; the reagent concentration is estimated to be about 2 M.

1) Contact the reagent-alcohol-diluent phase with an equal volume of 10% sodium carbonate.

2) Centrifuge both phases and observe for the presence of a third phase.

3a) When third phase is present, add from a calibrated dropper a 10% solution of the alcohol in kerosene, shaking and centrifuging after each addition until the third phase just disappears.

3b) If no third phase is present, add a measured amount of alcohol-free kerosene solution containing reagent at a known concentration higher than that in the original solution. Mix, centrifuge and observe for third phase. Repeat until a third phase is observed, then backtitrate as described in 3a.

4) From volumes added and the known original reagent (dialkylphosphoric acid) concentration* calculate the final reagent concentration.

5) Determine from the miscibility curve of Figures 6, 7, or 8 the quantity of alcohol required to maintain miscibility, and from this value subtract the amount of alcohol added in step 3a or 3b. The difference is the amount of alcohol in the original sample.

As mentioned previously (Section IV), duplicate analyses by this procedure were in good agreement, the variation in determinations being ordinarily no greater than 4% of the total loss of alcohol, i.e., plus or minus one drop of the kerosene-10% alcohol titrant, in the samples usually handled.

Distribution Of Alcohol To Acidic Solutions

Several tests have been made to determine the losses of various alcohols from the organic solvent by distribution to, or solubility in, the acid sulfate liquors. Some of the experimental results are listed in Table 24. In each test a single volume of organic solvent, 0.1 M di(2-ethylhexyl)phosphoric acid in kerosene-2% (wt/vol) alcohol, was equilibrated with several hundred volumes of of the aqueous solution. After separation the amount of alcohol remaining in the organic phase was determined according to the method outlined in the preceding section.

---

*As determined by pH titration of an aliquot of the organic phase.

Table 24

DISTRIBUTION OF ALCOHOL TO ACIDIC SOLUTIONS

Aqueous Composition			Phase Ratio	Equilibrium Conc. of Alcohol	
pH	SO_4 (M)	Alcohol	(aq/org)	w/v % in Org	ppm in Aq
1	0.5	2-Ethyl-hexanol	300	0.81	40
1	0.2	"	400	.60	36
1.7	0.2	"	400	.60	36
1	0.5	Capryl	800	.48	19
1	0.5	4-Ethyl-octanol	800	1.76	3

In order to determine whether the losses observed were saturation limited or were following a distribution law, a distribution coefficient for 2-ethylhexanol was calculated from the first experiment (0.5 M sulfate solution) and found to be

$$D^{aq}_{org} = 4.9 \times 10^{-3}$$

Using this, a calculation was made for the expected loss of 2-ethylhexanol after ten extraction stages in which 10 ml of the organic phase described above was contacted with 10 successive 200 ml volumes of the acid liquor (0.5 M SO_4, pH = 1). According to the calculation, 120 mg of 2-ethyl-hexanol should be lost to the total aqueous phase. An actual experiment was then made, following the above procedure, and the alcohol loss was determined by methods previously described. The measured loss was 130 mg, in good agreement with the calculated value.

Since the alcohol loss appears to follow a distribution relationship and since the equilibrium alcohol concentrations in the organic solvents shown in Table 24 are lower than would be present in process application, it follows directly that the concentrations shown in the aqueous solution are lower than would be experienced in actual practice.

The correspondence of the alcohol loss to a distribution relationship permits a calculation of losses to be expected in practice. As stated earlier, the alcohol concentration in a 0.1 M solution of di(2-ethylhexyl)phosphoric acid in kerosene would ordinarily be held during processing at 2 w/v percent. Using this value, along with distribution coefficients determined from data in Table 24, the expected losses of the various alcohols to the different liquors have been calculated and the data are listed in Table 25.

Table 25

ALCOHOL LOSS TO ACIDIC SOLUTIONS FROM KEROSENE SOLUTIONS MODIFIED WITH 2 W/V PERCENT OF VARIOUS ALCOHOLS

Aqueous Composition		Alcohol	Dist. Coeff.* D^{aq}_{org}	Calculated Conc. of Alcohol Expected in Aqueous (ppm)
pH	SO_4			
1	0.5	2-ethyl-hexanol	4.9×10^{-3}	98
1	0.2	"	6.0×10^{-3}	120
1.7	0.2	"	6.0×10^{-3}	120
1	0.5	Capryl	4×10^{-3}	80
1	0.5	4-ethyl-octanol	1.7×10^{-4}	3

*Calculated from Table 24.

In each case the indicated alcohol loss is small but significant. Thus, if the liquor contacted in an extraction process contained 1 g U/l the expected alcohol consumptions on a lb/(lb of U_3O_8 recovered) basis would be 0.085 lb for

2-ethylhexanol, 0.068 lb for capryl alcohol, and 0.003 lb for 4-ethyloctanol. The lower loss of the longer (branched) chain 4-ethyloctanol demonstrates an advantage to be gained in process application by using alcohols of higher molecular weight. The ethyloctanol itself is not presently available in quantity but other alcohols should also be useful and some are available at a reasonable price, e.g., primary branched decyl alcohols (21¢/lb) and primary branched tridecyl alcohols (24¢/lb).

Distribution Of Alcohol To Alkaline Solutions

Losses of 2-ethylhexanol, capryl alcohol and 4-ethyloctanol to solutions 10% (wt/vol) in sodium carbonate were determined in the same manner as that used for the acidic liquors above. In each case 0.1 M di(2-ethylhexyl)phosphoric acid in a kerosene diluent containing 2 w/v % of the appropriate alcohol was contacted with the aqueous solution at a high aqueous/organic phase ratio. Assuming conformity to the distribution law, the measured equilibrium concentrations of alcohol remaining in the organic phase were used to calculate the following distribution coefficients.

For 2-ethylhexanol: $D^{aq}_{org} = 2 \times 10^{-3}$

For capryl alcohol: $D^{aq}_{org} = 3 \times 10^{-3}$

For 4-ethyloctanol: $D^{aq}_{org} = < 10^{-6}$

The losses to the more highly salted sodium carbonate solutions were somewhat lower than for the acidic liquors. In any process application using sodium carbonate in the stripping cycle, the quantity of such liquor would be so low ($\sim$1/50 the leach liquor volume) and the uranium concentration so high ($\sim$50 g U_3O_8/l) that losses of the order shown above would be insignificant from a cost standpoint.

[redacted]

VI. EXTRACTION OF URANIUM FROM LEACH LIQUORS

In a previous section, data were presented for extraction of uranium and other metals from sulfate solutions which ordinarily contained only a single metal ion. The following section describes experiments showing the properties of di(2-ethylhexyl)phosphoric acid when used as an extractant for uranium from synthetic and actual leach liquors similar to those encountered during processing of some types of Western ores.

Most of the data are presented as extraction isotherms or equilibrium curves obtained from single-stage and cascade extractions. Such curves are ordinarily useful for the extrapolation of laboratory data to extractions in continuous multistage operations. Thus, from a solution of particular composition, it is usually possible to predict uranium concentration levels which may be reached in the organic phase at any desired phase ratio, the number of extraction stages required to achieve complete extraction, the extraction coefficients at each extraction stage, etc.

In addition to the single-stage tests, preliminary closed-cycle extraction-stripping runs have been made in continuous countercurrent extraction equipment. The results from this work are also summarized below.

Sulfate Liquors

Isotherms have been determined for the extraction of uranium with di(2-ethylhexyl)phosphoric acid from three different sulfate liquors; the compositions of these liquors are described in Table 26. Liquor S-2 is similar in major components to those that have been obtained during processing of ores from the Marysvale district, Utah. Liquor S-3 has less iron and aluminum and no fluoride, but contains some vanadium. Liquor S-1 is nearly identical with S-2 except for the absence of iron.

Data from cascade extractions (organic extract contacted with several successive portions of fresh aqueous liquor) with di(2-ethylhexyl)phosphoric acid from liquors S-1 and S-2 are shown in Figure 10. Extraction of uranium with 0.1 M reagent from liquor S-2 was considerably better when the iron in solution had been mostly reduced (with sulfur dioxide) and the resulting isotherm resembled closely the one obtained from the iron-free sulfate liquor S-1. The

[redacted]

ORNL-LR-Dwg. 7083

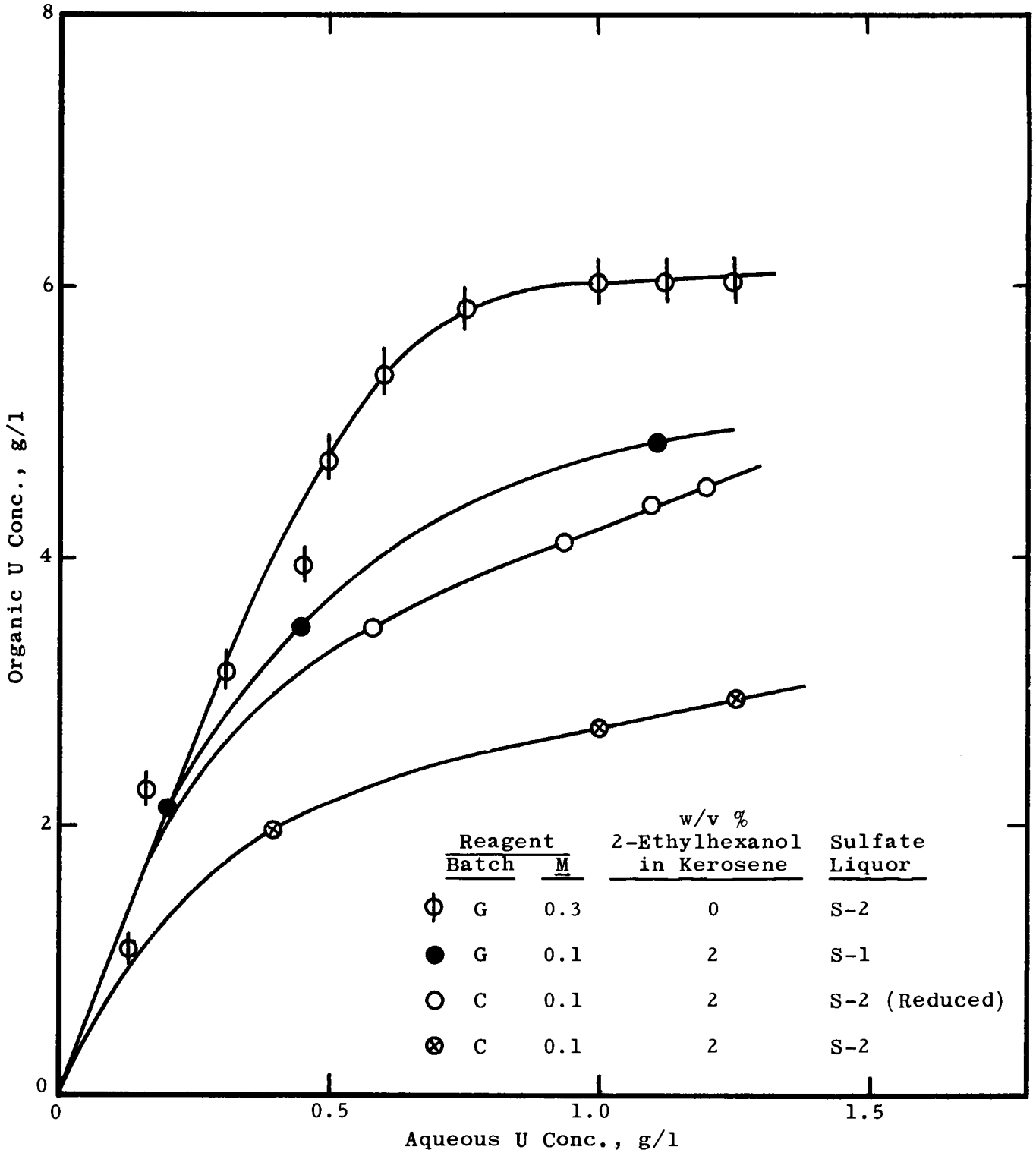


Figure 10

URANIUM EXTRACTION ISOTHERMS

with
Di(2-ethylhexyl)phosphoric Acid
from
Sulfate Liquors

Table 26

ANALYSES OF SYNTHETIC SULFATE LIQUORS

Component	grams/liter S-1	S-2	S-3
U(VI)	1.2	[illegible]	[illegible]
V(V)	----	----	0.8
Fe(III)	----	5.6	2.0
Al	3.6	3.0	2.1
SO_4	50	50	50
F	2	2	---
pH	0.9	0.9	1.0

difference in extraction behavior was a direct reflection of the extraction of iron, the concentration of iron in the final organic extract from the unreduced solutions being 0.8 g/l while that from the reduced solution was only 0.03 g/l.

The period of contact in each stage of the tests described in Figure 10 was two minutes so that according to the rate data presented previously the extract concentrations should not have been at equilibrium with respect to the iron and aluminum extraction. To obtain initial information on the effect of contact time, two isotherms were determined for sulfate liquor S-3 (not reduced). In one isotherm the contact time for each single-stage extraction (at varied aqueous-organic phase ratios) was 5 minutes, and for the other, 120 minutes. From Figure 11, it may be noted that an appreciable quantity of the uranium which had been extracted at the short period of time was replaced by iron during the longer contact. Thus, the uranium dropped from 3.3 g/l to 1.2 g/l while the iron increased from 0.07 g/l to 1.4 g/l. These data serve to demonstrate the importance of hold-up time in extracting liquors containing appreciable Fe(III) and also the difficulty in using laboratory batch tests for predicting operation with such liquors in a countercurrent system. Further measurements of Fe(III) tolerance in the extraction system are being made in continuous countercurrent equipment under simulated plant conditions (see below).

An isotherm for the extraction of uranium from unreduced liquor S-2 with 0.3 M di(2-ethylhexyl)phosphoric acid

[redacted]

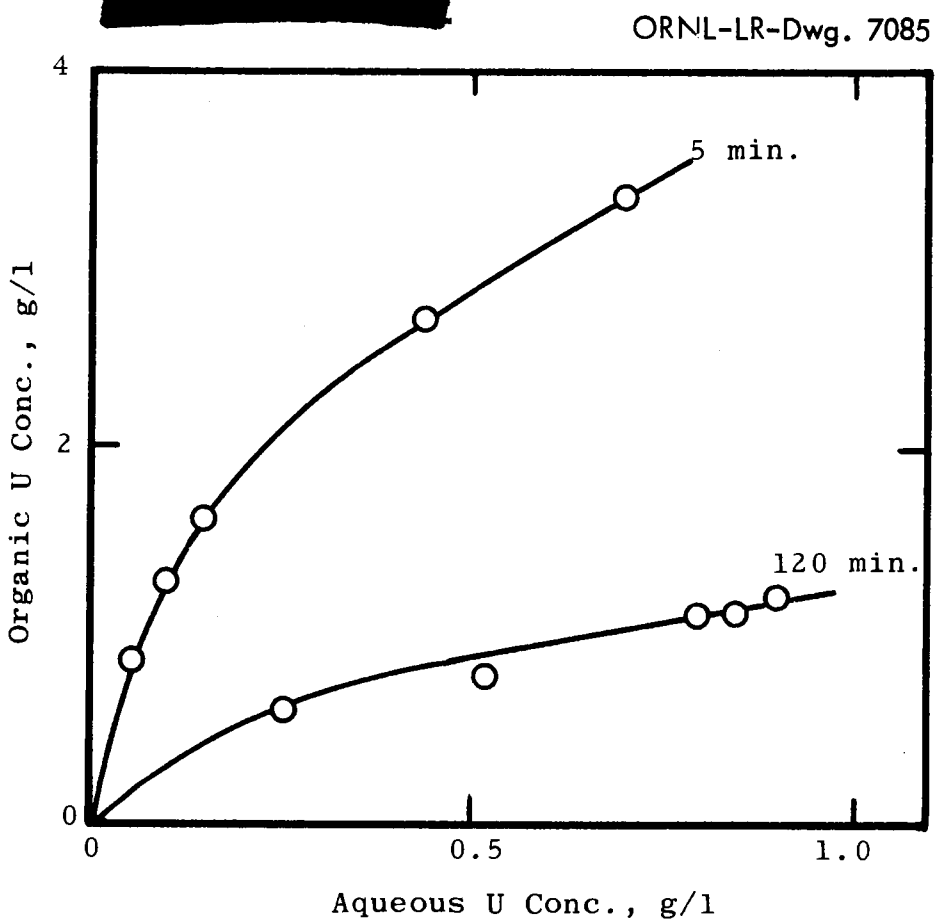


Figure 11

EFFECT OF CONTACT TIME UPON EXTRACTION

with

Di(2-ethylhexyl)phosphoric Acid, Batch I
0.1 M/kerosene + 1.6 w/v % capryl alcohol

from

Sulfate Liquor, S-3

(2 minute contacts) is shown in Figure 10. The uranium extraction was increased but apparently at some expense to selectivity over Fe(III). At indicated loading the uranium concentration was 17 percent of the theoretical limit (2 organophosphates per uranium) compared to >25 percent in tests with 0.1 M reagent under the same conditions. The iron extractions at loading were correspondingly greater. If the liquor had been reduced, the reagent concentration would have proved to be of a much greater advantage.

Sulfate-Chloride Liquors

Liquors containing both chloride and sulfate are produced in the salt-roast acid-leach process for treating Western ores. Depending upon the amount of hydrochloric acid recovered from the off-gases, and thus the amount of sulfuric acid required for fortification, the ratio of sulfate to chloride may vary over a considerable range. Isotherms for extraction with di(2-ethylhexyl)phosphoric acid from these liquors have been made as a function of liquor composition, degree of liquor (iron) reduction, liquor pH, and extractant concentrations.

The compositions of the liquors used in these tests are shown in Table 27. Two of the liquors are described as

Table 27

COMPOSITION OF SULFATE-CHLORIDE LEACH LIQUORS

	Composition (g/l)				
	High Chloride		Low Chloride		
Component	C-1	C-2	C-3	C-4	C-5
U(VI)	2.8	2.7	0.9	1.3	1.2
V(total)	2.3[a]	2.3	1.3	1.3	1.3
Fe(total)	1.0[a]	1.0[b]	1.0	0.8[b]	1.0
Al	1.7	1.8	0.4	0.4	0.4
SO_4	8.8	9	20	20	20
Cl	17	17	6	6	6
PO_4	0.8	---	---	---	---
pH	1.2	1.2	1.0	1.0	1.7

a) Partially reduced.
b) Prepared from $FeSO_4$ (97% Fe^{+2}).

"high chloride" and the others as "low chloride." The high chloride liquor C-1 was an actual leach liquor obtained from a plant using the salt-roast, acid-leach process where the amount of recovered hydrochloric acid was high with little sulfuric acid being required. Liquor C-2 was a synthetic liquor and had a similar high chloride concentration. The low chloride liquors, C-3, -4, and -5, were all synthetic liquors.

Isotherms for extraction from the high chloride liquors are shown in Figure 12 and for the low chloride liquors in Figure 13.

In both series of tests, the most effective extractions of uranium were again obtained from liquors in which the iron was most completely reduced. The effect of increased reagent concentration on increasing uranium extraction is demonstrated in Figure 12 for the high chloride liquors and the beneficial effect from increasing the liquor pH is shown in Figure 13 for the low chloride liquors. Although these latter variables were examined for only one series of liquors, similar trends have been obtained in pure solutions and will hold for any of these liquors, the magnitude of the effects depending upon the liquor composition.

As indicated by the data of Appendix B, di(2-ethylhexyl)phosphoric acid has a greater ability to extract uranium from solutions containing chloride ion than from a solution containing an equivalent concentration of sulfate ion. This observation is confirmed by comparison of the isotherms from sulfate liquor S-2 (Figure 10) and high chloride liquor C-2 (Figure 12). The anionic concentration in each liquor was $\sim$0.5 M, but the concentration of uranium in the organic extract, when there was 1 gram of uranium in the aqueous feed, was 8 g U/l from the chloride-sulfate liquor and 4.2 g U/l from the sulfate solution.

Bench-Scale Countercurrent Extraction Studies

Preliminary tests with di(2-ethylhexyl)phosphoric acid in continuous countercurrent extractions have been made to determine the physical performance of the extraction and stripping cycles and the tolerance of the system for ferric iron. The liquors used in the tests were of the following composition: U = 1.1 g/l, Fe_{total} = 3.0 g/l, Al = 2.7 g/l, SO_4 = 30 g/l, pH = 1.3. Keeping the total iron constant, the concentration of Fe(III) was varied from 0 to 0.6 g/l, corresponding to 100 and 80% reduction of the total iron in the liquor.

[redacted]

ORNL-LR-Dwg. 7082

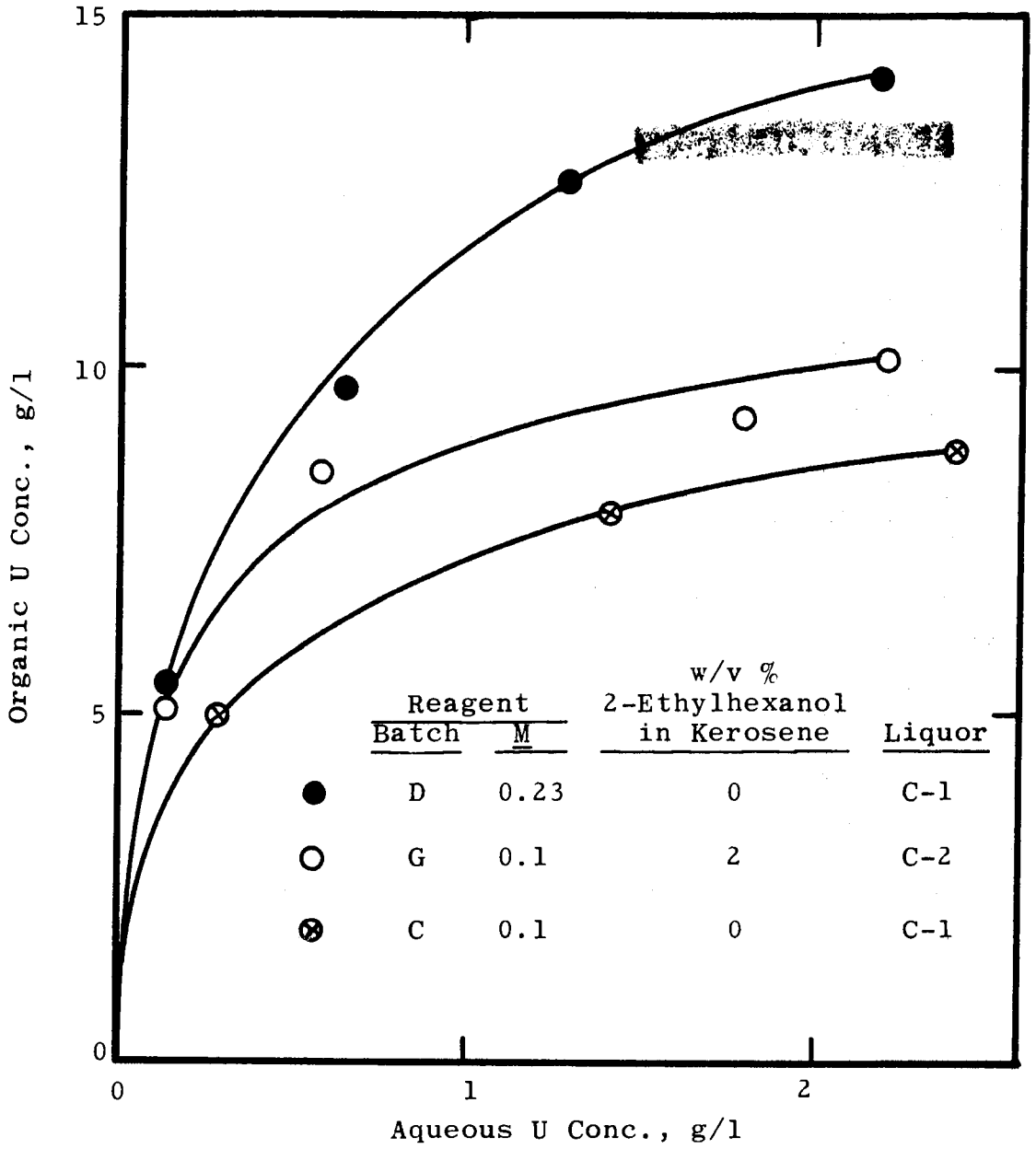


Figure 12

URANIUM EXTRACTION ISOTHERMS

with
Di(2-ethylhexyl)phosphoric Acid
from
Chloride-Sulfate Liquor (high chloride)

[redacted]

[redacted]

ORNL-LR-Dwg. 7086

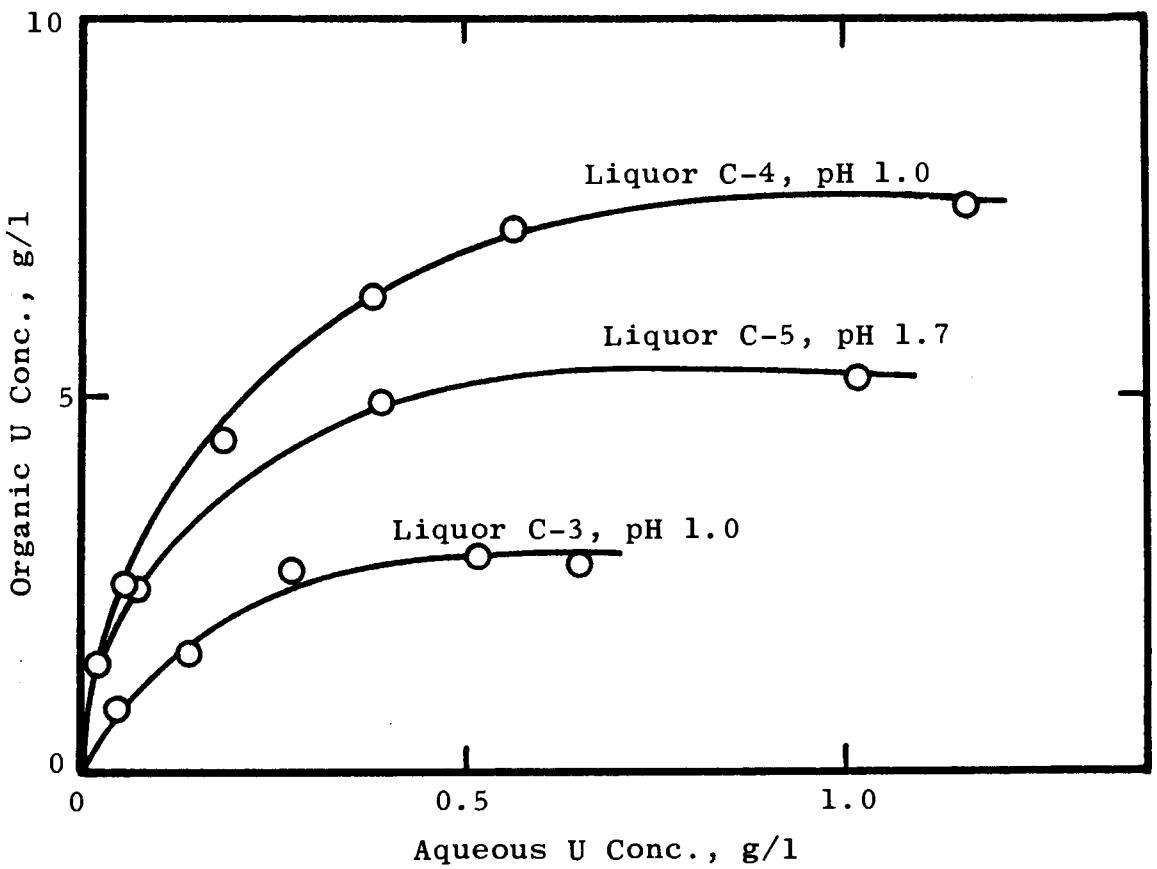


Figure 13

URANIUM EXTRACTION ISOTHERMS

with
Di(2-ethylhexyl)phosphoric Acid, Batch G
0.1 M/kerosene + 2 w/v % 2-ethylhexanol
from
Chloride-sulfate liquors (low chloride)

The experiments were run with 3 mixer-settler units (~80% stage efficiency) in the extraction cycle coupled with 2 mixer-settler units in the stripping cycle. Provision was made for partial recycle of the extracting phase within each stage as previously described by workers at Dow Chemical Company[13]. An internal phase ratio of 5 (organic/aqueous) was maintained within each mixer. To insure that no entrained aqueous feed would enter the stripping section, the pregnant organic phase was scrubbed with 0.5% sulfuric acid in a single-stage contactor. This treatment removed only negligible amounts of uranium, iron, and aluminum from the organic extract. Di(2-ethylhexyl)phosphoric acid (0.1 M in kerosene with 1.4 w/v % capryl alcohol) and sodium carbonate (10 w/v %) were used as the extracting and stripping agents. The flow ratios of feed:organic:strip were about 23:4.5:1 with an aqueous feed of approximately 6 liters/hr. Aqueous residence time in each mixer was 45 seconds at an agitator speed of ~800 rpm. (At 500 rpm extraction was unsatisfactory. Flooding was not observed at the maximum speed of the agitator, 1000 rpm.) Total hold-up time for organic in the complete extraction cycle was about 90 minutes.

Detailed patterns of the test results are shown with the aid of Figures 14 and 15. The flowsheet for each test is presented schematically and analyses for the various streams are given at appropriate locations on the diagrams. In several instances, two numbers are reported for the same variable. These indicate stream concentrations when the run was (a) approximately one-half over, and (b) at the end of the run. The duration of the test in each case was long enough for the total volume of organic extract to have cycled twice through the entire system.

Total extraction of uranium was 99.3 percent in the test with no ferric iron, and 98.4 percent at the level of 0.6 g Fe(III)/l. A fourth mixer-settler unit would have been sufficient to achieve >99 percent extraction in the latter case. Phase separations in all tests were rapid and clear.

The concentration of uranium in the pregnant organic phases varied from 5.1 - 5.5 g U/l in all tests, depending upon the feed uranium concentration. The concentration of iron in the organic phase decreased from 0.4 g Fe/l at 80% reduction to 0.05 g Fe/l at complete reduction. Aluminum extraction was low throughout, i.e., about 0.04 g/l in the organic phase.

In these first tests, 10 percent sodium carbonate solution was used as the stripping reagent. Since emphas

[redacted]

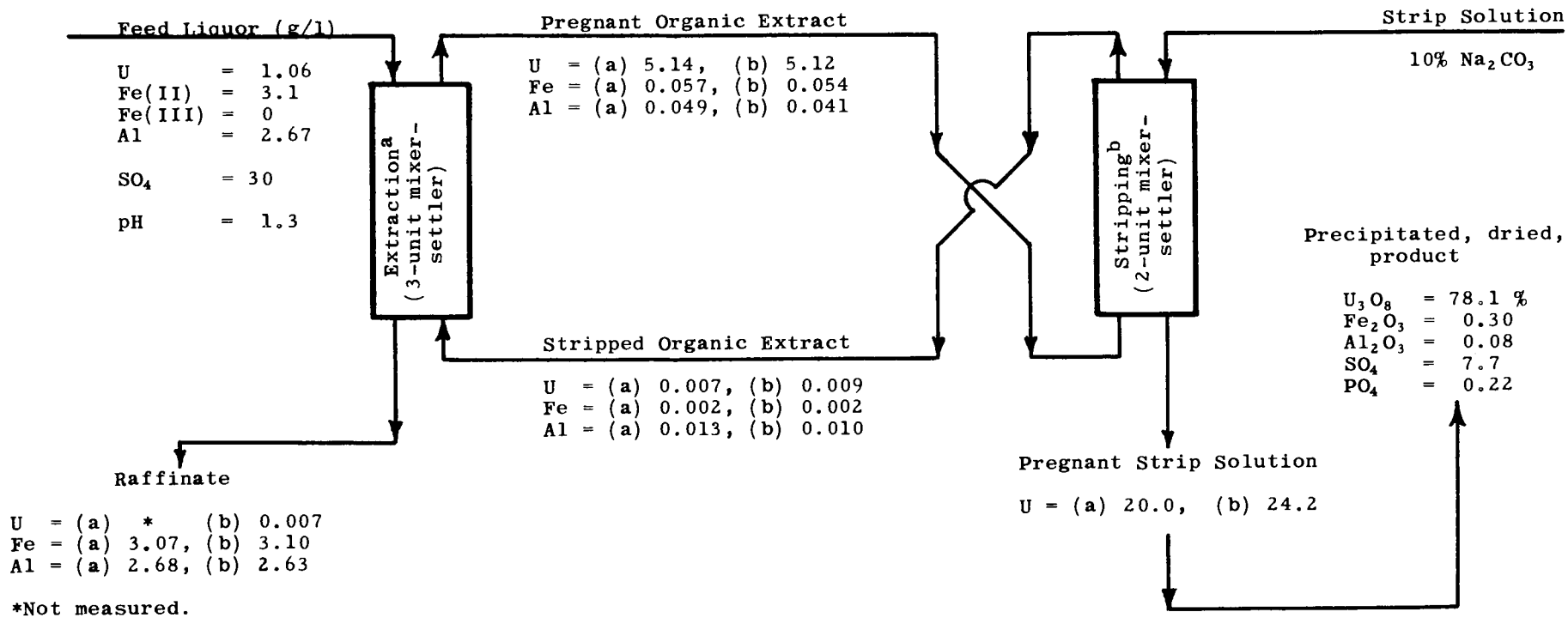
Figure 14

COUNTERCURRENT EXTRACTION OF SYNTHETIC SULFATE LIQUOR WITH

DI(2-ETHYLHEXYL)PHOSPHORIC ACID (100% Reduction of Iron)

Organic Extractant: 0.1 M Di(2-ethylhexyl)phosphoric Acid, Batch I, in kerosene, modified with 1.4 w/v % capryl alcohol.
Phase Ratios, aqueous feed:organic extractant:strip solution ∽ 22:4.7:1
Aqueous Feed Rate: 115 ml/min.

(Analyses in g/l indicated at completion of ~ 1 and ~ 2 complete cycles of organic extractant.)



(a) Cumulative extraction of 55% in 1st unit, 94% in 2nd unit, 99.3% in 3rd unit.
(b) 96% U stripped in 1st unit.

ORNL-LR-Dwg. 7078

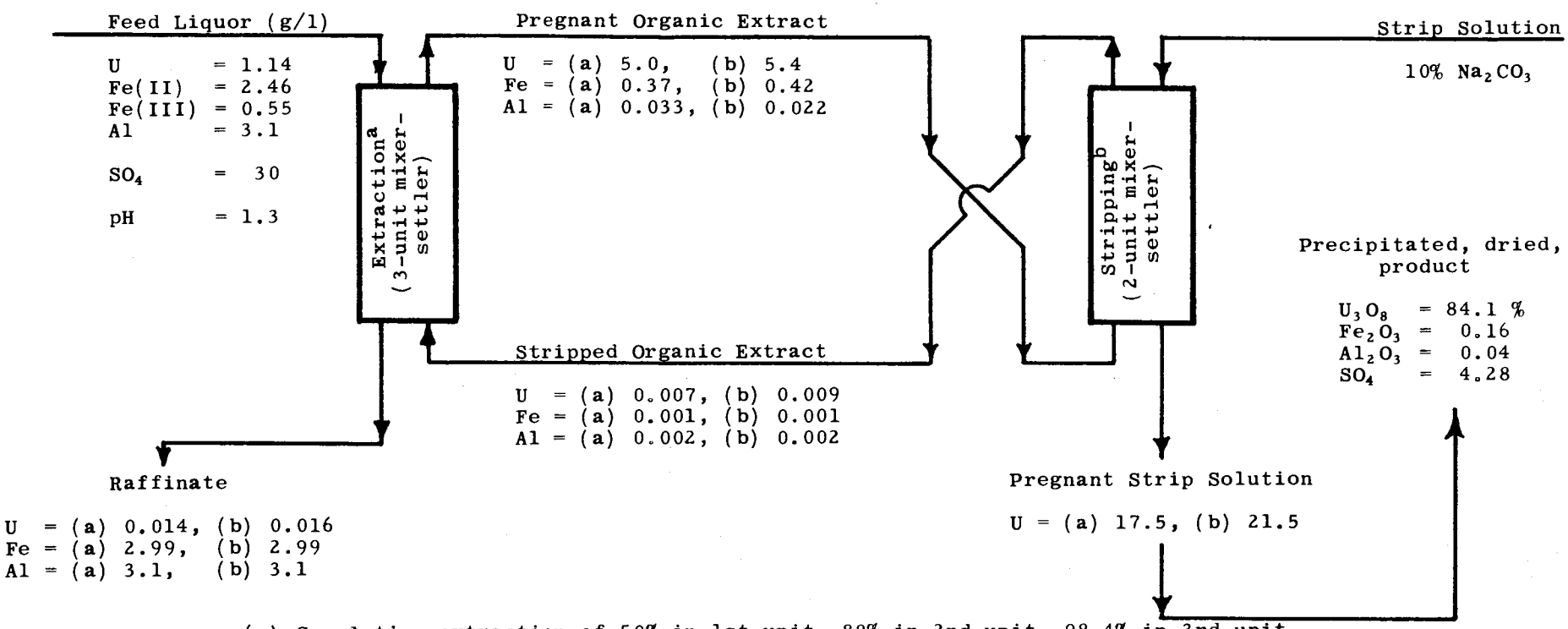
[redacted]

Figure 15

COUNTERCURRENT EXTRACTION OF SYNTHETIC SULFATE LIQUOR WITH DI(2-ETHYLHEXYL)PHOSPHORIC ACID (80% Reduction of Iron)

Organic Extractant: 0.1 M Di(2-ethylhexyl)phosphoric Acid, Batch I, in kerosene, modified with 1.4 w/v % capryl alcohol.
Phase Ratios, aqueous feed:organic extractant:strip solution ~ 22:4.7:1
Aqueous Feed Rate: 115 ml/min.

(Analyses in g/l indicated at completion of ~ 1 and ~ 2 complete cycles of organic extractant.)



(a) Cumulative extraction of 50% in 1st unit, 88% in 2nd unit, 98.4% in 3rd unit.
(b) 86% U stripped in 1st unit.

had been placed on performance rather than on reagent utilization, no attempt was made to load the carbonate stripping solution to the levels described in the section on alkaline stripping. The equilibrium strip solutions contained only 22-25 g U/l and, consequently, the utilization of reagent was only half that possible (Table 20). To achieve the maximum loading, it would have been necessary to control a flow of sodium carbonate solution equal to only 2-3 ml/min. In several subsequent tests (not shown), 5% Na_2CO_3 has been used in the stripping cycle. Efficient stripping was achieved in these tests and the uranium loading in the strip solution was about 22 g U/l. This corresponds to near maximum effective utilization of the sodium carbonate reagent and serves to confirm the conclusions made on the basis of the batch tests described previously.

As the analyses of the barren organic phases indicate (see figures), two stripping stages were adequate to effect 99.9 percent removal of uranium as well as almost all of the iron and aluminum. No particular difference in the physical operation of the stripping cycle was observed as the concentration of oxidized iron increased. The precipitation of hydroxides in the first stripping unit caused a weak emulsion to be formed which levelled off with continued operation. In some cases the emulsion was further controlled by addition of a small amount of Sharples Nonic 218. The precipitate settled rapidly into the aqueous phase leaving the extractant clear, essentially barren of all metals, and ready for recycling without further treatment. The dry weight of the hydroxide precipitate recovered from the test on the 80 percent reduced solution amounted ~0.1 gram per liter of the aqueous feed processed.

The product was obtained by filtering the sodium carbonate strip solution, destroying the carbonate with sulfuric acid, and precipitating the uranium with ammonia. The precipitates were washed and dried. The products contained 78-84% U_3O_8, and iron and aluminum oxides combined amounted to less than 0.4%. The appreciable sulfate content indicates that the grade could have been improved with more complete washing of the precipitate.

Slurry Extraction

Preliminary experiments have also been conducted in which di(2-ethylhexyl)phosphoric acid has been used to extract uranium from slurries of Western ores and Leached Zone material in acid sulfate solutions. Batch shake-out, mixer-settler, and pulse column tests have given promising results with respect to uranium extraction, physical handling and reagent loss. This program of testing will be reported separately.

VII. ESTIMATED REAGENT COSTS FOR RECOVERY OF URANIUM FROM SULFATE LIQUORS WITH DI(2-ETHYLHEXYL)PHOSPHORIC ACID USING AN ALKALINE STRIP

Preliminary estimates have been made (Table 28) of the chemical costs in recovery of uranium from sulfate leach liquors with di(2-ethylhexyl)phosphoric acid using an alkaline strip. The cost calculations presented in the table are based only on small-scale tests and known uranium chemistry and, thus, must be treated as tentative. Costs for stripping with acid or acid-salt solutions have not been considered since the data available at this time are insufficient to support a comparative estimate.

Assumptions For Calculations In Table 28

1) The average feed liquor is assumed to contain 20-50 gms SO_4/l at a pH of 1-1.7. The uranium level in the liquor has been set at 1 g U/l (1.18 g U_3O_8/l).

2) It is assumed that most of the iron in the liquor has been reduced to the divalent state. Reduction of the liquor for this purpose has not been studied as a unit operation and reagent costs for this step are not included.

3) The extractant is 0.1 M di(2-ethylhexyl)phosphoric acid in kerosene, modified with 2 w/v % of a long-chain alcohol. Use of greater extractant concentrations would not create a large change in the total reagent costs.

4) Under average operational circumstances, it is expected that the uranium loading in the organic phase would be 4 g U/l (i.e., 4.72 g U_3O_8/l).

5) For purposes of this estimate, it is assumed that uranium is recovered from a sodium carbonate strip solution by acidification with sulfuric acid to drive off carbon dioxide and subsequent precipitation with ammonia. A 10% sodium carbonate solution is assumed as the stripping agent with a uranium loading at 50 g U_3O_8/l.

6) The unit costs for chemicals were taken according to Table 29.

Table 28

TOTAL REAGENT COST*

Source of Cost	¢/lb U_3O_8 Using 0.1 M Di(2-ethylhexyl)phosphoric Acid in Kerosene with 2% (wt/vol) 2-Ethylhexanol	2% (wt/vol) Capryl Alcohol	2% (wt/vol) 4-Ethyloctanol
Dissolved in Raffinate			
Di(2-ethylhexyl)phosphoric Acid	< 0.3	< 0.3	< 0.3
Alcohol	2.2	1.3	0.2
Dissolved in Strip Solution			
Di(2-ethylhexyl)phosphoric Acid	< 0.1	< 0.1	< 0.1
Alcohol	< 0.1	< 0.1	< 0.1
Entrainment of Solvent in Raffinate	1.7	1.7	1.8
Stripping and Product Recovery			
Na_2CO_3	4.6	4.6	4.6
H_2SO_4	2.0	2.0	2.0
NH_3	1.5	1.5	1.5
	12.5	11.6	10.6

*Costs calculated according to the assumptions listed on page 77. If a liquor at the same uranium level but lower sulfate (i.e., 0.2 M instead of 0.5 M sulfate) were treated, the total costs shown would be about 0.5¢/lb of U_3O_8 higher. This is due to the greater loss of alcohol to solutions of lower ionic concentration.

Table 29

UNIT CHEMICAL COSTS

Reagent	Unit Price
Di(2-ethylhexyl)phosphoric Acid (95%)	60¢/lb
2-Ethylhexanol	25¢/lb
Capryl Alcohol	19¢/lb
4-Ethyloctanol	40¢/lb*
Kerosene	14¢/gal
Sodium Carbonate	2.32¢/lb
Sulfuric Acid (97%)	1.35¢/lb
Ammonia	5.9¢/lb

Total Solvent	
0.1 M Di(2-ethylhexyl)phosphoric Acid in kerosene containing 2% (wt/vol) 2-ethylhexanol	34¢/gal
0.1 M Di(2-ethylhexyl)phosphoric Acid in kerosene containing 2% (wt/vol) capryl alcohol	33¢/gal
0.1 M Di(2-ethylhexyl)phosphoric Acid in kerosene containing 2% (wt/vol) 4-ethyloctanol	36¢/gal

*Estimated - not in commercial supply.

Remarks On Table 28

Reagent Losses By Solubility In Acid Liquors. Solubility losses of the di(2-ethylhexyl)phosphoric acid extractant to the liquor are low (see Section V) and give negligible contribution to the chemical costs. Losses of the shorter-chain alcohols through distribution to the liquor are significant and an advantage in using the longer-chain alcohol is evidenced even though the unit cost (Table 29) is higher. Other long-chain alcohols are now appearing on the market at a moderate price and, thus, might be superior to any of those shown from a cost standpoint, e.g., decyl alcohols (21¢/lb) and tridecyl alcohols (24¢/lb).

Reagent Losses By Solubility In Strip Solutions. The uranium concentrations in the loaded strip solutions are high and, thus, the reagent losses to these solutions are negligibly low on a cost-per-lb of U_3O_8 basis.

Reagent Losses By Entrainment In The Raffinate. Pilot plant experience with solvent extraction of clear liquors, using other reagents, has indicated organic entrainment losses of less than 0.01 percent by volume of raffinate. For present calculations, an organic volume loss of 0.05 percent has been assumed to allow for periods of bad operation, evaporation, and spillages.

Entrainment losses to slurries would be expected to be higher than experience has shown for clear liquors. Although many of the preliminary tests have been encouraging, the data were random and are not sufficient as yet to establish the losses in slurry application. The amount of this loss, of course, will be the important factor in comparative chemical costs for clear liquor and slurry processing.

Reagent Costs For Stripping And Recovery From The Strip Solution. The largest portion of the chemical costs is comprised by the reagents for stripping and product recovery from the strip solution. The product recovery process used for the calculations in Table 28 may not be the best for this purpose. For example, lower costs might be obtained if the uranium were precipitated from the sodium carbonate solutions with sodium hydroxide and the supernatant (filtrate) regenerated with carbon dioxide for further recycle. In either case, if the uranium were loaded to a greater concentration in the organic solvent (i.e., $>$ 4 g U/l) somewhat lower costs would result provided appropriate adjustments were made in the volume and concentration (Na_2CO_3 conc.) of the strip solution.

VIII. VANADIUM EXTRACTION AND STRIPPING

Although the vanadium extraction coefficients with di(2-ethylhexyl)phosphoric acid are much lower than those for uranium (Table 3), it is possible to extract vanadium from reduced liquors by use of higher reagent concentrations or by a combination of increased reagent and pH levels. Both alkaline and acid stripping methods are effective in removing the vanadium from the organic extract. A brief description of the extraction and stripping results obtained thus far are given below.

Extraction From Sulfate Solutions

Extractions of vanadium from sulfate liquors with 0.2 M di(2-ethylhexyl)phosphoric acid over a pH range from 1 to 3 are shown in Table 30. Under these conditions, the extrac-

Table 30

EXTRACTION OF OXIDIZED AND REDUCED VANADIUM FROM SULFATE SOLUTIONS

0.2 M Di(2-ethylhexyl)phosphoric Acid, Batch F, in kerosene
0.04 M Vanadium
0.5 M SO_4

Phase Ratio, aqueous/organic = 2

Agitation Time - 2 minutes, hand shaking

Initial pH	Extraction Coefficient V(V)	V(IV)*
1.0	0.2	1.1
1.5	---	4.3
2.0	0.7	7.5
3.0	0.2	16

*Coefficients affected by vanadium loading of the organic phase.

tion coefficient for oxidized vanadium(V) was never larger than 1, and seemed to pass through a maximum in this range. Extraction coefficients for reduced vanadium(IV), on the other hand, continued to increase from a value of 1 at pH = 1 to a value of 16 at pH = 3.

Since the vanadium level in the tests of Table 30 was fairly high, the extraction coefficients, as shown, should have been appreciably affected (lowered) by reagent loading. Consequently, similar tests have been made with more dilute vanadium(IV) solutions and these results are presented in Table 31. In this case there is a 20-fold in-

Table 31

EXTRACTION OF VANADIUM(IV) AS A FUNCTION OF pH AND REAGENT CONCENTRATION

Di(2-ethylhexyl)phosphoric Acid, Batch G, in kerosene
A. 0.4 M, 4% (wt/vol) 2-ethylhexanol
B. 0.2 M, 3% " "

0.01 M Vanadium(IV)

0.5 M SO_4

Phase Ratio, aqueous/organic
A. 2
B. 1

Agitation Time - 2 minutes, hand shaking

A			B		
Initial pH	Final pH	E_a^o	Initial pH	Final pH	E_a^o
1.12	1.07	1	1.12	1.08	0.3
2.05	1.92	20	2.05	1.93	7
3.20	2.50	50	3.20	2.50	25

crease in extraction coefficient in the pH range 1-2, e.g., a value of 1 was obtained with 0.4 M reagent at pH 1 and 20 at pH 2. The kerosene-reagent solution in these latter

tests contained 2-ethylhexanol, 3% (wt/vol) being added to the 0.2 M solution and 4% to the 0.4 M solution. Where the extraction coefficients are not affected by reagent loading, it is apparent that (similar to the experience with uranium) the addition of alcohol decreased the vanadium extraction coefficients (compare E_a^o = 0.3 for 0.2 M reagent in Table 31 with E_a^o = 1 for the same concentration in Table 30). Different amounts of alcohol were used in the tests of Table 31 and, thus, the effect of reagent concentration cannot be independently determined from these data. It is interesting to note, however, that under the particular conditions of the tests and in the pH range 1-2, the extraction coefficient was more than doubled when the reagent concentration was increased by a factor of 2.

In general, it may be concluded from the data that useful extraction of vanadium from sulfate liquors can be achieved if the vanadium is reduced and high reagent concentrations are used. In addition, it will be advantageous to adjust the liquor pH to the maximum possible value short of precipitation. The effect of sulfate in the liquor has not been studied but it is probable that, as in the case for uranium, the vanadium extraction would increase with decreasing sulfate concentration. Information on extraction rates is also lacking at this time.

In view of the high reagent concentration and the ability of the reagent to extract ferric iron (see above), it would be necessary that the iron in the liquor, as well as the vanadium, be reduced. Even with this precaution it would be expected that extractions of unwanted metals in a vanadium process would be more of a problem than in a uranium process where much lower extractant concentrations can be used.

Extractions From Sulfate-Chloride Liquors

Using 0.4 M di(2-ethylhexyl)phosphoric acid in kerosene (4% alcohol) as the extractant, extraction isotherms have been determined for reduced (i.e., all vanadium and most of the iron reduced) sulfate-chloride liquors which, except for the absence of uranium, are similar in composition to those obtained in the currently used "salt-roast, acid-leach" process[21] for carnotite ores. These data are presented in Figures 16 and 17. The isotherms from the solution with the higher sulfate/chloride ratio (Figure 16) show nearly a tenfold advantage by increasing the pH from about 1 to 1.8. At the higher pH, the maximum vanadium concentration obtained in the organic phase was ~7 g V/l and appeared to be near the loading limit. At either pH, all of the ferric iron originally present in the aqueous liquor was extracted.

[redacted]

ORNL-LR-Dwg. 7074

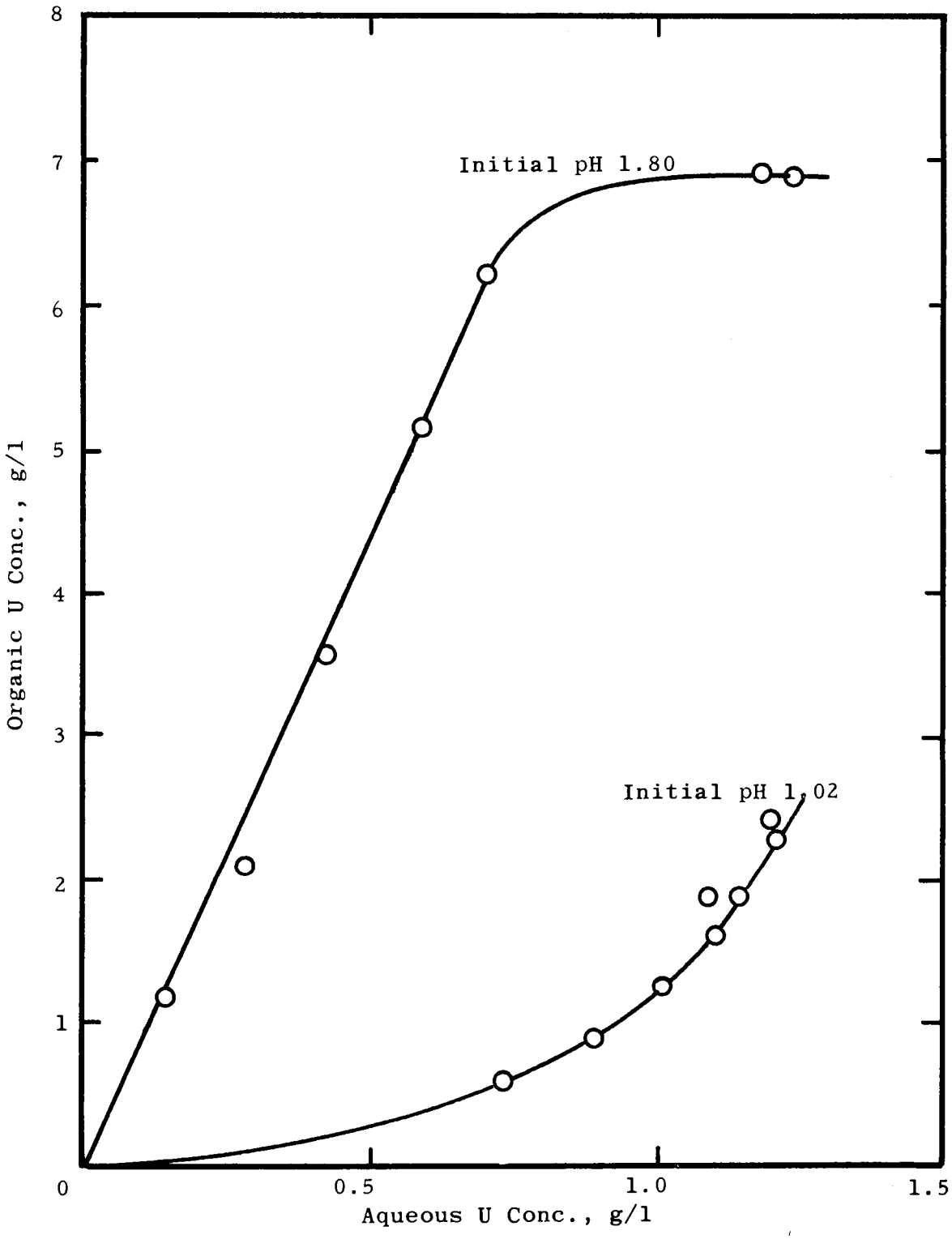


Figure 16

VANADIUM EXTRACTION ISOTHERMS

with
Di(2-ethylhexyl)phosphoric Acid, Batch G
0.1 M/kerosene + 4 w/v % 2-ethylhexanol
from
Chloride-sulfate liquor (low chloride)

[redacted]

ORNL-LR-Dwg. 7081

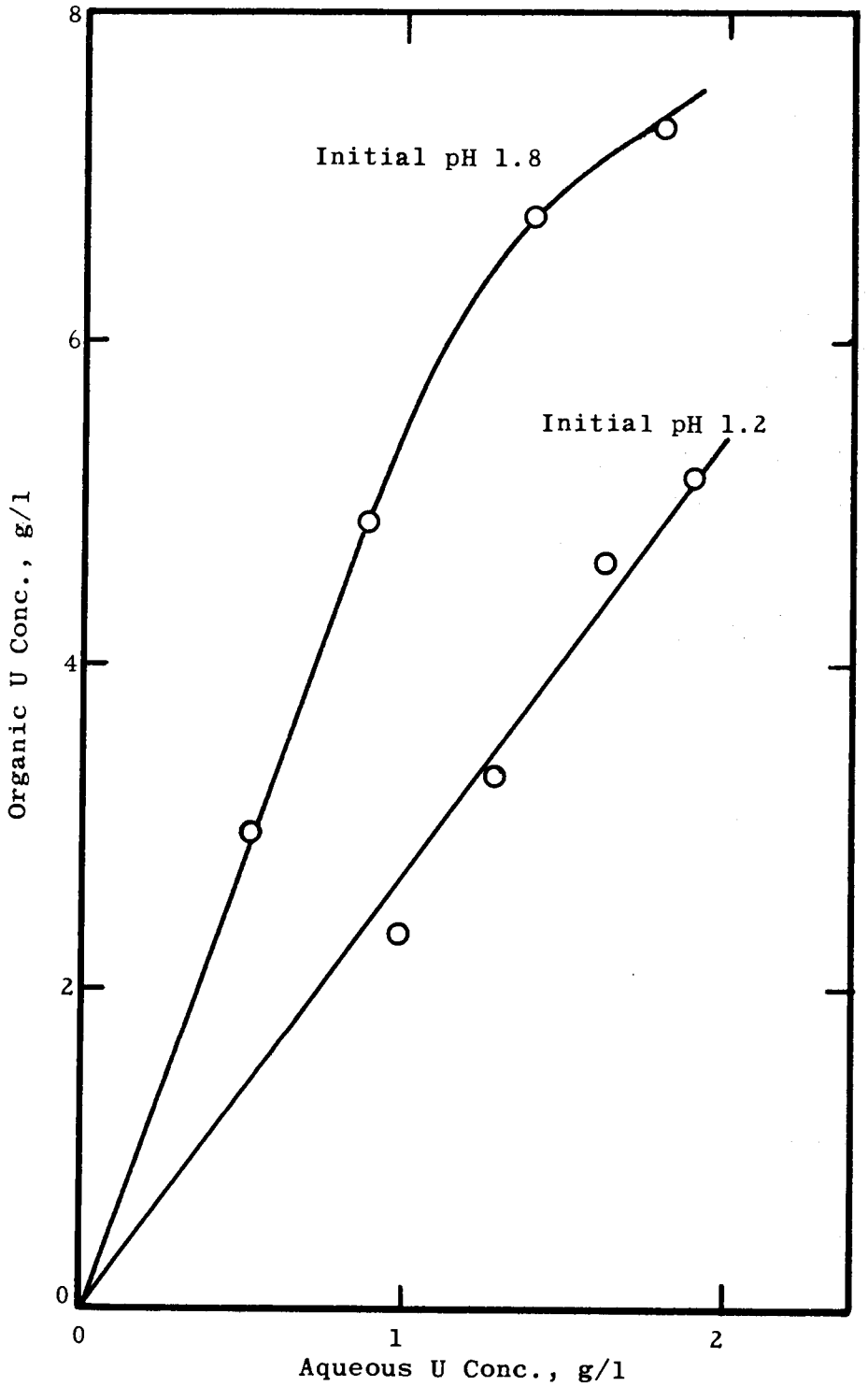


Figure 17

VANADIUM EXTRACTION ISOTHERMS

with
Di(2-ethylhexyl)phosphoric Acid, Batch G
0.4 M/kerosene + 4 w/v % 2-ethylhexanol
from
Chloride-sulfate liquor (high chloride)

In the tests with the higher chloride, lower sulfate liquor (Figure 17), the advantage gained by increasing the pH was not as significant, e.g., initial coefficients varied from ~3 to ~6 upon raising the pH from 1.2 to 1.8. Again, the vanadium in the organic phase reached about 7 g V/l and almost all of the ferric iron was extracted.

Vanadium Stripping

Cursory studies have shown the possibility of using either acid or alkaline reagents for stripping vanadium from the organic extract. In examining the alkaline stripping possibilities, a 0.4 M di(2-ethylhexyl)phosphoric acid-kerosene solution (4% wt/vol 2-ethylhexanol) containing 5.2 g V(IV)/l was contacted in one case with an equal volume of 10% NaOH solution and in another case with 10% Na_2CO_3 solution. With both reagents, 94% of the vanadium had reported to the aqueous solution after the single, 2 minute contact. Although precipitation of V(IV) was not noted in these particular tests, precipitation might be generally anticipated in alkaline stripping. In such case, the precipitation could presumably be prevented, or the precipitate dissolved, by addition of an oxidant to convert V(IV) to the soluble vanadate.

Third phase formation was avoided during the alkaline strip by the presence of alcohol in the organic solvent. The alcohol requirements for maintaining reagent-diluent compatibility in an alkaline vanadium-stripping cycle should be the same as those described previously for uranium.

Stripping data with hydrochloric and sulfuric acid, from the same organic solution used above, are presented in Table 32. Coefficients greater than 20 are obtained with both acids at concentrations of 1 molar. It should be noted, however, that the organic extract used in these tests contained 2-ethylhexanol which has been shown to decrease vanadium extraction coefficients (page 83). Thus, if the extraction from acid solutions occurs according to a reversible reaction it should be more difficult to strip vanadium with acids from a solvent containing no alcohol. Studies of the alcohol effect in this respect have not been made. Stripping with acid solutions containing an oxidant have also not been examined. More effective stripping might be possible in this case since the extraction coefficients for V(V) from acid liquors are apparently lower than for V(IV).

Table 32

ACID STRIPPING OF VANADIUM (IV)

Organic Phase: 0.4 M Di(2-ethylhexyl)phosphoric Acid, Batch G, in kerosene + 4% 2-ethylhexanol

Phase Ratio, aqueous/organic = 2

Agitation Time - 2 minutes, hand shaking

Acid Conc. M	Stripping Coefficient, S_o^a	
	HCl	H_2SO_4
0.1	0.1	0.3
0.2	0.5	1
0.5	2.3	16
1.0	22	26

The tests made thus far on both vanadium extraction and stripping have been limited in number and do not supply sufficient information for definitive description of a process operation. On the other hand, the information is sufficient to suggest process possibilities for vanadium recovery with di(2-ethylhexyl)phosphoric acid, either (1) by simultaneous extraction of uranium and vanadium from the leach liquor with separation of the two elements being accomplished by selective stripping or by subsequent processing, or (2) by extraction of vanadium from the liquor after uranium removal in a primary extraction cycle. The latter approach has been investigated by the Dow Chemical Company with the long-chained monoalkylphosphoric acids. Further studies of vanadium recovery with dialkylphosphoric acids will be made but on a low priority basis in view of the recent move toward de-emphasis of vanadium production on the part of the AEC.

IX. SUMMARY

Since most of test work described has been directly concerned with the development of a complete process for recovering uranium from ore leach liquors, the test results are summarized from this viewpoint. In Figure 18, a flow-sheet is shown which presents in general terms an extraction-stripping cycle (in this particular case, an alkaline stripping cycle) for the recovery of uranium from sulfate liquors with di(2-ethylhexyl)phosphoric acid. Although testing of the process in a completely continuous counter-current system is still on a preliminary bench-scale basis, the operation thus far has been satisfactory and in agreement with the laboratory single-stage measurements. In the following summary both the single and multiple stage data are considered in respect to the pertinent sections of the process flow diagram.

Some information concerned less directly with the process or variations thereof is not included in the summary, but may be located by reference to the Table of Contents or the Appendices. Specifically, extractions of uranium from sulfate liquors with several other dialkyl-phosphoric acids are described in Appendix C and extraction of uranium with di(2-ethylhexyl)phosphoric acid from acid solutions other than sulfate liquors are described in Appendix B.

Feed Liquor

1) The studies thus far have been directed primarily toward the extraction and recovery of uranium from liquors obtained (1) by direct sulfuric acid leaching of Western ores or (2) by leaching salt-roast calcines with a sulfuric-hydrochloric acid mixture according to methods used in some of the existing Western mills. These liquors have responded satisfactorily to the extraction process. In addition, favorable extraction results have been obtained in preliminary tests with liquor-slime slurries so that it may not be necessary to remove undissolved solids after the leaching operation.

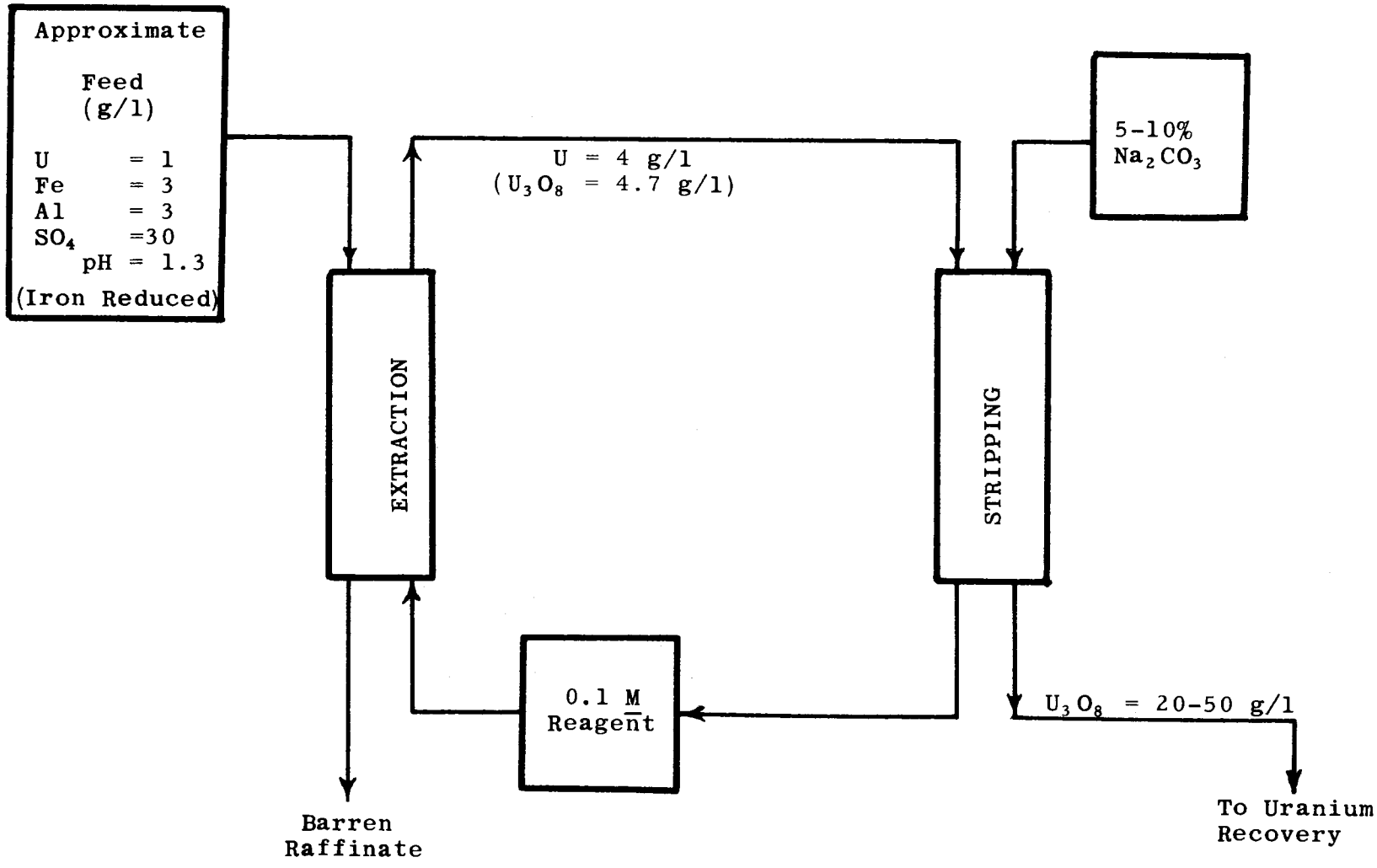
2) The extraction coefficients for uranium from the liquors decrease with increasing sulfate concentration and increase with increasing pH. Over the range of conditions usually encountered in ore liquors the extractions have been satisfactory when the concentration of di(2-ethyl-

[redacted]

ORNL-LR-Dwg. 7079

Figure 18

TENTATIVE FLOWSHEET FOR URANIUM RECOVERY FROM SULFATE LIQUORS WITH 0.1 M DI(2-ETHYLHEXYL)PHOSPHORIC ACID IN 98% KEROSENE - 2 W/V % ALCOHOL



hexyl)phosphoric acid in the organic phase was 0.1 molar. With liquors of unusually high sulfate or low pH, it might be profitable to simultaneously adjust both factors to a better range by adding calcium carbonate (calcite). Such a step should not affect the overall operating cost since neutralization of the acid liquor after the extraction would be necessary to precipitate vanadium and/or prepare the liquor for waste disposal.

3) Extraction coefficients for ferrous iron with di(2-ethylhexyl)phosphoric acid are extremely low whereas ferric iron is appreciably extracted, but at a rate much slower than that for uranium. Because of the slow extraction, it should be possible to tolerate a certain level of ferric iron in the process and thus a complete reduction, even of high iron liquors, prior to extraction should not be necessary. Preliminary bench-scale countercurrent tests of the flowsheet in Figure 18 have given good results on a liquor containing 3 g Fe/liter, of which 0.6 g/l was Fe(III).

4) Aluminum has not proved to be a problem in extractions with di(2-ethylhexyl)phosphoric acid since the rate of extraction is slow and the extraction coefficient after attainment of equilibrium is small. Di(3,5,5-trimethylhexyl)- and di(diisobutylmethyl)phosphoric acids also extracted small amounts of aluminum. Di-n-octylphosphoric acid, on the other hand, precipitated aluminum and hence is not applicable to the types of liquor considered here.

5) Titanium, thorium, and molybdenum are extracted by the di(2-ethylhexyl)phosphoric acid, but fortunately these elements are not appreciable contaminants in most of the Western domestic ores. In cases where molybdenum is extracted, separation of uranium from molybdenum would be expected as a natural result of the subsequent stripping and precipitation operations. Other metals more common to the ores, such as calcium, copper, chromium, manganese, have not shown appreciable extractions at the di(2-ethylhexyl)phosphoric acid concentrations which would be used in a uranium recovery circuit.

Solvent

1) In almost all of the process studies made thus far, a solution of di(2-ethylhexyl)phosphoric acid in kerosene, usually modified with a small amount of a long-chain

alcohol, has been used as the extraction solvent. This particular reagent was selected over the other dialkylphosphoric acids because of its potential availability in quantity at a reasonable price (see Appendix A). On the basis of extraction characteristics alone, several other reagents within the same class would be expected to give equal, or perhaps in some cases superior, performance.

2) The uranium extraction coefficient varied nearly as the square of the di(2-ethylhexyl)phosphoric acid concentration and may thus be adjusted over a range according to the liquor being treated. Under ordinary circumstances, an extractant concentration of 0.1 M is contemplated.

3) Modification of the kerosene with solvents such as the long-chain alcohols is a requirement of the alkaline stripping process for prevention of third phase formation (sodium dialkylphosphate salt) during contact with the sodium carbonate solutions. The quantities of alcohol required for this purpose vary with the extraction reagent concentration according to a linear relationship (see Figures 6, 7 and 8). In process studies, the amounts of alcohol used have been in excess of, ordinarily double, the threshold requirements. In the extraction part of the process cycle, the presence of alcohol causes a decrease in extraction efficiency. However, the effect is not sufficiently severe to prevent utility of the process.

Extraction

1) Using 0.1 M di(2-ethylhexyl)phosphoric acid in kerosene (2% capryl alcohol) at an aqueous to organic ratio of 4 to 1, typical sulfate liquors of the type described in Figure 18, have been essentially completely extracted in three mixer-settler units. With liquors more difficult to extract, i.e., higher sulfate, higher ferric iron or lower pH, the possibility of using additional units would be balanced against the possibility of increasing the extractant concentration or volume, decreasing ferric iron by further liquor reduction, or decreasing the sulfate and increasing the pH by addition of calcium carbonate.

2) The uranium concentration attainable in the organic phase could be varied dependent upon the grade of liquor treated and the optimizing of other extraction

variables. In the process shown in Figure 18 (liquor containing 1 g U/l), the uranium concentration in the pregnant solvent is 4 g U/l (4.7 g U_3O_8/l), consistent with the aqueous to organic feed ratio of 4.

Raffinate

1) The raffinate from the extraction process would contain only a few ppm uranium, i.e., the uranium recovery would be greater than 99% and probably greater than 99.5%. Also, the amounts of extraction reagents dissolved in and expelled with the raffinate would be low. For example, the measured solubility loss of di(2-ethylhexyl)phosphoric acid was less than 5 ppm and the measured loss of capryl alcohol at conditions shown in the flowsheet was less than 80 ppm. Lower solubilities would be experienced with longer-chain alcohols.

2) The amounts of solvent expected to be lost with the raffinate by physical entrainment would vary with the type of equipment used and thus should best be measured on a larger, pilot plant, scale. However, pilot plant tests with other solvents have shown very low entrainment losses to clear liquors under good operational conditions. With slime-slurries, low entrainment losses have also been indicated in some preliminary small scale continuous tests.

Stripping

1) The di(2-ethylhexyl)phosphoric acid is amenable to an alkaline strip provided a small amount of long-chain alcohol is present in the kerosene diluent (see above). In most applications a two-stage strip with 10% sodium carbonate would probably be used and the resultant uranium concentration in the loaded strip solution would be in the order of 50 g U_3O_8/l. The losses of extraction reagent during stripping, through solubility in the strip solution, are negligible on a cost-per-pound-of-uranium-recovered basis.

2) In addition to uranium, other metals extracted in much smaller quantities, e.g., iron, aluminum, titanium, vanadium and molybdenum, are removed from the solvent by the sodium carbonate strip. Some of these, e.g., iron, aluminum and titanium, are precipitated as the respective hydroxides whereas others, e.g., molybdenum,

are dissolved in the alkaline solution. The presence of small amounts of precipitated solids in the stripping system has not created a serious problem in the continuous mixer-settler runs made thus far. In tests where appreciable quantities of ferric iron were intentionally extracted, and hence precipitated during stripping, a weak emulsion formed in the first stripping stage but leveled off with continued operation. If desired, the emulsion formation could be further controlled by adding a small amount of wetting agent. The precipitate settled rapidly into the aqueous phase leaving the organic clear and barren of metals for ready recycle.

3) Insofar as they have been tested, certain other branched dialkylphosphoric acids have shown amenability to alkaline stripping similar to that shown by di(2-ethylhexyl)phosphoric acid. The di-n-octyl compound was not compatible, however, since precipitation of the sodium salt could not be prevented even with large additions of alcohol to the kerosene diluent. Monoalkylphosphoric acids (at least the branched compounds) have indicated acceptable response to alkaline stripping, with low reagent losses, if the alkyl chains are sufficiently large.

4) Stripping of uranium from di(2-ethylhexyl)phosphoric acid can be accomplished by acid and acid-salt solutions, although the studies so far are not as complete as for the alkaline method. Since the stripping reactions in this case are the reverse of those for extraction, the stripping coefficients for di(2-ethylhexyl)phosphoric acid are higher than would be obtained with other similar reagents having a higher extraction coefficient. Stripping with Na_2SO_4-H_2SO_4 solutions and HCl solutions of moderate concentrations should receive further study.

Product

Standard chemical procedures can be used for recovery of uranium from the pregnant strip solutions. Products were obtained from bench-scale tests of the extraction alkaline strip process shown in Figure 18 by destroying the carbonate with sulfuric acid and precipitating the uranium with ammonium hydroxide. The dried cakes analyzed 78-84% U_3O_8 with iron and aluminum oxides, combined, amounting to less than 0.4%. A small amount of ferric hydroxide formed in the sodium carbonate strip during this test and was filtered off prior to the acid addition.

Reagent Costs

On the basis of laboratory measurements made thus far, the overall chemical costs, excluding costs for reducing iron(III), are indicated to be in the order of 10.6 to 12.5 cents per pound of U_3O_8 recovered from average type reduced liquors containing about 1 g U/l. Further establishment of these costs and the operational feasibility will await the completion of continuous countercurrent tests now in progress. The liquor reduction step will also be examined.

Vanadium Recovery

Vanadium may also be extracted from reduced liquors by di(2-ethylhexyl)phosphoric acid if the extractant concentration is sufficiently high. Stripping of the vanadium may again be accomplished with either acid or alkaline reagents. Only preliminary studies have been made of the process possibilities but the results are sufficiently encouraging to warrant further work.

X. FUTURE WORK

1) Further continuous countercurrent extraction studies of various extraction-stripping cycles with di(2-ethylhexyl)phosphoric acid are being made as a means of examining the major variables in process chemistry under simulated process conditions. Simultaneously, slurry extraction studies are being conducted by the Engineering Section under the direction of Mr. H. M. McLeod.

2) Since the presence of alcohol in the kerosene, to prevent third phase formation during alkaline stripping, causes a lowering of the uranium extraction coefficient, other possible diluent extenders will be examined.

3) Continued systematic studies will be made of the comparative extraction properties of various pure alkylphosphoric acids.

4) The vanadium extraction possibilities with dialkylphosphoric acids will receive further study.

XI. ACKNOWLEDGEMENTS

The bench-scale countercurrent extraction tests were made by Mr. A. D. Kelmers.

Tracer tests with di(2-ethylhexyl)phosphinic acid were made by Dr. W. H. Baldwin of the Oak Ridge National Laboratory Chemical Division.

Most of the analyses were performed by the Y-12 Section of the Oak Ridge National Laboratory Analytical Division under the direction of Mr. C. D. Susano.

Several of the compounds were prepared by the Research Laboratories of the Virginia-Carolina Chemical Corporation, Richmond, Virginia and one was prepared by the Carbide and Carbon Chemicals Company, South Charleston, West Virginia.

XII. REFERENCES

1. "Progress Report, Uranium Chemistry of Raw Materials Section, July 1, 1951 to September 30, 1951," Oak Ridge National Laboratory - Y-12, Y-823, November 30, 1951.

2. "Progress Report, Uranium Chemistry of Raw Materials Section, October 1, 1951 to December 31, 1951," Oak Ridge National Laboratory, ORNL-1220, January 25, 1952.

3. "Progress Report, Uranium Chemistry of Raw Materials Section, January 1, 1952 to March 31, 1952," Oak Ridge National Laboratory, ORNL-1308, May 23, 1952.

   "Progress Report, Uranium Chemistry of Raw Materials Section, April 1, 1952 to June 30, 1952," Oak Ridge National Laboratory, ORNL-1384, October 23, 1952.

4. "Progress Report, Uranium Chemistry of Raw Materials Section, Part II. Studies in Uranium Chemistry: Solvent Extraction, July 1, 1952 to September 30, 1952," Oak Ridge National Laboratory, ORNL-1480, December 6, 1952.

5. "Progress Report, Chemical Research Section, November 1949," Hanford Engineering Works, HW-17453, December 20, 1949.

6. Stewart, D. C., University of California Radiation Laboratory, UCRL-585, January 26, 1950.

7. "Progress Report, Chemical Research Section, March 1950," Hanford Engineering Works, HW-17542, April 17, 1950.

8. "Progress Report, Chemical Research Section, July 1950," Hanford Engineering Works, HW-18646, August 21, 1950.

9. Stewart, D. C. and T. E. Hicks, "Alkyl Phosphoric Acid Extractions," University of California Radiation Laboratory, UCRL-861, August 9, 1950.

10. "Progress Report, Chemical Research Section, August 1950," Hanford Engineering Works, HW-18880, September 19, 1950.

11. "Progress Report, Chemical Research Section, Sept. 1950," Hanford Engineering Works, HW-19155, October 16, 1950.

12. "The Recovery of Uranium from Industrial Phosphoric Acids by Solvent Extraction. Part I. Summary Status Report. Part II. Index of Monthly Progress Reports," The Dow Chemical Company, DOW-81, July 14, 1952.

"Monthly Progress Reports," The Dow Chemical Company: DOW-83, August 6, 1952; DOW-84, September 12, 1952; DOW-85, October 3, 1952; DOW-87, November 3, 1952.

13. Valle-Riestra, J. F., "Carnotite Solvent Extraction Process - Process Description," The Dow Chemical Company, DOW-123, November 10, 1954.

14. Stewart, D. C., "Recovery of Heavy Elements From Sea-Water," Argonne National Laboratory, ANL-5154, December 1953.

15. Coleman, C. F., "Extraction of Uranium from LZ Nitric Acid Leach Liquor," Oak Ridge National Laboratory, Y-B34-3, January 12, 1953.

16. "July-August Progress Report," The Dow Chemical Company, DOW-120, September 1, 1954.

17. Blake, C. A., R. S. Lowrie, D. G. Hill, K. B. Brown, "Studies in the Carbonate-Uranium System: Part I. Investigations in the Four Component System UO_3-Na_2O-CO_2-H_2O," Oak Ridge National Laboratory, AECD-3280 (Y-673), Declassified November 26, 1951.

18. Brown, K. B. and J. M. Schmitt, "Studies in the Carbonate Uranium System: Part II. The Solubility of Sodium Uranyl Tricarbonate in Solutions of Certain Sodium Salts," Oak Ridge National Laboratory, AECD-3229 (Y-678), Declassified September 6, 1951.

19. Valle-Riestra, J. F., "Proposed HCl Recovery System - Salt Lake City Pilot Plant," The Dow Chemical Company, DOW-119, August 20, 1954.

20. "January-February Progress Report," The Dow Chemical Company, DOW-127, March 1, 1955.

21. Saine, V. L. and K. B. Brown, "Studies of Recovery Processes for Western Uranium-Bearing Ores: Part I. A Critical Examination of the Salt-Roast, Acid-Leach Process for Western Uranium Ores," Oak Ridge National Laboratory, AECD-3241 (Y-499), Declassified September 19, 1951.

APPENDIX A. PREPARATION, PURITY, STABILITY, AND AVAILABILITY OF REAGENTS

Preparation

A general review of the methods for preparing alkylphosphoric acids has been given by Kosolapoff.[1] Two of the common methods are described by the following equations:

$$ROH + P_2O_5 \longrightarrow (RO)_2PO_2H + ROPO_3H_2 + \text{pyro acids and poly acids} \quad (1)$$

$$(RO)_3PO \xrightarrow{NaOH} (RO)_2PO_2Na \xrightarrow{HCl} (RO)_2PO_2H \quad (2)$$

where $ROH \equiv$ alcohol with alkyl group R

$ROPO_3H_2 \equiv$ monoalkylphosphoric acid

$(RO)_2PO_2H \equiv$ dialkylphosphoric acid

$(RO)_3PO \equiv$ trialkylphosphate

Because phosphorus pentoxide has a structure (P_4O_{10}) containing -P-O-P- linkages, poly-, pyro-, and metaphosphoric acids are formed in the first reaction in addition to the alkylorthophosphoric acids. (Such reaction mixtures have been used successfully in the extraction of uranium from commercial phosphoric acids[2].) When the alkylorthophosphoric acids are required free of the other types, it has been customary to treat the reaction mixture by acid hydrolysis or by steam distillation in order to destroy the polymeric by-products[1,3]. Experience at this laboratory has shown that some of these polymeric acids are fairly stable toward hydrolysis, and unless rather exhaustive treatment with acid is given to the mixture they can remain and be mistakenly identified with the dialkylphosphoric acids.

The ortho acids have been separated by the usual techniques of selective partitioning between two immiscible liquid solvents[4]. Ethylene glycol and petroleum ether, for example, have proved effective in the separation of the 2-ethylhexyl-phosphoric acids. It is also possible to separate these acids by taking advantage of the relative

solubilities of their sodium salts in alkaline solutions of appropriate concentration. The sodium salt of mono(2-ethylhexyl)phosphoric acid, for example (see p. 51), is quite soluble in 10% sodium carbonate or hydroxide solution, while that of the di(2-ethylhexyl)phosphoric acid is insoluble in such solutions, although it is readily soluble in water.

The de-alkylation of the trialkylphosphate shown in the second equation can be made nearly specific for the formation of the dialkylphosphoric acid. The unreacted trialkylphosphate and the alcohol by-product can be separated by extracting these neutral impurities into an organic solvent, while the sodium salt of the dialkylphosphoric acid remains dissolved in water.

Table 1 describes the reagents used in these experiments, their source, method of preparation, and acid equivalence as indicated by titrations with aqueous sodium hydroxide in a 75-25 ethanol-water medium.

Purity

In the absence of pyro- and polyphosphoric acid, titration curves for mono- and dialkylphosphoric acids exhibit sharp, well-defined inflections. The monoalkyl acids show two inflections corresponding to the two hydrogen ions, the strength of which are not greatly different from the corresponding ones of orthophosphoric acid. The dialkylphosphoric acids show but one inflection, representing an acid strength nearly equal to the stronger hydrogen ion of the monoalkyl reagents. Comparative acid strengths of several alkylphosphoric acids are shown in Table 2.

Titration to the two successive inflection points provides a differential analysis of mono- and dialkylorthophosphoric acids in mixtures which contain only these two acid species.* The titer to the first end point is equivalent to the dialkylphosphoric acid plus the stronger hydrogen ion of the monoalkylphosphoric acid, and the additional titer from the first to the second end point is

---

*Some of the reagents as received were found to contain iron, presumably from corrosion of reaction vessels. Any metal ion must be removed from the reagent mixture by thorough acid stripping before the differential titration can be used.

Table 1

DESCRIPTION OF REAGENTS

Alkyl Group	Mol Wt	Batch No	Theo. meq/g	Acid Assay meq/g[a] Strong Acid	Acid Assay meq/g[a] Weak Acid	Source[b]	Remarks
			- Dialkylphosphoric Acids -				
2-Ethylhexyl	322	C	3.11	2.80	<0.1	ORNL	Separated from mixture
		F		3.09	<0.1	ORNL	" " "
		G		3.04	<0.1	C&C	Separated at ORNL from Tergitol P-28
		I		2.87	<0.1	C&C	As received
		J		3.10	<0.1	C&C	Separated at ORNL from Tergitol P-28
n-Octyl	322	A	3.11	2.99	<0.1	ORNL	Separated from mixture
Octyl-2	322	A	3.11	3.06	<0.1	ORNL	Separated from mixture
3,5,5-Trimethylhexyl	350	A	2.86	2.78	<0.1	VC	As received
Diisobutylmethyl	350	A	2.86	2.72	<0.1	VC	As received
		D		>2.72	<0.1	VC	Separated at ORNL from portion of Batch A

Table 1 (Cont'd.)

DESCRIPTION OF REAGENTS

Alkyl Group	Mol Wt.	Batch No.	Theo. meq/g	Acid Assay meq/g[a] Strong Acid	Acid Assay meq/g[a] Weak Acid	Source[b]	Remarks
- Monoalkylphosphoric Acids -							
n-Butyl	154	A	6.49	6.17	6.01	ORNL	Separated from mixture
Iso-amyl	168	A	5.95	4.74	4.87	ORNL	" " "
2-Ethylhexyl	210	F	4.76	4.55	4.59	ORNL	" " "
n-Octyl	210	A	4.76	4.52	4.62	ORNL	" " "
Octyl-2	210	A	4.76	4.70	4.78	ORNL	" " "
3,5,5-Trimethylhexyl	224	A	4.46	4.34	4.43	VC	As received
Diisobutylmethyl	224	B	4.46	4.35	4.59	VC	" "
Dodecyl[c]	266	B	3.76	----	----	ORNL	Hydrolysis product of alc-P_2O_5-reaction mixture
4-Ethyl-1-isobutylmethyl	294	A	3.40	2.91	2.91	VC	As received
Heptadecyl[d]	337	B	2.97	----	----	ORNL	Hydrolysis product of alc-P_2O_5-reaction mixture

Table 1 (Cont'd.)

DESCRIPTION OF REAGENTS

Notes:

a) Based on differential titration in 75-25 ethanol-water mixture with aqueous sodium hydroxide.

b) ORNL - Oak Ridge National Laboratory.
C&C - Carbide and Carbon Chemicals Company.
VC - Virginia-Carolina Chemical Corporation.

c) Prepared from 2,6,8-trimethylnonanol-4 by reacting with P_2O_5 in kerosene. Reaction mixture hydrolyzed 3 hours with 6 M HCl until no excess strong acid detectable. Final concentration in kerosene, 0.47 M.

d) Prepared from 3,9-diethyltridecanol-6 as in note (c).

Table 2

RELATIVE ACID STRENGTHS

OF SOME ALKYLPHOSPHORIC ACIDS

Alkyl Group	Monoalkyl Acid			Dialkyl Acid	
	Batch	pA_1*	pA_2*	Batch	pA_1*
n-Octyl	A	3.4	8.2	A	2.9
2-Ethylhexyl	F	3.1	8.4	G	3.2
Octyl-2	A	3.8	9.0	A	3.6
Diisobutylmethyl	B	4.1	9.3	A	4.4
		---	---	D	4.4
3,5,5-Trimethylhexyl	A	3.7	8.6	A	3.0
2,6,8-Trimethylnonyl-4 (DDPA)**	B	4.2	9.6		---
4-Ethyl-1-isobutyloctyl	A	4.2	9.6		---
3,9-Diethyltridecyl-6 (HDPA)**	B	4.1	9.4		---
H_3PO_4		4.0	8.4		

*Acid strength as represented by the measured apparent pH of the 75-25 alcohol-water mixture at the point of half-neutralization.

pA_1 ≡ pH of half-neutralization of stronger hydrogen ion.
pA_2 ≡ pH of half-neutralization of weaker hydrogen ion.

Results of a similar titration of the first two hydrogen ions of inorganic phosphoric acid are included for comparison. Note that the apparent pH's in the alcoholic medium cannot be compared directly with pH in aqueous solution.

**Kerosene solution titrated in alcohol-water mixture. Check tests with mono- and di(2-ethylhexyl)phosphoric acids showed that this has no appreciable effect upon the pH of half-neutralization.

equivalent to the weaker hydrogen ion of the monoalkylphosphoric acid. When there is only a small amount of the monoalkyl acid present in a large amount of the dialkyl acid the two inflections merge; however, the resulting shape of the titration curve differs sufficiently from that shown by the pure dialkyl acid to serve as a qualitative test. Thus, it has been found possible to detect less than 0.1 meq (~1 wt %) of mono(2-ethylhexyl)phosphoric acid per gram of di(2-ethylhexyl)phosphoric acid. None of the dialkylphosphoric acids listed in Table 1 showed even this much monoalkylphosphoric acid present.

The monoalkylphosphoric acids listed in Table 1 were probably somewhat less pure than the dialkyl acids, and the purity was more difficult to assess. However, it seems safe to conclude that the mono-n-butyl- and mono(diisobutylmethyl)phosphoric acids contained less than 10% of the corresponding dialkylphosphoric acids, and that the other monoalkyl acids listed contained less than 5%.

The difference between total meq/g found and theoretical meq/g (about 5% for most of the compounds listed) represents nonacidic impurity, which is believed to consist principally of the corresponding alcohol and trialkylphosphate. At the levels so indicated, these compounds should have little or no effect on the extraction results described in this report.

Homologous purity depended on the homologous purity of the starting materials, and although differences may be expected in other compounds of a homologous series, it is not likely that they are present to an extent causing changes in chemical or physical properties which are important in the present tests.

The extraction behavior in itself can sometimes be used for indirect confirmation of reagent purity. For example, the uranium extraction isotherm with di(2-ethylhexyl)phosphoric acid (Batch G) shown in Table 5 and Figure 4 (Section II), calculated on the basis of free reagent concentration, showed essentially the same inherent extraction coefficient at high loading as at low loading. This would not have been the case if the reagent had contained a small amount of a contaminant with much higher extraction power.

Stability

Degradation of the alkylphosphoric acids has not been observed in any of the tests described in this report.

Preliminary stability studies have been reported at Hanford Engineering Works[5,6] which indicate good stability of the n-butylphosphoric acids to acid hydrolysis by 3 M nitric acid at 76°C under intermittant agitation (half-life of 8 days for dibutylphosphoric acid, 18 days for monobutylphosphoric acid). Since reagent stability has not been a factor of importance in the present tests, no further studies have been made in this laboratory.

Availability

Di(2-ethylhexyl)phosphoric acid is available from Carbide and Carbon Chemicals Company, South Charleston, W. Va. The following is an excerpt from a communication[7] which describes the tentative price structure:

> ".... [Carbide and Carbon Chemicals Company has] sold and will sell development quantities [of di(2-ethylhexyl)phosphoric acid] in the range of 1000 pounds for $1.50 per pound. For larger quantities in the range of 10,000 to 20,000 pounds per month, a price of $0.75 per pound is felt to be possible. If the use were to grow to the range of 50,000 pounds per month, it is possible that the price could be in the range of $0.50 per pound. Since di(2-ethylhexyl)phosphoric acid is not a commercial chemical at the present time, ... [Carbide has] not had production experience to indicate the lower price ranges. A guide.... [is] the $0.50 - 0.70 per pound price range. These prices apply to a 95 percent material and if a less pure product [can be used], some economies might be possible."

Carbide is currently marketing a 25% solution of the sodium salt of di(2-ethylhexyl)phosphoric acid in water under the trade name of Tergitol Wetting Agent, P-28. Its price is listed as:

Quantity	Cents/lb of 25% Solution
CL (in drums)	18.5
LCL	19
LDL	24

Very pure di(2-ethylhexyl)phosphoric acid (Batches G and J) has been recovered from this solution by preliminary

scrubbing of the Tergitol with petroleum ether, followed by acidification with hydrochloric acid and extraction of the reagent into petroleum ether.

Mixtures of alkylphosphoric acids are also being marketed by other chemical companies which handle organophosphorus compounds, e.g., Victor Chemical Company and Monsanto Chemical Company. Acids prepared from the following alcohols are representative of available mixtures: butyl, amyl, isoamyl, 2-ethylhexyl, isooctyl, lauryl, stearyl, etc.

REFERENCES FOR APPENDIX A

1. Kosolapoff, G. M., "Organophosphorus Compounds," J. Wiley & Sons, 1950.

2. "The Recovery of Uranium from Industrial Phosphoric Acids by Solvent Extraction. Part I. Summary Status Report. Part II. Index of Monthly Progress Reports," The Dow Chemical Company, DOW-81, July 14, 1952.

   "Monthly Progress Reports," The Dow Chemical Company: DOW-83, August 6, 1952; DOW-84, September 12, 1952; DOW-85, October 3, 1952; DOW-87, November 3, 1952.

3. "Organophosphorus Compounds - Definitive Report, January 1, 1953 - December 10, 1953," Virginia-Carolina Chemical Corporation.

4. "Technique of Organic Chemistry, Vol. III," Interscience Publishers, Inc., N. Y., 1950.

5. "Progress Report, Chemical Research Section, October 1950," Hanford Engineering Works, HW-19503, November 17, 1950.

6. "Progress Report, Chemical Research Section, November 1950," Hanford Engineering Works, HW-19739, December 18, 1950.

7. Letter to K. B. Brown from R. W. Eddy, Carbide and Carbon Chemicals Company, 30 E. 42nd Street, New York 17, N. Y., February 1, 1955.

APPENDIX B. EXTRACTIONS FROM NITRATE, CHLORIDE, AND PHOSPHATE SOLUTIONS

As a part of the general screening program on uranium extractants, tests are ordinarily made with nitrate, chloride, and phosphate solutions as well as with sulfate solutions described in the foregoing report. Some of the results from extraction tests with these other solutions are discussed briefly below.

Nitrate Solutions

Extractions of uranium from acidic nitrate salt solutions and from nitric acid solutions with di(2-ethylhexyl)-phosphoric acid are listed in Tables 1 and 2. The following observations may be drawn from these data.

1) The extractions of uranium with the dialkylphosphoric acid reagent are better from the nitrate solutions than from sulfate solutions at comparable concentration and pH levels. This result is expected since, in contrast to sulfate ions, the nitrate ions have little tendency to complex with (and thus compete against the extractant for) the uranyl ions.

2) At similar concentrations of hydrogen ion and extractant (Table 1), the uranium extractions were increased by increasing the nitrate concentration in the aqueous phase. Since the magnitude of the changes are greater than expected from changes in ionic strength, an additional extraction mechanism is apparently in effect at the higher nitrate levels, similar perhaps to that deduced for explaining extractions with trialkylphosphates.

3) In extractions from fairly concentrated nitric acid solutions (Table 2), the "nitrate effect" was large enough to offset the deleterious effect from increased hydrogen ion concentration as shown in Equation (1) (Section II). Appreciable extractions were obtained, for example, even from 6 M acid.

4) Increased extractions from sulfate liquors were also obtained by adding appreciable quantities of nitrate salts to the aqueous phase (Table 3). Similar results have been reported previously for dialkylphosphinic acids.[1]

Table 1

EXTRACTION FROM NITRATE SOLUTIONS

0.01 M Di(2-ethylhexyl)phosphoric Acid (Batch G) in kerosene (1.3% 2-ethylhexanol)
Phase Ratio: aqueous/organic = 1/2
U Conc. in Aq: 1 g U/l
Contact Time: 2 minutes (hand shaking)

Nitrate M	Initial pH	E_a^o
0.5	0.5	1.2
	1.65	28
1.5	0.6	2
	1.7	50
4.0	0.75	15
	1.5	400
6.0	0.7	40
	1.85	>500

Table 2

EXTRACTIONS FROM NITRIC ACID SOLUTIONS

0.1 M Di(2-ethylhexyl)phosphoric Acid (Batch G) in kerosene (2% 2-ethylhexanol)
Phase Ratio: aqueous/organic = 1/2
U Conc. in Aq: 1 g U/l
Contact Time: 2 minutes (hand shaking)

HNO_3 (M)	E_a^o
0.5	70
1.5	15
4.0	15
6.0	20

Table 3

EFFECT OF NITRATE ON EXTRACTION

FROM SULFATE SOLUTIONS

0.05 M Di(2-ethylhexyl)phosphoric Acid (Batch F) in carbon tetrachloride

Solution Composition: 0.5 M SO_4, pH = 1.2
1 g U/l

Phase Ratio: aqueous/organic = 1

Contact Time: 20 min (end-over-end mixing)

Nitrate (M)	U Extracted %	E_a^o
0	78	3.5
0.2	78	3.5
0.8	82	4.5
2.0	90	9
3.6	92	12

In view of the data described above, a thorough study of the factors governing uranium extraction from nitrate solution by dialkylphosphoric acids would be of interest. The function of alcohol in the kerosene diluent, and the effects of other diluents, should be included as a part of this study.

Chloride Solutions

Extractions of uranium from hydrochloric acid solution with di(2-ethylhexyl)phosphoric acid are shown in Table 4.

Table 4

EXTRACTION FROM HYDROCHLORIC ACID SOLUTIONS

0.1 M Di(2-ethylhexyl)phosphoric Acid (Batch G) in kerosene (2% 2-ethylhexanol)

U Conc. in aq: 1 g U/l

Phase Ratio: aqueous/organic = 1

Contact Time: 2 min (hand shaking)

HCl (M)	E_a^o
0.5	75
1.5	6
4.0	0.4
6.0	0.15

It may be noted that,

1) at comparable conditions the extraction from chloride solutions are greater than from sulfate solutions. This, again, is an expected result for reasons given under (1) above.

2) a "chloride effect," similar to the "nitrate effect" described earlier, was not observed within the range

of acid concentrations tested. Thus, the extractions were lower with each increase in acid concentration. These tests are similar to, and in agreement with, the stripping experiments presented in the body of this report.

Phosphate Solutions

Extractions of uranium from phosphate solutions with di(2-ethylhexyl)phosphoric acid are presented in Tables 5 and 6. From these data the following observations may be made.

1) The extractions from phosphate solutions, under comparable conditions, are lower than from sulfate solutions and much lower than from nitrate or chloride solutions.

2) Although useful extraction coefficients could be obtained at moderate phosphate levels, the extractions from concentrated phosphate or phosphoric acid solutions, similar to those encountered in commercial practices, were extremely low.

3) No important differences were found in the extractability of U(IV) or U(VI) from the solutions studied.

Table 5

EXTRACTIONS FROM PHOSPHORIC ACID SOLUTIONS WITH DI(2-ETHYLHEXYL)PHOSPHORIC ACID IN KEROSENE

U Conc. in Aq: 100 ppm

H_3PO_4 M	Ox. State of U	Extractant Conc. M	Phase Ratio aq/org	E_a^o
0.5	VI	0.1*	1/1	6
1.5	VI	0.1*	1/1	0.2
3.3	VI	0.1*	1/1	0.04
5.3	VI	0.1*	1/1	$<$ 0.01
3.3	VI	0.25**	1/2	0.4
3.3	IV	0.25**	1/2	0.4

*2% 2-ethylhexanol in kerosene. Reagent Batch G. 2 minutes contact time (hand shaking).

**No alcohol used. Reagent Batch C. 20 minutes contact time (end-over-end agitation).

Table 6

EXTRACTION FROM PHOSPHATE SOLUTIONS:

EFFECT OF REAGENT CONCENTRATION

Di(2-ethylhexyl)phosphoric Acid, Batch G

1 g U/liter (~0.004 M)

Phase Ratio, aqueous/organic = 1

Agitation, 2 minutes by hand

Reagent M	Diluent	Alcohol* %	PO_4 M	pH	E_a^o
0.1	Kerosene	1.9	0.5	0.9	6
.2	"	2.6	"	"	35
.5	"	4.7	"	"	270
1.0	"	8.2	"	"	800
0.2	Kerosene	2.6	5.3	1.0	0.03
.5	"	4.7	"	"	.2
1.0	"	8.2	"	"	.7

*2-Ethylhexanol added to the kerosene diluent.

REFERENCES FOR APPENDIX B

1. "Progress Report, Uranium Chemistry of Raw Materials Section, Part II. Studies in Uranium Chemistry: Solvent Extraction, July 1, 1952 to September 30, 1952," Oak Ridge National Laboratory, ORNL-1480, December 6, 1952.

APPENDIX C. COMPARISON OF URANIUM EXTRACTION ABILITY OF SEVERAL ALKYLPHOSPHORIC ACIDS

As a part of the general program[1-5] to investigate and evaluate various organic compounds as solvent extraction reagents, series of alkylphosphoric acids have been prepared and subjected to preliminary comparison in uranium extraction tests. The ability to compare the extraction power of these compounds depends upon the confidence which may be placed in the purity of the reagents and in the proper evaluation of other factors which may influence extraction, such as loss of reagent by distribution to the aqueous phase and reagent stability. Di(2-ethylhexyl)phosphoric acid has been shown to have negligible distribution to acidic liquors (page 57) and, since the other dialkylphosphoric acids all had equal or greater molecular weights, the loss of reagent concentration and the formation of water-soluble organophosphorus complexes were considered to be negligible factors in the comparison of their uranium extraction properties. The dialkyl reagents were contaminated with less than 1 percent of monoalkylphosphoric acid, and the remaining non-acidic material should have had little or no effect on the extraction results described in this report.

Comparison of the extraction powers of the monoalkyl acids has been more difficult, and the results are less reliable. With only one alkyl group in the molecule, these reagents are more soluble in aqueous liquors than are the corresponding dialkyl reagents, and the loss of reagent to the aqueous phase during extraction was probably significant with the smaller of the alkyls used. In addition, these reagents were probably less pure than the dialkyl reagents, although the impurities most likely to be present (trialkylphosphate, dialkylphosphoric acid, alcohol) should not have any great effect on the extraction results.

Most of the comparison extractions have been made from sulfate and phosphate solutions with 0.1 M reagent in carbon tetrachloride. This diluent has been used in extractant screening tests because of its ability to dissolve many and varied organic compounds and because its high density aids phase separation. Two of the reagents (monododecyl- and monoheptadecylphosphoric acids) were synthesized directly in kerosene (page 101) so that comparison of these with other reagents was made in this diluent.

Comparisons of the ability of the reagents to extract uranium from a 0.5 M sulfate solution at pH 1 are presented in Tables 1 and 2. These show that the monoalkyl reagents had much higher extraction coefficients than did the dialkyl reagents prepared from the same alcohols. The results with the mono(2-ethylhexyl), di(2-ethylhexyl), and mono(tetradecyl) reagents show that extractions in carbon tetrachloride were lower than extractions in kerosene, and that the difference was much greater for the dialkyl reagents than for the monoalkyl reagents. Thus, it appears that carbon tetrachloride was a poor choice of diluent for intercomparison of these two classes of compounds, and Table 1 should be used only for comparison of mono- with mono- and di- with di- reagents.

Uranium extraction ability of the dialkylphosphoric acids showed correlation with the relative acid strength of the compounds, and both extraction ability and acid strength could be correlated with the extent of branching of the organic side chains. Figure 1 demonstrates this apparent relationship between the uranium extraction coefficient and the relative acid strength (cf. Appendix A, Table 2). A more extensive treatment of these data will be presented separately later.

Within the group of three long-chain monoalkylphosphoric acids (Table 2) made from similarly constituted secondary alcohols (i.e., with branching in vicinity of the phosphorus atom nearly identical, different mainly in the length of chains beyond the points of branching) there was but slight variation in either extraction ability or acid strength. The reagent prepared from the primary alcohol, 3,5,5-trimethylhexanol, had appreciably higher extraction ability (even with carbon tetrachloride as the diluent, Table 1) and acid strength. For the reasons mentioned above, comparison of the reagents in the octyl series is more difficult, but it appears that under the conditions of the tests the compound made from the secondary alcohol, octanol-2 (capryl alcohol), had lower uranium extraction ability than did those prepared from either of the primary alcohols, n-octanol or 2-ethylhexanol.

The extractions from sulfate solutions are extended in Tables 3 and 4 to sulfate solutions of higher concentration (1.7 M) and to phosphate solutions. With the possible exception of the diisobutylmethyl phosphoric acids, the relative extraction ability of these compounds remained the same in extractions from each of these solutions. In agreement with the more detailed experiments with di(2-ethylhexyl)-phosphoric acid, 1) extraction was lower from a phosphate solution than from a sulfate solution at the same molar concentration, 2) extraction decreased with increasing sulfate or phosphate concentrations, and 3) extraction increased with pH level.

Table 1

COMPARISON OF EXTRACTION ABILITY OF SEVERAL ALKYLPHOSPHORIC ACIDS IN CARBON TETRACHLORIDE

0.1 M Reagent in carbon tetrachloride

0.5 M Sulfate, pH = 1, 0.004 M U

Phase Ratio, aqueous/organic = 1

Agitation Time, 10 min (wrist-action shaker)

Alkyl Group	Dialkylphosphoric Acid		Monoalkylphosphoric Acid	
	Batch No.	E_a^o	Batch No.	E_a^o
n-Octyl	A	90	A	580
2-Ethylhexyl	G	17	F	~2000
Octyl-2	A	11	A	220
Diisobutylmethyl	D	3	B	450
3,5,5-Trimethyl-hexyl	A	40	A	>1000
4-Ethyl-1-isobutyloctyl		--	A	190

Table 2

COMPARISON OF EXTRACTION ABILITY OF SEVERAL ALKYLPHOSPHORIC ACIDS IN KEROSENE

0.1 M Reagent in kerosene

0.5 M Sulfate, pH = 1, 0.004 M U

Phase Ratio, aqueous/organic = 1

Agitation Time = 10 min (wrist-action shaker)

Alkylphosphoric Acid	Batch No.	E_a^o
Mono(2-ethylhexyl)	F	~2500
Mono(heptadecyl)[a]	B	370
Mono(dodecyl)[b]	B	275
Mono(tetradecyl)[c]	A	435
Di(2-ethylhexyl)	G	135

a) Prepared from 3,9-diethyltridecanol-6 (p. 101).

b) Prepared from 2,6,8-trimethylnonanol-4 (p. 101).

c) Prepared from 4-ethyl-1-isobutyloctanol.

[redacted]

ORNL-LR-Dwg. 7084

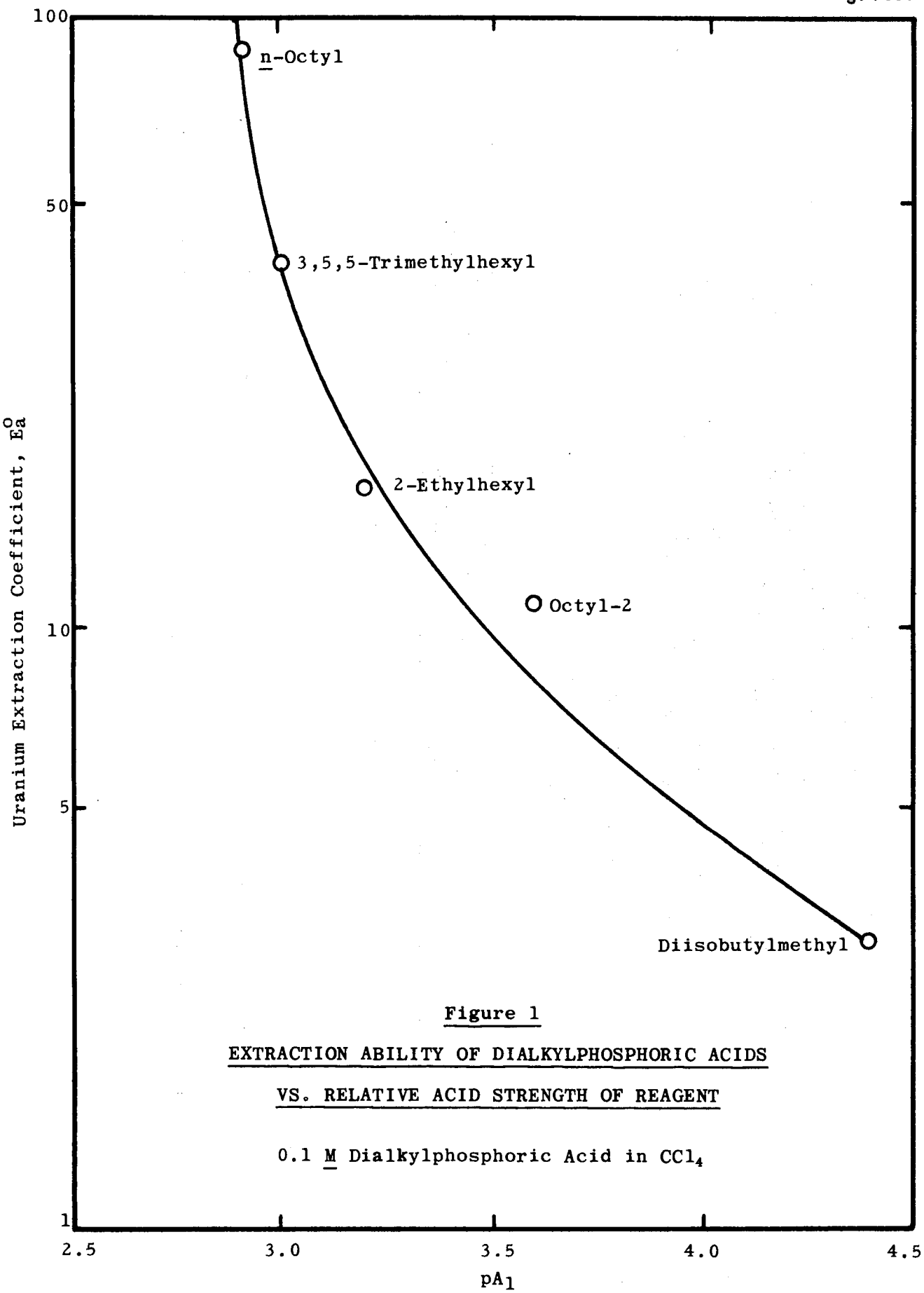


Figure 1

EXTRACTION ABILITY OF DIALKYLPHOSPHORIC ACIDS VS. RELATIVE ACID STRENGTH OF REAGENT

0.1 M Dialkylphosphoric Acid in CCl_4

Table 3

COMPARISON OF EXTRACTION ABILITY OF SEVERAL DIALKYLPHOSPHORIC ACIDS FROM SULFATE AND PHOSPHATE SOLUTIONS

0.1 M Reagent in carbon tetrachloride

0.004 M U

Phase Ratio, aqueous/organic = 1

Agitation Time = 20 min

		E_a^o				
		Sulfate		Phosphate		
Dialkylphosphoric Acid	Batch No.	0.5 M pH = 1	1.7 M pH = 1.2	0.4 M pH = 1.2	1.4 M pH = 1.3	1.4 M pH = 2.0
n-Octyl	A	90	25	30	0.8	2
Octyl-2	A	11	3	2	0.1	0.2
3,5,5-Trimethylhexyl	A	40	7	8	0.4	0.6
Diisobutylmethyl	A	6	2	2	1.1	1.0
	D	3	1	2	0.8	0.6

Table 4

COMPARISON OF EXTRACTION ABILITY OF SEVERAL MONOALKYLPHOSPHORIC ACIDS FROM SULFATE AND PHOSPHATE SOLUTIONS

0.1 M Reagent in carbon tetrachloride

0.004 M U

Phase Ratio, aqueous/organic = 1

Agitation Time = 10 min

		E_a^o				
		Sulfate		Phosphate		
Monoalkylphosphoric Acid	Batch No.	0.5 M pH = 1	1.5 M pH = 1.0	0.4 M pH = 1.2	1.4 M pH = 1.3	1.4 M pH = 2.0
n-Octyl	A	580	250	160	12	20
2-Ethylhexyl	F	>1000	560	240	18	30
Octyl-2	A	220	75	20	2	5
3,5,5-Trimethylhexyl	A	>1000	590	290	20	30
Diisobutylmethyl	B	450	130	75	6	15
4-Ethyl-1-isobutyloctyl	A	190	50	25	2	7

[redacted]

REFERENCES FOR APPENDIX C

1. "Progress Report, Uranium Chemistry of Raw Materials Section, July 1, 1951 to September 30, 1951," Oak Ridge National Laboratory - Y-12, Y-823, November 30, 1951.

2. "Progress Report, Uranium Chemistry of Raw Materials Section, October 1, 1951 to December 31, 1951," Oak Ridge National Laboratory, ORNL-1220, January 25, 1952.

3. "Progress Report, Uranium Chemistry of Raw Materials Section, January 1, 1952 to March 31, 1952," Oak Ridge National Laboratory, ORNL-1308, May 23, 1952

4. "Progress Report, Uranium Chemistry of Raw Materials Section, April 1, 1952 to June 30, 1952," Oak Ridge National Laboratory, ORNL-1384, October 23, 1952.

5. "Progress Report, Uranium Chemistry of Raw Materials Section, Part II. Studies in Uranium Chemistry: Solvent Extraction, July 1, 1952 to September 30, 1952," Oak Ridge National Laboratory, ORNL-1480, December 6, 1952.

[redacted]